

# JNMM

JOURNAL OF  
THE INSTITUTE OF  
NUCLEAR MATERIALS MANAGEMENT



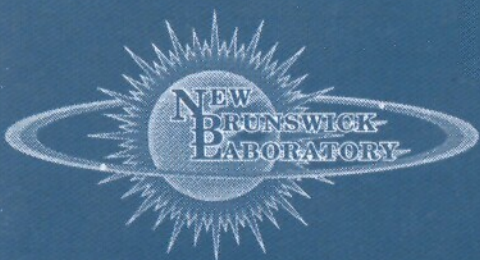
# 1949

## NEW BRUNSWICK LABORATORY

## 40TH ANNIVERSARY



# 1989



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Volume XVIII, Number 1 • November 1989

**NEW BRUNSWICK  
LABORATORY 40<sup>TH</sup>  
ANNIVERSARY  
1949-1989**

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### On the Cover:

Top photo: The early days at New Brunswick Laboratory in Argonne, Illinois. Bottom photo: New Brunswick Laboratory today. See "Life Begins at 40" by Samuel C. T. McDowell for a history of NBL's growth, relocation and contributions to the nuclear safeguards industry.

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SOCIETY OF  
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INSTIT. OF NUCLEAR MATERIALS MANAGEMENT

This issue contains the papers presented at the celebration of the fortieth anniversary of the founding of the New Brunswick Laboratory by the new United States Atomic Energy Commission. During World War II it was necessary to determine the physical and chemical properties of uranium and plutonium and to develop the methods to measure these materials as accurately as possible. After the war the Atomic Energy Commission established an analytical laboratory for nuclear materials in New Brunswick, New Jersey, as is described in several of the following papers. In 1975 the Atomic Energy Commission decided that it would be wise to relocate this laboratory on the site of Argonne National Laboratory. After considerable discussion it was decided to retain the name, New Brunswick Laboratory, because this name was well known to nuclear chemists around the world although the name may be confusing to the newcomers to the field.

To add to the confusion, the Atomic Energy Commission was split into the Nuclear Regulatory Commission and the Energy Research and Development Administration in 1974 and the latter became the Department of Energy in 1977. This might be referred to as fission and transmutation.

Members and friends of the Institute of Nuclear Materials Management should find the papers in this issue of great interest. The measurements of nuclear materials by chemical analytical means are rarely discussed at the big safeguards meetings or in the safeguards journals, although they are essential to all measurements for nuclear safeguards and production purposes.

The anniversary symposium was organized by Dr. Carleton D. Bingham, director, and the staff of the New Brunswick Laboratory. As you will see, the papers cover the past history of the development of nuclear and radio-chemistry, the present sta-



tus of these disciplines, and tentative forecasts for the future. The developments in radio-chemistry have found many applications in other fields and other developments of chemical techniques have contributed to the present status of measurements of nuclear materials.

Although most of the authors are Americans, it is obvious that this development has been a truly international undertaking.

This is probably the most complete presentation of the history and status of nuclear analytical measurements to have been recorded. The Institute is honored to have the opportunity to publish this very valuable document.

*Dr. William A. Higinbotham  
Brookhaven National Laboratory  
Upton, New York*

## Members and Friends of the INMM

As I begin my second year as INMM chairman it is appropriate that we look at what we have accomplished during the past year and forward to the future. One of the goals we set for each other was to increase participation in the leadership of the Institute. That has happened during the past year and some of your colleagues have agreed to serve as vice chairman for our standing committees. Hopefully this will lead to more avenues of input to the committees from the membership at large. The Officers and Executive Committee are genuinely interested in your ideas concerning our future. A downside to the increased participation was that our membership decreased by about six percent. In 1990 we will be working to reverse that trend. Currently a new membership brochure is being prepared and you will be receiving a bulletin from me "for your eyes only." Please make this membership drive your drive and invite at least one new member.



During the last five years each annual meeting has been larger than the previous meeting. This trend continued in Orlando. There were more than 200 papers and the largest attendance for any meeting. The Technical Program Committee is already working to make the 1990 Annual Meeting a better meeting than Orlando. However, the trend for more papers will be broken in FY-1990. The Executive Committee has instructed the Technical Program Committee that there should be no more than 200 papers. This step has been taken because of

the physical problems associated with running more than five concurrent sessions and as part of an effort to keep the proceedings in one volume. Let me know your thoughts on this format for the meeting.

During 1990 Vince DeVito will be preparing the history of the INMM. If you have documents, photographs or memorabilia from the early days give Vince a call. In addition to looking at the history, we intend to totally review and update, as necessary, the long range plan. If you are interested in participating in either of these efforts give me a call.

Best wishes for a happy holiday season and a prosperous New Year!

*John F. Lemming  
EG&G Mound Applied Technologies  
Miamisburg, Ohio*

## Letter

The article in the January, 1989 issue of *JNMM* by Dixy Lee Ray, "The role of Plutonium as a Resource Now and in the Future", contains an error that weakens the force of her argument. The article was originally presented as the keynote address at the 29th Annual Meeting of the INMM and the error occurs in the meeting proceedings as well.

In supporting the use of plutonium recycle in civilian power reactors via reprocessing and possibility breeder production, Dr. Ray made the following statement with respect to Pu-239 bred in existing power reactors (fueled by low-enriched uranium): "Some of it does in fact burn in power reactors, enough to account for about 1.3 percent of the reactor's total energy production." This figure for energy production by Pu-239 is low by more than an order of magnitude.

By means of a simple point-reactor computer program, we have calculated the fuel and energy characteristics as a function of burnup (time at full power) of a 3000 thermal-megawatt light-water reactor fueled by 100 metric tons of 3% enriched uranium. At a burnup of 30 MWD/kgU (1000 full-power days), the cumulative energy production from the fission of U-235 is about 60%. The remaining 40% results from the fission of bred Pu-239 and Pu-241, with the former contributing far more because of its much higher abundance; their averaged fission cross sections are about equal.

Also plotted are the instantaneous U-235 fission fraction and the fractional burnup of U-235. These two additional curves provide another way of understanding the basic point under discussion.

Though the computer program is simple, its results for this problem are reasonable, as is evident from the rough agreement for the burnup-dependent production of the plutonium isotopes with abundances calculated independently for a similar

but not identical reactor (see, e.g., *Light Water Reactor Nuclear Fuel Cycle*, eds. R.G. Wymer and B.L. Vondra, Jr., CRC Press, Inc., Boca Raton, FL, 1981). At a burnup of 33 MWD/kgU, the correspondences are as follows, with our numbers as a basis: Pu-239, +2.5%; Pu-240, -15%; Pu-241, +23%; and Pu-242, +5%.

We have informed Dr. Ray of the general nature of the correction in advance of submission to *JNMM*. She is of course pleased that the correction strengthens her thesis.

In conclusion, the cumulative energy production from plutonium fission in an ordinary LWR is about 40% by the time a burnup of 30 MWD/kgU is reached, with the bulk of that arising from Pu-239.

*Yours sincerely,  
Leslie G. Fishbone  
Ming-Shih Lu  
Brookhaven National Laboratory  
Upton, New York*

## Kirkland Bruce Stewart 1922-1989

The safeguards community is saddened by the recent death of Kirk Stewart, whose importance to the development of statistical concepts in safeguards-related work has sadly gone unrecognized by all but a few individuals who were privileged to associate with him. I was one of those individuals, and want to use this opportunity to remark on his contributions, many of which were of seminal importance.

Kirk's contributions are not widely known because he was of a retiring nature, reluctant to participate in meetings and symposia. He did publish in a number of journals and authored several in-house reports whose importance at first were unrecognized, because he was often far ahead of his time. As a prime example, Kirk did extensive work on the so-called minimum-variance MUF over 30 years ago. He published this work in respected statistical journals and in Hanford reports. After lying dormant for years, this work resurfaced about 10 years ago when so much activity on evaluating sequences of MUFs was initiated by several authors. With the resurgence of activity in this problem area, Kirk's pioneering efforts finally became more generally appreciated. As another example, Kirk was a principal author in a 1974 Battelle report that introduced the idea of partial defects and the need to increase bias tester sample sizes to be responsive to the existence of such defects. It is my recollection that he was instrumental in introducing and developing this concept which is now basic to inspection sampling plans. I could cite other cases, for there are many, but my point has been made. I sum up Kirk's professional contributions by stating that the safeguards community's perception of their importance is far overshadowed by their actual importance.

On a personal note, although we later discovered that we had lived for years in the 1930's within a few blocks of one another in Tacoma, I did not meet Kirk until the summer of 1955 when he was interviewed for a position with our Statistics group at Hanford under Carl Bennett. In response to a query by Kirk during our time together, I assured him that one could play golf all winter in Richland with the possible exception of one or two weeks. He joined our group in September. On November 11 it started snowing, and when the snow eventually disappeared in April, the local golf course became flooded. By June he was finally able to play golf. The fact that our friendship flourished during this harsh winter was one small evidence of the type of person Kirk was.

As just implied, Kirk was an avid golfer, and an excellent one. He chose not to golf competitively, but not because of any misgivings that he might not perform his best. In his quiet way, he was a tremendously competitive individual who was not satisfied when he did not perform to his standards in any arena. He golfed with great competence, always long and down the middle. He never agonized over a shot but was an unerringly excellent shotmaster who quickly made up his mind what needed to be done, and just did it. His skills and accomplishments far surpassed those of most of the "agonizers" with whom he played.

Kirk excelled in whatever he did. He was excellent at tennis and at table tennis. In his early years in the Tri-City area of Washington, there was a local high-school phenomenon who was highly touted in the press. In one of Kirk's rare entries into competitive sports, he met this young, rising star in the finals of a local tournament. Although nearing the "young veterans," status, Kirk demolished his opponent, with very little obvious effort. He was also an excellent bridge player who had the ability

to decide very quickly on how a hand should be played, and executed his strategy rapidly and to perfection with very little apparent thought.

Above all, Kirk Stewart was a gentleman. Never having married, we often invited him to our house. Our children loved having him around. Although in later years our paths went in different directions, we kept in touch via correspondence and too-infrequent telephone conversations. I shall miss him.

*John L. Jaech  
International Atomic Energy Agency  
Vienna, Austria*

## Election Results

According to Article III, Section 6, of the INMM Bylaws, "The Secretary shall notify each member in good standing the results of the election by October 1 of each year." This notice in the Journal shall be construed as having met that obligation.

In accordance with Article III, Section 4, of the INMM Bylaws, the Nominating Committee selected and properly submitted to the Secretary the following candidates for Officers and Members-at-Large for the Executive Committee of the INMM:

*For Chairman*

- John Lemming

*For Vice Chairman*

- Darryl Smith

*For Secretary*

- Vincent DeVito

*For Treasurer*

- Robert Curl

*For Members-at-Large*

- Rokaya Al-Ayat
- Patricia Baird
- Donald Six
- Ivan Waddoups

In accordance with Article III, Section 5, a ballot was mailed to each of the Institute's 731 members, of which 298 returned ballots.

There were no petitions for candidates to be added to the ballot; however, there were write-ins.\*

As a result of the balloting, the Officers and Members-at-Large of the Executive Committee beginning October 1, 1989 are as follows:

*Chairman*

- John Lemming

*Vice Chairman*

- Darryl Smith

*Secretary*

- Vincent DeVito

*Treasurer*

- Robert Curl

*Members-at-Large*

- Kenneth Sanders  
September 30, 1990
- James Tape  
September 30, 1990
- Patricia Baird  
September 30, 1991
- Donald Six  
September 30, 1991
- Japan Chapter Representative
- Vienna Chapter Representative

*Past Chairman*

- Charles Vaughan  
September 30, 1990

\* Write-ins

*Chairman*

- Nicholas Roberts

*Vice Chairman*

- Laura Thomas
- Charles Pietri

*Secretary*

- Charles Pietri

*Members-at-Large*

- Yvonne Ferris
- Thomas Collopy
- Obie Amacker

## Another Successful Gathering of Eagles—The 30th Anniversary Annual INMM Meeting!

You may not be able to present a paper at the 1990 Annual Meeting—if you fail to submit your abstract/summary by the February 1, 1990 deadline.

The success of this year's meeting stressed INMM capabilities and logistics skills to the breaking point. We will definitely limit the number of papers to be presented next year and undoubtedly reduce the number of sessions. This year, 226 papers were presented—an all-time record—but then we have said that each year for the past five years, too. There were 783 attendees (including family) and 526 meeting participants. We had up to seven concurrent sessions for a total of 31 sessions, 22 posters and demonstrations, and 29 exhibitors—all within three days. The bulk of the papers were authored (or co-authored) by representatives from the following organizations: IAEA (13), LANL (19), LLNL (13), Sandia (39), Westinghouse SR (18), and USDOE (18). There is, of course, some overlap in these figures arising from co-authorship.

What a way to celebrate the Institute's Annual Meeting Thirtieth Anniversary!

Each year we've tried to improve our Annual Meeting program, meet the needs of our limited community, and attract others to the INMM family. Although the Technical Program Committee is, in itself, its severest critic, we always solicit comments from our attendees but never seem to get suggestions for major improvement in our technical program activities. This year the Committee formalized the critique process with a tear-out form in the Final Program. (We also sent inquiries to Session Chairmen.) We received 26 replies—less than a 5% sampling of the total meeting participants. Our statisticians would say that this response was probably too small to make definitive conclusions but perhaps significant enough to take into consideration. (Yvonne Ferris would undoubtedly say that most attendees,

by their lack of formal response, were highly satisfied and who—but another statistician—would dare to argue with Yvonne?) Here are the results summarized in a qualitative manner:

Most participants reporting found the variety of papers presented, hotel accommodations and services, meeting location, rooms, facilities, Final Program, Chairman's Reception, banquet, onsite registration, spouses amenities, Speakers' Breakfast, exhibits, and posters/demonstrations—acceptable to outstanding. Two respondents (probably West Coasters!) said the Speakers' Breakfast was too early. Several found the Plenary Session unacceptable while the remaining 85 percent was evenly divided between acceptable and outstanding. It's unfortunate that no reason for dissatisfaction was given—tell us, specifically, what topics and who you want to hear. The committee meeting dates, times, and accommodations were generally acceptable or better. We hit the jackpot with responses on the sessions: split decision on number of sessions ("just right" to "too many"); length of meeting responses varied 2:3 from "too short" to "just right"; number of paper responses ranged 3:1 from "just right" to "too many". Several attendees commented that the Posters/Demonstrations Session (organized by Roy Cardwell) were great but needed more attention to logistics and scheduling. (We're making plans to do just that for the next meeting.) Some general comments about the banquet: excellent food, good location, fine fellowship, and short speeches.

The Technical Program Committee and others got a lot of good verbal comments about the quality of the papers, the hotel, and the meeting, in general. (Hardly anyone likes to tell you bad stuff face-to-face.) To those of you who stopped by to give us your views, my thanks; to those who made the effort to complete the cri-

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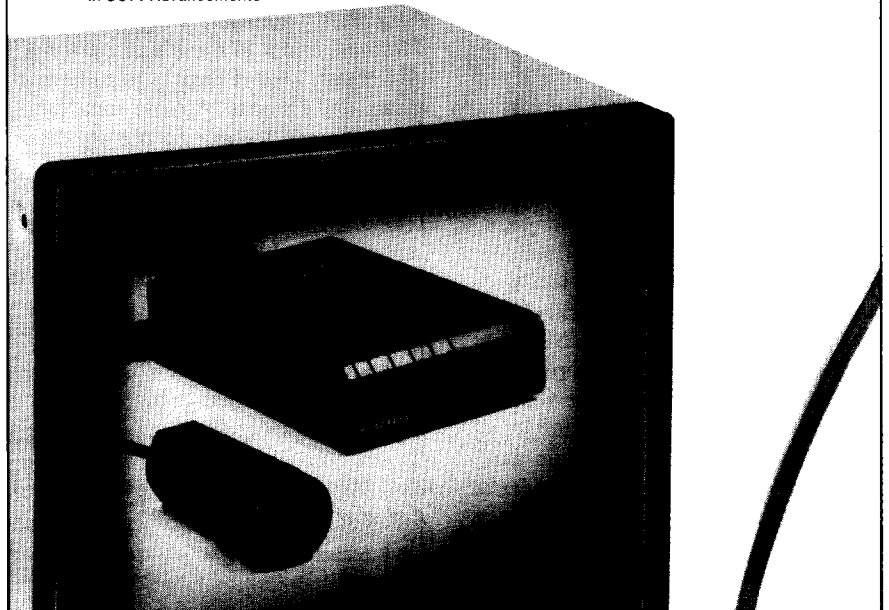
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tique form and write letters, in detail, I thank you profusely. Our peers considered this meeting to be successful and the major credit has to go to the participants—the speakers, authors, and session chairmen whose effort and dedication provided the substance and the sizzle!

Although it was a great meeting, not everything went the way we had planned. We were fortunate, through the behind-the-scenes efforts of Ken Sanders, to get Richard T. Kennedy, Ambassador at Large, as our Plenary Speaker, but we were not able to get his Soviet counterpart, Ambassador Roland Timerbaev. (We had originally planned a duet on non-proliferation from both the United States and the Soviet Union perspectives—a more than interesting dialogue.) Nevertheless, Ambassador Kennedy not only gave an illuminating talk but a very revealing private interview later; we plan to publish the interview in the January 1990 issue of the *Journal*. Surprisingly, the Ambassador actually stayed for the entire meeting; he attended the Chairman's Reception, some of the sessions, the exhibits, and the banquet. We know that he and his wife certainly enjoyed the meeting; he wrote later saying that he was honored by the Institute's invitation and doubly honored by the cordial reception!

Several days before each Annual Meeting takes place, the Technical Program Committee begins to plan the next one. (I guess we figure that there's no more good—or harm—we can do to the current one!) Plans for the 1990 meeting include: a full session on arms control and treaty verification (we now have an INMM Committee exploring this topical area), another series of waste management sessions to stimulate and attract participants (Ed Johnson carried a major effort in putting together this year's program), new technology transfer activities, and explosives detection technology (some exciting directions and applications). But we

need your ideas—What would you like to see and hear?

Another innovative venture we hope to introduce in the coming year is the submission of abstracts and summaries by authors to INMM via computer word processing files on floppy disks to expedite the production of the preliminary and final meeting programs, and to reduce costs. We are working with the INMM HQ staff to define a practical system that we can all use.

I can promise you another fine meeting next year, unequivocally. What I can't promise is that we can be fortunate enough to have the superb hotel accommodations and services we enjoyed this year—no matter they will be great. Again, much thanks is due to the INMM Headquarters Office management and staff for their efforts in the arrangements, logistics, and coordination of the meeting. And, finally, as I do each year, I sincerely appreciate the collective efforts of the Technical Program Committee who worked harder than ever this year to put on the meeting for the Institute: R. Al-Ayat, J. Arendt, W. Belew, K. Byers, R. Cardwell (posters/demonstrations), J. Clark, C. Hodge, W. Lamb, N. Roberts, C. Sonnier, J. Tape, L. Thomas, and J. Williams. (I personally thank Darryl Smith, John Lemming, and Dennis Mangan for their support—and for letting me cry on their towel when things got hectic!) My apologies to the hundreds of others that I have not specifically recognized who helped make the meeting a winner.

See you in 1990! Please get those abstracts in on time!

*Charles Pietri, Chairman  
INMM Technical Program  
Committee  
U.S. Department of Energy  
Argonne, Illinois*

## Professional Recognition Program Committee

The Professional Recognition Program Committee met in July of 1989.

### Attendees:

Ken Sanders, Terri Olascoaga, Don Jewell, Bill Cook, Wendell Belew, Leon Green, Dick Duda, Paul Ebel, and Takeshi Osabe

### Discussion Subjects:

#### 1. Committee Charter

The charter, as approved by the Executive Committee was discussed. The committee charter is as follows:

"The Professional Recognition Program Committee is to develop, implement, and maintain a program that will increase the awareness of achievement of INMM members in the areas of nuclear materials management. This program shall contain recognition levels for INMM members who are contributing to the advancement of the general profession of nuclear materials management. The program shall be separate and distinct from the individual service awards program."

#### 2. "Straw Man" Recognition Program Previously Created by Ad Hoc Committee

This committee discussed all aspects of the "Straw Man" program and also reviewed two sheets of written program suggestions (from Dick Duda and Leon Green). As a result of the discussion, the committee chairman (Paul Ebel) prepared a draft which incorporated most of the major ideas. That draft is currently being reviewed by the committee members.

#### 3. Professional Recognition Program Major Ideas

The committee members made many suggestions for the features of the program. Some of the major attributes suggested were:

1. Keep the program simple, easy to fill out, and easy to administer.
2. Have the application for recognition consideration be a part of the yearly membership application so

- all members can be evaluated without having to fill out another form.
3. Create 3 to 5 recognition levels and provide different colored badges for each level to be used at the annual meeting and at all other INMM activities throughout the year.
  4. Use weighting of different activities to increase participation in particular targeted INMM activities.
  5. Include recognition in recent activities (last 5 years) in MC&A, C&S, Physical Security, and Waste Management.
  6. Have the committee evaluate every INMM member every year just before the annual meeting. This will involve evaluating about 900 members. *The evaluation of the Level I and II members will be nearly automatic, and can be done by the INMM Staff.* The evaluation of Levels III and IV will be more subjective and will require a meeting of the Professional Recognition Program Committee.
  7. Budget some money to support the administrative activities of the committee and to purchase the badges and certificates.
  8. Have the level rating system reward community outreach as well as participation in INMM specific activities.
  9. Create a certificate for each level of recognition.
  10. Publish the final program plan in the INMM Journal so members can prepare to complete the forms.
  11. Do not give credit for education levels because members can make major contributions without a high level of education (and vice versa).

12. Have the evaluation take into account the effects of cultural norms of participants such as in the Japan Chapter and the Vienna Chapter.
13. Do not charge a fee for submission of an application for recognition evaluation.

#### **4. Draft of INMM Professional Recognition Program Forms**

After the committee meeting, the chairman created a new draft of the "INMM Yearly Membership Questionnaire" and a table of the "INMM Typical Recognition Level Requirements." A copy of those documents are attached to these minutes. The committee members are asked to comment on those documents and on the program as implied by the forms. Please send the comments to the committee chairman by December 1, 1989, for consideration and preparation of a final program.

#### **(Draft) "INMM Yearly Membership Questionnaire"**

This questionnaire would be incorporated into the membership application so the data would be available on all members. All members would be evaluated by the committee each year prior to the annual meeting of the INMM. At the annual meeting, members would receive their recognition, their different colored badges, and their certificates. Those who are unable to attend would be mailed a certificate and a plastic, colored badge for use at all INMM meetings (local, regional, or international).

#### **(Draft) "INMM Typical Recognition Level Requirements"**

These guidelines would be used by the committee to evaluate the membership questionnaires. These guidelines would be changed every few years to reflect the current emphasis desired by the INMM Executive Committee. The Levels I and II would be nearly automatic and could be determined by the INMM Staff. The Levels III and IV would be more

subjective and require an INMM Professional Recognition Committee meeting to decide on the levels. Committee comments and the actual committee deliberation and evaluation process will not be made generally available. There will be no quotas for each level. The decision of the committee will be final for that year, but an appeal can be made in writing to the committee for consideration in the following year.

*Paul E. Ebel, Chairman  
INMM Professional Recognition  
Program Committee  
BE Inc.  
Barnwell, South Carolina*

## Japan Chapter

### 1. 1989-1991 New Officers of Japan Chapter

The following officers were elected for the 1989-1991 and approved by the 29th Executive Committee Meeting which was held October 3, 1988 in Tokyo.

*Chairman*

Hirata, Mitsuho (NUSTEC)

*Vice Chairman*

Haginoya, Tohru (NMCC)

*Secretary*

Osabe, Takeshi  
(Japan Nuclear Fuel, Co. Ltd.)

*Treasurer*

Seki, Yoshinobu  
(Mitsubishi Metal Corp.)

*Member at Large*

Mori, Kazuhisa (JAIF)

Kurihara, Hiroyoshi (PNC)

Hara, Reinosuke

(Seiko Instruments and Electronics, Ltd.)

Iwamoto, Harumitsu

(Nuclear Fuel Transport Co. Ltd.)

### 2. Executive Committee Meeting

The 30th, 31st, 32nd, 33rd, and 34th Executive Committee Meetings have been held at the NMCC Headquarters in Tokyo on November 7, 1988, December 23, 1988, March 10, 1989, June 2, 1989, and June 8, 1989, respectively. Financial Report (see attached) and the Business Report for the 1987-1988 were reviewed and authorized, then the plan of chapter's activities as listed below for the 1989-1990 have been discussed and approved at the 30th Meeting. Mr. Hiroyoshi Kurihara was elected as a Program Chairman of the 10th Annual Meeting of the Chapter.

### 3. Plan of the activities for the 1989-1990

#### 3.1 Annual Meeting

The 10th Annual Meeting was held in Tokyo on June 9, 1989. The meeting program and photographs will be featured in a special commemorative section of the January 1990 issue of *JNMM*.

#### 3.2 INMM Journal Translation Services

Abstracts of the papers and messages from the INMM of the Journal have been translated into Japanese and distributed to members as a chapter's new activity being served from Volume XVII, Number 1, October 1988 issue.

### 4. Membership

Members of the Japan Chapter as of the end of June, 1989 are 145 in total, increasing since June, 1988 (124 in total as of the end of September, 1988). Members are from the following organization; Scientific Institution—59, University—6, Electric Utilities—4, Industries—70, Government—5, Journalist—1.

## Physical Protection

The presently scheduled and planned activities of the Technical Working Group on Physical Protection are listed below:

- Workshop, "Package Search Techniques," is currently being considered, but has not been tentatively scheduled. Such a workshop would concentrate on better and more effective methods of searching packages which enter restricted areas. If you have an interest in such a workshop please contact Donald Kasum, Nuclear Regulatory Commission (301) 492-3379.
- Workshop, "Security Personnel Training," another workshop on this topic is being considered for the spring of 1990.

Workshops on other subjects of interest to physical protection personnel will be considered if enough interest is expressed. Additional details about the group activities are given below.

### General

I see a general decrease in funding and interest in Physical Security throughout the Department of Energy. The reason is twofold, the DOE had upgraded most of their sites already and the bulk of the money is now being directed to *Environmental, Safety, and Health (ES&H)* issues. Therefore, there will probably be fewer Workshops on Physical Security and there will be fewer attendees at the Workshops which are held. To supplement this loss in revenue to the Institute, we should strive to fill the ES&H needs of the community.

### Detecting Outsiders and Insiders by Integrating the Elements of Delay, Intrusion Detection, and Entry Control into Physical Security Systems

Workshops on this general topic area have been very interesting and well-attended in the past. The most recent one was held November 6-9, 1989, at the Cavalier Hotel, Virginia Beach, VA. James C. Hamilton, (614)

897-2204, Martin Marietta Energy the workshop Chairman. Approximately 50 persons attended the workshop.

### Security Personnel Training

The next workshop on this topic will probably be scheduled in the spring of 1990. Fred Crane, ERCI is helping to locate Workshop Co-Chairmen.

*James D. Williams, Chairman  
INMM Technical Working Group  
on Physical Protection  
Sandia National Laboratories  
Albuquerque, New Mexico*

## Materials Control and Accountability

The Technical Working Group for Materials Control and Accountability is sponsoring a technical workshop entitled "Assessing Safeguards Performance."

This workshop will focus on some of the current issues in safeguards today, namely the challenges of assessing safeguards performance and resolution of anomalies. The meeting will be held December 4-6, 1989 at the Sheraton Gunter Hotel in San Antonio, Texas. The workshop format will consist of several sessions in which a few presented papers will be followed by smaller group discussions. Each discussion group will be facilitated by a moderator and designed to cover the same topics, allowing each attendee to address the same issues.

Status: The hotel contract is signed, and the workshop brochures were mailed to INMM members the week of October 9. Potential speakers and group moderators are being contacted with commitments for participation from approximately half of the needed speakers and moderators received to date. The current list of

speakers and moderators is attached. A preliminary budget was prepared by Barb Scott based on an assumed attendance of 50 members and 20 non-members with a bottom line of income over expense of \$8,921.

### Technical Workshop Assessing Safeguards Performance

*Safeguards Performance Objectives  
(invited speakers)*

Speakers  
Gary Carnival—RFP  
Walt Kane—TSO

Moderators  
Joe Rivers—DOE/HQ  
Don Jewell—DOE/CTA  
Ken Byers

#### *Safeguards Modules*

Speakers  
Tom Williams—DOE/SRO  
Don Emon—DOE/HQ

Moderators  
Martha Williams—NRC

#### *Anomaly Resolution*

Speakers  
Alan Lamont—LLNL  
Brian Smith—Battelle Richland  
Mike McNeely—Y-12

Moderators  
Fran Davis—Westinghouse Savannah Co.  
Rich Strittmatter—Los Alamos National Lab

## Waste Management

The following summarizes the activities of the Technical Working Group on Radioactive Waste Management for the period July 1989 through October 1989:

1. The preliminary program for the INMM Spent Fuel Management Seminar VII was developed and candidate speakers are being contacted. This meeting will be held at Loew's L'Enfant Plaza Hotel, Washington, D.C., January 17-19, 1990.
2. The TWG developed its proposed budget for the 1989-1990 fiscal year and forwarded it to the INMM Treasurer.
3. E.R. Johnson attended a meeting of the Steering Committee for the forthcoming International High Level Radioactive Waste Management Conference and Exposition at UNLV in Las Vegas on October 18, 1989. The conference which is being sponsored by a number of technical societies, including INMM, will be held April 8-12, 1990 at Caesar's Palace, Las Vegas, Nev.

The next meeting of the Steering Committee is scheduled for December 8, 1989 in Washington, D.C.

N.B. McLeod attended a meeting to select papers for the conference on October 16-17, 1989 in Las Vegas.

*E.R. Johnson, Chairman  
INMM Technical Working Group  
on Waste Management  
E.R. Johnson Associates  
Reston, Virginia*

# Before NBL

■  
*Clement J. Rodden*  
*Founding Director*  
*New Brunswick Laboratory*  
■

## ABSTRACT

*A first-hand historical overview is given of some of the nuclear material measurements and measurement problems that were addressed prior to and at the beginning of the Manhattan Project.*

When Bing first asked me to address you at the 40th anniversary of the New Brunswick Laboratory, my first reaction was that, due to failing eyesight, I was unable to travel. He then suggested a videotape, but an 86-year-old man is nothing to look at. Finally, an audio tape was agreed upon. This type of presentation has the advantage that the chairman can stop it by the flick of a switch. I hope you will bear with me for some ancient history, some of which may not appear pertinent.

During the early 1930's, I did my thesis on the magnetic susceptibility of certain rare earth elements. But, owing to the job market, I thought I would do better in micro-analysis. There were three Austrian chemists who specialized in micro-analysis at New York University—Alba, Pekla and Nedel. [In those days, we had no videotape instruction; one learned by actually doing the work.] In addition to being a teaching fellow, I was able to absorb enough so that I got a job as a micro-analyst at George Washington University Medical School in Washington D.C. After about two years, Harry Bright of the Chemistry Department of the National Bureau of Standards came in one day and asked if I would like a job as micro-analyst at the Bureau. Even though the salary of a P-1 was \$500.00 less than I was making, I decided to go to the Bureau, as my interest was in inorganic chemistry.

After a few years at the Bureau doing inorganic and organic micro-analysis, I developed a method for the spectrophotometric determination of certain rare earths. In January 1940, we received portions of graphite electrodes from Columbia University for the determination of free and combined hydrogen by microchemical methods. In March 1940, uranium power was analyzed for hydrogen and absorbed water. In December 1940, the Bureau started work on uranium isotope separation and the Chemistry Department prepared the samples.

In January 1941, Fermi, who had been running some neutron absorption tests on graphite, had come to the conclusion that the major absorption of neutrons was by boron. Fermi had requested boron analysis from a commercial laboratory, but the results did not confirm his conclusion. This was so important that Fermi asked Lyman Briggs, the Bureau Director, and chairman of the Uranium Committee, to see what the Bureau could do. With the help of the Bureau's glass blower who made some quart flasks, a satisfactory method was developed and the results confirmed Fermi's conclusion. It took but a month, and from then on, Section Four—Chemistry was in business.

Graphite was purchased from U.S. Graphite; we received samples from all steps of their operation. The final product showed two parts-per-million (ppm) boron which came mostly from the foundry coke. Dana Mitchell of Columbia and I went to U.S. Graphite in Saginaw, but no great process was made on improving the graphite. However, during lunch, one of their engineers said that he had run out of foundry coke at one time and had substituted petroleum coke and that the resulting product was satisfactory. Owing to the fact that the company was making electrodes for magnesium production, no change could be made (in the production process).

Shortly after, contact was made with Spear Carbon that made graphite from petroleum coke. We analyzed samples from all steps of the production toward the end of 1941. The boron concentration was less than one ppm.

From early 1941, Szilard used to come down to the Bureau, and in the course of the conversation about uranium metal, I told him I could make some massive uranium metal, since I had been at the University of New Hampshire in 1926 when Prof. Charles James had made massive uranium metal by reducing uranium tetrachloride with calcium. I told him I had made massive molybdenum in 1929 (using a similar process) at the University of New Hampshire. Dr. Briggs arranged that I could use a small building at NBS for this purpose. The metal was made and its melting point was found to be about 1100° C. This was about 750° below what was in the literature. This was startling, but in the right direction. The British were skepti-

cal, and a small portion was sent for them to melt. About this time, measurements of powdered uranium metal from Metal Hydride Co. showed high boron concentration. It was found that the usual calcium metal of commerce was highly contaminated with boron. We decided to distill the calcium; this produced essentially boron-free calcium.

In 1940, Scribner and Mullin at the Bureau developed a spectrographic method for the analysis of uranium oxide using gallium oxide as a carrier. This method was applicable to most all impurity elements except the rare earths, which have the highest neutron capture cross-section in the whole periodic table. Since most of the ores of uranium contain rare earths, it was necessary to solve this problem. At first, uranium nitrate was repeatedly crystallized to separate the rare earth fraction. This was not too satisfactory. Jim Harper of the Bureau extracted uranyl nitrate with ether and found his procedure separated rare earth and many other impurities. This process proved a godsend and Mallinckrodt Chemical Co. used it for purifying uranium on the commercial scale. We also used this procedure to separate rare earths which then could be analyzed spectrographically.

In 1942, Spedding at Ames used a method similar to that of James for making massive uranium metal and samples of uranium turnings were received at NBS until Ames got their analysis program going.

The quality of the uranium ore supply was always a problem. Early on, some came from the Belgian Congo and from Canada. These sources had impurities, the worst of which were the rare earths. If you consider that one of these, gadolinium, had a danger coefficient of about 8,000, compared to 2,000 for boron in uranium metal, you see the magnitude of the problem. The ether extraction of uranyl nitrate was the solution to this problem.

The Manhattan District of the Corps of Engineers took over in late 1942. The Bureau was a member of the Central Laboratory with the Met Lab of Chicago, the Frick Lab at Princeton under Furman, and the Spectrographic Lab at MIT with Harrison and Rockwell Kent III. This group supplied contractors with needed help through the war. The Met Lab had to back out in August 1943, because of other work starting on plutonium. This kept up during the war. The younger generation should read Atomic Energy for Military Purposes by H. D. Smythe to get an idea of the impossible problems that were solved.

There were less impossible problems also to be solved. On one occasion, we sent a group to Colorado to check on uranium ore being supplied from that area. We flew in on a Piper Cub. The lab had been set up in a hurry. It was winter and one morning the water and drain lines in an open cut were frozen. That didn't bother the contractor; a little gasoline and match solved that problem.

The Analytical Chemistry of the Manhattan Project took a fair amount of time, especially with clerical personnel supplied by the Army. The clearance problem necessitated much repetition of papers, but when you considered the scope, it wasn't too bad.

After the war, the Bureau was not the place for uranium work. In 1948, it was decided that the work should be moved. A former Navy pump factory building in New

Brunswick, New Jersey was obtained and converted. This meant chemical, spectrographic, mass spectrographic, radiochemical and electronics laboratories; later on (in 1959), a plutonium laboratory was added. Essentially all the work being done at the Bureau was moved in 1949, along with a large part of the Bureau personnel.

The emphasis was on accounting for quantities of uranium and plutonium in the nuclear fuel cycle. NBL was the principal laboratory for this work. One of the first jobs at NBL was to publish *The Analytical Chemistry of the Manhattan Project*, followed by *The Analysis of Essential Nuclear Reactor Materials* in 1964 and *Selected Measurement Methods for Plutonium and Uranium in the Nuclear Fuel Cycle* in 1972. These were all cooperative works done by dedicated workers. More international work was started and oxide continued to be supplied by those at the Bureau.

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Clement J. Rodden received his B.S. in chemistry from the University of New Hampshire and his M.S. from New York University where he prepared a thesis on the magnetic susceptibility of certain rare earth elements. He joined the National Bureau of Standards (NBS) in 1937 where his expertise in microanalysis made early contributions to the analysis of nuclear materials. In 1949, Dr. Rodden led a group of scientists from NBS to a laboratory that was established by the Atomic Energy Commission in New Brunswick, New Jersey, where he served as NBL's Director until his retirement in 1970. He authored or edited a number of landmark references on the analytical chemistry of uranium and plutonium that remain in wide use today.

# Silver, Copper, and "Honest-to-God Copper"

■  
Glenn T. Seaborg  
Associate Director-at-Large  
Lawrence Berkeley Laboratory  
University of California  
Berkeley, California  
■

## ABSTRACT

*The discovery of the transuranic element now known as plutonium and its subsequently scaled-up production during the Manhattan Project was enabled by many people solving difficult chemical problems. The early history surrounding the discovery of plutonium is described.*

This 40th Anniversary of the New Brunswick Laboratory reminds me that I first came across your founding director, Clem Rodden, more than 40 years ago. Our paths crossed early in 1943 when I was working at the wartime Metallurgical Laboratory and he was at the Bureau of Standards. We had a problem, at that time, of preparing plutonium in a high state of purity. It seemed to be necessary to remove light element impurities down to less than a part-per-million, and I remember that I got in touch with Clem Rodden in order to enlist his help in how to solve this very difficult problem.

This anniversary comes very close to the 50th anniversary of the discovery of nuclear fission, and also close to the 50th anniversary of the discovery of the first transuranium elements which took place in 1940 and 1941. I think it might be proper to reminisce a little bit regarding the method we used for the analysis of plutonium in those earliest days. We measured the alpha radiation from plutonium using a proportional counter and then, very soon thereafter, an ionization chamber connected to a linear amplifier here at the Berkeley campus of the University of California, working in room 303 of Gilman Hall.

The first identification of plutonium came as a result of a bombardment that we made on December 14, 1940. We bombarded uranium oxide with deuterons in the 60-inch cyclotron. Actually, what we did is just sort of plastered the uranium oxide onto a copper backing plate and then, after the end of the bombardment, dissolved the uranium oxide and made our chemical separation. Participating in this discovery experiment were Arthur Wahl, Joseph Kennedy and Ed McMillian. We found this alpha particle radioactivity which we suspected was due to the new element with the atomic number 94. We actually were able to chemically identify the element in an experiment

that we conducted during the stormy night of February 23, 1941, here in room 307 on the Berkeley campus. This room has been cited as an historic landmark as a result of this experiment.

Actually we didn't find the isotope with the mass number 239 in the first experiment, we found-synthesized and identified an isotope with the mass number 238, but it was very soon thereafter that we succeeded in identifying the important isotope, the fissionable isotope, plutonium-239, the isotope of course, that your laboratory is so much concerned with. Emilio Segre joined us in the experiments that led to the identification of plutonium-239.

It might be interesting to reminisce a bit about the naming of this element. The work was carried on under the self-imposed secrecy in view of its potential implications for national security. We actually used code names at that time for element 93 which we referred to as "silver" and for element 94 which we referred to as "copper" and this worked fine until for some reason it became necessary to use real copper in our work and since we continued to call element 94 copper in our work, on occasion we had to refer to the real thing as "honest-to-God copper." The first time a true name for element 94 seemed necessary was in writing the report to the Uranium Committee in Washington in March of 1942. I remember very clearly the debates within our small group as to what that name should be. It eventually became obvious to us that we should follow the lead of Ed McMillian who had named element 93 neptunium after Neptune, which is the next planet after Uranus. Thus, we decided to name element 94 for Pluto, the next planet beyond Neptune, but this is a little known story. It seemed to us that one way of using the base Pluto was to name the element "plutium." We debated the question of whether the name should be plutium or plutonium, we liked the sound of plutonium so much better, that we finally decided to take the name that sounded better. Then there was the matter of the need for a symbol, and here too, a great deal of debate was engendered because although the symbol might have been Pl, we liked the sound Pu, and for the reason you might suspect. So we

decided on Pu, and I might add we expected a much greater reaction after it was declassified, than we ever received. The first weighing of plutonium took place after we had moved to the Metallurgical Laboratory at the University of Chicago, on September 10, 1942. This sample was an oxide of plutonium which weighed 2.77 micrograms and the weighing took place in Room 405 of the Jones Laboratory on the University of Chicago Campus. This weighing was performed with a balance made of quartz fibers so thin that you could hardly see them, and it was performed by Burris Cunningham and Louis Werner. Room 405 at Jones Laboratory has also been named a National Landmark.

I must say that you have come a long way in your methods of analysis for plutonium since those early days. I think that the work being carried on at the New

Brunswick Laboratory is very important. I think it is very fitting that you observe, in this manner, the 40th anniversary of the founding of the laboratory and I'm very pleased to have been asked to play a small role in the observance of the 40th anniversary.

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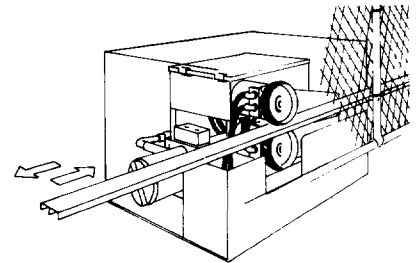
Glenn T. Seaborg received his B.A. in chemistry from UCLA and his Ph.D. from the University of California, Berkeley. He was a co-discoverer of plutonium and established the basis for the position of the actinide elements in the Periodic Table. He served as Chairman of the Atomic Energy Commission during the early development of the peaceful uses of nuclear energy. Dr. Seaborg is currently Associate Director-at-Large of the Lawrence Berkeley Laboratory of the University of California.

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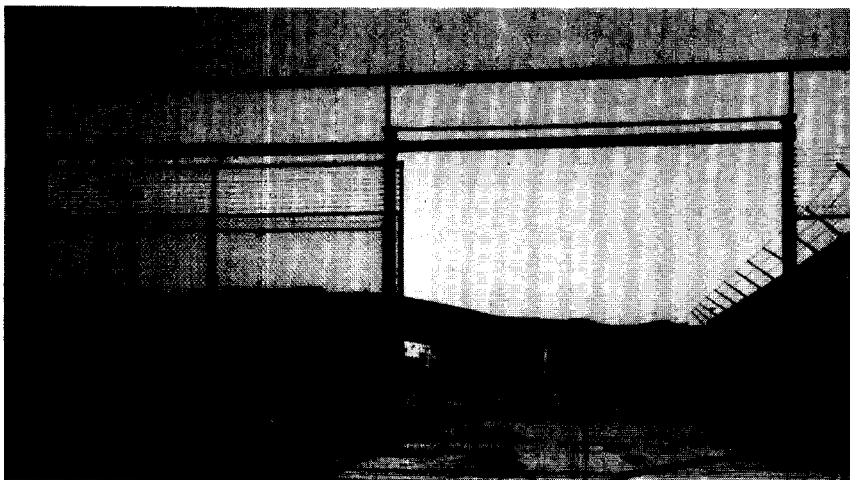
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# In The Beginning— Measurements of Uranium

James C. White  
Oak Ridge National Laboratory, Retired  
Oak Ridge, Tennessee

## ABSTRACT

*After World War II, Oak Ridge continued to be involved in measurements of uranium materials, both for the weapons program and for early reactor development programs. These early tasks, and some of the people involved in them, are recalled.*

I can't help but think that, if the decision had gone differently back 20-some years ago, we'd be holding this meeting in Oak Ridge because we had competed with a number of other localities for hosting the new New Brunswick Laboratory. If that had happened, we'd be looking at Dogwood trees and azaleas; that sure beats the bare trees here in Illinois right now.

In looking at this "In the Beginning," and looking at the other speakers here, Bing, you should have provided us with a beard, a rope, and a shepherd's crook. After hearing the real old days, the "Adam and Eve Day" from Clem (Rodden) and Seaborg, what I want to do is reminisce and tell you some of the experiences that impressed me over the years in those early days of the uranium business.

My first encounter with uranium was in high school chemistry class when our chemistry prof showed us an ashtray that was colored orange, and pronounced that to be due to the presence of uranium. He added that was the only known use for uranium at that time. That was about 1937 or 1938—in that order.

I went through chemistry at Indiana University and I don't recall ever hearing the word "uranium." I was in the service on an island in the Pacific when I heard that the atomic bomb had been dropped on Hiroshima and that uranium had been used. I guess that was the second time I remember the word.

I went to graduate school and really didn't hear much about uranium there either, until I ended up in Oak Ridge. In those days a newly admitted Ph.D. was supposed to know everything; when I came to Oak Ridge, I didn't know anything about uranium, but I was put in charge of a small group to oversee uranium analyses. The first thing I did was to hustle myself to the Reports Office (of course, they were highly classified) looking for anything on the chemi-

cal analysis of uranium. I couldn't find a thing! All uranium was known as Tuballoy. (I've forgotten exactly how the word came into being—perhaps someone here can tell us.) There was no symbol cataloged for uranium; the symbol used was "T"—it took a little getting used to.

In addition to that, one couldn't throw away any solutions that remotely contained uranium. You had to put it in some big plastic containers at that time. They were different sizes because there were different enrichments—depleted, normal and enriched—that you had to keep separate. That was my first introduction into the world of uranium accountability, and that stayed with me for the next 36 years until I retired.

I recall one incident in particular about uranium accountability. One of my best friends was in charge of the chemistry program for the Aircraft Nuclear Propulsion (ANP) Program. For those of you too young to remember that, the idea was to build a reactor in an airplane that would fly until the fuel became depleted, then land for refuelling. (That concept would never "fly" today, I'm sure.) However, the Molten Salt Breeder project evolved from ANP. It was one of the first of the circulating high-temperature fuel reactors. The fuel was eutectic mixture of sodium, beryllium, zirconium and uranium fluorides. Somehow, several kilograms of material had gotten lost; no one could find it. We analyzed everything possible; samples—of all types—kept pouring into the laboratory in an effort to locate the material. It finally got to the point where they brought in the FBI to watch everything we did from the taking of the sample right through to the final determination. In those days we had mechanical calculators. One would enter, for example, 32.61 milliliters of titrant (two significant figures beyond the decimal) and 2.6432 grams/ml; then push a button and numbers would spin around like a slot machine and out would come a number with 15 numbers to the right of the decimal. We would write down the final determination, say, 86.19 grams—two significant decimal places. The Agent could not understand why we threw out so many numbers in reporting the result. We gave him a short crash course in significant figures, which he failed to comprehend. He lit-

erally went bezerk when duplicate samples failed to give the same answer. At times, I thought my career was going to end much sooner than I had anticipated from the threatening mutterings of the Agent about what happened to people who lost or stole uranium.

The Homogeneous Reactor Project (HRP) developed a reactor fueled with a uranyl sulfate solution that circulated through the core surrounded by a thorium oxide slurry. The reactor concept could not surmount the corrosion difficulties, but it had many interesting uranium analytical problems involving macro concentration of uranium. The Raw Materials Program was designed to win uranium at the few hundred parts-per-million level from ore found primarily in the Western states. The samples were mainly from research into organo-nitrogen and phosphorous compounds that could preferentially extract the uranium from the ores. These of course were levels in the micro range. Thus we had the gamut of the concentrations to work with.

This range in concentration levels led to my first contacts with the folks who produced standards—the National Bureau of Standards, the US Geological Survey, and of course, the New Brunswick Laboratory. I had worked in a steel mill lab for a few months before I went to graduate school, so I was familiar with standards, but I wasn't familiar with inventory differences. I suppose I learned more about uranium chemistry trying to resolve inventory differences than from anything else. Prof. Hobart Willard, the venerable analytical chemist from the University of Michigan, was a consultant of ours and was very involved in precise uranium determinations.

Being involved in uranium analyses meant being involved in round robins—another term whose genesis I never understood. None of the conference tables were ever round and the only relevance to ornithology was what individuals thought of the folks whose results didn't agree with their numbers. Nonetheless, it was a great way to meet your colleagues and get away from Oak Ridge in order to replenish the necessities of life that were unavailable in Tennessee from the Central Liquor Store in Washington.

Many friendships were made in those days. In 1957 we launched the First Conference on Analytical Chemistry in Nuclear Reactor Technology—which incidentally continues today under a different name and at a different site—in Gatlinburg in the Great Smoky Mountains. Clem Rodden was a featured speaker on the analytical chemistry of uranium and its compounds. I remember the talk even today for its brevity! (We almost went into night sessions.) There were so many parties interested in uranium chemistry from so many countries, that, by the time everyone had his say, we were exhausted. In succeeding years, we had further papers on uranium—in the fuel cycle and recycle for example—but none has stayed in my memory more than that first one. The real value of the conference in those days was that it brought together many analytical chemists from all over the world and stimulated vigorous and worthwhile discussions on many topics. Another topic certain to cause a discussion was whose standard was best. I know we had a supply of very pure uranium

metal that was purer than the NBS  $U_3O_8$  standard—the only problem was that we didn't have very much of it. The US Geological Survey had some standards for fluorimetric analyses, but they were running out too. There was plenty to talk about and plenty of good talkers, too!

The one indispensable text—the analytical chemist's bible—was the *Analytical Chemistry of the Manhattan Project*. Clem Rodden was appointed chairman of the Manhattan Project Analytical Committee in 1945; the committee decided to gather together all the information concerning the analytical chemistry used in the project. That turned out to be a wise decision that I am sure was applauded wherever and whenever analytical chemists gathered. The chapter on uranium analytical chemistry was compiled by Clem Rodden and Jim Warf. It included 459 references which is a slight indication of how thorough the compilation was. The phrase "all you ever wanted to know about uranium and then some" is appropriate. I dare say that this chapter was probably used more extensively by more analytical chemists than any other chapter written in the project and for years to come. Many methods for the determination of uranium were developed, most of which were included in this text. All seemed to have their champions which, of course, led to competition for the method of choice. That struggle continued for years and has been fuel for many a meeting. This is a result of the fact that uranium was probably the most exhaustively studied element, from the analysis standpoint, of all the elements. It is all there in that book. Among those who contributed to this mighty undertaking were the late Prof. Howell Furman from Princeton, who made major contributions to uranium analytical chemistry, Prof. "Buck" Rogers, now Professor Emeritus at the University of Georgia, and many others from Oak Ridge. Albert Smales, from the UK, became such a baseball fan while at Oak Ridge that he kept up with the league standings even after he returned to England. For those who did not know Albert, he was a very imposing figure who did not suffer fools lightly. Fools were often those who deigned to disagree with him. He was a superb analytical chemist. How he would relate to the oversight that today's chemists endure is something to ponder with wonder!

Oddly enough by today's standards, money wasn't much of an issue for a long time. When Oak Ridge projects ran low on funds, Alvin Weinberg went to Washington and got more. Still we were expected to keep costs down since analytical work was an overhead item. There were thousands of samples of various kinds to be run requiring different methods of determination. This was particularly true of the Raw Materials Project. Speed was of the essence. Often the chemists literally camped in the analytical lab watching their samples like a mother hen. Since we had a young, mostly female, technician work force and young male chemists, there were some interesting supervisory problems to resolve. Some of my fondest memories are of the technicians we trained to do the fluorimetric determinations of uranium. I recall C. D. Susano, my boss in those days, telling me about a crackerjack technician he was hiring. He discovered her in the food line of a popular cafeteria in Knoxville. She was a whirling dervish who literally

ran rather than walked in the lab. She retired last year and was still quick as a cat. Coincidentally, she was a great athlete whom I saw playing women's baseball for the Fort Wayne Daisies in 1946!

Ethyl ether was used in those days to extract uranium—a rather dangerous step. Perchloric acid was used to dissolve uranium ores and would spill over onto a plywood board which held the platinum dishes in which the samples were dissolved. Periodically, the ether would flame up and, on occasion, the plywood would ignite and we'd have a lively conflagration. When the building that housed our labs was torn down years later, the health physicists said the debris would have to be buried and the safety people breathed a sigh of relief. That debris now is, in part, the subject of environmental cleanup that is expected to cost billions of dollars at Oak Ridge alone. There are now thousands more samples to be run for years to come. It is ironic that the element uranium that was virtually unknown until the Manhattan Project began in the 1940s and was the subject of so many analytical determinations has had renewed notoriety and will continue to be a heavily analyzed element. It can be said that uranium is the analytical chemist's best friend.

I suppose to many people today it will come as a shock that we didn't have quality assurance in the early days. What we had was called quality control and we survived very nicely. We did have statisticians, but I recall that most of them were also analytical chemists. We had uranium controls of all sorts, in which NBL played a key role. The kind of statistical quality control we practiced was what was taught in quantitative analysis and accounted in no small way for the large number of determinations that were done. Duplicates were de rigueur and triplicates were not all uncommon. Although there was relatively little confusion between "accuracy" and "precision," we did encounter the interchangeability of the terms "standard deviation" and "coefficient of variation" from time to time. In 1963, Ralph Jones of the AEC Division of Nuclear Materials Management compiled the report *Selected Measurement Methods for Plutonium and Uranium in the Nuclear Fuel Cycle* (TID-7029) that included a lengthy and complicated chapter on Statistics of Measurement that helped get folks together. The report is an excellent follow-up on the progress made from the time that Clem Rodden's committee compiled their series. Later, the professional statisticians took over and they ruled the roost—even to this day. A certain amount of obfuscation is desirable in any scientific endeavor to prevent clear understanding by laypersons, let alone scientists, and the statisticians provide that very well. I observe that when the press (and the public) try to understand uranium accountability.

There are a lot of fine people that were in this business, and I'm really pleased today to see a number of them. It's too bad that some of the others that have now gone on and have not been able to have such an opportunity to reminisce such as this. We owe an awful lot, and I don't think the general public or even the general scientific public, really appreciates all that was done in those early days. There hasn't been a great deal of real development in the

field of uranium analytical chemistry since those days. It shows the thoroughness of the work that was done. Instrumentation now is much better, but the basic chemistry that was developed in those days is still current and working today.

Bing, I thank you for the opportunity, and the invitation. It's just a joy to see so many people I haven't seen for many years. Thank you very much.

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James C. White received his B.S. in chemistry from Indiana University and his M.S. and Ph.D. from Ohio State University. From 1950 to 1976, he was with the Analytical Chemistry Division of the Oak Ridge National Laboratory—serving as Division Director from 1972 to 1976. From 1976 until his retirement in 1986, he served in several technical management positions for the ORGDP and Y-12 Plants. He chaired the IUPAC Commission on Radiochemistry and Nuclear Techniques.

# Measurements of Plutonium

■  
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■

## ABSTRACT

*Based on reviews of the early and recent literature concerning comparative measurements of plutonium, sources of measurement error are discussed—in particular those related to mass spectrometric isotope dilution.*

When Jim (White) was talking about how far back he went concerning the analytical chemistry of uranium, I tried to recall when my first nuclear experience was. I think it was in freshman chemistry in college. We had something you held up to the light and looked through it. You saw occasional flashes of light inside. They told us that was caused by radioactivity. The instrument was called a spintariscope.

I had the distinct opportunity of working at Brown University as a graduate student, as a teacher of physical chemistry, and then back as a graduate student. During that period, the Manhattan Project was going on at Brown University and I was working for Charlie Krause. Jim White said that alcohol wasn't available in Oak Ridge. General Groves told Charlie Krause that alcohol was not allowed; Charlie told the General that he wouldn't come. The General decided that Charlie Krause's suitcase wasn't going to be searched. We always knew how many days the old man was going to be gone by how many bottles of Irish whiskey he had in his suitcase.

I came to Argonne in 1951 and went through some initial experiences in the Analytical Laboratory. Argonne was just recovering from the situation of a lost gram of uranium-235 and had undergone the famous Hickenlooper investigation. [Bert Hickenlooper was a senator from Iowa who announced from the floor of the senate that bomb material was missing at Argonne National Laboratory. Eventually they did say they found it. They held up a thing, an FBI man took a picture of it, and they went on their ways.] The lab was still in cardiac arrest when I arrived at Argonne.

My next experience was shipper/receiver differences. I think Argonne ran the first breeder reactor in EBR-I. My laboratory associate, Cy Volger, had the responsibility for isolating the first plutonium from the blanket of EBR-I.

We found more than they said they sent us—120 mg was isolated, and the papers said 80 mg. What did we do? We balanced the books around the wastepot, then fixed the wastepot in such a way that no one could analyze it.

I'm going to dedicate my talk about plutonium to Mr. Plutonium—Mr. Analytical Chemistry of Plutonium, (And God, I wish he were here today!) —Charlie Metz. Charlie Metz was a father to us all. He was my surrogate father as far as a plutonium chemist was concerned. It was great to get on the telephone and call Charlie and ask what to do. He'd tell you. He was a good man. He ran a great laboratory. It was the finest plutonium laboratory in the United States—in the world. As I see it, New Brunswick is carrying on in the name of Charlie Metz in many ways. Clem Rodden was a uranium chemist; he was the father of the uranium chemistry; he knew more about uranium analytical chemistry, in his time, than anyone else. Charlie Metz knew all about plutonium (I think Charlie would agree with me) and I would like to dedicate this talk to him.

First of all—Epigram—Santayana: "Those who do not learn from the past are doomed to repeat it." You must read the literature! I am writing a book about the analytical chemistry of plutonium. To give this talk came at a very opportune time. I've spent more time in preparing for this talk than any other talk I've given. I want to divide the talk into three parts: radiometric methods, titrimetric methods and mass-spectrometric methods. Let's start in the beginning. As Seaborg indicated, he started with radiometric methods. We had 2-pi proportional counters, and we still have 2-pi proportional counters, and don't anyone forget them. They are great instruments—they are simple, they work and they can give extremely reliable results.

When I started at Argonne, I was trained for a month in the Analytical Laboratory by a woman named Florence Ferry. Florence had a high school education, maybe a year at Joliet Junior College. She showed me how to do plutonium analysis. We co-precipitated the plutonium with a little bit of lanthanum fluoride, washed the precipitate, pulled it into a transfer pipette, slurried it onto a stainless steel plate, dried it, counted it in a 2-pi proportional coun-

ter. We did  $\pm 1\%$  analytical work right along. I mean accuracy and precision. We knew the isotopic composition, hence the specific activity, of plutonium, because we ran the laboratory in such a way that didn't accept samples unless they gave us a piece of plutonium they were working with. Most samples, in those days were Purex processing samples on which they were trying to achieve decontamination factors of  $10^6$ . We did 2-pi alpha counting on sample aliquotes from a thousand-fold dilution. We had good methods and the radiometric methods progressed. By the middle of the 1960's we were solvent-extracting the plutonium into methyl isobutyl ketone according to methods of Maeck and Rein at the Idaho Chemical Processing Plant—a superior separation procedure. We were counting the samples by liquid scintillation counting. Since the chemists and engineers didn't need results to any better than  $\pm 1\%$ , we gave them  $\pm 1\%$ . We made a brief investigation of how well we could do liquid scintillation counting of plutonium. We were able to demonstrate 0.1% accuracy.

The 1950's were characterized by the Hanford/Rocky Flats shipper/receiver difference problem. Hanford shipped plutonium nitrate solutions that were greater than one M  $\text{HNO}_3$ . Hanford would analyze them before they shipped them and Rocky Flats would analyze them after they received them and they would compare results. There was something very unique about the results—they never agreed! I mean there were one percent, two percent, three percent differences between the two laboratories. What made the problem more interesting was that one laboratory was not always the high one. There were problems. I don't know if they ever resolved them. I don't know if they knew what was the problem.

The AEC said maybe we needed to work on the analytical methods. With the advent of private industry getting into the nuclear business, the AEC told us—they ordered us—to write a manual. I served on the plutonium committee with Charlie Metz as the chairman. The manual was TID-7029—*Selected Measurement Methods for Plutonium and Uranium in the Nuclear Fuel Cycle*. It has good analytical procedures in it. We started comparing the

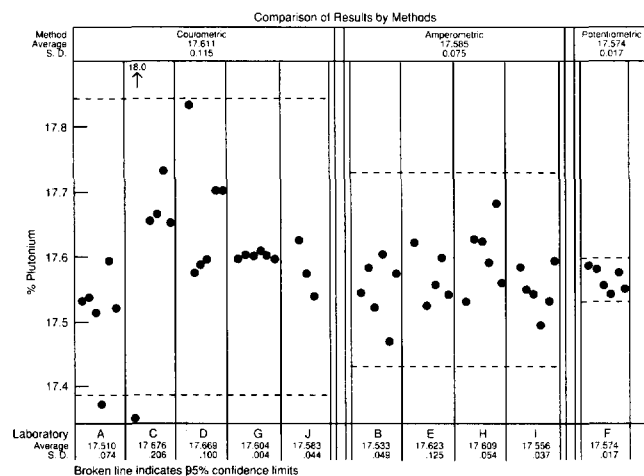


Figure 1.

measurements from TID-7029. New Brunswick put together a group of samples and sent them to various laboratories. The results of the comparative measurements were reported in NBL-231.<sup>1</sup>

In the early 1960's, "W-D" (W.D. Shults) was doing controlled-potential coulometric analysis at Oak Ridge National Laboratory and Metz and Waterbury were doing controlled-potential coulometric analyses at Los Alamos. Clem Rodden and coworkers at New Brunswick were doing potentiometric titrations. The people who worked with me at Argonne—Charlie Seils and Bob Meyer—developed an amperometric method of titration.

By the middle 1960's, we had a plutonium metal standard that was as good as any other standard for any other element in the periodic table for the calibration of our methods. Maybe there have been some slight improvements, but we had a real standard. We had analytical methods that were comparable to those that T.W. Richards used to win a Nobel Prize for his chemical determinations of atomic weights.

Figure 1 represents data from New Brunswick Laboratory's, what I call, the "Sample of the Month Club." Each month the participating laboratories received a sample of unknown composition. They were to analyze it and report the results back to NBL. NBL compiled the results into a report—NBL-256.<sup>2</sup> The figure compares plutonium determinations by controlled-potential coulometry, amperometric titration and potentiometric titration. The results are coded, but if you know who the people doing the work are, you could break the code. The best coulometry work is from Lab G. That's Los Alamos—Metz and Waterbury were doing the best coulometry work in those days. NBL was the only lab doing potentiometric titration (Lab F)—that wasn't tough. As far as the amperometric titrations were concerned, I made a guess and got that right. As you can see, basically we have pretty good quality work for a first comparison. I think part of the problems observed involved the dissolution of the samples. The samples were not easy to dissolve. Controlled-potential coulometry obviously had trouble because some laboratories reported significant difficulties. The next comparison is of laborato-

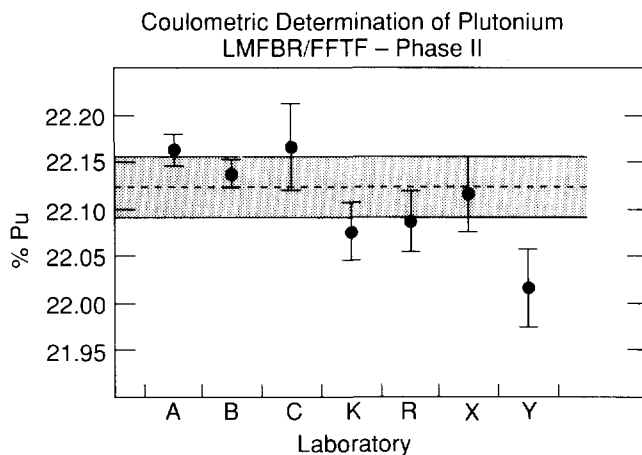


Figure 2.

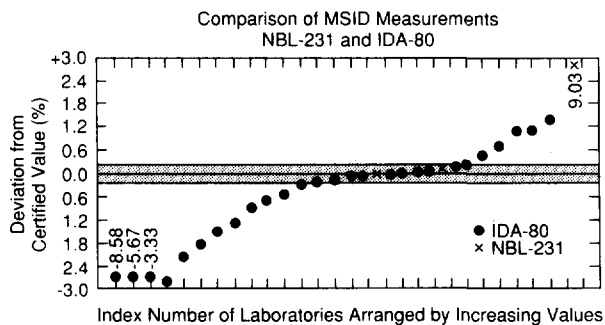


Figure 3.

ries applying to be contractors for the manufacture of Fast Flux Test Facility (FFTF) fuel—a (U,Pu)O<sub>2</sub> material. In Figure 2, we have the data from the second phase.<sup>3</sup> Laboratory B is Los Alamos. In the second phase, two of the laboratories that had been doing the amperometric method of Seils, Meyer and Larsen switched to controlled-potential coulometry—the method prescribed for this intercomparison.

Good work is being done at New Brunswick now in controlled-potential coulometric determinations of plutonium with an accuracy of nearly  $\pm 0.01\%$ . That includes the separation/purification procedure where they absorb the plutonium onto a Dowex-1 anion-exchange column, then elute it.

Now let's switch to mass-spectrometry—to a mass spectrometric isotope dilution (MSID) method of analysis. How well a laboratory can perform mass spectrometric measurements should be a measure of how well it might be able to perform MSID analyses. I said "might." Figure 3, compares performance data reported by the three laboratories in NBL-231 (x's) on measurements of plutonium concentration by MSID with performance data reported by 27

laboratories in 15 countries in the IDA-80 (o's) program.<sup>4</sup> This isn't progress; there are still problems. It isn't all the mass spectroscopist's problem; some of it is. There are problems with the chemistry that's involved.

There is an important paper in a journal called *Analytical Letters* that Bill Lyon edits. An experiment conducted at Los Alamos by Fred Marsh, Bob Abernathy and Jim Rein investigated problems with MSID analysis.<sup>5</sup> They mixed equal quantities of tetravalent Pu-239 and hexavalent Pu-242 and investigated the isotopic exchange methods reported by 10 different laboratories. Their results are summarized in Figure 4. One method oxidized with manganese in 5 M HNO<sub>3</sub>, then reduced with nitrite. It didn't oxidize the plutonium! Another method oxidized with manganese at 60° C, then reduced with nitrite. The recovery, requiring reduction from the hexavalent state, is only 1%. Don't these people read the literature? The documents from Hanford in the 1950's indicated that nitrite doesn't reduce plutonium from 6 to 4. It doesn't work at a molar level; how can one expect it to work at a micro level? Ben Rider (GE-Vallecitos), Alan Fudge (UK-Harwell) and I wrote the method that involved reduced of Pu(III) with hydrazine or hydroxylamine, followed by oxidation to Pu(IV) with nitrite. The method works great! As I look at the data from the ten procedures, nine of them appear to have problems with the chemistry. Why did they use 5 M HNO<sub>3</sub> in the oxidation? The rate is inversely proportional to the acid concentration; why didn't they do it in 1 M acid?

(Seaborg himself said if you heat plutonium in 1 M HNO<sub>3</sub>, you'll oxidize it to the hexavalent state.) I don't understand.

We must get around to the real world sometime. We have titrimetric and controlled-potential coulometric methods that can be performed to 0.01%; I'm not sure they

Chemical Treatments					Effect of Chemical Treatments on Pu Sorption		
Treatment	Reagents	Temp, °C	Reaction Time, Min	Resin Bead Contact	Total Pu Sorbed on Resin, % **	Stoichiometric Ratio of Pu to Initial Ratio **	Conclusion
1	2 mmol HClO <sub>4</sub> + 0.1 mmol HF	Fume	To dryness	40-hour static	65 +/- 5	1.010 +/- 0.014	Erratic, Pu(VI) incompletely reduced
2	a. 2 mmol HClO <sub>4</sub> + 0.1 mmol HF b. 0.005 umol H <sub>2</sub> O <sub>2</sub> *	Fume	To dryness	2-hour dynamic	38 +/- 9	1.007 +/- 0.012	Erratic, sorption decreased
3	a. 2 mmol HClO <sub>4</sub> + 0.1 mmol HF b. 0.06 umol H <sub>2</sub> O <sub>2</sub> *	Fume	To dryness	2-hour dynamic	41 +/- 4	0.988 +/- 0.016	Erratic, possible complexation or precipitation of Pu(IV) by peroxide
4	a. 2 mmol HClO <sub>4</sub> + 0.1 mmol HF b. 0.6 umol H <sub>2</sub> O <sub>2</sub> *	Fume	To dryness	2-hour dynamic	35 +/- 11	0.979 +/- 0.001	Possible complexation or precipitation of Pu(IV) by peroxide
5	2 mmol HClO <sub>4</sub> + 0.1 mmol HF + 0.02 mmol H <sub>2</sub> SO <sub>4</sub>	Fume	To dryness	2-hour dynamic	5 +/- 4	0.978 +/- 0.003	Periodate maintains Pu(VI) in presence of resin
6	a. 0.005 mmol KMnO <sub>4</sub> in 5M HNO <sub>3</sub> b. 0.02 mmol NaNO <sub>2</sub>	Room	15, dynamic	40-hour dynamic	38 +/- 2	11.3 +/- 1.0	Pu(IV) only slightly oxidized by unheated KMnO <sub>4</sub> , Pu(VI) not reduced by NaNO <sub>2</sub>
7	a. 0.005 mmol KMnO <sub>4</sub> in 5M HNO <sub>3</sub> b. 0.02 mmol NaNO <sub>2</sub>	60	20, static	2-hour dynamic	1.3 +/- 0.2	0.992 +/- 0.003	Pu(IV) oxidized by heated KMnO <sub>4</sub> , Pu(VI) not reduced by NaNO <sub>2</sub>
8	a. 0.005 mmol KMnO <sub>4</sub> in 5M HNO <sub>3</sub> b. 0.025 mmol H <sub>2</sub> O <sub>2</sub>	Room	15, dynamic	3-hour dynamic	58 +/- 2	1.179 +/- 0.043	Pu(IV) only slightly oxidized by unheated KMnO <sub>4</sub> , Pu(VI) incompletely reduced by H <sub>2</sub> O <sub>2</sub>
9	a. 0.005 mmol KMnO <sub>4</sub> in 5M HNO <sub>3</sub> b. 0.025 mmol H <sub>2</sub> O <sub>2</sub>	60	20, static	2-hour dynamic	17 +/- 1	0.994 +/- 0.001	Pu(IV) oxidized by heated KMnO <sub>4</sub> , Pu(VI) incompletely reduced by heated H <sub>2</sub> O <sub>2</sub>
10	a. 0.04 mmol Fe(III) + 0.15 mmol sulfuric acid in 5M HNO <sub>3</sub> b. 0.9 mmol NaNO <sub>2</sub>	60	20, static	2-hour dynamic	69 +/- 2	0.999 +/- 0.003	Only effective treatment

\* Added to 8M HNO<sub>3</sub> used for resin contact

\*\* Uncertainty units are standard deviation (number of replicates is 6, except 3 for treatments 2, 6, and 8)

Figure 4. Isotopic Equilibrium of Plutonium

can be performed that well on real samples. The real world's samples are those that come out of the final ion-exchange column in the Purex process. In the final exchange column, the feed going into the column is Pu(IV) in tributyl phosphate solution; the solution coming out is Pu(IV) and 1 M HNO<sub>3</sub>; and the column scrub solution is 0.1 M HNO<sub>3</sub>. If you read the literature, Ockenden and Welch<sup>6</sup> reported in 1956 that if you prepare a solution that is 0.1 M nitric acid and 0.001 molar in Pu(IV), within a half-hour you will have a significant visual—spectrophotometric—evidence, that plutonium polymers have formed and that a significant quantity no longer sticks on the Dowex-1, but passes right through. If you think of 0.1 M nitric acid scrub solution hitting aTBP-loaded column and that polymers are not being formed, that's why there were problems with Hanford/Rocky Flats shipper/receiver differences. There were plutonium polymers that the analytical procedures were not taking care of. The plutonium product solution is not going to be Pu(IV) monomer; there's going to be Pu(IV) polymer and there's going to be Pu(VI). One needs to apply the process that Marsh used. Consider what problems can arise; devise and perform experiments to resolve them.

The first question in any chemist's mind is, "Do I have a representative sample?" If you don't, you don't have anything and shouldn't do the analysis. If you're doing MSID and you've diluted the sample solution down to ug/g and let it stand for a little while, if it contained polymer, you may no longer be able to obtain a representative sample to load onto your filament. The polymer has absorbed onto the wall of the container; it's dead. There's no question about it. If you have a solution containing microgram quantities of both Pu(IV) and Pu(VI) that you've heated to dryness, then added some nitric acid and heated a little and taken up an aliquot in a pipette, you've done an isotopic separation. The Pu(IV) is more readily soluble than the Pu(VI) that was in solution. It's absolutely imperative in isotope dilution that everything go back into solution if isotopic equilibrium has not been established. Chemical conversion—we have had studies made of the kinetics; we have a bunch of literature that came out of the West Stands, Seaborg's works. You go back and find a lot of that information was done with microgram or nanogram amounts. You can't find that sort of thing in the literature that the analytical chemist needs. I'm trying to provide it, I'm writing a book. I'm not selling the book now.

The Koran says, "Take your necessary precautions against your enemies;" you must know the chemistry of plutonium to treat polymers and to assure isotopic exchange to be able to do mass spectrometric isotope dilution analysis. Jefferson said, "Eternal vigilance is the price of liberty." This is a part of what NBL is about. Your analytical chemistry is only as good as your quality control program; if you're out of control, you can't be analyzing samples. If you can analyze samples with a high degree of accuracy that all can agree on, shipper/receiver differences will disappear.

I'd like to close with a little vignette of the past. There is a laboratory in the US that prepares a standard sample of plutonium in drinking water. The concentration of plu-

tonium in drinking water in the sample they submitted is about 10 picocuries/liter (about 100 picogram/liter to be measured radiochemically. The directions say to first shake the bottle for 30 minutes; the implication is, if you don't shake it, you will get the wrong answers. That's true, if you don't shake it you will get the wrong answer. Pursuing this further, I asked how they prepared the standard. I was told they pipetted Pu(IV) nitrate into triply distilled water. I referred them to a paper by Oldham and Larsen that indicated drinking water contained hexavalent plutonium, and that drinking water was not triply distilled water. In adding such a small quantity of plutonium—not at concentrations for the mass spectroscopist, but four or five orders of magnitude lower—they were forming polymers. At this point I was told, "This is the way we have always done it." This ended our conversation.

We have problems to face; we must deal with them. We must learn from the past, and stop assuming what we're doing is right. We must do it right!

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Robert P. Larsen received his B.A. in chemistry from Kalamazoo College and his Ph.D. in physical chemistry from Brown University. He taught at Brown, Amherst and Ohio Wesleyan from 1944-1951. He joined Argonne National Laboratory (ANL) in 1951 and has done research in applied radiochemistry for the Chemical Engineering Division and the Radiological and Environmental Research Division. He retired in 1984, but has remained at ANL as a consultant and Special Term Appointee.

# Mass Spectrometry of Nuclear Materials— Attention to Detail

■  
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■

## ABSTRACT

*Measurements of the  $^{235}\text{U}/^{238}\text{U}$  ratio in product-quality material have improved from uncertainties of 0.1 percent (rel) to 0.2 percent since the Manhattan Project. The hardware and procedural changes responsible for these measurement improvements are traced and discussed.*

My task today is to discuss the evolution of the surface and thermal ionization isotopic mass spectrometer measurements. As I have done for more than 30 years I will use the ratio of ratio plot of the original measurements done on the uranium standards. These measurements were made by a number of cooperating laboratories and did indeed represent just about all the different systems used for isotopic measurement at this point in time. The base numbers are values supplied by Oak Ridge who prepared the original oxides. The values were presumed valid to 0.1 percent on the 235-238 ratio (precision only); the relationship to absolute was not shown. Table I gives the values used as the base data. The 235/238 ratio's were modified somewhat from the Oak Ridge values because of improved values for minor isotopes done at NBS. The data column far right hand written are the values from the most recent certificates that I have available. Pictogram 1 shows the ratio of ratio plot of the surface and thermal instruments. As you can see, these measurements do not add an awful lot of knowledge of the standards.

Though we did not know it at the time, what we had done was the first systems calibrations. The system calibration defines in no uncertain terms just how good the system is, the systematic shift that three or four groups show is usually associated with the element being analyzed, the scatter around the line is a measure of your limitations imposed by failures of various components of the measurement itself.

During the intervening 30 years I have seen this same data when if plotted would look exactly like the 1958 data with only a slight reduction in scatter. The most recent case only a few years ago with the data from a new instrument done by a highly skilled operator.

Between 1958 and 1963 I did indeed make a few changes to the surface and thermal instruments and dropped the scatter level from one to two percent level to 0.2 percent. The changes are well defined and very easy to justify. In no particular order they were the following.

1. Controlling the ionizing filament temperature first by setting a given Re ion beam intensity and later with the use of a good micro optical pyrometer.
2. The modification of the single scale recorder to expanded scale (Figure 1) is very simple and very inexpensive on L&N recorders. Some of the other brands require new slide wires.

Hindsight makes explaining the difference in non-linearity of a single scale recorder versus an expanded scale easy. If you just look at the mechanics of a recorder

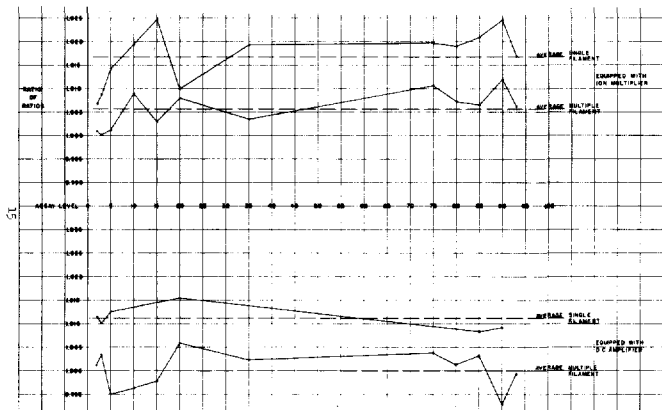
Table I  
Isotopic Composition of Uranium Standards  
NBS Best Estimates from Pooled Data

	<u>U234</u>	<u>U235</u>	<u>U236</u>	<u>U238</u>	<u>235/238</u>	
U005	0.0023	0.4894	0.0046	99.5037	0.004918	4919
U010	0.0056	1.0031	0.0065	98.9848	0.010134	10140
U015	0.0085	1.531	0.0163	98.444	0.01555	15565
U020	0.0124	2.037	0.0162	97.934	0.02080	2081
U030	0.0189	3.046	0.0202	96.915	0.03143	3143
U050	0.0280	5.006	0.0481	94.918	0.05274	5278
U100	0.0672	10.189	0.0372	89.707	0.11358	11360
U150	0.09901	15.296	0.0662	84.539	0.1809	18109
U200	0.1247	20.005	0.211	79.659	0.2511	25126
U350	0.2493	35.177	0.167	64.407	0.5462	5465
U750	0.5914	75.360	0.249	23.800	3.166	3166
U800	0.6559	80.276	0.246	18.823	4.265	4266
U850	0.6429	85.142	0.371	13.844	6.150	6148
U900	0.7771	90.198	0.332	8.693	10.375	10375
U930	1.0813	93.335	0.204	5.380	17.348	17349
	234 by 233 dilution 5%				OR Cert. .1%	



and believe that there might be a tenth of a division dead zone and one to two tenths nonlinearity you define a system that limits the intercomparison of two potentials to something like 0.5 percent. Think about the effect of a nearly full scale signal and a signal only ten or so divisions of full scale. Wear of the slide wire also has a very serious effect on the accuracy of comparing any two potentials; most of the wear is, of course, at the zero or baseline so that after a very short time almost any and all recorders have a very pronounced "S" shaped response.

On a more modern vein I should add that this same S-shaped response creeps into the response of single scale amplifiers independent of the number significant figures of the output volt meter. To my own personal knowledge



Pictogram 1. Experimental  $^{235}\text{U}/^{238}\text{U}$  vs NBS Estimate 1958

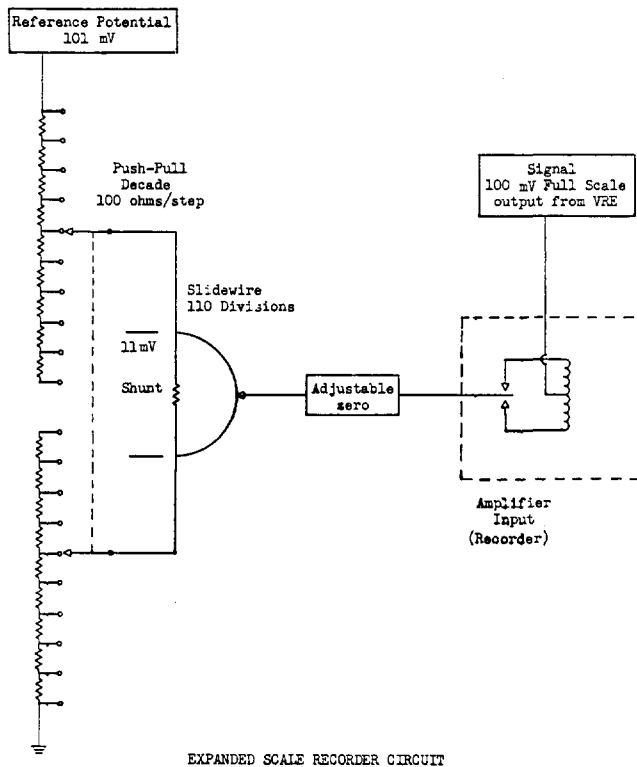


Figure 1.

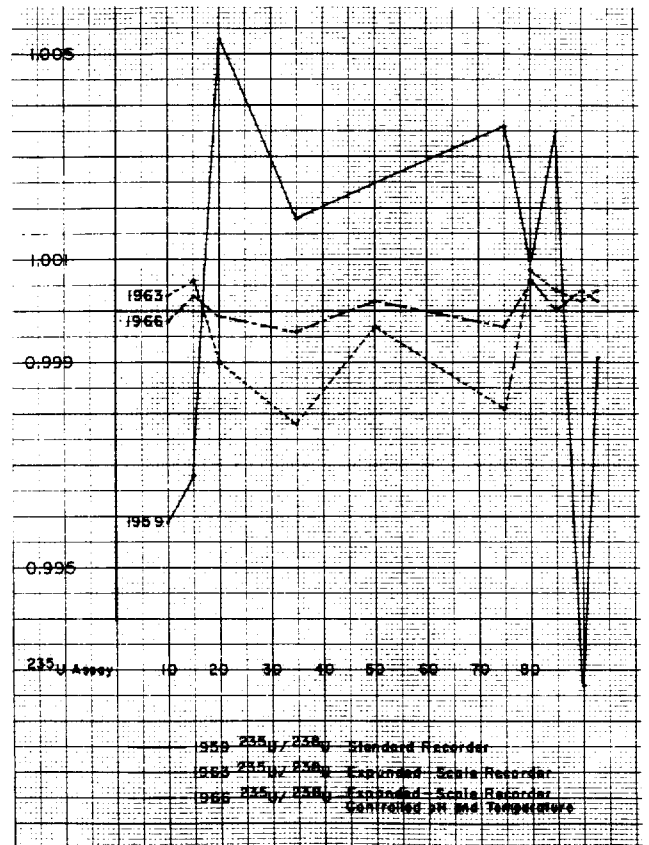
only the old Cary 31s and the somewhat newer Cary 401s avoid this problem.

3. The calibration of the attenuators on the amplifier does contribute also to the overall accuracy on a system using Cary amplifiers.
4. The liquid nitrogen cold finger copied from KAPL lab makes one of the most dramatic changes in an instrument's ability, because you then operate with a much more controlled atmosphere in and around the filaments.
5. Adding a degas step when using large samples with the cold finger gets rid of a major portion of the water and acid acid vapor.

Between 1963 and 1966 the final steps necessary for the transition from 0.2 percent to 0.02 percent were made in pictogram 2.

To effect this transition required some major changes in the ion optics.

1. First and foremost was the introduction of the cubic suppressed collector. During the analysis of a number of Rubidium samples it was found that the observed ratio was actually dependent on the accelerating voltage. At the time this was first observed, the ratio came to a steady state at something below 2 kilovolts and at higher voltages the baseline was to square at the base peaks. And at the same time, if you scanned a fairly wide mass range, there were always some humps and valleys in the baseline. By



Pictogram 2. Experimental  $^{235}\text{U}/^{238}\text{U}$  vs Theoretical  $^{235}\text{U}/^{238}\text{U}$

installing a baffle some distance forward of the defining slit and definitely smaller in the "Z" axis than the defining slit itself, part of this problem was removed. The next step was the addition of two small permanent magnets to twist the electrons out of the beam. This got rid of a large percentage of the too sharp of angles at the base of the peaks but did nothing for various humps and dips farther out on the baseline.

The addition of the suppression grids between the transmission grid and the defining slit. With this collector the Rubidium ratio is constant to well above five kilovolts but

still shows some response above six kilovolts. The simple collector with just "Z" limiting baffle and magnets begins to fail at something over four kilovolt and show more response the more it is used (as it gets dirty it really gets much worse). When both types are clean (new) at 4.5 kilovolts you can't really tell any difference between them. To the first approximation the cubic suppressed "Z" baffled with magnets never changes over long period of time and condition. A collector without the transmission grids but with the "Z" limiting baffle and magnets works somewhere between but does degrade with use. To my own knowledge I know of no set of data collected any instrument without the cubic suppression system that can be corrected by a single factor to the 0.02 level, I have seen some data at this level but it has been corrected by a family of factors. The only factor that I believe is valid is the filament fraction correction, any other factors are going to vary with time and conditions.

2. The final design of the source that I settled on is about 30 times more efficient than the source we started with and does indeed focus in the "Z" axis at the collector. This source is sufficiently reproducible so that all instruments equipped with it have the same transmission efficiency.

The next tables, Table II: High Temperature, Table III: Low Temperature and Table IV: mixed, are just demonstration analysis to show the level of control that can be obtained if you try. Fifteen single analysis on 15 different samples using two different heating patterns and then ten analysis on one set of five samples alternating the heating pattern. This data was produced for a talk I gave in 1966 and have included a copy of the talk as an addendum to the typed copy of today's talk that I have turned in to the sponsors of this meeting.

The only changes to the measurement during the interval 1966-1989 have been automation and sample size. Automation makes the operation of the instrument much easier and supplies instant precision but without a great deal of care a serious loss of accuracy. It took several years of effort to develop the automated systems to the level of accuracy as the old expanded scale recorder.

**Table II**  
Comparison of the Calculated  $U^{235} / U^{238}$  Ratio to the Observed  $U^{235} / U^{238}$  Ratio for High Temperature Analyses of Synthetic Uranium Samples

Group 1		Group 2		Group 3	
Approximate Ratio 1:9		Approximate Ratio 1:1		Approximate Ratio 9:1	
Mixture	Ratio of Ratios	Mixture	Ratio of Ratios	Mixture	Ratio of Ratios
1	0.99857	1	0.99742	1	0.99780
2	0.99852	2	0.99795	2	0.99786
3	0.99846	3	0.99720	3	0.99793
4	0.99830	4	0.99851	4	0.99800
5	0.99783	5	0.99779	5	0.99718
	0.99822		0.99777		0.99775

Average bias for high temperature analysis = 0.99794

**Table III**  
Comparison of the Calculated  $U^{235} / U^{238}$  Ratio to the Observed  $U^{235} / U^{238}$  Ratio for Low Temperature Analyses of Synthetic Uranium Samples

Group 1		Group 2		Group 3	
Approximate Ratio 1:9		Approximate Ratio 1:1		Approximate Ratio 9:1	
Mixture	Ratio of Ratios	Mixture	Ratio of Ratios	Mixture	Ratio of Ratios
1	0.99564	1	0.99584	1	0.99597
2	0.99523	2	0.99476	2	0.99590
3	0.99574	3	0.99521	3	0.99619
4	0.99498	4	0.99567	4	0.99586
5	0.99520	5	0.99563	5	0.99608
	0.99534		0.99542		0.99600

Average bias for low temperature analysis = 0.99562

**Table IV**  
Alternate High Temperature and Low Temperature Analyses for Synthetic 9:1 Uranium Samples

Sample Number	Observed $U^{235} / U^{238}$	Analytical Pattern	Corrected $U^{235} / U^{238}$	Calculated $U^{235} / U^{238}$	Ratio $U^{235} / U^{238}$ Corr. $U^{235} / U^{238}$
3	9.08386	LT	9.044	9.048	1.0004
2	9.02307	HT	9.004	9.004	1.0000
1	9.02257	LT	8.983	8.979	0.9996
5	8.97284	HT	8.956	8.950	0.9993
4	9.05800	LT	9.018	9.023	1.0006
3	9.06294	HT	9.050	9.048	0.9998
2	9.03922	LT	9.000	9.004	1.0004
1	9.00090	HT	8.982	8.979	0.9997
4	9.06001	LT	9.020	9.023	1.0003
5	8.97193	HT	8.953	8.950	0.9997
					0.99998

HT -- Denotes high temperature analysis. The correction factor for HT is 0.99794.  
LT -- Denotes low temperature analysis. The correction factor for LT is 0.99562

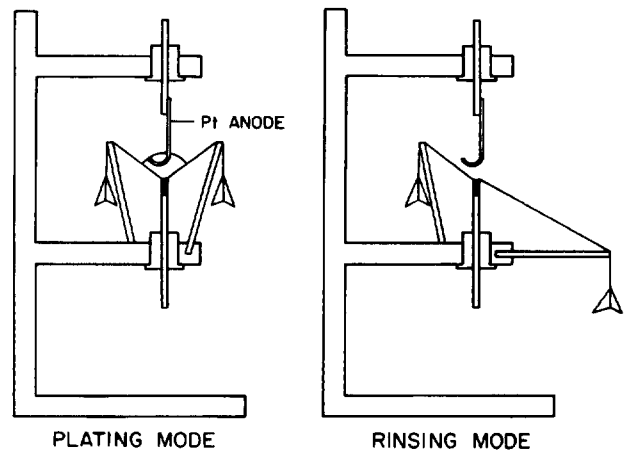


Figure 2.

As far as sample size is concerned it has almost lost meaning. If you use Dick Perrin's plating method and a single stage pulse counter, you can take sample size down to the attogram level. Figure 2 is a sketch of his plating rig using teflon tape to hold the sample drop at the filament. Over plating with platinum for the transuranics allows you to generate more than adequate signal at very low temperatures, low enough so that there are almost no background peaks. The plating step is also a purification step of several orders of magnitude. This loading technique is almost the only real improvement for the transuranics that has come along in the last 20 years. Unfortunately, the chemical preparation blank does get hellish and I think I will leave you with my thought for the day, which is that no mass spectrometer measurement is

better than the chemistry that went into it and that as you go down in sample size you will see blank problems that will make you wonder about the results of some of your larger samples.

---

William R. Shields received his B.S. in chemistry from the University of Washington. From 1953 to 1958 he served in the mass spectrometry group at Goodyear Atomic as shift supervisor, then head of the mass spectrometry development group. From 1958 to 1974 he was with the National Bureau of Standards as Project Leader for the Uranium Standards Project then as Section Chief of the Analytical Mass Spectrometry Section. Since 1974, he has been consulting in isotope ratio mass spectrometry.

# Measurements of Minor and Trace Elements in Nuclear Materials

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## ABSTRACT

*The Ames Laboratory, under Frank Spedding, had the task, among others, of producing high-purity uranium metal fuel for the reactor at the University of Chicago. Existing methods had to be modified and new methods had to be developed to attain the measurement sensitivity necessary to characterize the uranium product.*

## INTRODUCTION

Early in 1942 a branch of the Manhattan Project was established at Iowa State College (now University) in Ames, under the leadership of Dr. F.H. Spedding. One division conducted research in the chemistry of uranium and other actinide metals, fission products, analytical chemistry, etc.; another division set up and operated a pilot plant for production of ultra-pure uranium metal for the new Chicago reactor. Many tons of uranium ingots were manufactured. These operations required the support of a team of analytical chemists and 40 to 60 technicians. Approximately 500 analyses were carried out daily.

Anecdote: Many of the laborers hired to carry out the production of uranium were untrained farm hands from the surrounding areas. One particular man, with a disdain for safety measures, refused to wear a mask when handling green salt ( $UF_4$ ). He inhaled so much of the powder that each morning his pillow was marked with green streaks near his nostrils. He was eventually discharged. Thirty or so years later he visited Iowa State, apparently hale and hearty.

The metallic uranium was produced by reducing uranium (IV) fluoride with magnesium. Co-reduction of thorium chloride and zinc chloride yielded a thorium-zinc alloy; vacuum casting caused the zinc to distil out, giving pure metallic thorium. Later pure rare-earth metals were prepared by modified techniques.

Anecdote: This incident dates from the winter of 1943-44. The author and two companions, Dr. A.S. Newton and Dr. Adolph Voigt, were driving a station wagon from the first nuclear reactor, the historic original one at the University of Chicago, to our laboratory in Ames. Our cargo was a lead box of uranium ingots from the reactor,

and they were fairly radioactive because of the fission products. Snow covered the landscape. About 3 a.m. we had a flat in the lonely Iowa prairie, and were dismayed to find that the jack was faulty. It had a lifting span of only three or four inches. Driven by desperation, we devised a system in which we jacked up the axle enough to slide one of the cylindrical uranium slugs or ingots underneath, lowered the car, and used the jack another time when it rested on a uranium ingot. In this way, alternately putting uranium under the axle and jack, we managed to raise the car by notches and change the tire.

A number of Manhattan Project Laboratories participated in developing the analytical procedures necessary to back up all production steps. In addition to the Ames laboratories, others were the University of Chicago, Oak Ridge, National Bureau of Standards, Columbia, MIT and other sites.

The principal analytical techniques developed are briefly described below.

## EMISSION SPECTROCHEMICAL ANALYSIS

The carrier distillation technique permits determination of about 70 elements in heavy metal oxides such as  $U_3O_8$ . The Ames laboratory employed a DC arc with graphite electrodes and grating spectrographs. Gallium oxide was generally used in the carrier distillation procedure, although on occasion silver chloride served in that capacity. Errors were usually within plus-or-minus 10 percent. Limits were in the fractional ppm range, for instance 0.01 ppm for boron and 0.07 ppm for cadmium. These two elements were especially important because of their high neutron-absorbing cross sections.

Anecdote: The housing from our arcing assembly discharged into an old chimney which was convenient. We later found that chimney swifts nested each spring at the bottom of column, and the young birds consequently were treated to a steady dose of uranium, thorium, gallium, many fission products, and various other bizarre substances. We never observed any abnormalities in the nestlings.

## FLUOROMETRIC ANALYSIS

Although exceedingly sensitive for many determinations, fluorometric techniques were rarely used at the Ames laboratories. This situation arose because quality instrumentation was not available, and also the suspicion that unknown constituents in various samples might act as quenchers. Time would not permit perfecting each procedure.

## SPECTROPHOTOMETRIC PROCEDURES

Methods based on absorption spectra were widely employed. In some cases an element could be determined without separation. For example, iron was routinely determined in uranium by developing the color with 1,10-phenanthroline, and using uranyl nitrate of the same concentration in reference cell.

In other analyses, the trace element had to be concentrated before determination in the spectrophotometer. This could be accomplished by solvent extraction of the trace element, or solvent extraction of the uranium matrix, leaving the analyte behind. Cadmium was converted to its dithizone chelate and extracted from uranyl nitrate; to determine aluminum, the uranyl nitrate was extracted away using an ether, and the aluminum determined in the residual aqueous phase. An alternative technique sometimes employed was the use of a mercury cathode to remove the minor element to be determined; the uranium remained in the aqueous phase.

An oxidation-resistant solvent was employed which would extract cerium (IV), namely tributyl phosphate. This was found also to be an excellent extractant for uranium and plutonium, and tributyl phosphate came to be used in the Purex process.

## CHROMATOGRAPHY

In the early days of the Manhattan Project, chromatography was still an arcane separation technique, and was not widely employed. Within a year or two, with the availability of ion-exchange resins, chromatographic procedures gradually became used more frequently. These were for both preparative and analytical purposes. In particular, fission products were separated and measured. Later the rare-earth metals were separated on a large scale.

## RADIOMETRIC METHODS

Counters of various types were of course routinely used to determine fission products and the more active actinides (neptunium, plutonium, the transplutonium elements). Often there were so many radioactive nuclides present that preliminary separations had to be effected prior to measurement.

## VACUUM FUSION TECHNIQUES

Only a few vacuum-fusion assemblies were in operation. They afforded one of the few methods in which trace oxygen could be determined in metals. In use, a sample of uranium metal, say, was fused in a graphite crucible using an induction furnace. The oxygen was expelled as carbon monoxide; any nitrogen was also discharged. The CO was converted to CO<sub>2</sub>, permitting easy separation from the ni-

trogen. Each component was then measured using a McLeod gauge. With suitable modification, hydrogen and carbon could also be determined.

## CLASSICAL CHEMICAL METHODS

Many old and well-established analytical techniques were adapted to the analysis of nuclear materials. Some examples follow.

- A. Nitrogen.—Nitrides of uranium and other metals were analyzed by the Dumas method. Combustion in the Dumas apparatus produced elemental nitrogen, which could be measured in a microburet. For trace nitrogen in uranium, large samples were employed. Nitride nitrogen was also determined by micro-Kjeldahl procedures. Both methods were suitable for ppm quantities.
- B. Carbon and Hydrogen.—Using large samples, the classical combustion analysis was used routinely.
- C. Fluorine.—In that uranium metal was made from its fluoride, traces of fluorine were always retained. The old technique of dissolving and distillation of SiF<sub>4</sub> was found to be satisfactory. Since the fluoride-specific electrode had not yet been invented, titration with thorium nitrate or spectrophotometry was used.
- D. Iodine.—Small-scale preparation of costly metals such as rare earth metals and plutonium were improved by reduction of a halide with calcium in the presence of elemental iodine. With excess calcium, reaction with iodine provided extra heat, and also resulted in a eutectic melt. The metals produced contained traces of iodine, which was determined by distillation and a classic colorimetric procedure.

## MACRO ANALYSES

Quite a number of analytical procedures on the macro scale were developed in the Ames laboratory. Two of these are outlined.

- A. Analysis of Fluorides.—Since many fluorides were employed in Manhattan Project work, they required numerous analyses. The pyrohydrolytic procedure consisted of heating a sample in steam at 900-1000 degrees Celcius using a platinum apparatus. The hydrogen fluoride which resulted was condensed and determined by acid-base titration. Weighing the residual metal oxide provided an accurate determination of the metal content. While this procedure was satisfactory for heavy metal fluorides (UF<sub>3</sub>, UF<sub>4</sub>, ThF<sub>4</sub>), light metal fluorides required mixing with U<sub>3</sub>O<sub>8</sub>. This accelerator promoted complete hydrolysis by forming a uranate. The method was modified to determine water in fluorides.
- B. Assaying Metallic Uranium.—A great deal of work on uranium hydride was conducted at Ames. Since the hydride is easily formed by reaction with hydrogen at 250 degrees Celcius and decomposes at higher temperatures, it was easy to take advantage of this behavior for assaying uranium turnings and

other crude metal. Using a moderate-sized sample, the metallic uranium portion was converted to  $UH_3$ , and this decomposed under vacuum. Measuring the volume of hydrogen evolved gave the elemental uranium content.

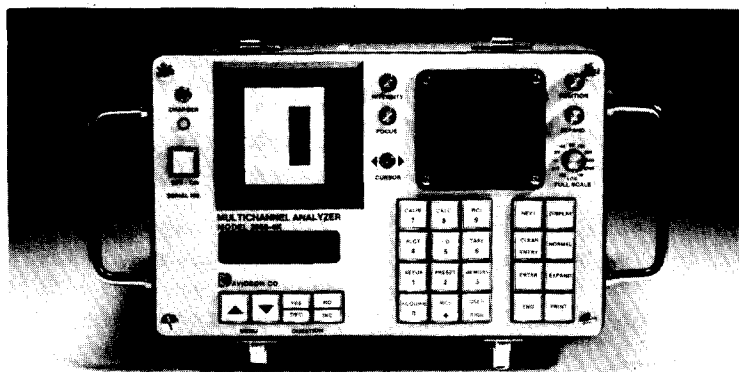
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James C. Warf received his B.S. in chemistry from the University of Tulsa and his Ph.D. from Iowa State. From 1942 to 1947, he was a group leader in the Manhattan Project at the Ames Laboratory. From 1948 to the present, he has served on the chemistry faculty of the University of Southern California, where he currently is a Professor, Emeritus. He has held Visiting Professorships at universities in Indonesia, Malaysia, and Vienna. Of the ten books that he has authored, six are in the Malaysian or Indonesian language.

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# Nuclear Reactors and The Nuclear Fuel Cycle

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## ABSTRACT

*The first sustained nuclear fission chain reaction was not at the University of Chicago, but at the Oklo site in the African country of Gabon. Proof of this remarkable phenomenon nearly 2 billion years later was provided by very careful mass spectrometric and analytical chemical measurements by French scientists. The U.S. experience in developing power-producing reactors and their related fuel and fuel cycles is discussed.*

## INTRODUCTION

It has been observed that the three ingredients of atomic energy, as it emerged in 1945 from war-time development by the Manhattan Engineer District (MED), were power, explosives and scientific tools.<sup>1</sup> The key development was the nuclear reactor, which can provide all three of the ingredients.

Strictly, the MED reactors are not the first known. It has since been established that self-sustaining nuclear fission chain-reactions occurred spontaneously during the early history of the Earth, about 1.9 billion years ago. The location is now in the African country of Gabon, at the site of the uranium ore deposits at Oklo. Proof of this remarkable phenomenon was provided by mass spectroscopy, which first revealed anomalies in the U-235 content of the ore mined at Oklo, and by other analytical chemistry techniques, which determined the nature of the fission products, especially the rare earths, that are still at the same locations near the reactors.<sup>2</sup> The Oklo reactors have probably had a philosophical impact, by demonstrating that fission chain-reactors did not require human intervention to start up or shut down. More practically, the detailed examination of the site has yielded geochemical data useful in considerations of long term storage of products of fission. But the engineering advances of the MED, as is discussed below, provided the foundation for subsequent reactor development.

In what follows, I consider mainly only reactors for electrical power generation and their related fuel and fuel cycle aspects. To limit the scope further, details of only the U.S. experience will be discussed. For the purpose of this

part of the Symposium, the emphasis is supposed to be retrospective—on early developments. However, it will be appropriate to refer to the present status of these same issues, and how we got there; and also to make some references to programs in other countries.

## 1. DEVELOPMENTS OF THE MANHATTAN ENGINEER DISTRICT

The principal purpose of the MED's reactor developments was to supply Pu-239 for military use. The reactors which fulfilled this purpose were large piles of natural uranium metal and graphite, cooled by Columbia River water. The procedure to obtain plutonium from the irradiated fuel included dissolution in acid, preferential co-precipitation with BiPO<sub>4</sub> and eventual separation of the pure metal. The fuel reprocessing was performed in large, specially designed chemical separations plants. A total of three was built and operated, one for each of the production reactors.

A low power, forced air-cooled version of the production reactors was built, along with pilot-scale facilities for metal separation—all this to provide construction and operation experience in advance of full scale plants. Also, a small reactor was built to check out the performance of a natural U metal-D<sub>2</sub>O moderator system. This design was a forerunner of the CANDU power reactors later developed in Canada, and of the production reactors later constructed

At the Savannah River Laboratory. Another small reactor evolved as part of the experimental program to test nuclear bomb physics. This one used a water-soluble salt of enriched uranium as fuel, dissolved in water as the moderator—the prototype both of homogeneous reactor and of enriched uranium reactors. (EU)\* Finally, to explore the use of Pu-239 in a controlled fission chain reaction, the MED produced a reactor with pure plutonium metal fuel and no moderator. Cooled by flowing mercury, it was an ancestor of later liquid metal, fast reactors. Table 1 summarizes the situation as of January 1, 1947 when the MED was replaced by the new Atomic Energy Commission (AEC), as required by the Atomic Energy Act of 1946. The first seven of these reactors (including the three produc-

Table 1  
Reactors Built by MED

<i>Designation</i>	<i>Location</i>	<i>Fuel</i>	<i>Moderator</i>	<i>Coolant</i>	<i>Purpose</i>
CP-1/CP-2	Argonne	<sup>N</sup> U Oxide and Metal	Graphite	Air, Convection	Research, Test
X-10	Oak Ridge	<sup>N</sup> U Metal	Graphite	Air, Forced	Research, Test
Water Boiler	Los Alamos	<sup>E</sup> U Salt	Water	Water	Research, Test
CP-3	Argonne	<sup>N</sup> U Metal	D <sub>2</sub> O	Water	Research, Test
B, D and F	Hanford	<sup>N</sup> U Metal	Graphite	Water	Production of Pu
Clementine	Los Alamos	Pu-239 metal	None	Mercury	Research

tion reactors and the three chemical separation plants) were built in an interval of less than three years, from December 1942 to 1945. The last one listed was completed in 1946.

Fuel for all of these reactors originated as imported uranium ore, principally from the Belgian Congo.<sup>5</sup> (An early, and serious problem for the AEC was to provide a U.S. source of supply). Compared with later evolution of the concept of the fuel cycle, the Hanford "cycle" was rudimentary. Uranium ore had to be mined, processed through several steps into U metal, and fabricated into fuel elements for loading into reactors. After optimal exposure to produce Pu of acceptable isotopic purity, the fuel was discharged for reprocessing to extract the Pu. Left behind were large volumes of high level waste (HLW) containing radioactive fission products, unburned uranium and, inevitably, unrecovered plutonium. The HLW was stored in underground tanks—149 in all—for eventual final disposition.<sup>6</sup>

It should be noted that the EU and (especially) Pu-239 reactors were "burners" of the fissionable isotopes. The NU reactors, including the production plants, did convert some of the burned U-235 into Pu-239, thus functioning as "converters".

Eight reactors were built—all related to the military objective of the MED. Yet, it was impossible to channel ideas about this new energy source toward this single goal. Especially at the Metallurgical Laboratory (later, Argonne National Laboratory, ANL) and then at Oak Ridge (later Oak Ridge National Laboratory, ORNL) these ideas crystallized into concepts for generating heat power at high temperature and practical quantity. Included was the concept of a true "breeder", which could produce more new fissionable material than was burned in operation of the reactor. The MED, which fostered the above effort (although hardly at high priority) nevertheless recognized early the wider application of "atomic power". In August 1944 General Leslie R. Groves who was in charge of the MED asked Professor Richard C. Tolman of Cal Tech to chair a committee "to look into the potential non-destructive uses of atomic energy".<sup>7,8</sup> Not the least remarkable aspect of the Tolman Committee was its timing. It was sent on its mission a year before the war was to end, and when not even all the production reactors had gone into operation. Among the observations in the Committee's

December 1944 report were these:

1. The government should urgently pursue research and development studies toward providing nuclear power to propel naval vessels; and
2. "The development of fission piles solely for the production of power for ordinary commercial use does *not* appear commercially sound *nor* advisable from the point of view of preserving national resources". (author's emphases)

A similar negative evaluation of commercial nuclear power was espoused by James B. Conant, president of Harvard University.<sup>9</sup> Dr. Conant, a noted chemist, was not a member of the Tolman Committee; but he, like Tolman, was an adviser to Groves. Conant's adverse attitude was based primarily on three factors: the requirement to handle unprecedented large quantities of radioactivity; the very great capital investments involved in plant and operations; and the persistent, overriding priority of military applications.

It's interesting to compare the reactor reality of today with these views of 45 years ago. There are now in the U.S. Navy some 100 vessels propelled by nuclear power, most of them submarines.<sup>10</sup> And there are no fewer than 111 licensed commercial nuclear power plants in the U.S.<sup>11</sup> Most (but not all) of the latter use enriched U fuel with water moderation, and are of designs related to the earliest naval propulsion reactor prototypes. They have a total generating capacity of 99,000 Mw, and turn out annually nearly 20 percent of the US electrical energy. So, despite the negative views of the Tolman Committee and others, there must have been enough incentive for commercial nuclear power to support substantial reactor development and deployment.

For various reasons, such has not been the case with the installations needed to process the spent fuel after discharge from the reactor, the so-called "back-end" of the fuel cycle. With minor exception, the spent fuel has been stored in pools of circulating cooling water, located at the reactor sites. No reprocessing of commercial fuels is in sight. The "once-through" fuel cycle is indicated in figure 1; but the situation is more accurately characterized as a "stowaway cycle" (See Table 4).

Federal legislation has been enacted to provide a repository for commercial fuel at Yucca Mountain, NV—but it will be years before it is operating.<sup>12</sup> A repository for high



level waste from the military reactors is nearing completion near Carlsbad, NM, and is in the licensing process.<sup>13</sup>

In summary, despite shortcomings (of which many were due to wartime circumstances) the MED operation provided useful experience in several areas important for future development of nuclear power. These include radiobiology and health physics; design, construction and operation of reactors both for production and research; fuel reprocessing; and—in the Clementine reactor—the possibility of fuel recycling.

It is not out of place to mention here that disagreements over the course and direction of MED's programs occurred and are documented.<sup>14</sup> Whether or not these can be extrapolated to the active anti-nuclear movement of today is conjecture. But a continuation of this wartime aspect of the MED's operations did influence the post-war emergence of scientists' and engineers' organizations. These participated effectively in the debates preceding the enactment of the Atomic Energy Act of 1946. That measure, which provided for a civilian Atomic Energy Commission, won out over other bills that would have kept military control of atomic energy.

## 2. ADVANCES BY THE AEC

The MED did, after all, initiate several projects on power reactors.<sup>15</sup> One was based on a homogeneous core of natural uranium and graphite, cooled either by helium or liquid bismuth (the "Daniels Pile"). Another concept utilized

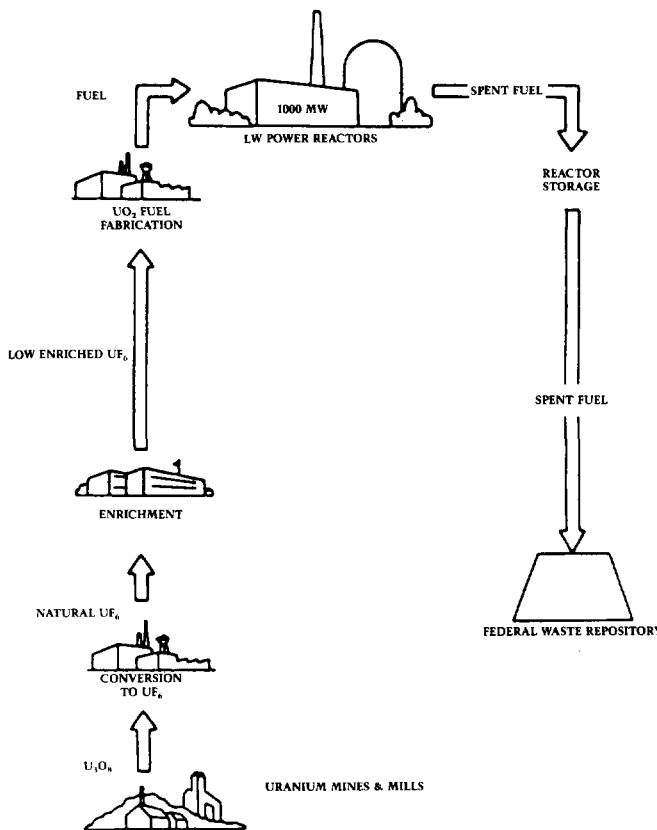


Figure 1. Light water reactor fuel cycle—no uranium or plutonium recycle (GESMO)

enriched uranium, and NaK or liquid sodium cooling. However, the AEC in its initial operations was beset by higher priority problems such as locating an indigenous supply of uranium ore and re-establishing an effective weapons program.<sup>16</sup> After review of the above power reactor projects by committee, AEC cancelled the first and downgraded the second.

Commencing in 1948 and extending over a period of about ten years, the early phase of the AEC power reactor program developed incrementally.<sup>17</sup> It experienced abrupt cancellations, re-starts and shifts in direction. A consistent objective was to engage US industry in reactor development, at first by the solicitation of proposals for designs that would produce both power and plutonium, and finally for power only. AEC offered many inducements such as subsidies for development, design, construction and operation of power reactors. Many companies became involved. The way things went is indicated by the experience—probably not the most glaring—of North American Aviation, Inc. (NAA) with its SRG design. This was a sodium cooled, graphite moderated, enriched uranium fueled reactor. (Table 2).<sup>18</sup>

It was not until 1953—halfway through this interval—that AEC formally recognized "the development of economic nuclear power as a national objective".<sup>19</sup> This was followed in 1954 by a substantial amendment of the Atomic Energy Act, which allowed private ownership of reactors, and lease or sale of fuel to reactor operators. Also enacted during this period was the Price-Anderson Act, which established a liability ceiling for reactor accidents. A distinctive change now appeared in the siting of power reactors. Very early practice had been to locate them—and all reactors—on Federal reservations in isolated, sparsely populated areas. Thus in 1951, electric power was first produced from nuclear fission by the Experimental Breeder

Table 2  
Summary of SGR History

Year	Action
1949	AEC contracts with NAA <sup>a</sup> for research & development on the SGR concept
1952	AEC plans to build a 10 Mw SGR. This would have been the U.S. nuclear power plant
1953	Plans cancelled by National Security Agency
1954	AEC contracts with NAA to build the 20 Mw Sodium Reactor Experiment (SRE)
1955	AEC accepts proposal to build a 240 Mw SGR for Consumers Public Power District (CPPD) at Hallam, Nebraska
1957	AEC finalizes contracts with NAA & CPPD. Construction starts

*Note*

<sup>a</sup> All NAA reactor development for AEC during this time interval was done by its Atomics International Division (AI). As of April 1989 it has been absorbed into Rockwell International's Rocketdyne Division.

Reactor (EBR-I) at the (then) National Reactor Test Station in Idaho; and by the Homogeneous Reactor Equipment (HRE) at Oak Ridge National Laboratory. But such early power reactors as Dresden-I (a BWR), and Shippingport (a PWR) were located near populated areas that were load centers for the respective utilities, Commonwealth Edison and Duquesne.

A glimpse at the AEC power reactor program after 10 years, shows the no fewer the nine different power reactor types either built, building or in active development. These included applications to central station power plants; ship propulsion, both naval and merchant marine; and auxiliary power in space. They are listed in Table 3 along with a brief description of the types of fuel used.<sup>20</sup>

It is worth noting that the first, and only, U.S. power plant reactor in space was one of the same type as the last entry in table 3. The reactor was designed to operate at 40 kw<sub>th</sub> and produce 500 watts of power continuously for year from its Si-Ge thermoelectric converter.<sup>21,22</sup> Launched by rocket aboard an Agena B Vehicle on April 5, 1965 into a 700-mile polar orbit, the reactor was prematurely shut down automatically by an unrelated fail-

Table 3  
Power Reactor Types as of 1957  
(Built, building, or in active development)

Designation	Application	Fuel
Fast breeder (LMFBR)	Power and fuel cycle	<sup>238</sup> U metal and alloys; Pu alloys
Intermediate spectrum (SIR)	Propulsion	( <sup>238</sup> U ...)
Pressurized water <sup>a</sup> (PWR)	Propulsion; power	<sup>235</sup> U alloys; <sup>238</sup> UO <sub>2</sub>
Boiling water <sup>a</sup> (BWR)	Power	<sup>235</sup> UO <sub>2</sub> ; <sup>238</sup> U alloys
Homogeneous (HRE)	Power	<sup>235</sup> UO <sub>2</sub> SO <sub>4</sub> in water (and D <sub>2</sub> O)
Organic moderated and cooled	Power	<sup>235</sup> UO <sub>2</sub> dispersion in steel; <sup>238</sup> U alloys
Sodium graphite	Power	<sup>235</sup> U; <sup>238</sup> U alloys; <sup>238</sup> U carbide
Plutonium recycle (PRTR)	Fuel cycle research	(U, Pu) O <sub>2</sub> <sup>b</sup>
Systems for Auxiliary Nuclear Power (SNAP)	Space power	<sup>238</sup> U metal, homogeneous <sup>c</sup> dispersion in Zr H <sub>x</sub> moderator

Notes

<sup>a</sup> Together, referred to now as LWR—Light water reactor

<sup>b</sup> The PRTR provided important (and the only) U.S. experience with recycling plutonium in a thermal spectrum reactor, although it did not generate electric power.

<sup>c</sup> Critical experiment completed, using a mixture of <sup>235</sup>UO<sub>2</sub> and ZrH<sub>x</sub>. All other SNAP reactors used homogeneous dispersion as above.

ure. Estimated orbit lifetime is 3,800 years, and the calculated total fission product activity as of April 1989 is less than 10 Ci.<sup>23</sup>

Several additional reactor systems have been demonstrated more recently. These include:

. MSRE

This research reactor used a core of molten fluorides, in which the fuel was <sup>233</sup>UF<sub>4</sub>. Although it generated no electric power, it was an important demonstration of a thermal spectrum U-233 system.

. HTGR

The high temperature gas-cooled reactor, a converter, operated with particulate <sup>235</sup>UO<sub>2</sub>-ThO<sub>2</sub> fuel, dispersed in a graphite moderator cooled by helium gas. Two power reactors have been built in the U.S., and a related design has been used in Europe.

. LWBR

The light water breeder reactor used a core of <sup>238</sup>UO<sub>2</sub>-ThO<sub>2</sub>, in the Shippingport PWR.<sup>24</sup>

However, it is the LWR-EUO<sub>2</sub> system that has emerged as the preferred U.S. power reactor with, so far, the stowaway fuel cycle indicated in Table 4. The metal-fueled LMFBR is still significant, as the only U.S. reactor system to operate (1946-1969) with fuel recycle.<sup>25</sup>

The large variety of reactor types indicated by Table three may, with hindsight, indicate a pre-occupation with the reactor—in which, after all, fuel resides only for a while on its journey through the cycle. Relatedly, the AEC program of that time may appear deficient in such areas as fissionable materials safeguards and waste handling. Yet very substantial efforts were made on other parts of the fuel cycle, as outlined below.

Table 4  
Fuel Cycle Definitions

Conventional

1. Mining
2. Milling
3. Conversion
4. Enrichment
5. Fuel Fabrication
6. Irradiation
7. Storage
8. Reprocessing
9. Reconversion
10. Re-Enrichment or Fissile Recycling
11. Shipping
12. Waste Management
13. Repository Storage

Once-Through

Steps 1 through 7, then 11 through 13

Stowaway

Steps 1 through 7

## Reprocessing

Alternative procedures were investigated in research and pilot scale projects. Initial emphasis was on improving Hanford practice (aqueous reprocessing), and culminated in the development of PUREX process. A much more efficient and lower-volume process than BiPO<sub>4</sub> co-precipitation, PUREX made use of solvent extraction by which an organic phase (such as tri-butyl phosphate) preferentially removed U and Pu from fission products.<sup>26</sup> PUREX plants at Idaho, Savannah River and Hanford have operated successfully to the present time since 1951, 1954 and 1956 respectively.<sup>27</sup> The PUREX flowsheet is indicated in Figure 2.

### PUREX waste storage as calcine

Aqueous waste solutions were evaporated and converted to a dry powder calcine, which was then stored in stainless steel canisters—the first storage of HLW in solid form.<sup>28</sup> As a waste form, calcine turned out to not to be acceptable for disposal in a repository (see below);<sup>29</sup> but for interim storage, the canister/calcine system has its advantages over storage of liquid HLW in tanks.

### Mined Geological Repository

Acting on a favorable evaluation by review committee of the National Academy of Science, ORNL investigated the potential of a bedded salt formation near Lyons, KS as a repository for indefinitely long storage of HLW.<sup>30</sup> Because of conditions local to the Lyons site, which included presence of unplugged boreholes left from prospecting for gas

and oil, the location turned out to be unsuitable. But ORNL's work opened up the search for a suitable repository in a practical way, and led to the present construction of the Waste Isolation Pilot Plant (WIPP), which is located in a bedded salt formation.

### Ultimate Wasteforms

Experiments in the 1950s showed the potential of borosilicate glass (Hanford) and of ceramics, such as aluminosilicates (Brookhaven) to fix and contain HLW.<sup>31</sup> The glass development work was the forerunner of the Borosilicate block plants now (1989) under construction at Savannah River and at Nuclear Fuel Services. Incorporation of HLW into the borosilicate glass blocks requires, of course, reprocessing. At present, use of this wasteform is limited to production reactor (military) fuel. As for ceramic development work, Department of Energy recently (1981) completed an intensive alternative (to glass) wasteform evaluation program that included several ceramic systems.<sup>32</sup>

## 3. THE FUEL CYCLE—AN INTERDEPENDENT SYSTEM

Despite the extensive effort on development of nuclear reactors, it is evident from Table 4 that reactor irradiation is only one step in the complete fuel cycle. Another step is reprocessing, which is essential for production reactors and breeders, where new fuel is the dominant product. It is *not* essential for power reactors if several requirements can be met, including an economical supply of fresh fuel, and a licensed repository for safe, indefinitely long storage of spent fuel. Historically, fuel cycle concepts including reprocessing as an integral step, developed early, in the considerations of breeder reactors. Nevertheless, it is appropriate here to review first, briefly, the development of reprocessing for other power reactor fuel.

It has been noted that the AEC program included substantial efforts to improve the reprocessing of production reactor fuel. With the successful experience of the PUREX plants, it was assumed the power reactor fuel would use the same process, with modifications of the head end to accommodate different fuel composition and burnup. The cost of reprocessing was assumed to be balanced by the income from sale to the AEC of the purified unburned uranium (as UF<sub>6</sub>) and plutonium (as PuO<sub>2</sub>). No reprocessing plant was built at an adequate scale to check out the assumptions; and despite tests to evaluate other key steps such as placement in a geological repository, AEC did not conduct appropriate trials of the complete cycle of Table 4, on which to base realistic cost estimates. Instead, at the end of the reactor development period summarized in Table 3, reprocessing costs were based on the analysis of a "reference fuel reprocessing plant", with an estimated capital cost of \$20.5 million (in 1957) and annual throughput capacity of 300 tons of fuel.<sup>33</sup> Although this was a PUREX plant, the analysis was limited to metal fuel.

AEC acted on the assumption, which appeared valid at the time, that commercial power reactor fuel reprocessing was merely an extension of chemical industry practice, and therefore should be left to private industry. Eventu-

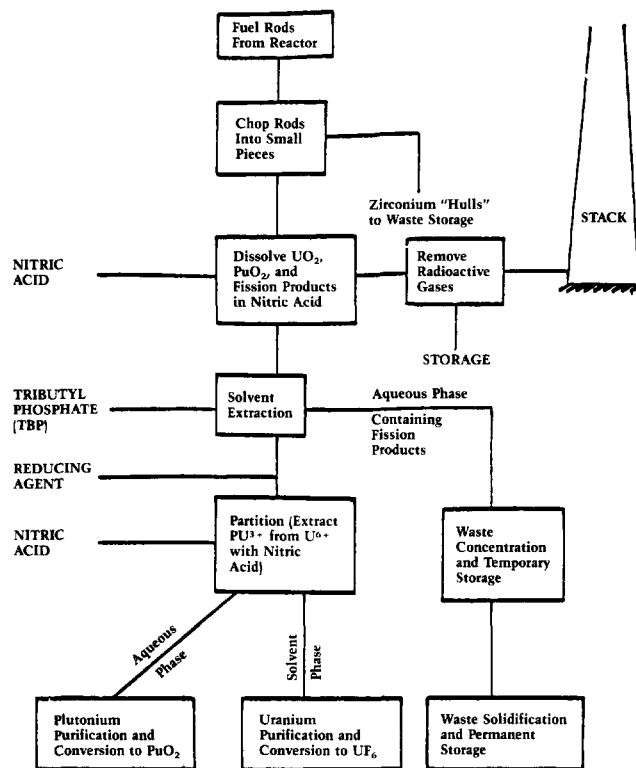


Figure 2. Schematic PUREX Flow Chart

ally, a commercial 300 ton PUREX plant would be built, the Nuclear Fuel Services installation at West Valley, NY, which was to be shut down after operating for six years (although not at design levels).<sup>34</sup>

The problems of commercial fuel reprocessing have in part been technological, as in the General Electric Facility at Morris, IL—built, but never operated with irradiated fuel.<sup>29</sup> However, plant siting, shifting Federal agency requirements and economics have been major factors, as in the Allied-Gulf Nuclear Services plant at Barnwell, SC—built but never operated.<sup>35</sup> Detailed plans have been developed for several other plants, but no construction started. Commercial fuel reprocessing was banned by order of President Ford in October 1976.<sup>36</sup> The ban was extended “indefinitely” by President Carter in April 1977, when he also instigated a two-year long International Fuel Cycle Evaluation (INFCE) project, conducted under the auspices of the International Atomic Energy Agency, a United Nations body. The purpose of INFCE was to identify diversion-resistant fuel cycles, which would safeguard against proliferation of nuclear weapons. In this, the INFCE was not successful; but it did show that without reprocessing, the once-through cycle was sustainable, and spent fuel was acceptable, if not ideal, waste form for repository disposal. Finally, INFCE evaluated the feasibility of centrally located international reprocessing facilities. This U.S. recourse to international action was reminiscent of the ideas first proposed by the U.S. to the U.N. in March 1946 for international control of atomic energy.

Although the ban was removed in September 1981 by order of President Reagan, no private industry has ventured into the field. As of today, with no commercial reprocessing available, and the opening of a repository for spent power reactor fuel probably decades away, the fuel must remain in interim storage. It is pertinent to compare here the experience of other countries, notably the U.K. and France, where aqueous reprocessing and fuel recycling have been conducted since inception of their nuclear power programs in the 1950s. Additionally, the French program has for several years included operation of a borosilicate glass block plant for incorporation of calcined HLW.<sup>37</sup> The blocks are then encased in stainless steel canisters which are retrievably stored in a facility that was designed to provide 40 years of convection air-cooling. By the end of the cooling period, a suitable geological repository is expected to become available.

In these countries, nuclear power development progressed differently from the U.S. for several reasons. Historically, they were able to plan their programs free of the wartime pressures of the MED, and its legacy. Also, they had fewer alternative energy sources than the U.S. And finally, not only reactor development and construction, but also electrical generation and distribution were essentially government monopolies.

In contrast to the U.S. experience with commercial fuel described above, is the successful fuel cycle approach pursued since the early 1950s by ANL as part of their development of the LMFBR (Liquid Metal-cooled Fast Breeder). The initial incentive for breeders was the concern that the

U.S. uranium ore supply was too limited for substantial deployment of reactors.<sup>38</sup> Emphasis was on the U-233/Pu-239 breeding cycle, but studies were also directed toward Th-232/U-233. The nuclear reactions are summarized in Figure 3. (The U-233 fuel for the MSRE was obtained via the thorium reactions—but that came much later, as did the LWBR.)

Of course, exploration and mining in the 1950s and since have turned up very substantial supplies of ore in the U.S. (and especially in Canada).<sup>39</sup> Nevertheless, the early emphasis on high breeding ratio and short doubling time dictated the use of metal reactor fuel. Further, it drove the development of low-decontamination, compact (“dry”) reprocessing chemistry, in contrast to the high-decontamination, aqueous chemistry used at Hanford.

Among the many alternatives to the latter, studied by MED chemists before the BiPO<sub>4</sub> co-precipitation procedure was selected, were the pyrometallurgical processes of melting, refining and oxide drossing. These were the process steps chosen by ANL for the combined operation plant in Idaho, the Experimental Breeder Reactor-II/Fuel Cycle Facility (EBR-II/FCF).<sup>40</sup> The flow sheet is indicated in Figure 4. \* A sketch of the FCF is shown in Figure 5. The FCF reprocessed nearly 5 metric tons of metal, and refabricated enough fuel elements for about eight complete reactor core loadings, in operation from September 1964 to January 1969. The mission of the EBR-II was changed in 1969, and fuel cycle operations were discontinued. However, laboratory-scale improvements in compact reprocessing at ANL are continuing up to the present, an almost unbroken line of development since the 1950s.<sup>41</sup> Collocation of the reactor, fuel reprocessing and fuel refabrication plant, and waste storage facility only half a mile away,† contributed to the successful operation of the closed fuel cycle. Of substantial importance as well the siting of the entire activity at the Idaho National Reactor Test Station.‡

One application of compact reprocessing to commercial fuel was investigated independently in the 1950s by NAA (AI). Conducted in connection with development of the SRE, the PRE (Pyro-chemical Refabrication Experiment) was applied to spent fuel (EU) metal from reactor. The process consisted of melt refining, oxide drossing, re-enrichment with U235, and re-fabrication.<sup>42</sup> Only small pilot scale experiments were conducted. Compact reprocessing

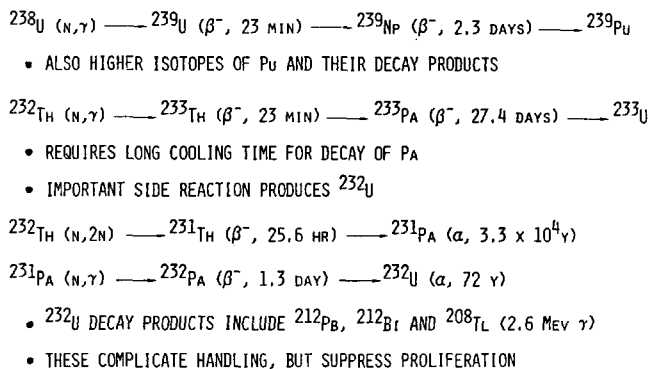


Figure 3. Nuclear reactions in breeders

applications were extended later to uranium oxide and carbide, and to thorium-bearing fuels, on a similar scale.<sup>43,44</sup>

## CONCLUSION

The MED provided both a head start on reactor technology, and a pervading influence in subsequent U.S. nuclear developments. The programs and policies of the AEC and its successor agencies supported evaluation of many alternative power reactor designs; produced a number of demonstration plants; and led to the construction of what is now the world's largest national nuclear power generating capacity. The programs also included investigations of

many important elements of the commercial power fuel cycle. To date, however, no large scale demonstration has been made—with particular emphasis on the “back-end”—of any complete fuel cycle, not even the “once-through”. An exception may emerge from the integrated fast breeder reactor/fuel cycle facility approach of ANL, whose successful demonstration of low-contamination reprocessing and remote fuel refabrication merits further development.

Nuclear power programs have taken a different course in other countries, where they have deployed fuel cycle operations more completely and on a larger scale. Their example is available to the U.S.—which is still engaging in formulating a consensus approach to solving the problems first identified during the MED era.

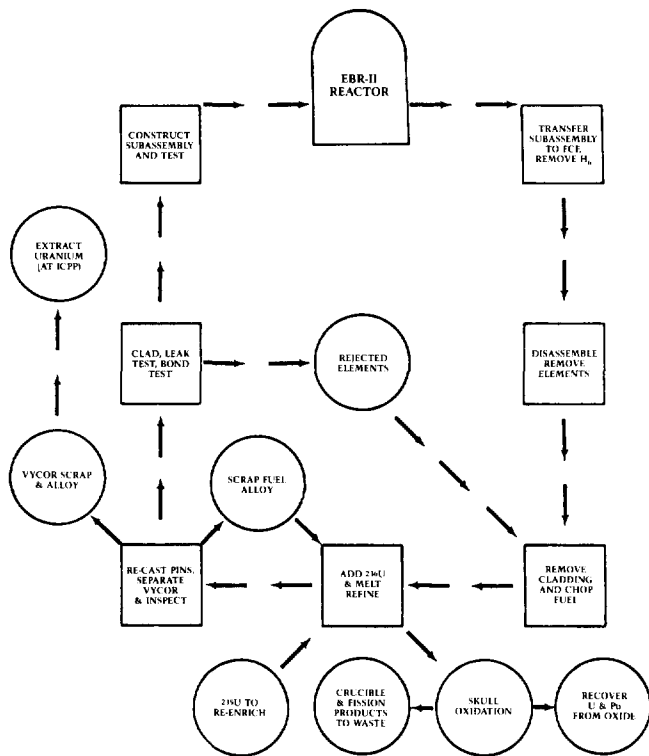


Figure 4. Schematic FCF Flowsheet

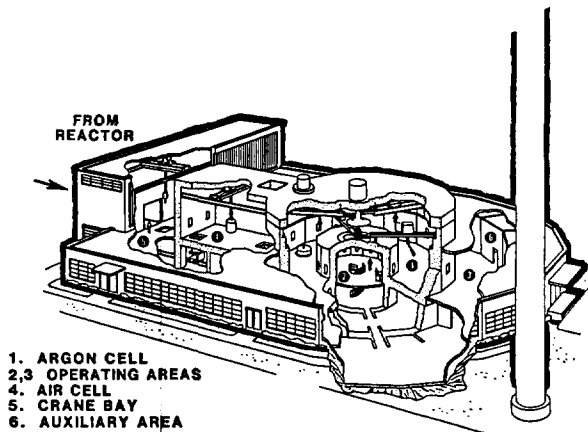


Figure 5. Perspective of the FCF

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\*The basic water boiler design was adapted and deployed as a research reactor by North American Aviation (NAA), utilizing fuel either fully enriched, for U.S. installations, or 20 percent enriched, for off-shore locations. This reactor was demonstrated to have exceptional safety against accidental release of excess reactivity.<sup>3,4</sup> It was the first reactor in California, and downtown Chicago—among other populated sites in the U.S.; and in West Germany (including West Berlin), Denmark and Japan, overseas. A total of 18 was built.

\*\*The sidestream to ICPP, a PUREX plant, was necessary to remove unburned EU from the fuel elements (whose enrichment has varied from 48 percent to 67 percent U-235 in successive designs). Process improvements indicate this will not be necessary in the future.

†The FCF was designed with some waste storage capacity. However, the Radioactive Scrap and Waste Facility (RSWF), in operation since 1965 has a much greater capacity for retrievable storage.

‡In operation since 1949, the name is now Idaho National Engineering Laboratory.

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Harry Pearlman received his B.A. from Cornell and his Ph.D. from the Massachusetts Institute of Technology. From 1942 to 1944, he was Chief Chemist for Remington Rand. From 1944 to 1946, he was a Senior Physicist for the Manhattan Engineer District, Oak Ridge, Tennessee. From 1946 to his retirement in 1982, he served Rockwell International (and its predecessor companies) both as an individual contributor and line/project manager of industrial research and development related to physical chemistry and material science of nuclear reactor technology. Since 1982, he has been an active consultant in radiation effects and material science.

# Analytical Chemistry and Measurement Science (What DOE Has Done for Analytical Chemistry)

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## ABSTRACT

Over the past forty years, analytical scientists within the DOE complex have had a tremendous impact on the field of analytical chemistry. This paper suggests six "high impact" research/development areas that either originated within or were brought to maturity with the DOE laboratories. "High impact" means they lead to new sub-disciplines or to new ways of doing business

## INTRODUCTION

The purpose of this paper is to bridge the gap between earlier papers in this symposium—which dealt with the early accomplishments of analytical chemistry within the atomic energy program—and later papers that will deal with recent accomplishments and challenges of tomorrow. The usual approach in a talk like this is to discuss what analytical chemistry has done for DOE (-ERDA, -AEC). This paper will take the opposite approach: it will consider what DOE has done for the field of analytical chemistry. The message is that we have had great impact on our own field. "Great impact" means that we have done things that lead to whole new subdisciplines or caused our discipline to a major detour in the way it does business.

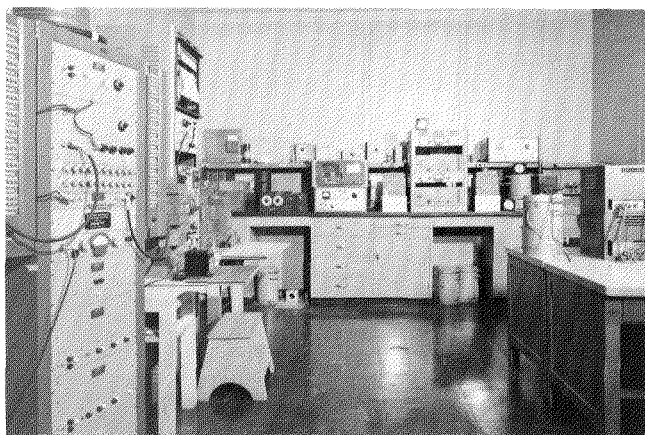


Figure 1. A vintage 1950 counting room. A 20-channel spectrometer is standing on the left.

The plan of this paper then is to present several DOE-derived contributions that have had a major impact on our discipline. Some old photographs will be used to illustrate the tremendous progress that we have made over the past forty years. Some related research opportunities will be suggested. Then, the almost incredible capabilities that we have today will be illustrated, using dollars as an analogy.

## SOME MAJOR CONTRIBUTIONS TO ANALYTICAL CHEMISTRY BY DOE SCIENTISTS

Six contributions are at the top of my list. (You may have other ideas about this.) Please note this disclaimer: we did not necessarily discover or invent these things, but we did bring them to analytical chemistry and made them viable within the field.

### 1. Nuclear and Radioactive Chemistry.

We had to learn to deal with radioactivity, of course—it was forced upon us. But, we did much more than deal with it. We developed a whole branch of analytical chemistry based upon radiochemistry, we extended it to tracer chem-

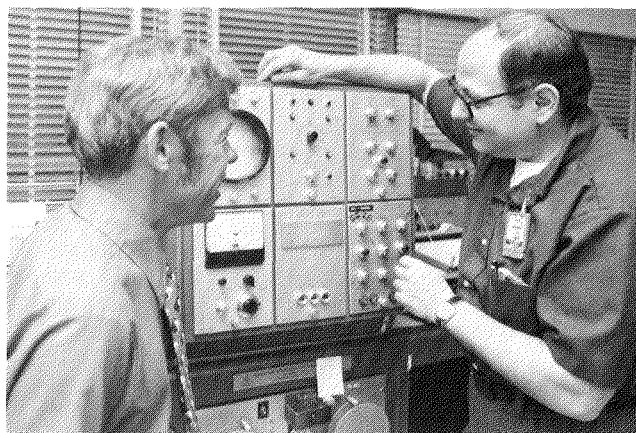


Figure 2. A 400-channel spectrometer, vintage 1964.





There is a real opportunity here today to apply expert systems to the base amount of knowledge that we have established in the area of inorganic separations. Expert systems offer a way to store our knowledge, use it efficiently, expedite methods development, trouble-shoot and tutor non-experts.

### 3. Operational Amplifiers in Analytical Instrumentation

(Figure 7) When Glenn Booman at Idaho Falls put operational amplifiers into an electrochemical instrument, he forever changed the nature of analytical instrumentation

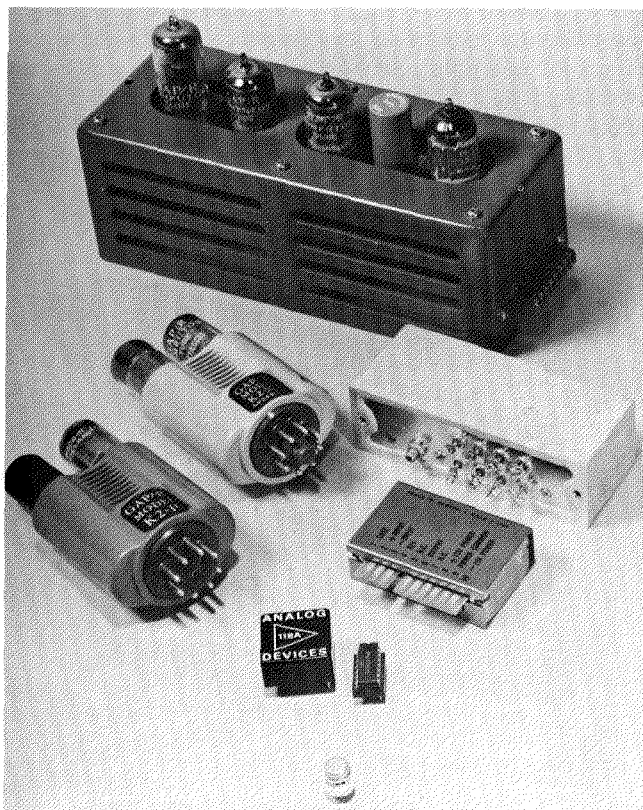


Figure 7. Operational amplifiers, vintage 1960.

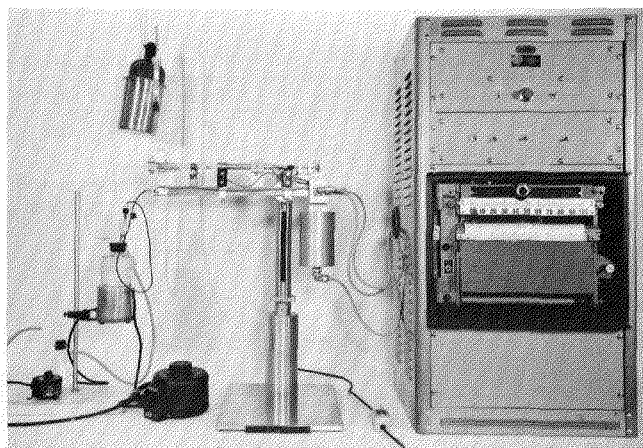


Figure 8. A servo-controlled potentiometric titrator, vintage 1960.

in general, and electroanalytical instrumentation in particular. Booman's device was a controlled-potential coulometric titrator, an instrument that had been impractical prior to the advent of operational amplifiers because manual potential control was tedious and the measurement of coulombs was difficult. Glenn's first application was the determination of uranium by reduction of  $U(VI)$  to  $U(IV)$  at a mercury pool electrode, and it was precise to a few tenths of a percent for samples of a few milligrams. Fred Scott almost immediately applied the new hardware to plutonium, using the  $Pu(III)$ ,  $Pu(IV)$  couple and a platinum electrode. Lots of work and lots of applications ensued, by Bob Stromatt, Jack Harrar, Bob Propst, myself and others. CPC became a workhorse for us for a while and it is still used in many laboratories to determine milligram quantities of uranium and/or plutonium precisely. In fact Wanda Mitchell, Dennis Troutman and Ken Lewis recently published a description of an automated CPC titrator that is in use today at the New Brunswick Laboratory.

Booman's concept of potential control by operational amplifier circuitry was extended by Myron Kelly and Dale Fisher to DME polarography and thence to voltammetry with solid electrodes. Thus, the whole idea of three-elect-

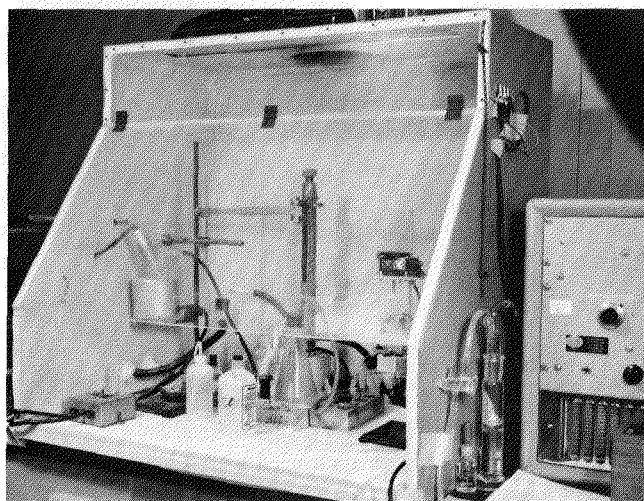


Figure 9. A titration box for plutonium, vintage 1960.

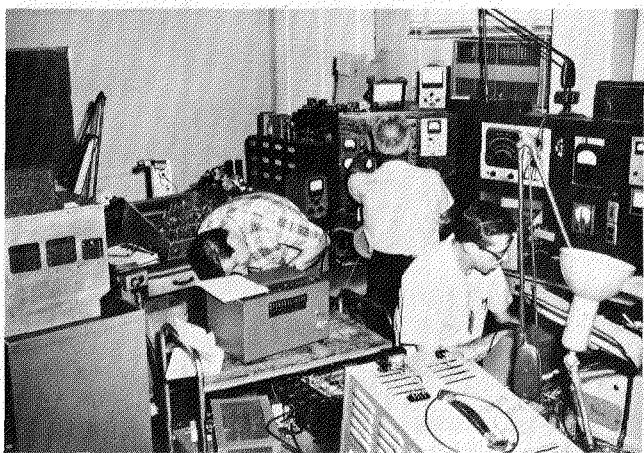


Figure 10. The operational amplifier era.

trode chemistry was born. It is the conventional way to do electroanalytical chemistry today. Both Fisher and Kelly won the ACS Chemical Instrumentation award for their work in instrumentation. The Princeton Applied Research Corporation—now a part of EG&G—was built upon this technology.

Figure 8 shows a servo-controlled potentiometer titrator that was developed during the op-amp era to determine milligram amounts of uranium and/or plutonium. It could be used in or out of a glove box or hot cell, but it wasn't easy. Figure 9 is a view of a box—not gloved—with a potentiometric titrator on the left and a coulometric titrator on the right. We could not work with milligram quantities of plutonium under these conditions today.

Figure 10 is included to illustrate the state of affairs in the operational amplifier era. It was a time of solder and wire and resistors and other electronic components. It was a time of hands-on instrumentation.

Future research and development in the general area of instrumentation is likely to emphasize sensors and methodology for in-line and at-line analysis.



Figure 11. A laboratory minicomputer system of the 1970s.

A. Multiple-Fusion Device and Miscellaneous Equipment Required for the Determination of Uranium by the Fluorometric Method

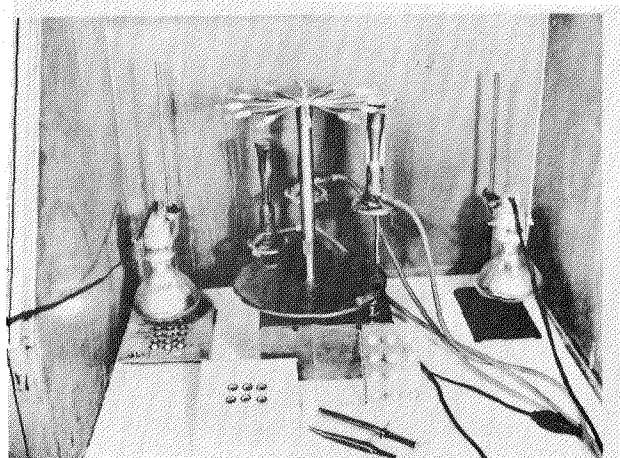


Figure 12. A pellet fusing device, vintage 1950.

#### 4. Minicomputers in Analytical Instrumentation.

Operational amplifiers were a great advance, a nice prelude to the minicomputer era. Jack Frazier at Livermore was first to see the enormous potential for minicomputers in analytical chemistry. We were all familiar with the PDP-8 series of computers that were so widely used in the 1970s. Jack had an earlier version—a PDP-7—and interfaced it to first mass spectrometers, then to other things. Interfacing to him meant developing the hardware that could be operated by the computer, as well as the software to control the hardware. His was a systems approach, which is trite today but was visionary then. Jack Frazier also won the ACS Chemical Instrumentation for his leadership in analytical instrumentation.

Jack Frazier, Myron Kelley (shown in Figure 11 with Jim White and a PDP-8I minicomputer), Jack Harrar, Dale Fisher, Sam Perone and many others made us think about our instrumentation in enlarged terms. We began to see that the computers expanded our horizons as well as our efficiency. They let us make measurements that we could not otherwise make. These men set the stage for the microcomputers that are so ubiquitous today.

Future research in this area is likely to be aimed at the development data management systems that are relational in nature, so that we or our clients can extract information from the database in virtually any format they choose, and manipulate it to suit the occasion.

#### 5. Optical Spectroscopy.

This is another area of analytical chemistry in which great advances have been made since the 1950s, and again it is one on which DOE-sponsored work has had tremendous impact. There are two techniques that warrant special mention here. One is fluorimetry and the other is inductively coupled plasma atomic spectrometry.

The fluorimetric determination of uranium illustrates just how far we have come. In the old days we put traces of uranium on NaF-LiF, fused them by flaming (Figure 12), and then measured the uranium by fluorescence (Figure 13). We could measure 0.1 ppm at a time when parts per thousand measurements were considered good. Typically, we improved hardware to improve the method: better fusion systems (Figure 14) and better fluorimeter systems (Figure 15). As has often happened, it took a change of concept to provide a quantum advance in methodology. Laser-based fluorescence plus carefully designed timing and measuring electronics have proved to be the next step, as

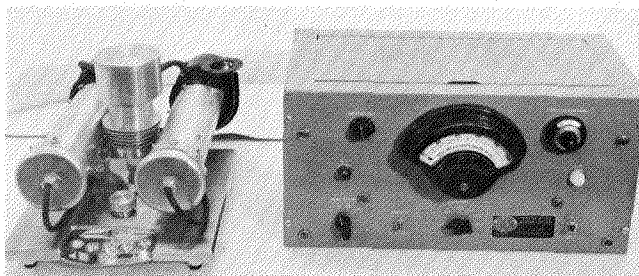


Figure 13. An early uranium fluorimeter.

There is a real opportunity here today to apply expert systems to the base amount of knowledge that we have established in the area of inorganic separations. Expert systems offer a way to store our knowledge, use it efficiently, expedite methods development, trouble-shoot and tutor non-experts.

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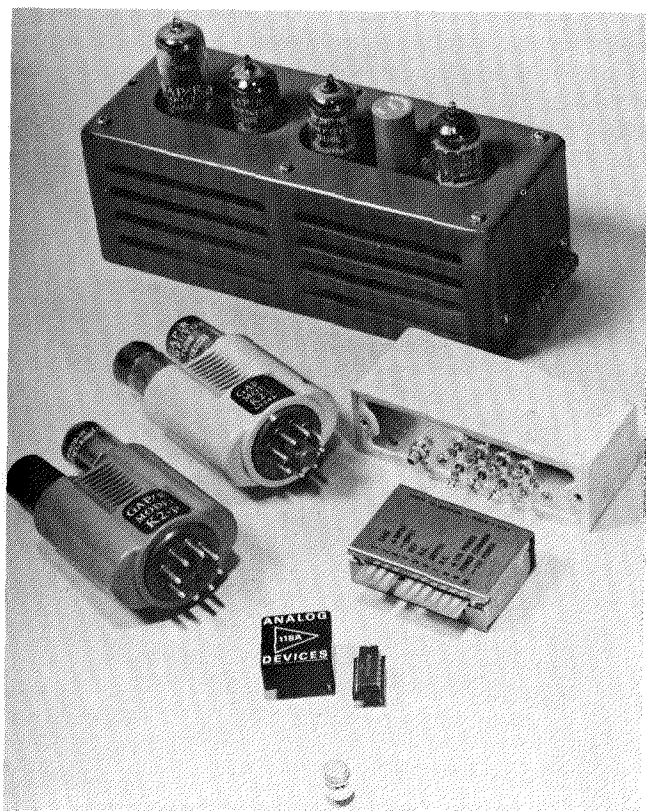


Figure 7. Operational amplifiers, vintage 1960.

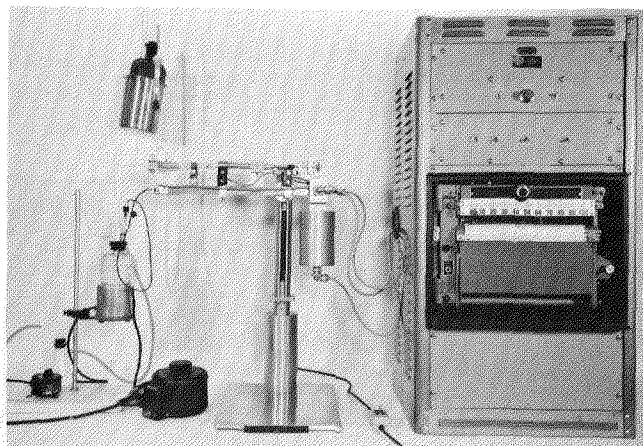


Figure 8. A servo-controlled potentiometric titrator, vintage 1960.

in general, and electroanalytical instrumentation in particular. Booman's device was a controlled-potential coulometric titrator, an instrument that had been impractical prior to the advent of operational amplifiers because manual potential control was tedious and the measurement of coulombs was difficult. Glenn's first application was the determination of uranium by reduction of U(VI) to U(IV) at a mercury pool electrode, and it was precise to a few tenths of a percent for samples of a few milligrams. Fred Scott almost immediately applied the new hardware to plutonium, using the Pu(III), Pu(IV) couple and a platinum electrode. Lots of work and lots of applications ensued, by Bob Stromatt, Jack Harrar, Bob Propst, myself and others. CPC became a workhorse for us for a while and it is still used in many laboratories to determine milligram quantities of uranium and/or plutonium precisely. In fact Wanda Mitchell, Dennis Troutman and Ken Lewis recently published a description of an automated CPC titrator that is in use today at the New Brunswick Laboratory.

Booman's concept of potential control by operational amplifier circuitry was extended by Myron Kelly and Dale Fisher to DME polarography and thence to voltammetry with solid electrodes. Thus, the whole idea of three-elect-

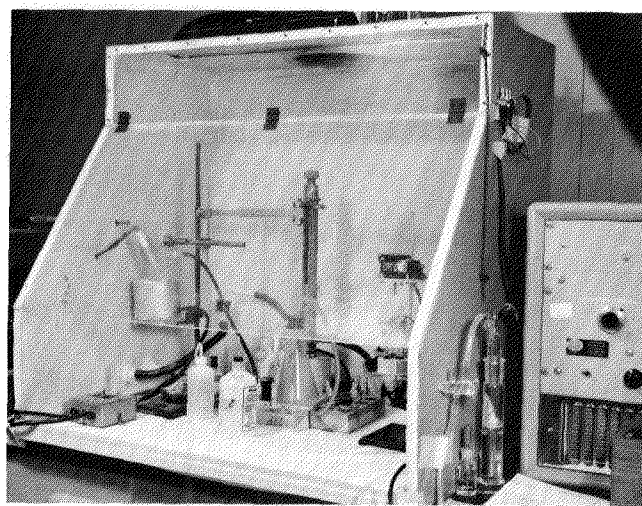


Figure 9. A titration box for plutonium, vintage 1960.



Figure 10. The operational amplifier era.

trode chemistry was born. It is the conventional way to do electroanalytical chemistry today. Both Fisher and Kelly won the ACS Chemical Instrumentation award for their work in instrumentation. The Princeton Applied Research Corporation—now a part of EG&G—was built upon this technology.

Figure 8 shows a servo-controlled potentiometer titrator that was developed during the op-amp era to determine milligram amounts of uranium and/or plutonium. It could be used in or out of a glove box or hot cell, but it wasn't easy. Figure 9 is a view of a box—not gloved—with a potentiometric titrator on the left and a coulometric titrator on the right. We could not work with milligram quantities of plutonium under these conditions today.

Figure 10 is included to illustrate the state of affairs in the operational amplifier era. It was a time of solder and wire and resistors and other electronic components. It was a time of hands-on instrumentation.

Future research and development in the general area of instrumentation is likely to emphasize sensors and methodology for in-line and at-line analysis.



Figure 11. A laboratory minicomputer system of the 1970s.

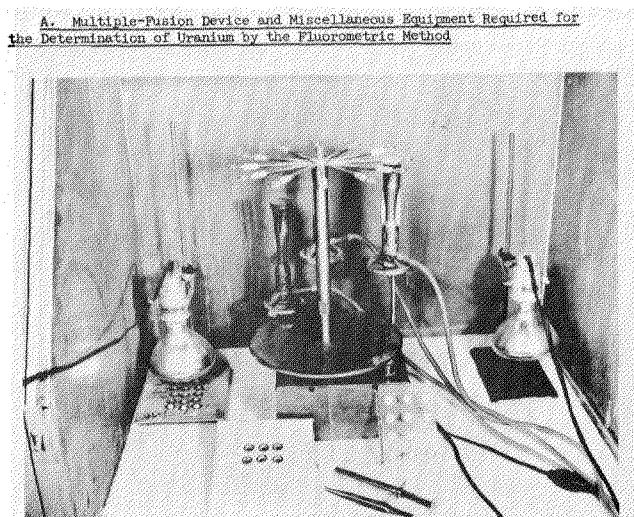


Figure 12. A pellet fusing device, vintage 1950.

#### 4. Minicomputers in Analytical Instrumentation.

Operational amplifiers were a great advance, a nice prelude to the minicomputer era. Jack Frazier at Livermore was first to see the enormous potential for minicomputers in analytical chemistry. We were all familiar with the PDP-8 series of computers that were so widely used in the 1970s. Jack had an earlier version—a PDP-7—and interfaced it to first mass spectrometers, then to other things. Interfacing to him meant developing the hardware that could be operated by the computer, as well as the software to control the hardware. His was a systems approach, which is trite today but was visionary then. Jack Frazier also won the ACS Chemical Instrumentation for his leadership in analytical instrumentation.

Jack Frazier, Myron Kelley (shown in Figure 11 with Jim White and a PDP-8I minicomputer), Jack Harrar, Dale Fisher, Sam Perone and many others made us think about our instrumentation in enlarged terms. We began to see that the computers expanded our horizons as well as our efficiency. They let us make measurements that we could not otherwise make. These men set the stage for the microcomputers that are so ubiquitous today.

Future research in this area is likely to be aimed at the development data management systems that are relational in nature, so that we or our clients can extract information from the database in virtually any format they choose, and manipulate it to suit the occasion.

#### 5. Optical Spectroscopy.

This is another area of analytical chemistry in which great advances have been made since the 1950s, and again it is one on which DOE-sponsored work has had tremendous impact. There are two techniques that warrant special mention here. One is fluorimetry and the other is inductively coupled plasma atomic spectrometry.

The fluorimetric determination of uranium illustrates just how far we have come. In the old days we put traces of uranium on NaF-LiF, fused them by flaming (Figure 12), and then measured the uranium by fluorescence (Figure 13). We could measure 0.1 ppm at a time when parts per thousand measurements were considered good. Typically, we improved hardware to improve the method: better fusion systems (Figure 14) and better fluorimeter systems (Figure 15). As has often happened, it took a change of concept to provide a quantum advance in methodology. Laser-based fluorescence plus carefully designed timing and measuring electronics have proved to be the next step, as

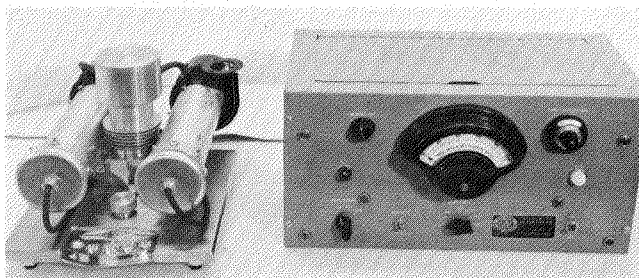


Figure 13. An early uranium fluorimeter.

indicated in Figure 16. A pulse from a nitrogen laser excites the uranium, which in this case is in solution. Measurements of fluorescence intensity are made as a function of time and extrapolated back to  $t=0$  to get the concentration dependent readout. This circumvents interference from impurities in the solvent. These measurements are quick, reliable and sensitive to the 0.05ppb level without pre-concentration.

Inductively coupled plasma spectrometry (Figure 17), is by far the DOE-sponsored development of the greatest impact on optical spectrometry. Velmer Fassel and his colleagues at the Ames Laboratory developed the inductively coupled plasma source, which is now in use in laboratories all over the world. The ICP was adopted promptly by the instrument companies and has become the standard method for trace element analysis in water. This technology caused the field of analytical chemistry to take a detour. The latest rage is to couple Fassel's ICP source with a mass spectrometer, thereby obtaining improved sensitivity and selectivity, plus isotopic information. There are at least six ICP/MS systems within the DOE laboratories now and several others are on the way. At about the same time, Sam Hurst, Jack Young and Marvin Payne developed a laser-based spectrometric technique that was claimed to detect a single atom. In fact, there has been one claim in

the literature of detecting half an atom. Half an atom! They must have done it with mirrors (or statistics).

Laser spectrometry is certain to be a prominent R and D area in analytical optical spectroscopy in the future. Laser offers tremendous resolution, control, and speed.

#### 6. Inorganic Mass Spectrometry.

Inorganic mass spectrometry— isotopic analysis, gas analysis, major and minor component analysis—must be included in any list of very significant contributions to measurement science via DOE. DOE labs have been slow to get into organic mass spectrometry, but they have been prime movers in isotopic and inorganic mass spectrometry.

### LASER-BASED FLUORIMETRY

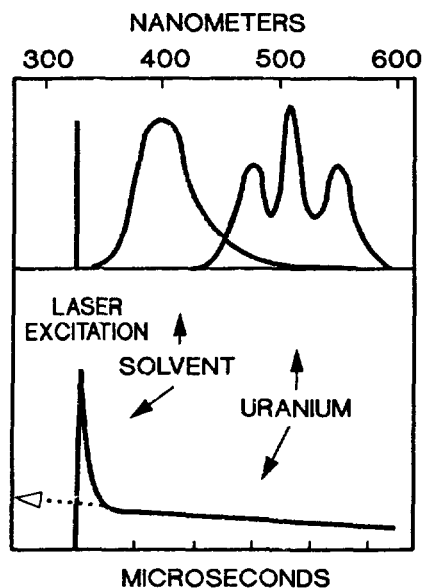


Figure 16. Laser-excited fluorescence of uranium.

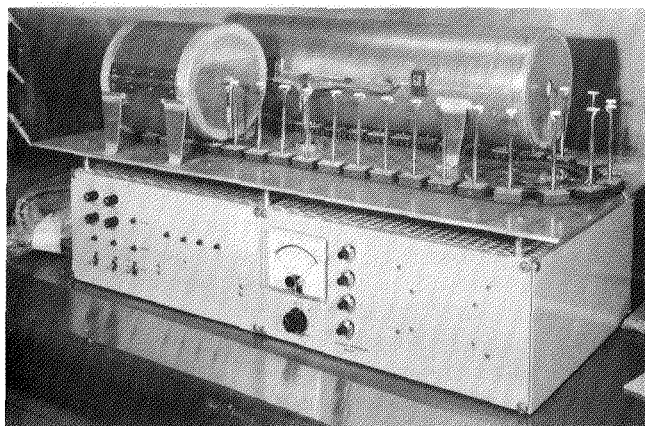


Figure 14. An advanced pellet fusing device, vintage 1970.

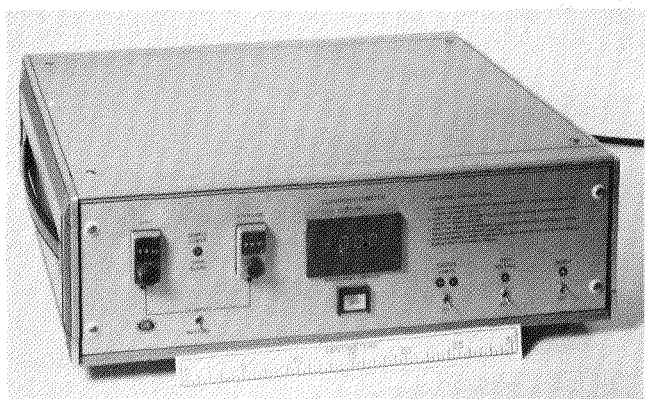


Figure 15. An advanced fluorimeter, vintage 1970.

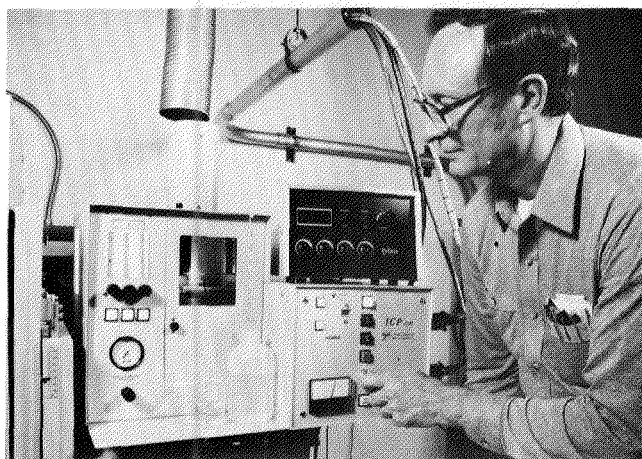


Figure 17. An inductively coupled plasma source for atomic emission spectrometry, vintage 1980.

try. We owe a great deal to people like Al Nier, Gus Cameron, Harry Svec, Leo Collins and others who not only developed the instruments and techniques, but also set the foundations and expectations upon which the field is built.

Figure 18 shows a two-stage machine the ORNL built for the IAEA Safeguards Analytical Laboratories in Vienna in the mid-1970s, for high precision isotopic analysis of uranium. This machine has now been supplanted by commercial instrumentation that can do fantastic things. Isotopic ratios can be measured with precision and accuracy of 0.01 percent. With gas machines, the precision and accuracy approaches 0.003 percent. Mass spectrometry has become the premier analytical technique today, in sensitivity, accuracy and applicability.

Research in analytical mass spectrometry in the future is likely to include trapped ion and laser-based techniques. Ion traps and ion cyclotron mass spectrometers are already attracting much attention in organic mass spectrometry, and resonance ionization mass spectrometry has already been shown to have great selectivity.

The above six areas of contribution were selected as having a major impact on the field of analytical chemistry. You may disagree with some of the choices, or perhaps with some of the future research opportunities that are mentioned. I hope you can agree with the premise that DOE scientists have changed the course of analytical chemistry.

## WHAT HAS HAPPENED TO US IN FOUR DECADES

I want to conclude by illustrating what has transpired in measurement science since NBL was established. To do that I want to use the height of a stack of dollar bills as my reference. A stack of one hundred dollar bills measures 0.75 inch. We can relate accuracy and precision to stacks of bills. Thus, in 1950 we could determine major constituents with an accuracy of 99.8-99.9 percent, or about one part per thousand. This is analogous to measuring all but one or two bills in a stack of bills 7.5 inches tall. Today we can do almost 100 times better. The analogy now is measuring all except one or two bills in a stack 750 inches

(62.5 feet) tall. I believe we have made good, but not spectacular, improvement insofar as accuracy is concerned.

The real gains have been made in sensitivity. When NBL was born, detection limits for ionic analyses were generally in the tens to hundreds of parts per million. Using the above analogy, detecting ten ppm corresponds to detecting one blank paper in 100,000 bills. This is about 750 inches or 62.5 feet of dollar bills. Today, we operate routinely at the part per billion level. The analogy is detection of one



Figure 19. Analytical chemistry, vintage 1950.

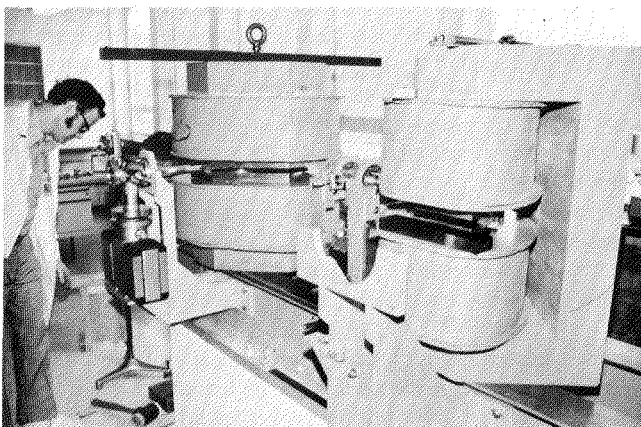


Figure 18. A two-stage mass spectrometer, vintage 1975.

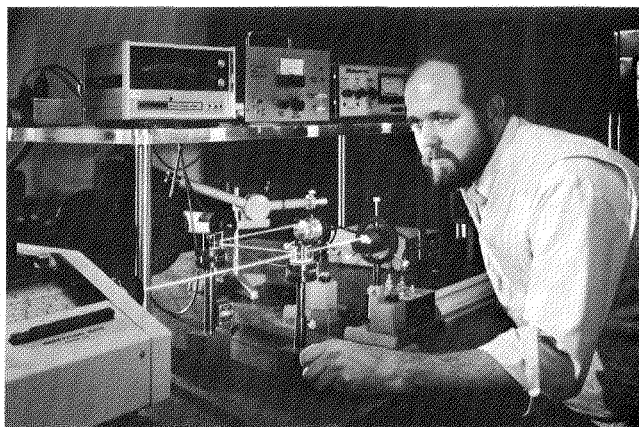
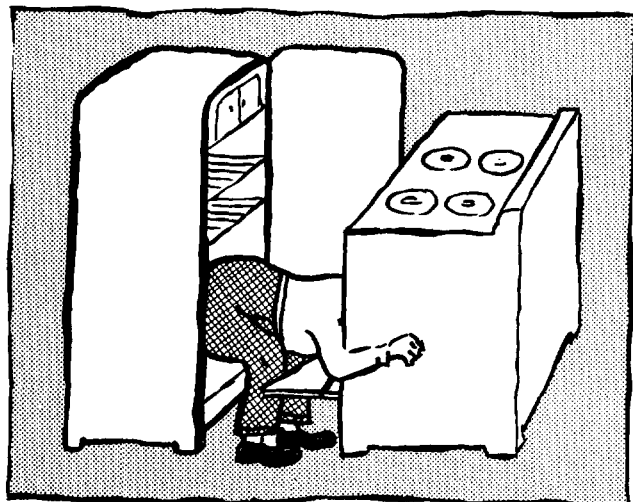


Figure 20. Analytical chemistry, vintage 1989.

### AVERAGES CAN BE MISLEADING



"ON THE AVERAGE, HE FEELS FINE!"

Figure 21. The law of averages.

blank piece of paper in a stack of bills about  $6.25 \times 10^5$  feet tall. To put it in context: we detect constituents in our samples at levels that correspond to one blank paper in a stack of bills as tall as 424 Empire State Buildings. We have unbelievable gains in practical sensitivity over the past forty years.

### CONCLUSION

Forty years ago, analytical chemistry was perceived primarily as "wet chemistry" (Figure 19). Today it is perceived as fancy instrumentation and computers (Figure 20). To get here from there, we have had to be technically

agile. We have had to learn new skills, develop and adopt new technology, and meet new challenges—and do so continually—over the years. It has been exciting and it has been fun. On the average, it has been fine (Figure 21).

Part of the fun, of course, has been knowing and working with the people at laboratories like NBL. The New Brunswick Laboratory has been involved in every one of the six areas of analytical chemistry that I discussed. It has been a force within the field. I congratulate NBL and wish it continued success between now and 2028.

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Wilbur D. (Dub) Shults received his B.S. and M.S. from Emory University, as one of the first group of AEC Fellows, and his Ph.D. from Indiana University after some ten years at ORNL. In 1976, he succeeded Jim White as Director of the Analytical Chemistry Division of ORNL, a position he still holds. He served, in 1981, as Chairman of the Analytical Chemistry Division of the American Chemical Society.

# Isotope Mass Spectrometry from 1968 to 1989

Paul De Bièvre

Central Bureau for Nuclear Measurements  
Commission of the European Communities  
Geel, Belgium

## ABSTRACT

The principal developments in isotope mass spectrometry are described with respect to instrument construction, detector technology, measurement precision, measurement accuracy, and reference materials. The dramatic increase in the application of isotope mass spectrometry is briefly summarized, with special emphasis on its use in safeguards of nuclear materials. The future potential versus the present achievements of the field are discussed.

Dearest colleagues, and Dr. Bingham, I feel very privileged and, indeed, honored at having been invited to attend this anniversary. When Bing called and subsequently wrote a letter, we agreed that I would cover a period of 20 years. I've taken the liberty, without asking permission, of bringing some reflections over the last 21 years. I'm not yet going to tell you why I changed to 21.

1. I would like to start with a pressing problem for 1989 and the years to come—the uncertainty of input measurements to a reprocessing plant. If we take a 10 cubic meter tank (a small tank when we think about reprocessing) and we assume systematic error in  $^{235}\text{U}$  measurements of a quarter of a percent—Bill Shields will certainly go along with that—and a half percent on plutonium, we have an accumulated uncertainty over one year of reprocessing, (which amounts roughly two hundred batches) of the order of 12.5 kg  $^{235}\text{U}$  (Fig. 1). That is for a small tank. Much larger tanks are being built right now, as you know. Fortunately, a number of the systematic errors in our measurements are variable and do cancel out to a large degree. Mother Nature helps us in that. Hence, the real uncertainty is not that large. But even if it's a factor of ten less, we are facing a problem and that problem is becoming larger and larger as the plants which are currently being built become bigger and bigger.

2. Isotope mass spectrometry which must measure all of this is in good shape (Fig. 2). The evolution is that industry and government have discovered the value of isotope mass spectrometry for control, reference and umpire purposes.

3. The last 21 years have seen the development of a number of analytical laboratories all over the world constituting a network of verification laboratories. I want, with this picture (Fig. 3) to put this talk directly in an international frame. We are facing an international problem with nuclear measurements and our task and duty is there.

4. No scientific measurements are absolute as you know, and the simple mind would say, let us all use common reference materials to calibrate them and make them comparable. It's something which has been done in various fields. Standards institutes were built for that purpose around 1900. For some reasons, the nuclear world has not been able to come up with common reference materials so that measurements would be traceable worldwide. I'm happy to report that (I almost said, despite the big systems of this world) one item did succeed, in the course of the last 20 years, and that is a set of five uranium isotopic reference materials to calibrate  $^{235}\text{U}$  measurements by

Typical batch amount	Systematic error	Uncertainty in U or Pu amount	Uncertainty in $^{235}\text{U}$ or $^{239}\text{Pu}$ amount	*Accumulated uncertainty on $^{235}\text{U}$ , $^{239}\text{Pu}$ over 200 batches
U (0.8% $^{235}\text{U}$ ) input (10m <sup>3</sup> tank) : 2500 kg (1% loss) : 2475 kg	0.25 % 0.25 %	6.25 kg 6.25 kg	49 g 49 g	9.8 kg 9.8 kg
Pu (60% $^{239}\text{Pu}$ ) input (10m <sup>3</sup> tank) : 225 kg output (1% loss) : 22 kg	0.5 % 0.25 %	113 g 55 g	68 g 33 g	13.6 kg 6.6 kg

Systematic errors in 'input' and 'output' batches of a reprocessing plant, roughly related to threshold amounts for nuclear explosion devices.

Figure 1.

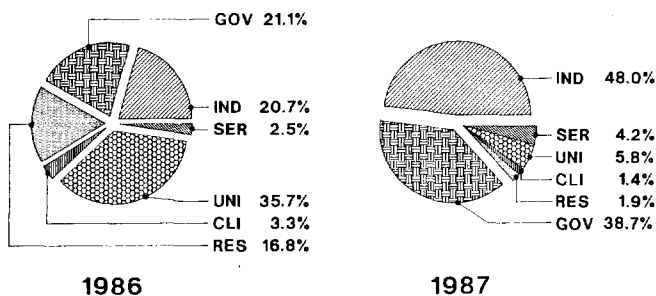


Figure 2.





It is a small (by now maybe not even important) example of what can happen without common RMs. An intermediate solution, by the way, would be at the least, a systematic approach, in verifying compatibility of existing reference materials.

5. Now some bad news. If one distributes to 31 laboratories worldwide, a sample of the same material and one asks them to do a measurement, this is what you get (Fig. 8). Why is that? Few of the scientific reasons which have been put forward, I think, are really true. Rather trivial causes must be looked for. It is my duty to state that the status of measurements in our nuclear community could be better.

I'm now going to answer why I picked out 21 years rather than 20. May 1968 had influence on human society to a much higher degree than we suspect, including on the world of accurate measurements, because it essentially promoted the feeling that a figure (i.e., the result of a measurement) was a figure and if it was put forward by somebody, there was no reason, as a matter of principle that it be less good or be better than a figure from somebody else.

The measurement situation is, in general, close to the one displayed in Fig. 8. I don't want to talk for NBL, but I know that the colleagues here at NBL are in sufficient agreement, that I can state that it is the duty of "standard" laboratories to put reference values in such a picture with a conservative uncertainty. This uncertainty should be a total uncertainty, yes, but still be smaller than the total spread amongst laboratories. Some steps have been done in trying to do that and it's a very difficult, demanding task. But there is no way around it. The picture which I just showed proves that reference materials on their own are not sufficient to get a measurement system in line. One needs regular "reference measurements." I know that it is difficult, I know that it is imposing, but it must be done.

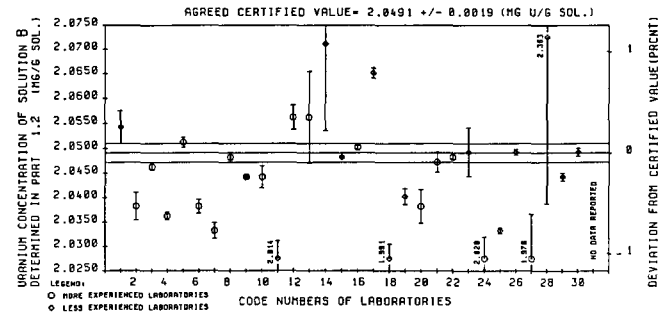


Figure 8.

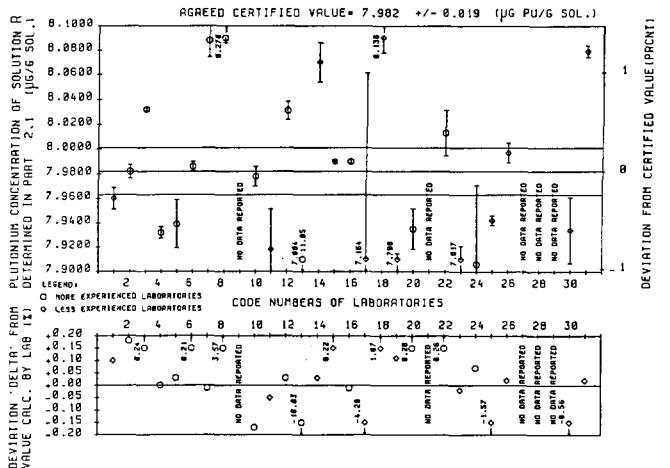
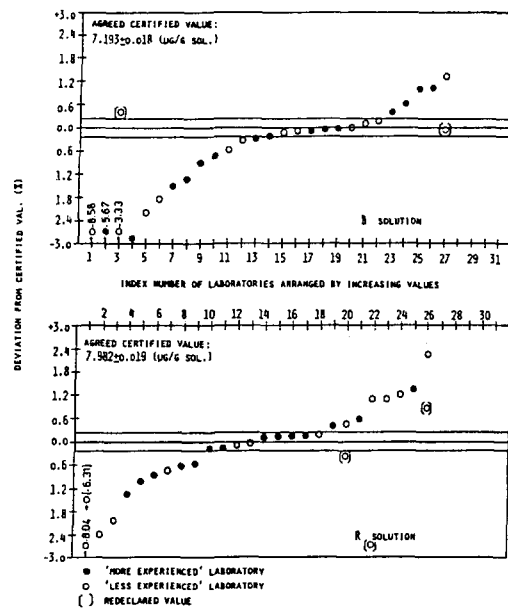
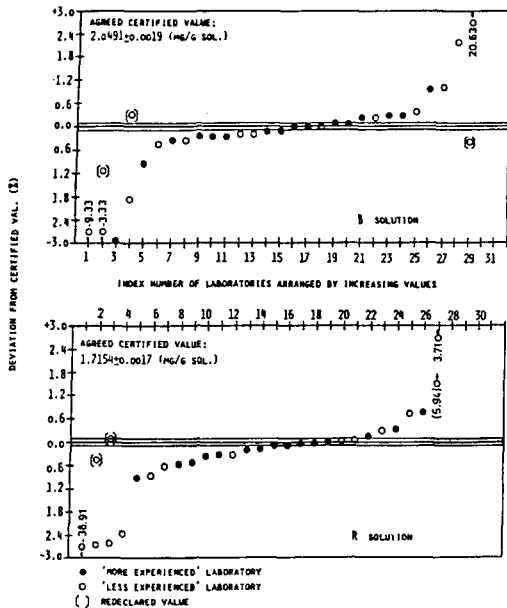


Figure 9.

For plutonium measurements the same pictures arise, although plutonium is not special at all in measurements. Using a synthetic plutonium sample the situation is, if anything, worse than in the case of measurements on plu-



IDA-80/FIG. 9: REPORTED URANIUM CONCENTRATIONS

IDA-80/FIG. 10: REPORTED PLUTONIUM CONCENTRATIONS

Figure 10

onium solutions containing fission products (Fig. 9). In addition, if one asks for the raw data from laboratories and one calculates the end results and compares them with the reported end results as calculated from the same raw data basis, this graph gives the differences in the calculations, in other words, Fig. 9, bottom part, displays the calculation errors. The plus-or-minus 0.2 percent scale is barely sufficient to contain half of the 31 results, 31 different laboratories, all over the world, including for the first time Russia, Brazil, Japan, India. A zero difference between the

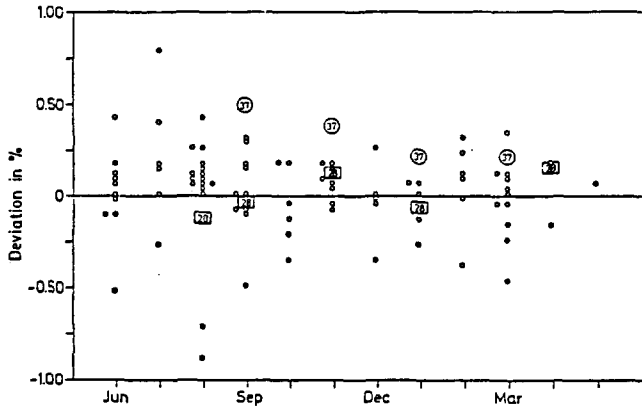
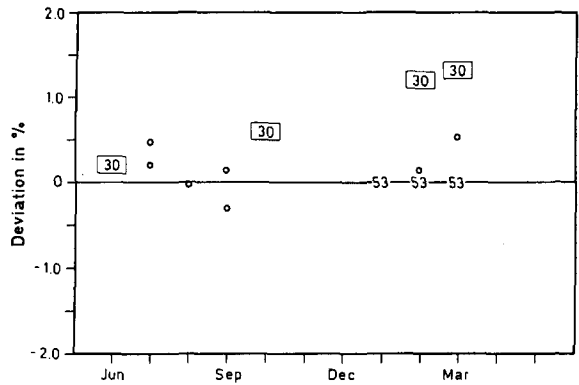


Fig. Interlaboratory evaluation of  $^{235}\text{U}/\text{U}$  (SALE 1978-1979).

Figure 11.



Interlaboratory evaluation of Pu element assay (SALE 1978-79)  
Drift with time: loss of control

Figure 12.

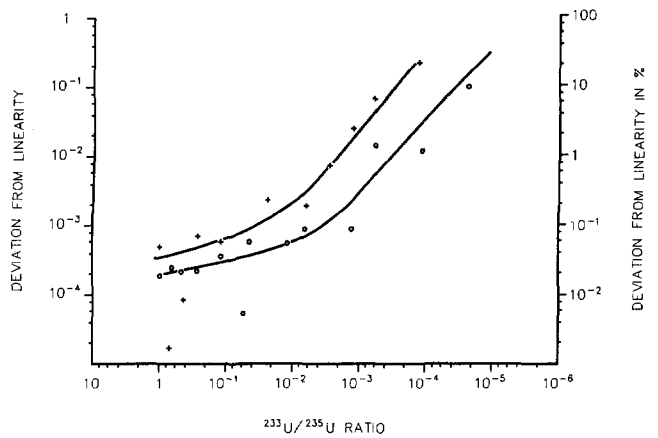
Code number	Description	Atomic isotope ratios		Unit	Price of Unit (ECU)
		$^{233}\text{U}/^{235}\text{U}$ $\pm 0.03\%$ of value	$^{235}\text{U}/^{238}\text{U}$ $\pm 0.00030$		
CBNM-IRM-072/1	Uranyl-nitrate solution	1.00033	0.99103	1 mg U in 1g solution	1000 per set
072/2		0.69967	0.99168		
072/3		0.49985	0.99212		
072/4		0.29987	0.99256		
072/5		0.10001	0.99299		
072/6		0.05091	0.99310		
072/7		0.01994	0.99317		
072/8		0.010165	0.99319		
072/9		0.0050000	0.99320		
072/10		0.0020012	0.99321		
072/11		0.00096892	0.99321		
072/12		0.00050088	0.99321		
072/13		0.00010182	0.99321		
072/14		0.000019996	0.99321		
072/15		0.0000019995	0.99321		

Figure 13.

two ways of calculating results from the same raw data is only found with one out of 31 laboratories! Don't we think that we have to do something about that in a fairly drastic way before we are questioned? If one asks these laboratories to identify themselves as more experienced (black dots), or less experienced (white dots), then the picture in Fig. 10 develops. In no case, not one single case, neither for element concentration nor for isotope measurements, was there any correlation between the self-declaration, and the actual result. In no case, I repeat.

Providing these pictures has to be done on a regular basis with externally submitted samples. That can lead to an improvement of the situation as exemplified in Fig. 11 taken from the New Brunswick Laboratory's SALE Program. However, such improvement is not necessarily the rule, as is visible from Fig. 12. Consequently, we have a regular program in Europe to provide such pictures regularly.

6. Another thing which has happened in the period 1968-1989 is the generalized acceptance that all isotopic measurements have to be calibrated by isotopic reference materials which themselves must be based on synthetic isotope mixtures. We have heard this morning about the set of uranium isotopic reference materials, which has



LINEARITY OF ISOTOPE MASS SPECTROMETER  
(Single Faraday  $\circ$ ) and Daly (+) collector)

MSL87002

Figure 14.

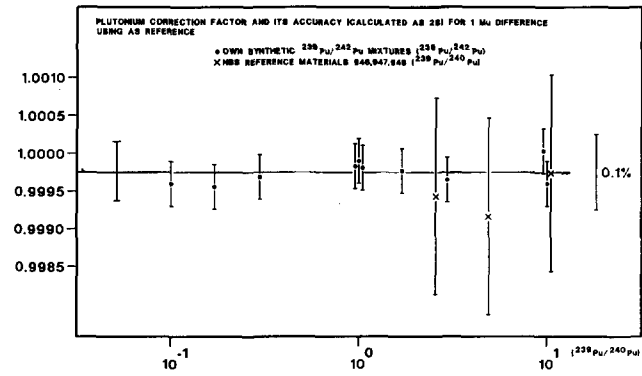


Figure 15.

come from this country (NBS) to the world and which have been so extensively used. We were forced at CBNM, against my professional conscience as a scientist so to say, to prepare a similar set of reference materials but maybe a second place in the world where this is done is not too bad. I really didn't see the need for it, but it is now there.

Much more important is the now generalized insight that one should always verify whether the K (the correction factor for isotope fractionation) is indeed linearly dependent on  $\Delta M$ , a very important thing which must be verified in order to extrapolate correction factors to allow

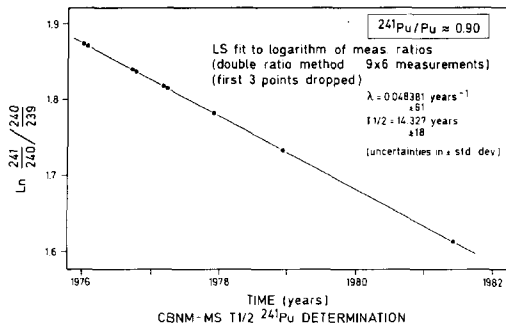


Figure 16.

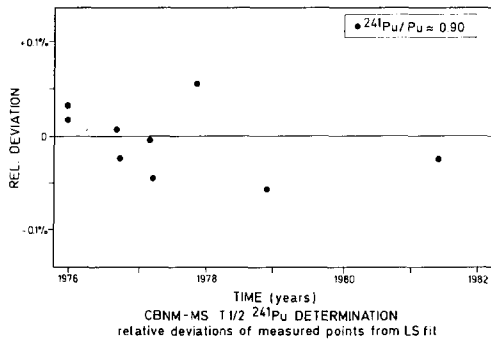


Figure 17.

$T_{1/2}$  Measurements  $^{241}\text{Pu}$   
(corrected for isotope fractionation)

t (days)	$R = \frac{^{241}\text{Pu}}{^{240}\text{Pu}} (s_{\text{int}})$	$r = \frac{^{240}\text{Pu}}{^{239}\text{Pu}} (s_{\text{int}})$
0	$22.8915 \pm 0.0040$ (0.02 %)	$3.5205 \pm 0.0011$ (0.03 %)
6	$22.8726 \pm 0.0076$ (0.03 %)	$3.5208 \pm 0.0018$ (0.05 %)
258	$22.1330 \pm 0.0069$ (0.03 %)	$3.5215 \pm 0.0016$ (0.04 %)
265	$22.1208 \pm 0.0090$ (0.04 %)	$3.5215 \pm 0.0015$ (0.04 %)
420	$21.6621 \pm 0.0086$ (0.04 %)	$3.5208 \pm 0.0011$ (0.03 %)
434	$21.6216 \pm 0.0088$ (0.04 %)	$3.5195 \pm 0.0008$ (0.02 %)
680	$20.9150 \pm 0.0091$ (0.04 %)	$3.5207 \pm 0.0008$ (0.02 %)
1057	$19.9304 \pm 0.0074$ (0.04 %)	$3.5214 \pm 0.0014$ (0.04 %)
1969	$17.6527 \pm 0.0096$ (0.05 %)	$3.5212 \pm 0.0023$ (0.06 %)
		$3.5208 \pm 0.0006$ (0.02 %)
		(1s, n = 9)

Figure 18.

calibrating other abundance ratios than those of available reference materials. A new and interesting set of RMs, is a series of U synthetic isotope mixtures with  $^{235}/^{238}$  ratios equal to unity, allowing one to correct for source mass discrimination, and with the third isotope ( $^{233}\text{U}$ ) going down in known steps over six orders to magnitude (Fig. 13). This allows one to verify whether the measurement system stays linear over these six orders of magnitude.

One of the curves in Fig. 14 has been measured in Australia and one in Geel. As one comes to measure 100 ppm, 10 ppm, or 1 ppm, one better do some very careful checks on the high sensitivity detectors.

7. Bringing a gift to New Brunswick Laboratory is difficult because of US Customs. Therefore, I brought a scientific gift which I don't think I have shown before. We have an operational facility now for mixing plutonium 239 and

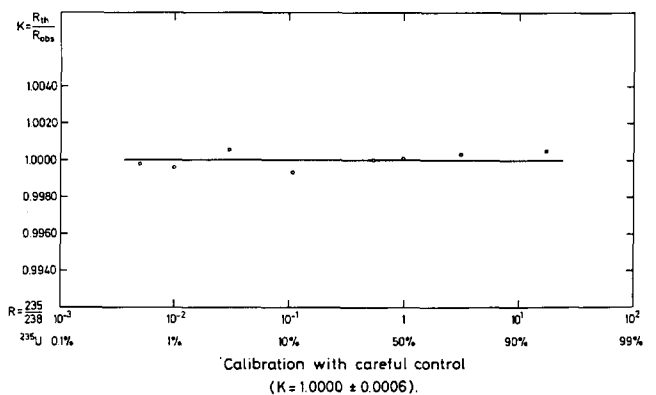
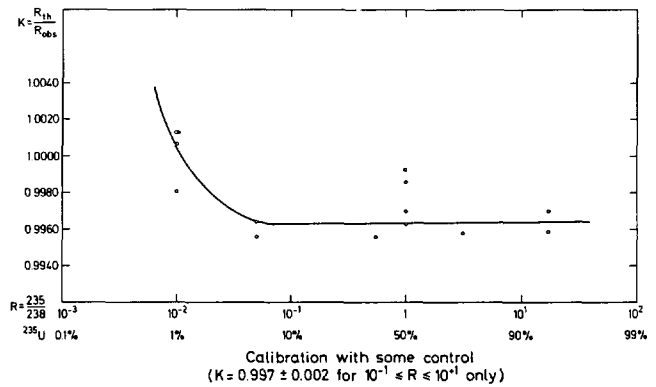
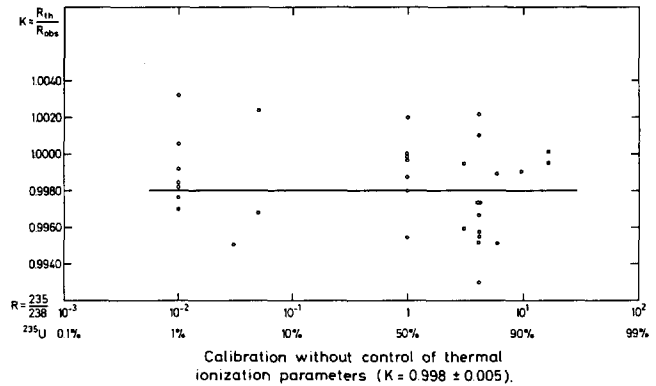


Figure 19.

242 isotopes essentially to an uncertainty of one part in  $10^4$  for a one mass-difference basis, and covering two orders of magnitude. We looked at the NBS (now NBL) plutonium isotopic standards and I am now addressing the New Brunswick Laboratory and the NBS colleagues with Bill Shields. They have been working on these three plutonium isotopic reference materials, but, at that time, had not yet put them on an absolute basis. These have now been put on an absolute basis, down at CBNM in Geel as is visible from the graph (Fig. 15). The 0.1% uncertainty limitation in any Pu isotopic measurement has now come down, a factor of three or so. Based on our plutonium synthetic isotope mixtures, we now also have a few pilot samples to calibrate gamma-spectrometry of plutonium. such measures at various places in this country can now be put on an absolute basis. I think that people who have used them are extremely enthusiastic about these first plutonium isotopic standards for gamma spectrometry.

8. Another thing which has evolved over the last 20 years is the introduction of the measurement of ratio-of-ratios in mass spectrometry. It is borrowed from the isotopic geologists, a very well organized, and in fact better quality set of isotopic measurement people than the nuclear. I apologize for the statement, but I think it must be made. If one does a ratio-of-ratio measurement such as in this six-year project to determine the half-life of plutonium-241, one can (Fig. 16) come up with a 0.02-year uncertainty. That was six to seven years ago, whereas the internationally recommended value from the IAEA today,

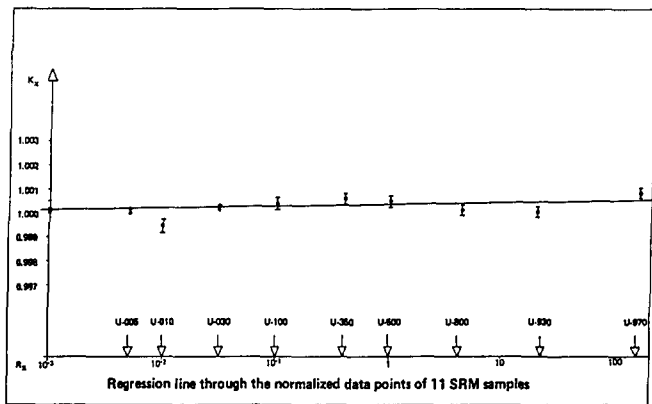


Figure 20.

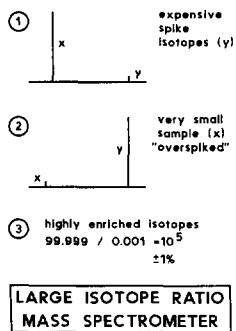


Figure 21.

still has a 0.2-year total uncertainty which is ten times worse.

Fig. 17 shows the maximum deviations from the best linear fit over six years. This directly illustrates the power of the ratio-of-ratio approach in isotope mass spectrometry. It is beautiful to see how the  $^{239}\text{Pu}/^{240}\text{Pu}$  ratio stays constant to within 0.02 percent (not standard deviation of the mean, but of the single determination) and how the ratio 241/240 gradually decayed over the six years (Fig. 18).

9. System calibration is one of the most useful things that has happened to isotope mass spectrometry. It dates back to the period before the period I'm supposed to review. However, because it is so important and because it has considerably improved, I am showing it here (Fig. 19). We changed the abscissa from linear in abundance to logarithmic in ratio—what it really ought to be for various

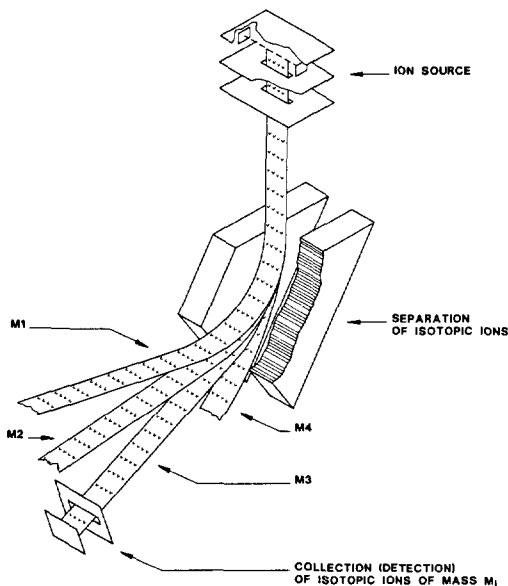


Figure 22.

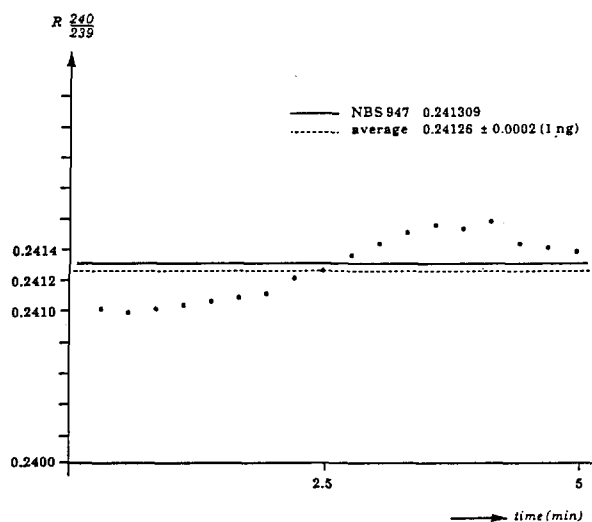


Figure 23.

reasons. One can determine the independence of an isotope ratio from  $\Delta M$  or plus-or-minus 0.5 percent, if one is sloppy; to plus-or-minus 0.2 percent if one is a little better. As far as I know, the third graph is the first system calibration of a commercial instrument (MAT TH5-1975 at CBNM) with a single standard deviation of 0.06 percent. By the way, even if your correction factor is equal to one, even with three or four zeroes, that does not allow you to cancel or forget or ignore the uncertainty with which the correction factor was established. Usually in the absence of systematic errors, people say they can forget about it—"we don't have them." Even the statement, "we don't have them" has its uncertainty and may not be forgotten in the cumulated total uncertainty of a measurement. Such system calibrations, including the logarithmic scale, are now included in commercial leaflets. Fig. 20 shows such a leaflet which is given to the customer as a proof of the quality of an instrument. I find that very encouraging.

10. Calibration with two or three orders of magnitude is good, but why not try to extend our measurement capability into what I call large isotope ratio mass spectrometry. People in this country, such as Dietz, and colleagues at General Electric, Schenectady, and also at NBS, Oak Ridge, and Los Alamos have tried to do that with a double magnetic tandem mass spectrometer. Fig. 21 shows three important examples why such instruments are needed: highly enriched isotopes, "over spiking" small samples,

and "underspiking" with rare enriched isotopes. I am happy to announce that a development order put out in 1983 by CBNM to one of the manufacturers, is about to succeed. It will probably achieve an abundance sensitivity of about  $10^{-8}$ .

11. We have seen, in this period of 21 years, the introduction of multi-collector systems which brings us, in practice, closer to the concept of a mass spectrometer measuring a ratio. As long as one is measuring on a single collector, one can immediately convert ion currents into ion current ratios, but one is actually not yet directly measuring ratios and that has consequences for fully orthodox uncertainty calculations, involving variances and co-variances. That is almost universally ignored. With multi-collector systems we are measuring, directly, isotope ratios and that is an interesting development. If one couples multi-collector systems which can measure, say, four isotopes at once, and one turns one of these ratios, or two of these isotopes—one ratio—into a built-in internal ratio

### ISOTOPIC MEASUREMENTS BY THQ

SAMPLE	IODINE (PPM)		ELEMENT ION	LOADING TECHNIQUE	STANDARD DEVIATION (MIX) ISOTOPE RATIO DETERMINATION
	THQ	SECTOR MS			
POWDERED MILK BCR 151	5.44 ± 0.12	5.34 ± 0.01	B	BO <sub>2</sub> SINGLE FIL./LANTHANUM	0.2 (10B/11B)
POWDERED MILK BCR 150	128 ± 0.03	132 ± 0.01	Cl	Cl <sup>-</sup> DUAL FIL.	0.2 (35Cl/37Cl)
POWDERED MILK BCR 83	0.32 ± 0.03	0.28 ± 0.01	Ca	Ca <sup>+</sup> DUAL FIL.	1.0 (40Ca/44Ca)
TUNA FISH	0.85 ± 0.08	0.83 ± 0.003	Ti	Ti <sup>+</sup> DUAL FIL.	0.2 (47Ti/48Ti)
BOVINE LIVER NBS 1577	0.31 ± 0.05	0.28 ± 0.01	V	V <sup>+</sup> DUAL FIL.	0.2 (50V/51V)
SAMPLE	BORON (PPM)		ELEMENT ION	LOADING TECHNIQUE	STANDARD DEVIATION (MIX) ISOTOPE RATIO DETERMINATION
	THQ	SECTOR MS			
WATER MOSS BCR 61	108.4 ± 3.6	108.2 ± 0.8	Cu	Cu <sup>+</sup> SINGLE FIL./SILICAGEL	0.7 (63Cu/65Cu)
SPINACH NBS 1570	30.2 ± 0.2	30.3 ± 0.1	Zn	Zn <sup>+</sup> SINGLE FIL./SILICAGEL	0.7 (66Zn/68Zn)
POWDERED MILK BCR 83	1.81	1.78	Ni	Ni <sup>+</sup> DUAL FIL./LANTHANUM	0.8 (78Ni/81Ni)
STEEL NBS 363	13.0 ± 0.2	12.6 ± 0.7	Zr	Zr <sup>+</sup> DUAL FIL.	0.2 (90Zr/92Zr)
ALUMINUM (MERCK)	2.75 ± 0.02	2.77 ± 0.05	Mo	Mo <sup>+</sup> SINGLE FIL./RESIN BEAD	0.5 (97Mo/98Mo)
SAMPLE	LEAD (PPM)		ELEMENT ION	LOADING TECHNIQUE	STANDARD DEVIATION (MIX) ISOTOPE RATIO DETERMINATION
	THQ	SECTOR MS			
BIDIST. WATER	0.23 ± 0.03	0.23 ± 0.05	Tc	TcO <sub>2</sub> SINGLE FIL./LANTHANUM	0.3 (97Tc/99Tc)
SAMPLE	LEAD (PPM)		ELEMENT ION	LOADING TECHNIQUE	STANDARD DEVIATION (MIX) ISOTOPE RATIO DETERMINATION
	THQ	SECTOR MS			
HUMAN BLOOD SERUM	92.8 ± 0.8	92.4 ± 0.1	Ru	Ru <sup>+</sup> SINGLE FIL./RESIN BEAD	0.7 (100Ru/102Ru)
ANIMAL BLOOD SERUM	95.7 ± 0.7	95.2 ± 0.4	Cd	Cd <sup>+</sup> SINGLE FIL./SILICAGEL	0.3 (114Cd/116Cd)
REFERENCE WATER SAMPLE	111.9 ± 0.8	111.4 ± 0.5	Sr	Sr <sup>+</sup> SINGLE FIL./SILICAGEL	0.4 (120Sr/122Sr)
SAMPLE	LEAD (PPM)		ELEMENT ION	LOADING TECHNIQUE	STANDARD DEVIATION (MIX) ISOTOPE RATIO DETERMINATION
	THQ	SECTOR MS			
HUMAN BLOOD SERUM	92.8 ± 0.8	92.4 ± 0.1	Ta	Ta <sup>+</sup> DUAL FIL./Ba(OH) <sub>2</sub>	0.8 (128Ta/129Ta)
ANIMAL BLOOD SERUM	95.7 ± 0.7	95.2 ± 0.4	I	I <sup>-</sup> DUAL FIL./LANTHANUM	0.3 (127I/129I)
REFERENCE WATER SAMPLE	111.9 ± 0.8	111.4 ± 0.5	Hf	Hf <sup>+</sup> DUAL FIL.	1.0 (179Hf/180Hf)
SAMPLE	LEAD (PPM)		ELEMENT ION	LOADING TECHNIQUE	STANDARD DEVIATION (MIX) ISOTOPE RATIO DETERMINATION
	THQ	SECTOR MS			
HUMAN BLOOD SERUM	92.8 ± 0.8	92.4 ± 0.1	Tl	Tl <sup>+</sup> SINGLE FIL./SILICAGEL	0.3 (203Tl/205Tl)
ANIMAL BLOOD SERUM	95.7 ± 0.7	95.2 ± 0.4	Pb	Pb <sup>+</sup> SINGLE FIL./SILICAGEL	0.3 (206Pb/208Pb)
REFERENCE WATER SAMPLE	111.9 ± 0.8	111.4 ± 0.5	U	U <sup>+</sup> DUAL FIL.	0.3 (235U/238U)

Figure 24.

The Isotope Mass Spectrometer (IMS) compares amounts by comparing numbers of atoms

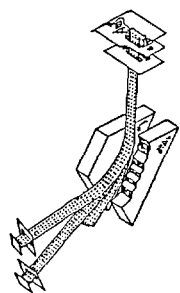


Figure 25.

It gives what "analysts" need :

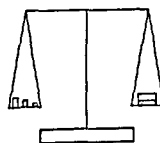
- 1) it sorts atoms (of qualitatively different species) on the basis of the SI quantity mass

units : the kg  
the u = 1.660 54 · 10<sup>-27</sup> kg

- 2) it counts atoms on the basis of the SI quantity for amount of substance

(unit : the mol = N<sub>A</sub> atoms/molecules/entities)

The balance, used in early chemistry compares amounts c comparing their weights or masses



From early times, weights (or masses) compared by a single instrument

the balance

Recognising its status, science gave a base (SI) unit :

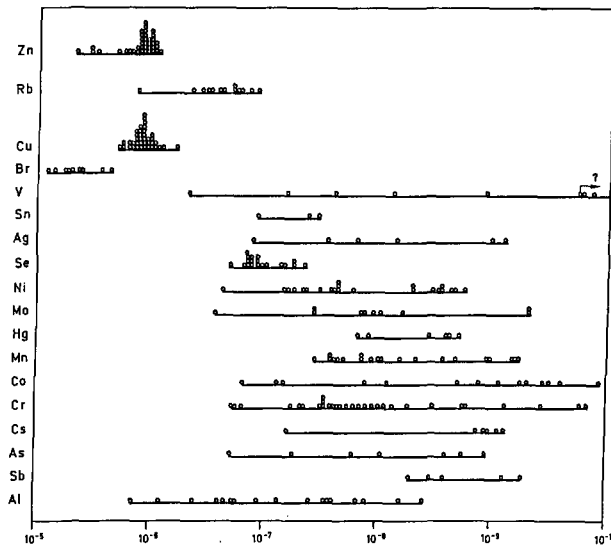
the kg

But the science and technology of the fact that atoms combine in simple numbers, so chemists cannot use directly, to compare amounts of substance.

They must divide each mass by its weights to get what they need

The balance does not take into account the nature of matter

Figure 26.



TRACE ELEMENTS IN BLOOD USING DATA SUMMARIZED BY VERSIECK AND CORNELIS IN g·ml<sup>-1</sup> (1980)

Figure 27.

standard (IRS), prospects for doing high accuracy isotope mass spectrometry become in principle, better by a factor of 10. You have seen in the example of the half life determination by ratio-of-ratio, what that means. The simple IRS reasoning illustrated in Fig. 22 holds a big potential for better accuracy in isotope mass spectrometry in the years to come. Twenty ppm in ratio-of-ratio neodymium measurements—by isotope geologists (that's  $2 \times 10^{-5}$ ), are possible and have been achieved.

12. Total evaporation of small samples has come through (Fig. 23). I would like to be careful about it—but it looks as if the total integration over the entire measurement time—total evaporation—gives, indeed, highly accurate results under in-field conditions.

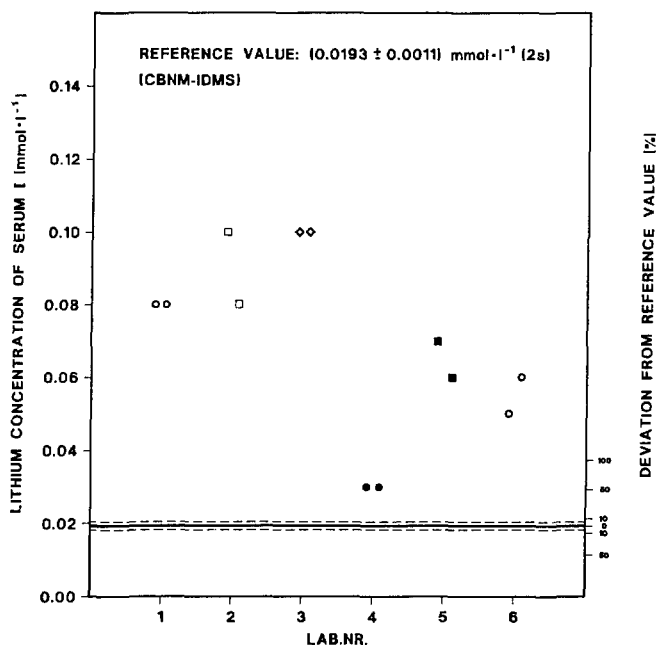


Figure 28.

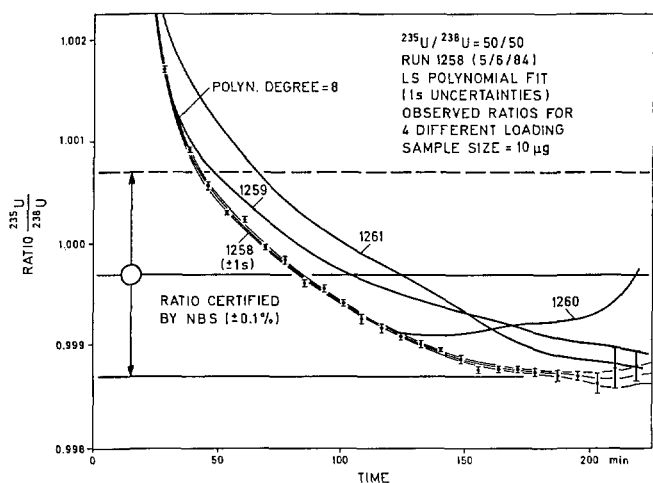


Figure 29.

13. Something which we must welcome is the reduction in price of isotope mass spectrometry by the advent of small thermal ionization quadrupole (THQ) spectrometers which will bring isotope dilution mass spectrometry within reach of more chemical laboratories. It is my prediction that a significant part of classical analytical chemistry measurements will be replaced by IDMS, and that evolution has already started for several elements as one can see from Fig. 24.

14. This brings us to isotope dilution mass spectrometry (IDMS). In former times, chemists used to determine amounts of substances by weighing, so weights, later masses, were given an international unit the kilogram. If one really thinks through the principle, one arrives at the conclusion that the determination of an unknown amount of substance should consist of a process of counting particles. This is exactly what IDMS does (Fig. 25). Our modern unit for measuring an amount of substance is not the kilogram anymore, but the mol, i.e., a number of particles. An isotope mass spectrometer can be used to determine numbers of particles. The balance doesn't. The balance needs atomic weights to convert weights into moles, a quantity which is proportional to numbers of particles. My simple statement here would be that the isotope mass spectrometer determines amounts of substance in the correct international unit and is on its way to replace the balance for a number of measurement applications (Fig. 26).

15. Trace concentrations by isotope-dilution mass spectrometry have become very important. In the period, 1960 until 1980, trace elements in human serum and blood have been determined by various laboratories using classical analytical methods, all over the world. In Fig. 27, each point is a published value for the natural content of this trace element in human blood. The observed concentrations vary over two to three orders of magnitude in published scientific literature. We don't worry here about a few percent, or 10 percent or 20 percent uncertainty on these trace elements. But we are worried by published scientific data going over three orders of magnitude. An undefendable situation! Isotope-dilution mass spectrometry

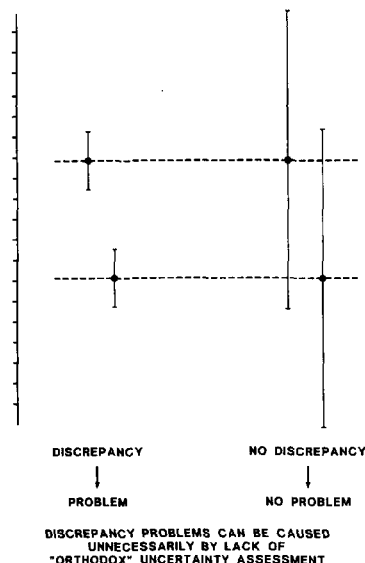


Figure 30.

has been used and will continue to be used to put references for other methods assaying trace elements in all sorts of matrices. If one asks clinical laboratories to determine lithium in human serum, one gets Fig. 28. If one would think that the most probable or best answer, is the average or most "democratic" answer, one couldn't be more wrong, as Fig. 28 shows. The reference value in this picture was carefully checked and put into the picture by isotope-dilution mass spectrometry.

What we must do as scientists, on every single occasion, is to fight the opacity of measurement procedures caused by automation of equipment and caused by "black box" software and by extensive use of "N," the number of measurements, to improve precision and give us a more optimistic uncertainty value than is actually deserved. And we must do it before we're going to be asked questions by the public on that.

16. In order to cure the highly unsatisfactory situation in assessing measurement uncertainties we've got to get rid of most of statistics and statisticians and work on the real causes of our errors back in the laboratory. I don't want to be mean to other scientific colleagues. I'm only saying that the misuse of extensive statistical procedures in measurement science has done lots of harm over the last 20 years.

17. I would like to conclude with a few more pictures. Fig. 29 is probably one of the most beautiful recordings ever made of an isotope fractionation over about two hundred minutes. You see the ratio come down and cross the absolute value. You see with what extremely high precision these point have been determined. A polynomial fit was done with N equal to eight. The standard deviation on a single point on the fit, and things like that, are then published as measurement uncertainty. If you redoes the measurement with another filament, one gets one of the other fits in the picture. A single point on any of these fits is *not* the result of the analysis, and its uncertainty should not be the uncertainty which is then published. We are folling ourselves if we do that, and we must try to clean up our mentality and philosophy on that. I carry Fig. 30 over the last three to four years as a standard item in my briefcase, because in any discussion, any conference I attend, I need it again and again. It exemplifies two measurements by

two different laboratories or people, on the same material. It shows the sort of mess we get ourselves into by wrong, or incomplete, or too optimistic assessments of the uncertainties of our measurement.

Even if one has a correction factor of unity for a possible or suspected systematic error determined with the aid of a reference material, that correction factor carries an uncertainty that is mostly ignored. We cannot do that. The uncertainty of determining the correction factor, is and should be, the same order as the uncertainty on the measurement of the unknown itself. By not taking this into account, we cut our uncertainty in half, we get ourselves in a mess. But if some people, or now more and more the general public are worrying whether these uncertainties hide real differences in the material balances of nuclear material, this matter is becoming very serious, and it ought to be addressed.

What can we do about all this? Well, I'm often asked to address these items at the end of a lecture. People expect the answers, "more budget, more automation." The items which I want to put to the audience as answers are not such things as further automation or more sophisticated software but those indicated in Fig. 31.

I recommend that the nuclear community have clear and short answers at the ready when they are going to be asked the question: How much material do you handle and how well do you know it?

Present Problems / Limitations  
for  
Accuracy of Isotopic Measurements  
(1986)

1. Devotion / Dedication / Reliability of staff
2. Training in chemical sample preparation
3. Support for this specialised work
4. "Orthodox" data treatment
5. Control of mass discrimination
6. Software programming
7. Verification of instrument linearity

Figure 31.

Paul De Bièvre received his Ph.D. from Gent University (Belgium). Since 1961 he has been at the Central Bureau for Nuclear Measurements—a Joint Research Center of the Commission of European Communities in Geel, Belgium. He has been Group Leader of Mass Spectrometry since 1976. He is a member of the IUPAC International Commission on Atomic Weights and Isotopic Abundances, serving from 1975 to 1983 as chair of the subcommittee addressing the Isotopic Composition of the Elements.



# Nondestructive Assay

■  
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■

## ABSTRACT

*Analytical chemistry and the physics of radiometric measurements have effected an interdisciplinary synergism into the broad field of nuclear material measurements and have given rise to nondestructive assay technology widely supporting domestic and international safeguards. The events leading up to the establishment of a safeguards R&D program and the subsequent contributions thereof to international safeguards are traced.*

I am doubly pleased to be here to participate in this special symposium honoring the 40th Anniversary of the establishment of the New Brunswick Laboratory. First, this proud and happy occasion for celebration also provides an excellent opportunity for all of us to review and consider together developments—past, present and future—in our common professional field of nuclear materials measurements. Secondly, I am pleased to be here because good old Chicago is where I got my start—the West Suburban Hospital on Austin Boulevard—way back in the “roaring 20s.”

Well time flew by, and after those incredibly short eighteen years between arrival into and departure from the family nest, I found myself, in the Fall of 1942, a freshman at the University of Chicago full of enthusiasm and determination to pursue my chosen professional field of analytical chemistry. However, like millions of others, my plans (and my life) were changed, drastically, by “the war” and the U.S. Navy (which in World War II actively recruited qualified science students to enlist in the Navy’s “V-12” College Training Program, switch their major to physics, and upon graduation, to fulfill their military service obligation as a shipboard Naval Radar Officer). So, some 40-plus years later here I am back in Chicago attending this 40th Anniversary Symposium, as a physicist reporting on Nondestructive Assay—whereas, but for the grace of God and the U.S. Navy, I might have come here as a chemist reporting on the “advances in automated coulometric titrimetry” or whatever—or indeed, I might not have been around to come here at all. So much for reminiscences and hypotheticals. What did strike me repeatedly, as I was contemplating the perspective and content of this overview paper,

was that our common professional field of nuclear material measurements embraces a truly synergistic blend of chemistry and physics—as a quick glance at our program and speakers will readily attest. As we all know from both intuition and experience, such interdisciplinary synergism operating between different professional disciplines and specialties is essential to innovation and on-going progress in any area of science, including our own broad field of nuclear material measurements. From the outset, this overview of Nondestructive Assay is presented from the perspective of a safeguards researcher who evolved along with the emerging issue and discipline of nuclear materials safeguards, because it is this discipline that has provided the major impetus and ongoing support for the accomplished of Nondestructive Assay technology on which I’ve been asked to speak.

Since the dawn of the nuclear age, the dangers and potential for misuse of nuclear fission energy and nuclear materials were recognized by many informed people. The Baruch plan for international cooperation and rigid controls on all nuclear activities was proposed in 1946, and was rejected in that same year. The Eisenhower “Atoms for Peace” program was put forth in 1953 to “promote international cooperation in the peaceful uses of nuclear energy” and, at the same time, “establish international controls to ensure that the products of this cooperation would not be diverted to military uses.” The Atoms for Peace program brought several innovations including the series of UN International Conferences on the Peaceful Uses of Atomic Energy (the Geneva Atoms for Peace Conferences, beginning in 1955); and the establishment of the International Atomic Energy Agency (IAEA) in 1957. All through the 1950s our research work with fissionable materials at Los Alamos (in the Critical Assemblies Group at Pajarito site), and my participation in both domestic and international technical fora, (starting, on the international level, with the first Geneva conference in 1955) had made me increasingly aware of a growing need for stringent controls on sensitive nuclear materials to ensure against their diversion and misuse (the broad issue now called nuclear safeguards).

From July 1963 to September 1965, I was on extended leave from Los Alamos to serve with the Headquarters staff of the IAEA in Vienna, Austria, under the leadership of IAEA Director General Sigvard Eklund. Fostered in large part by the Atoms for Peace program, throughout the 1960s peaceful nuclear energy programs flourished in many countries because supplier nations, including the United States, offered a very attractive long-term source of nuclear fuel, in part intended to discourage the development of other supply sources. Also during the 1960s the number of nuclear weapons nations increased from three to five with the addition of France in 1960 and the Peoples Republic of China in 1964. These and other developments gave rise to increasing concerns about nuclear weapons proliferation—both “horizontal” and “vertical.” Thus during the course of my 1963-65 assignment with the IAEA in Vienna, my earlier concerns about the coming need for tight controls over nuclear materials were strongly confirmed—and to this was now added a new and broader problem: the global challenge of nuclear proliferation.

By the time I returned to the United States in the Fall of 1965, I had become firmly convinced the our country should take the lead in this key area of nuclear safeguards; I further felt that Los Alamos itself was quite unique in having both the expertise and the facilities that would be essential for the required R&D effort, including (1) the full range of materials processing, fabrication and recovery facilities for special nuclear materials; (2) the world’s leading facility and expertise in all types of critical assembly operations; and (3) top-notch instrumentation and measurement know-how, which could be further staffed up as needed. After a lengthy series of presentations, briefings, etc. to the Atomic Energy Commission, the Congressional Joint Committee on Atomic Energy and others, the Los Alamos Safeguards R&D Program was funded and launched on December 1, 1966. Six months later the AEC established the Office of Safeguards and Material Management at its Washington Headquarters, as well as a new Division of Safeguards in the AEC Regulatory Branch (now the Nuclear Regulatory Commission).

The special nuclear materials expertise and facilities at Los Alamos as noted above (i.e. nuclear instrumentation and measurement know-how; nuclear materials processing and fabrication knowledge and expertise; as well as extensive critical assembly operations) were foreseen as an ideal home base for a highly productive safeguards R&D program. Two events early on in the program helped to give the U.S. safeguards high visibility throughout the the worldwide nuclear community. These were (1) the official visit to the Los Alamos safeguards program by IAEA Director General Sigvard Eklund in October, 1968; (2) the AEC International Symposium on Safeguards Research and Development held at Los Alamos in October, 1969, (see Figure 1). Over 400 symposium participants came from the United States and abroad to review progress in the nuclear safeguards field, with emphasis on new technical developments and an extensive exhibit of newly developed safeguards instrumentation. Among the many distinguished participants at the 1969 Symposium was Clement J. Rodden, former Director of the AEC’s New

Brunswick Laboratory, who was directly succeeded by Carleton Bingham, our host for this NBL 40th Anniversary Symposium, and present Director of the New Brunswick Laboratory. Figure 2 shows “Clem” Rodden with Los Alamos Laboratory Director, Norris E. Bradbury as they toured the instrumentation exhibit area of the Los Alamos Safeguards R&D laboratory.

## AEC Symposium on Nuclear Safeguards

LOS ALAMOS SCIENTIFIC LABORATORY

OCTOBER 27-30, 1969



Figure 1. At the 1969 AEC Symposium on Nuclear Safeguards, GE Vice President A.E. Schubert (top) describes “Safeguards Activities Within Industry”; (above), the late Delmar L. Crowson, Director of the AEC’s Office of Safeguards and Materials Management and R.P. Wischow, head of Safeguards, AEC Regulatory Branch, lead discussion in the opening plenary session of the Symposium.

Over the years as nuclear activities expanded in many countries around the world, safeguards concerns increased correspondingly, and steadily greater requirements were placed on nuclear material measurement capabilities (e.g., with respect to detection sensitivity, timeliness, accuracy, and representative sampling) for the many forms and configurations of materials found in the nuclear fuel cycle. This, in turn, led to the development and implementation of a new measurement technology to supplement, and complement, the traditional destructive assay methods of sampling and chemical assay. This new technology—now commonly known as nondestructive assay, NDA—is based on direct physical measurements of unique characteristics or “signatures” of fissionable materials. Nondestructive assay techniques fall into two major categories, passive and active. Passive assay uses naturally emitted gamma-ray and/or neutron radiations as direct signatures of fis-

sionable materials. Active assay involves irradiation with neutrons or photons to induce fissions in the sample to be assayed. The resulting fission-produced neutron or gamma-ray signatures are analyzed to determine quantitatively the amount of fissionable material present.

For more than 20 years safeguards research and development in the United States, and more recently in several other countries, have developed, tested, and implemented a broad range of passive and active NDA instruments and measurement/accountability systems that are now widely employed in safeguarding nuclear materials in nuclear facilities of all types. NDA instruments range in size and complexity from small portable units (e.g. for on-site use by safeguards inspectors) to large in-situ NDA measurement systems designed for routine in-plant use not only for safeguard and accountability, but also for process control, quality control and critical safety. In this paper, we survey briefly the major categories of gamma-ray and neutron-based passive and active assay techniques, give representative examples of NDA instruments currently in use, and cite some notable instances of ongoing state-of-the-art NDA technique development.



Figure 2. Clement J. Rodden, former Director of the New Brunswick Laboratory chats with Norris E. Bradbury, former Director of the Los Alamos National Laboratory (with the author looking on) at the AEC's Symposium on Nuclear Safeguards held at Los Alamos in October, 1969.

First, in the area of passive gamma-ray assay, many different instruments have evolved employing the two well-known types of gamma-ray detectors; i.e. low resolution NaI(Tl) scintillation detectors and the high-resolution germanium solid-state detectors. Necessary corrections for sample attenuation are carried out using either an external gamma-ray source or by suitable analysis of the measured response to the sample's own internal gamma rays. Gamma-ray measurements using the so-called "enrichment meter" principle are based on the fact that for fixed detector-sample geometry and for samples that are thick

relative to the penetration depth of the 185.7-keV  $^{235}\text{U}$  gamma rays, the count rate due to the 185.7-keV gamma rays is directly proportional to enrichment. When performed with care, NDA enrichment measurements can achieve 0.1 to 0.2 percent precision at one standard deviation, measurement biases of similar magnitude.

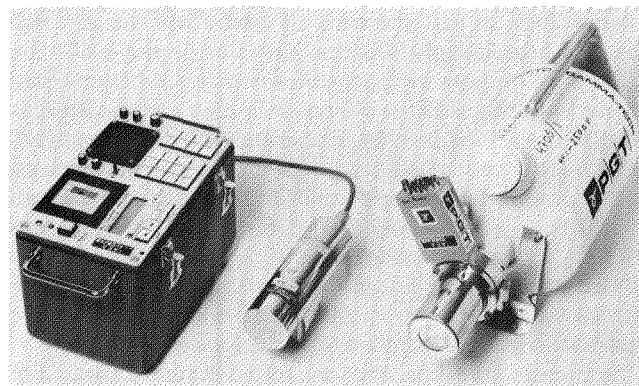


Figure 3. The Portable Mini-MCA (PMCA) is an "intelligent" battery-operated multi-channel analyzer (at left) that can display and record gamma-ray spectra from a NaI detector (center) or a high-resolution Germanium detector (at right). Using suitable standards, the PMCA can provide accurate, on-the-spot measurement of U enrichment as well as total  $^{235}\text{U}$  content, and can also be used for some Pu verification applications.

In the case of plutonium isotopic composition measurements by gamma-ray spectroscopy, achievable accuracies are typically the order of one percent or better for  $^{239}\text{Pu}$  and  $^{241}\text{Pu}$ . The well-known and widely used Portable Mini MCA, (Figure 3) is a battery powered 2K/4K multi-channel analyzer that can acquire, display, analyze and record gamma-ray spectra from either NaI or high resolution germanium detectors. A second instrument, the Segmented Gamma Scanner<sup>1</sup> is used for measuring samples up to 200 liters in volume and employing a transmission source that is viewed through a horizontal collimator slit to assay the sample as a series of horizontal segments, and then measuring sample response and the transmission correction segment by segment. In the case of solid materials (e.g. scrap and solid waste) an important source of bias can arise when lumps are present in the sample to be assayed; a method of detection and correction for the presence of lumps is under development that involves assaying the sample at different gamma-ray energies.<sup>1</sup> Another noteworthy example of an attenuation-corrected passive gamma-ray assay system is the Nuclear Material Assay System<sup>2</sup> for assay of  $^{235}\text{U}$  in solution at the Savannah River High Enriched Uranium (HEU) Facility. This system can assay over 20,000 samples per year with measurement accuracies near 0.1 percent. The Solution Assay System was honored as a 1988 "R&D-100 Award" winner. (see figure 4)

The second major category of NDA techniques is active gamma-ray densitometry and x-ray fluorescence. In the densitometer a gamma-ray beam is passed through an assay sample, and a gamma-ray detector measures the transmit-

ted beam whose reduced intensity is a function of the gamma-ray energy and the amount, or concentration, of nuclear material between the source and detector. The isotopic sources,  $^{57}\text{Co}$  and  $^{75}\text{Se}$ —with 122.0-keV and 121.7-keV gamma rays respectively—nicely (and fortunately) bracket the 121.7 keV K-absorption of plutonium. These sources are utilized in the so-called compact K-edge densitometer developed for in-line concentration measurements of Pu solutions in glove box lines without breaching or affecting in any way the glove box containment. An installed  $^{57}\text{Co}$ - $^{75}\text{Se}$  K-edge densitometer system has been used for nearly 10 years for assay of product solution in the analytical laboratory of the Tokai fuel reprocessing plant at Tokai-Mura, Japan.<sup>3</sup> (See Figure 5). Generally the accuracy and precision of K-edge densitometer measurements are better than one percent and can approach 0.1 percent.

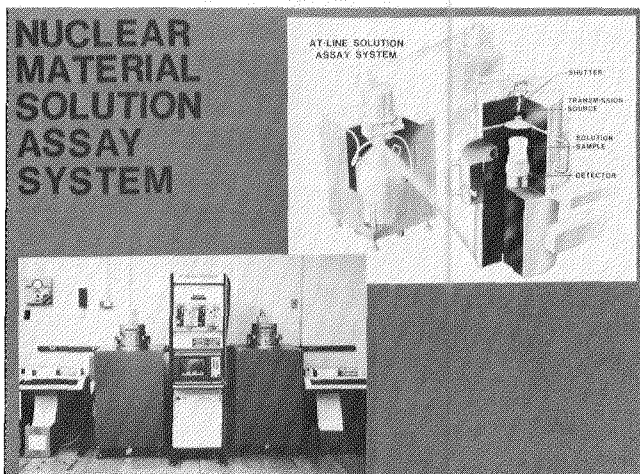


Figure 4. Nuclear Material Solution Assay System installed in the High Enriched Uranium (HEU) Facility at the DOE's Savannah River Plant. The system can assay over 20,000 samples per year with measurement accuracies near 0.1%. This system received the prestigious "R&D-100 Award" in 1988.

In the complementary technique of x-ray fluorescence (XRF), again a gamma-ray beam is passed through an assay sample, but here the absorbed, rather than the transmitted, gamma rays are used to provide an assay signal. The absorbing atoms are raised to excited states from which they decay by emission of x-rays; the energies of these x-rays are uniquely characteristic of the elements in the absorbing material, and their intensities are proportional to the amounts present. Gamma-ray densitometry and x-ray fluorescence have been applied most successfully to the measurement of uranium and plutonium concentrations in solutions. The two techniques are complementary; i.e. densitometry is best suited for SNM concentrations above about 10 g/l, whereas XRF is best suited for concentrations below this level. At least two hybrid assay systems have been built that combine densitometry and XRF. One is used to assay uranium and plutonium in light-water-reactor reprocessing solutions at Kernforschungszentrum Karlsruhe in the Federal Republic of Germany,<sup>4</sup> and the other is designed for routine use in

the recovery section of the Los Alamos plutonium facility.<sup>5</sup>

Concerning advanced NDA technique development in the area of gamma-ray assay, two novel methods for determination of Pu concentration (and isotopic distribution) have recently been developed that require no external radioactive sources or x-ray generators, but rely only on the natural radiations from Pu. The methods are ideally suited to the assay of reasonably pure Pu solutions such as the product solutions of a reprocessing plant and the eluate solutions from anion exchange columns. The methods can be applied to aged or freshly separated Pu and can be used to measure Pu concentrations in pipes or tanks. The first method uses the MGA2 isotopic program developed at Lawrence Livermore National Laboratory.<sup>6</sup> In this program a relative detection efficiency curve is fitted from 59 keV to 208 keV including the discontinuity at the Pu K-absorption edge. For fixed sample thickness, the magnitude of the discontinuity is proportional to the Pu solutions with concentrations ranging from 60 g/l to 320 g/l it was found that Pu concentrations can be determined to be 1.9 percent with precisions of about 1.5 percent.

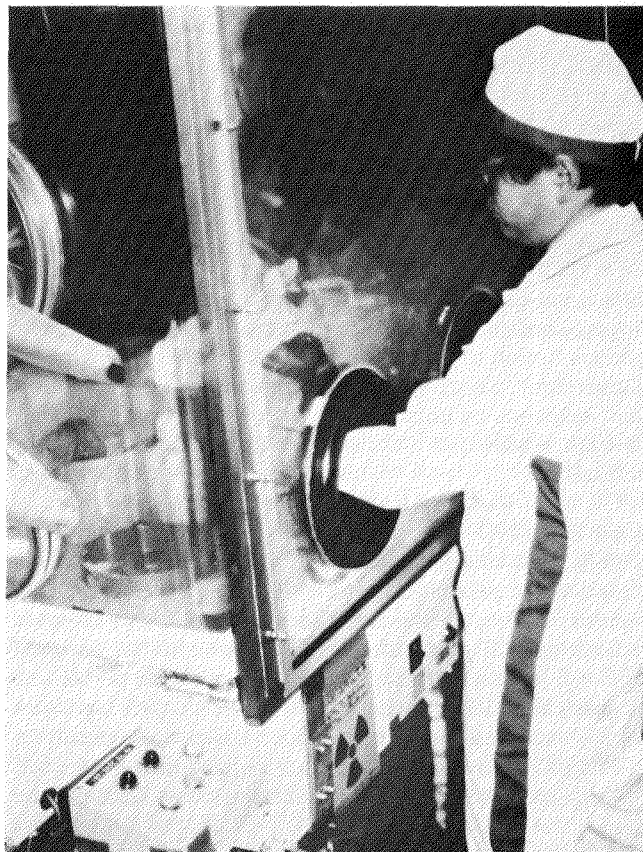


Figure 5. Operator assays Pu nitrate product solution using the K-edge densitometer in the chemical analytical laboratory of the Tokai Reprocessing Plant, Tokai-Mura, Japan. The stainless steel cover for the counting well is seen at the left inside the glove box.

The second method<sup>7</sup> uses the ratio of a pair of gamma-ray or x-ray peaks from the Pu sample: one above the K-absorption edge and one below the edge so that the absorption coefficients ( $\mu$ ) are substantially different. The  $\mu$  values of 129-keV gamma ( $^{239}\text{Pu}$ ) and 111-keV x-ray (U K from  $^{241}\text{Pu}$ ) differ substantially, so the ratio of these two lines is a strong function of Pu concentration, and for a fixed solution thickness the function can be used to determine Pu concentration from a measurement of the 111/129 ratio. Applying this ratio method to Pu solutions with concentrations ranging from 10 g/l to 320 g/l, Pu concentrations were determined to 0.26 percent with precisions of about 0.2 percent. Calculations show that while the ratio method is insensitive to the amount of low-Z absorber ( $Z < 10$ ), for best results the medium-Z matrix ( $Z < 40$ ) in the solution should be less than six percent of the Pu concentration and the high-Z matrix should be less than three percent of the Pu concentration. Thus if the concentration of impurities in the Pu solution is less than the amounts given above, the ratio method can be used to determine Pu concentrations from 10 g/l to 300 g/l with less than 0.5 percent bias. When the solution is very thick, the ratio approaches a unique asymptotic value, with the very practical result that the ratio method can therefore be used to determine Pu concentrations in tanks or bottles without drawing samples.

Turning now to neutron-based NDA techniques, we address first passive neutron methods; it will be recalled the neutrons originating in nuclear materials are primarily due to (1) spontaneous fission (largely in Pu-238, 240 and 242) and (2)  $(\alpha, n)^*$  reactions in light elements (e.g., in the commonly used compounds of uranium and plutonium, notably the oxides, carbides, and fluorides, or in B, Be or Li impurities). An additional source of neutrons can arise, especially in larger samples, from induced-fission multiplication in the sample. Passive neutron NDA is typically carried out using neutron coincidence counting (with  $^3\text{He}$  proportional-counter neutron detectors) to measure spontaneous fission of the even-numbered plutonium isotopes. "Coincident" neutrons are distinguished from  $(\alpha, n)$  "singles" neutrons by coincidence counting techniques based on high resolution "shift register" coincidence electronics.<sup>8</sup>

The well-known High Level Neutron Coincidence Counter, HLNC<sup>9</sup> (See Figure 6) is widely used for the assay of bulk plutonium samples ranging from 10-g to several kilograms of plutonium, and  $^{240}\text{Pu}$  content from a few percent to about 30 percent. The HLNC can assay samples containing 500 g or more of plutonium in 300 seconds with a precision and accuracy the order of one percent or better. The utility of the basic HLNC system has been greatly extended by the development of a whole family of HLNC-like detectors with specialized detector heads, but all employing the same basic "shift-register" coincidence electronics.<sup>8</sup>

A method was developed several years ago to correct for sample self-multiplication effects based on measurement of the real coincidence rate,  $R$ , together with the ratio of real coincidence rate,  $R$ , to total neutron rate,  $T$ , i.e., the "reals to totals" ratio.<sup>10</sup> However, this method requires

knowing or being able to calculate the contribution of  $(\alpha, n)$  neutrons. Conventional coincidence counting has worked reasonably well for pure  $\text{PuO}_2$  materials; however for highly multiplying samples, impure oxides, samples with high  $^{241}\text{Am}$  content, and salts with high  $(\alpha, n)$  yields, the procedure generally fails because of the unknown multiplication and induced fission rates.

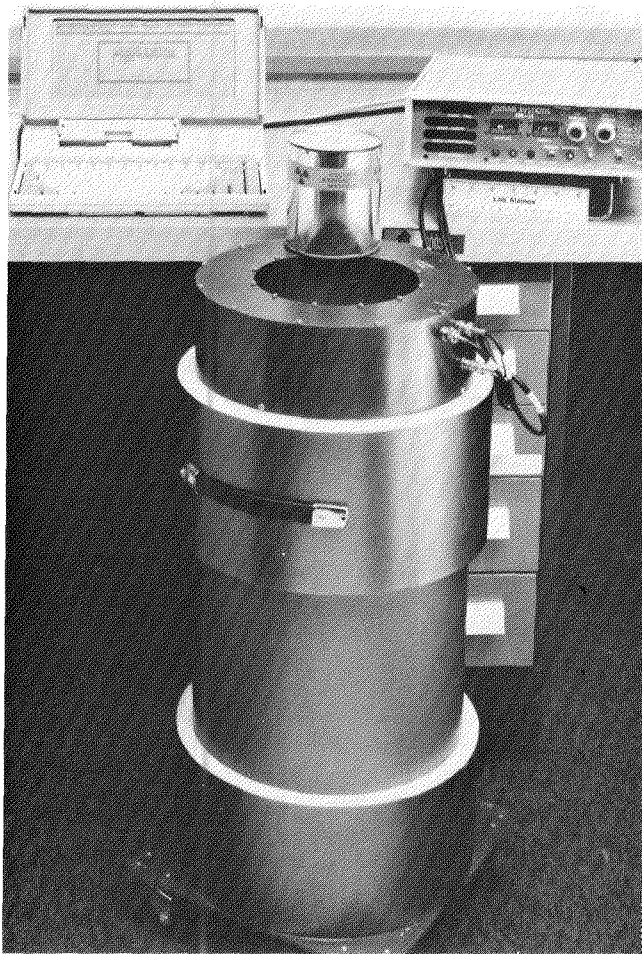


Figure 6. The High-Level Neutron Coincidence Counter, widely used for assay of plutonium samples ranging from 10 g to several kilograms with measurement precision and accuracy of  $\sim 1\%$  or better. The HLNC is used routinely by IAEA and EURATOM safeguards inspectors in nuclear installations around the world.

Major R&D emphasis in passive neutron assay techniques continues to be focused on finding better way to measure and correct for sample multiplication effects. In the general case of passive neutron counting there are three principal unknown variables: plutonium mass, sample self multiplication, and  $(\alpha, n)$  rate; however, there are only two measured parameters in conventional coincidence counting i.e. "real" neutron coincidence rate,  $R$ , and total neutron count rate,  $T$ . Among a number of possible approaches,<sup>11</sup> this basic problem of "one-too-many unknowns" is currently being addressed at Los Alamos in

two quite different ways, although each involves the development of an innovative neutron counting system. One is a fast neutron counter using liquid scintillator detectors, and gamma-ray/neutron pulse shape discrimination.<sup>12</sup> This detection system is designed to measure all three of the unknown quantities noted above, and to minimize interference from gamma-ray response of the scintillators.

The second innovative neutron counting system is the "neutron multiplicity counter"<sup>13</sup> designed to investigate the use of neutron multiplicity distributions for NDA of plutonium samples. The neutron multiplicity counter (overall dimensions about 80 cm diameter by about 70 cm high) is shown in Figure 7. The neutrons are detected by a total of 130 <sup>3</sup>He detectors configured in five concentric rings; the sample cavity is 15-cm in diameter, and the body of the counter is surrounded by 5 cm of polyethylene reflector. Neutron multiplication has been determined by analysis of measured neutron multiplicity distributions for samples of pure plutonium oxide with varying <sup>240</sup>Pu fractions (5-20 percent); for plutonium oxide mixed with matrix materials having various ( $\alpha, n$ ) yields; and for pure and impure plutonium metal. Mass uncertainties from counting statistics range from 0.3 percent for about one kg pure Pu metal to 1.4 percent for about one kg pure PuO<sub>2</sub> with ( $\alpha, n$ )/SF neutron ratios below about one, (SF = Spontaneous Fission). The most promising applications of the neutron multiplicity counter are assay of impure metal samples up to several kg and impure oxide samples up to about one kg, both with ( $\alpha, n$ )/SF ratios < 2.

Turning from passive to active neutron assay, here the fission process itself is employed directly to stimulate (or induce) a desired assay signature. The NDA of <sup>235</sup>U materials provides a very practical case in point: because <sup>235</sup>U does not have a passive neutron signature, <sup>235</sup>U-bearing samples are irradiated with neutrons to induce fissions in the <sup>235</sup>U, and the resulting emitted fission neutrons (prompt and/or delayed) provide a signature for accurate NDA. Examples are given below of state-of-art active neutron NDA instruments that utilize prompt neutron as well as delayed neutron response measurements (and also delayed gamma-ray response) to determine fissile material content with attainable accuracies of one percent or better.

First we cite the Active Well Coincidence Counter (AWCC) used for assay of <sup>235</sup>U content in enriched uranium materials. Two ( $\alpha, n$ ) neutron sources (AmLi, each about  $5 \times 10^4$  n/s) located above and below the sample well used to interrogate the sample, and the induced fission neutrons are counted with standard shift-register coincidence electronics. Coincidence counting discriminates against the single ( $\alpha, n$ ) neutrons from AmLi sources while detecting coincident neutrons from neutron-induced fissions in the <sup>235</sup>U present in the sample. The AWCC is used to measure bulk UO<sub>2</sub> samples, high enrichment uranium metals, LWR fuel, pellets, <sup>233</sup>U-Th fuel materials having high gamma-ray backgrounds, and more recently even mixed-oxide samples.<sup>14</sup> A second important application of active neutron coincidence counting is the Uranium Neutron Coincidence Collar (UNCL). The UNCL can be operated in both the active and the passive mode to

measure <sup>235</sup>U and the <sup>238</sup>U content, respectively, of both PWR and BWR light-water reactor assemblies. In the active mode a low intensity ( $5 \times 10^4$  n/s) AmLi neutron source interrogates the fuel assembly, and the induced prompt neutrons (from <sup>235</sup>U fission) are coincidence counted. When no interrogation source is present, the passive neutron coincidence rate (from <sup>238</sup>U spontaneous fission) gives a measure of the <sup>238</sup>U in the fuel. The <sup>235</sup>U response sensitivity enables detection of the removal or substitution of 3-4 rods in the PWR assembly and one rod in a BWR assembly.



Figure 7. The "Neutron Multiplicity Counter" in operation at the Los Alamos safeguards R&D laboratory. The outer shield is ~ 80 cm diameter by ~ 70 cm high, and the central sample cavity is 15 cm in diameter.

The so-called "<sup>252</sup>Cf Shuffler"<sup>15</sup> illustrates the application of active neutron interrogation together with delayed neutron response measurements. The heart of the <sup>252</sup>Cf Shuffler is an annular detector into which the sample is placed. A large <sup>252</sup>Cf source (107 to 1010 n/s) is repetitively cycled (shuffled) into and out of the detector cavity region to irradiate the sample and induce fissions in the <sup>235</sup>U present. Between successive <sup>252</sup>Cf neutron irradiations the detector is gated "on" to count delayed neutrons from the induced <sup>235</sup>U fissions. Properly calibrated, this delayed neutron signal then provides a measure of the amount of <sup>235</sup>U in the sample. The shuffler technique has been adapted to container sizes ranging from small vials to 200-l (55-gallon) drums. Shuffler systems can measure highly radioactive samples, such as irradiated fuel and reprocessing waste, because the <sup>252</sup>Cf source strength can be increased as necessary to override the background radiation. Figure 8 illustrates a <sup>252</sup>Cf Shuffler system installed at the U.K. prototype fast reactor reprocessing plant in Dou-

nreay, Scotland under a joint evaluation project between the United States and the United Kingdom. The shuffler system has been used nearly continuously over the past five years for the assay of plutonium in hot scrap and leached hulls in the head end of the reprocessing plant. Another large  $^{252}\text{Cf}$  shuffler system has been installed at the Fluorinel and Fuel Storage (FAST) Facility in Idaho, where it is in routine use for fissile assay of irradiated, highly enriched uranium fuel assemblies (with assay precisions of two to three percent).<sup>16</sup>

Finally we cite an active neutron interrogation system that utilizes not delayed neutron but delayed gamma-ray response: the automated  $^{252}\text{Cf}$  fuel rod scanner, developed early in the Los Alamos Safeguards R&D program, is used for quantitative assay of both light-water-reactor and fast-breeder-reactor fuel rods. The fuel rods are irradiated with a  $^{252}\text{Cf}$  neutron source to induce fissions in the fissile fuel ( $^{235}\text{U}$  or  $^{239}\text{Pu}$ ) loading the rods. Measurements of the delayed gamma rays from induced fissions in the fuel rods are then used to determine pellet-to pellet uniformity of loading, and total fissile content, i.e. grams  $^{235}\text{U}$  or  $^{239}\text{Pu}$ , to better than 0.5 percent accuracy. Fuel rod scanners are today widely used—for process and quality control, as well as material accounting and control—in commercial nuclear fuel manufacturing plants in many countries.

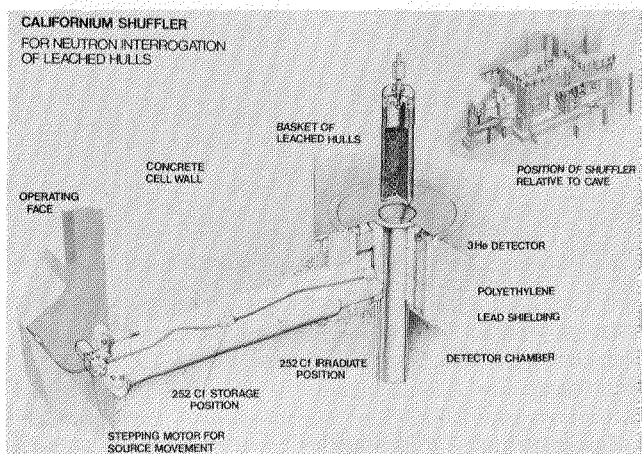


Figure 8. The " $^{252}\text{Cf}$  Shuffler" used for neutron interrogation and delayed neutron assay of plutonium in leached hulls (from spent fast reactor fuel) in the head end of a reprocessing plant. The Shuffler can also be used for routine precision assay of  $^{235}\text{U}$  content in irradiated highly enriched uranium fuel assemblies.

Much of the current NDA development effort is directed toward modifying and improving existing techniques; e.g., improved methods for neutron multiplication correction, gamma-ray peak area evaluation, and gamma-ray attenuation in heterogeneous materials, as well as ongoing development and improvements in the important NDA area of calorimetric assay techniques and procedures.<sup>17</sup> One example of work on new technique development is the application of laser-induced breakdown spectroscopy to high-sensitivity measurements of flowing uranium and plutonium solutions as well as to highly-radioactive solu-

tions.<sup>18</sup> Clearly a key area of ongoing concern in safeguards R&D is the development and field implementation of good measurement standards and calibration procedures, and the accurate determination of bias and precision for NDA techniques. Noteworthy in this connection is the use of Monte Carlo simulations<sup>19</sup> to determine calibration parameters for neutron coincidence assay of mixed-oxide fuel elements, and the potential for more ef-

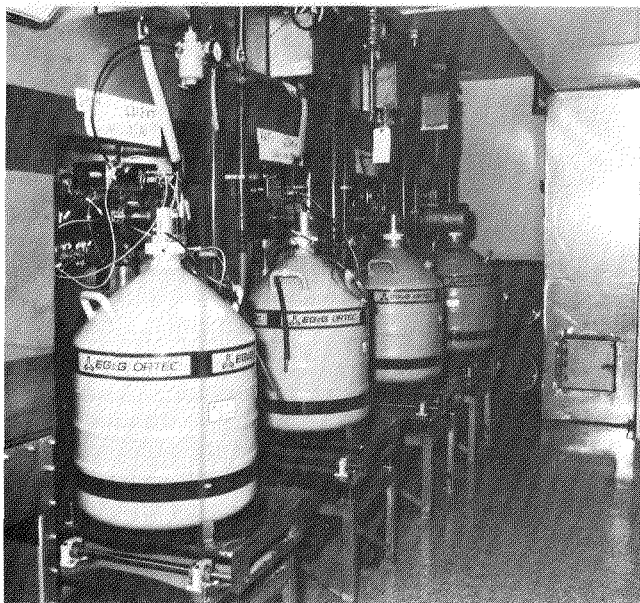
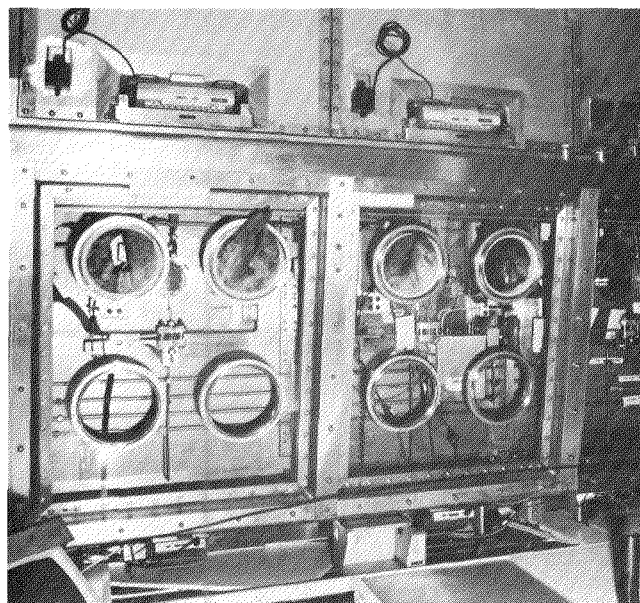


Figure 9. High resolution gamma-ray spectrometers (for solids isotopic analyses) recently installed in the sample assay room of the new plutonium scrap recovery facility at the DOE Savannah River Plant. (Upper and lower photos are front and rear views of glove box line). The pictured spectrometers are part of a complete integrated NDA system, which also includes a feed assay neutron coincidence counter and four calorimeters.

fective, less costly inspector verification of finished reactor fuel elements by reducing reliance on expensive physical standards.

The nation's Safeguards R&D program is committed to the development and application of state-of-the-art NDA instruments, techniques and systems to meet the requirements of government and commercial nuclear facilities, as well as the needs of safeguards inspection authorities,

both domestic and international. A highly productive cooperative R&D effort between instrument developers, safeguards systems analysts, and materials processing experts is actively ongoing today with the overall objective of developing integrated, "near-real-time" material accounting and control systems for demonstration, test and evaluation in various facility types. A timely case in point is the recently installed integrated system of automated NDA instrumentation (gamma-ray spectrometers supplied by Livermore, neutron coincidence counter by Los Alamos and calorimeters by Mound) for nuclear materials accounting and process control in the new plutonium scrap recovery facility at the U.S. Department of Energy's Savannah River Plant in South Carolina (See Figure 9). The entire NDA integrated system is presently undergoing full-scale test and evaluation at the Savannah recovery facility.

Figures 10 and 11 are intended to give a general indication of the scope of Los Alamos safeguards technology transfer to industry, as well as test/evaluation/implementation activities of both DOE contractor and private sector facilities around the United States. Similarly on the international level, through our ongoing support and close cooperation with the IAEA, Los Alamos provides assistance in the implementation of modern safeguards technology thereby helping the Agency meet its expanding inspection and verification commitments for all types of facilities under IAEA safeguards.

Finally, we cite one further example of ongoing safeguards technical support and cooperative activities at the international level. Under a formal US-Japan agreement for cooperation in the peaceful uses of nuclear energy, a number of NDA instruments are currently being developed by the U.S. Safeguards R&D program in cooperation with the Japanese PNC (Power and Nuclear Fuel Development Corporation); these instruments will be used for in-line measurement of mixed-oxide (MOX) fuel for Japan's fast breeder reactors, MONJU and JOYO, as well as future plutonium-recycle light water reactors. NDA instruments to be installed in the PFPF will measure feed materials, process materials, fuel pellet fabrication, handling and transfer, fuel pins in trays, complete MOX fuel assemblies, as well as process-line holdup, scrap and waste. All material handling and processing operations are carried out by automated, remote control so that all the in-process MOX material is, in effect, confined within a sealed "containment envelope" from the input of feed material to the final output of finished MOX fuel assemblies. The PFPF facility represents a very significant advancement in modern nuclear fuel fabrication technology and, such, represents a correspondingly significant challenge and opportunity for the development, test and implementation of state-of-the-art safeguards technology in the state-of-the-art high-throughput nuclear production facility.

The importance of technology and hardware notwithstanding, the actual implementation of effective and workable safeguards must in the final analysis be carried out by people—and moreover by qualified people with the requisite training, knowledge and motivation. Toward the absolutely essential goal of effective safeguards training and

## TECHNOLOGY TRANSFER

### Los Alamos-Designed Instruments Manufactured by US Vendors

- Portable MCA (Davidson/ORTEC)
- HLNCC/HLNCC II (IRT, JOMAR)
- AWCC (NNC, JOMAR)
- Inventory Sample Counter (JOMAR)
- Neutron Coincidence Collar (IRT, JOMAR)
- Fuel Rod Scanners (NNC, IRT)
- SGS (Canberra, JOMAR)
- GRAND-1 (Davidson)

*This instrumentation is purchased by foreign facilities, EURATOM, the IAEA, and US nuclear facilities.*

**Los Alamos**  
Safeguards Assay Group, N-1

Figure 10. Although not a complete listing, this illustration should help provide an indication of the extent of industry interactions and technology transfer activities of the Los Alamos Safeguards R&D Program.

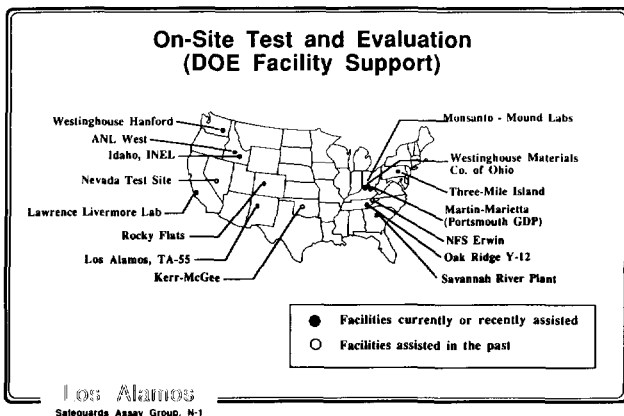


Figure 11. This map is intended to give a general indication of the scope of Los Alamos safeguards technology applications, test/evaluation, and implementation at both DOE contractor and private industry facilities around the United States.



technology transfer, the United States has led the way in developing and conducting well over a dozen safeguards training courses each year for inspectors and safeguards professionals from throughout the United States and countries around the world (See Figure 12). Indicative of the importance attached to safeguards training and technology transfer, since 1980 every new IAEA (International Atomic Energy Agency) inspector has been required to complete the Los Alamos NDA training course for IAEA inspectors. To date this has involved a total of some 400 IAEA people. Many years of experience have shown that the IAEA inspector courses as well as other international and domestic safeguards training courses contribute not only to the technical effectiveness, acceptance and credibility of safeguards, but also help to build a spirit of cooperation, mutual confidence, and a shared sense of professional commitment among safeguards people from around the world.

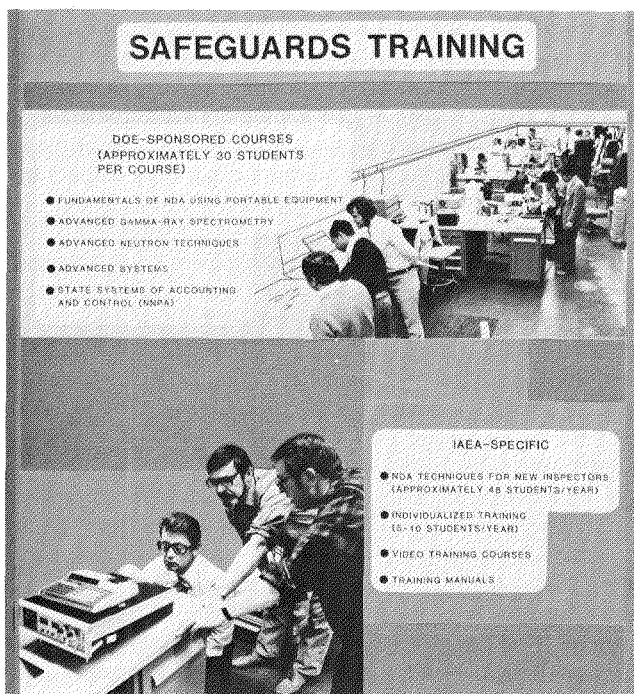


Figure 12. "Capsule summary" of the Los Alamos Safeguards Training Program, involving approximately 10 courses per year, with a total of some 200 participants annually from around the United States and countries throughout the world.

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# Neutron Activation Analysis and Gamma Ray Spectrometry

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## ABSTRACT

A scientometric study of the citations and publication data has been made to show the present state of neutron activation analysis (NAA) and applied nuclear chemistry as compared to other analytical techniques.

## INTRODUCTION

Scientometrics involves the use of quantitative methods to investigate science viewed as an information process. Scientometric studies can be useful in ascertaining which methods have been most employed for various analytical determinations as well as for predicting which methods will be used in the future and which appear to be losing favor with the analytical community. Published papers in the technical literature are the primary source materials for scientometric studies; statistical methods and computer techniques are the tools. The SCIENCE CITATION INDEX (SCI), published by the Institute for Scientific Information, Philadelphia, PA is the primary source for much of the data used in these studies, but additional information comes from other compilations and from the journals themselves.

Most technical papers contain references to other work; these are called citations. A basic assumption in scientometric studies is that a highly cited paper is of more importance to the scientific community than a little cited one. Citation counts have been suggested as one way in which the importance of a paper (and thus a piece of research) can be judged. The SCI lists citations to the papers published in all major journals in the world; thus both authors and journals can be evaluated on the basis of citations to them. Obviously publication in some journals is thought to be more prestigious than publication in others: there is a pecking order here and the measure of order is called the impact factor. Since most of the data used in this paper comes from only one or two sources with essentially the same impact factor no further discussion of this and other aspects of general scientometrics will be made. The recent handbook by Braun, Bujdoso and Schubert<sup>1</sup> is an excellent source for further information.

## LITERATURE GROWTH AND DECAY

The doubling time of publications in a particular field is an interesting and informative datum. The doubling time is defined as the time required for a given quantity to double in size; in our discussion it is the time for a number of publications on a given subject to double. When numerical data are plotted on the abscissa on a log scale as the function of time on a linear scale the resulting plot resembles a decay curve reflected upwards 90°. Figure 1 compares the cumulative growth of the world literature of analytical

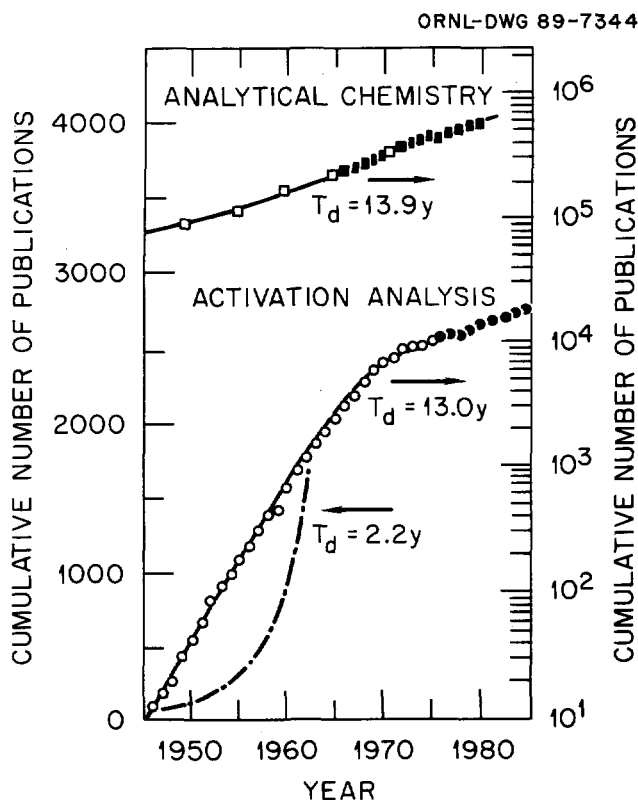


Figure 1. Cumulative growth of the literature of analytical chemistry and activation analysis

chemistry and neutron activation analysis (NAA). Note that in the beginning the growth rate of NAA was quite rapid (doubling time of ca. 2.2 years), but that about 1970 it began to level off, and now appears to be running about parallel with the field of analytical chemistry. These doubling times compare favorably with those for chemistry (14.5y), physics (19y) and biology (16y)<sup>2</sup>.

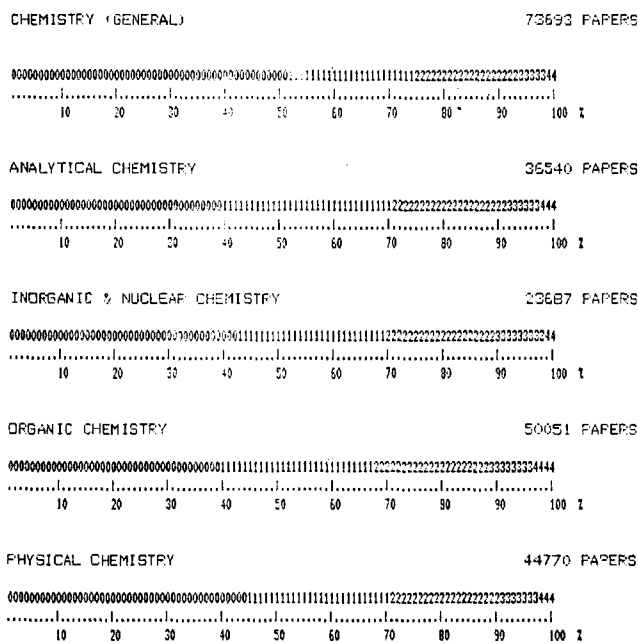


Figure 2. Characteristic citation scales for analytical chemistry as compared to four selected chemistry subfields—0: uncited paper, 1: poorly cited paper, 2: fairly cited paper, 3: remarkably cited paper, 4: outstandingly cited paper

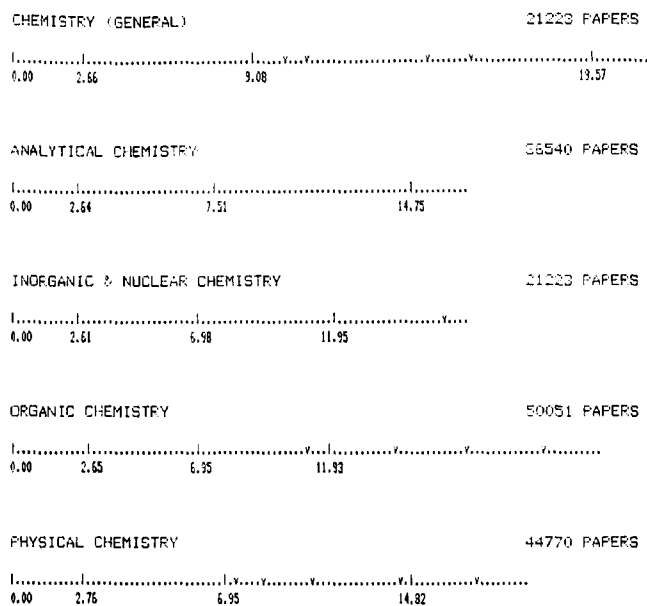


Figure 3. The distribution of papers over the rank categories for analytical chemistry as compared to four selected chemistry subfields.

But the total number of papers tells us nothing about quality. Rescher<sup>3</sup> defines a quantity # such that in a total population of papers /p/ at a time t, there will be p/t/ papers at each level as follows # = 1, at least routine; # = 0.75, at least significant; # = 0.50, at least important; # = 0.25, at least very important. According to Rescher the literature of # quality grows with a doubling time  $t_d/\#$ . Thus, for both analytical chemistry and with NAA doubling times of about 13 years, the doubling times for the last three # levels are 17.3, 26.0 and 52 years. One might conclude from this that most of the papers published in the literature are of very little value. But who is to say which is the valuable grain of wheat amidst all the chaff. After years have passed one may look at citations and see which papers seem to have had major impacts on science.

### CITING AND CITATION CLASSICS

Braun and coworkers<sup>4</sup> have developed a method of characteristic scales by which papers can be assigned to categories that are defined by the number of citations they receive. Using the SCI they have selected five subfields of chemistry: general chemistry, analytical, inorganic and nuclear, organic and physical. Publications assigned to these subfields have been determined for for a five year period (1981-1985). Figure 2 shows the results of this categorization where the 0 area indicates an uncited paper; 1, poorly cited; 2, fairly cited; 3, remarkable cited; and 4, outstandingly cited. Note the while inorganic and nuclear finds itself in the middle relative to total number of papers cited (i.e. fewest uncited), it ranks at the bottom in the outstandingly cited category. Figure 3 shows threshold values for each category for each subfield of chemistry. Note that in inorganic and nuclear a paper would have to be cited 12 times to be in the outstanding category; this is about three citations less than for analytical chemistry itself.

How about these most cited papers from analytical chemistry? In 1984 SCI published a list of the most cited articles from the literature of analytical chemistry. The list comprised 62 articles of which 48 came from *Analytical Chemistry*. Braun and co-workers<sup>5</sup> have categorized these papers by research topic. Spectrophotometry led the list with 15, followed by general chemistry with six, radioanalysis with four, and paper chromatography, electroanalysis, ion exchange and statistical evaluation all with three each. The distribution of total citations went from almost 10,000 citations (one paper, authors later received the Nobel Prize), almost 9,000 (one paper), 5000 (one paper), 2200 (one paper) and then a gradual sloping off to several hundred. All were published before 1972, with 23 in the period 1950-1959 and 19 in the period 1960-1969. It should be pointed out here that analytical papers of all types are not highly cited, especially compared to biology papers. The most cited articles in the *Journal of Radioanalytical Chemistry* are shown in Table 1<sup>6</sup>. Note that five of these six come from essentially the same time span as those from analytical chemistry, and that numbers 5 and 6 cover much the same subject and account for 40 percent of the total citations. All are method type papers and all

Table 1.  
Most-cited articles, 1968-1982, published in the  
Journal of Radioanalytical Chemistry arranged in  
alphabetic order first author<sup>14</sup>

No.	1968-1982 citations*	Bibliographic data
1.	64 (4.9)	ADAMS, F., DAMS, R., A compilation of Precisely Determined Gamma-Transition Energies of Radionuclides Produced by Reactor Irradiation. <i>J. Radioanal. Chem.</i> , 3 (1969) 99.
2.	77 (9.6)	BOWEN, H.J.M., Problems in the Elementary Analysis of Standard Biological Material. <i>J. Radioanal. Chem.</i> , 19 (1974) 215.
3.	95 (9.5)	COOKSON, J.S., FERGUSON, A.T.G., PILLING, F.D., Proton Microbeams. Their Production and Use. <i>J. Radioanal. Chem.</i> , 12 (1972) 39.
4.	51 (3.6)	CROCKET, J.H., KEAYS, R. R., HSEIH, S., Determination of Some Precious Metals by Neutron Activation Analysis. <i>J. Radioanal. Chem.</i> , 1 (1968) 487.
5.	115 (8.2)	GIRARDI, F., SABBIONI, E., Selective Removal of Radio-Sodium From Neutron-Activated Materials by Retention on Hydrated Antimony Pentoxide. <i>J. Radioanal. Chem.</i> , 1 (1968) 169.
6.	73 (6.1)	GIRARDI, F., PIETRA, R., SABBIONI, E., Radiochemical Separations by Retention on Ionic Precipitates. Adsorption Tests on 11 Materials. <i>J. Radioanal. Chem.</i> , 5 (1970) 141.

\*Citation/year data are in parentheses.

show the applied nature of radiochemistry and NAA even 20 years ago.

## INFORMATION FROM INSTRUMENTATION

Modern analytical chemistry is really instrumentation and its application. Thus, a study of the types of instrumentation used in reported research can be very informative as to the state of certain techniques. Braun<sup>7</sup> selected a set of 15 elements, and for each element the individual use of instrumental analytical technique was counted in the subject index of *Analytical Abstracts* for the period 1981-1984. Table 2 gives the results of this survey. Note that NAA is a distant fourth place. These instrumental techniques were merged into five categories, and their

Table 2.  
Frequency distribution of the uses of instrumental  
techniques in 1981-1984 research papers

World Total		
Technique	No. of uses	%
atomic-absorption spectrophotometry	1648	24.1
spectrophotometry	1271	18.5
emission spectrometry	1005	14.7
neutron-activation analysis	585	8.5
x-ray fluorescence	452	6.6
thin-layer chromatography	149	2.2
high performance liquid chromatography	117	1.7
atomic-emission spectrometry	116	1.7
polarography	94	1.4
ionchromatography	81	1.2
differential pulse polarography	61	0.9
ionselective electrode	59	0.9
flow injection analysis	57	0.8
kinetic methods	56	0.8
fluorimetry	52	0.8
anodic stripping voltammetry	49	0.7
voltammetry	47	0.7
inductively coupled plasma	46	0.7

uses for determinations of 15 elements calculated. These results are given in Table 3. Here nuclear is a distant second, used only 1/5 as much as optical methods.

In a related study Braun tabulated the frequency distribution of instrumental techniques used in 1883-1984 research paper. Table 4 lists some of the results obtained.

## ASKING THE EXPERTS

What have been the top advances in analytical chemistry during the past few years? One way to answer this question is to ask the experts. Braun sent a circular letter to 186 analytical chemistry gatekeepers. (A gatekeeper is one who exerts influence on a field as editor, reviewer, etc.) Table 5 is a merged summary of top advances as seen by analytical chemists. Braun also tabulated the methods

Table 3.  
Percentage distribution of the uses of merged instrumental analytical techniques in 1981-1984 research papers

World total

Technique <sup>2</sup>	Element															Total (%)
	Ag (%)	As (%)	Au (%)	Bi (%)	Co (%)	Cr (%)	Cu (%)	Fe (%)	Ga (%)	Hg (%)	Mn (%)	Mo (%)	Sb (%)	U (%)	V (%)	
DPT	59.1	70.4	59.1	67.9	62.9	70.2	66.3	70.8	71.6	65.9	73.2	70.1	59.5	47.2	74.7	66.9
NUCL	14.1	15.1	25.9	3.3	13.6	14.0	8.2	13.5	11.9	12.9	16.2	12.6	21.6	29.1	11.1	13.8
ELEC	15.7	7.8	10.0	15.9	9.5	7.4	14.6	5.6	12.8	9.8	3.9	9.6	11.4	13.9	7.2	9.8
CHROM	3.5	4.2	2.7	9.3	10.0	5.8	6.8	5.2	1.8	9.1	4.1	4.8	3.4	6.8	3.6	5.8
MISC	7.7	2.5	2.3	3.7	4.1	2.6	4.1	4.9	1.8	2.3	2.6	3.0	4.2	2.9	3.4	3.7
	100	100	100	100	100	100	100	100	100	100	100	100	100	100	100	100

used in the 133 most cited papers in analytical chemistry as listed in SCI. Table 6 shows the results. It is noteworthy that nuclear analysis ranks fourth in both comparisons.

A tabulation of instrumental methods used in the IAEA 64 laboratory round robin intercomparison of elements in environmental water samples showed atomic absorption leading (55 percent). NAA was a distant second (22 percent).

Finally one can ask the experts by looking at co-citation clusters. In this method one ascertains which papers are being cited together; presumably if two papers are often cited together this is an indication of an important development of trend. Using this technique Small<sup>9</sup> identified emerging specialty "hot spot" clusters as shown in Table 7. Note that nuclear techniques are nowhere listed.

Table 4.  
Frequency distribution of uses of NAA  
in 1983-1984 research papers

Country	# of uses	%
USA	73	13.3
UK	1	0.6
FRG	2	5.5
FR	5	12.3
USSR	38	7.1
JP	10	2.9
ASIA	15	2.8
LATIN AMER.	2	6.1
E. EUROPE	26	7.1
OTHER DEV. CTRS.	35	6.2

Table 5.  
Merged summary of top advances as seen  
by analytical chemists

Rank	Topic	Responses <sup>a</sup> (No.)
1.	Advances in spectroscopy and spectrometry	156
2.	Chromatography	127
3.	Advances in electroanalytical chemistry	79
4.	Nuclear analytical chemistry	77
5.	Continuous flow analysis	23
6.	Surface analytical chemistry	22
7.	Immunoanalytical chemistry	21
8.	Chemometrics	18
9.	Polydentate complexing ligands	14
10.	Organic reagents	6
	Thermoanalytical chemistry	6

<sup>a</sup>e.g., different advances in spectroscopy and spectrometry were mentioned a total of 156 times in the responses of the 69 respondents.

## CONCLUSION

From the data presented above, the conclusion should be self-evident. Nuclear techniques, like many new analytical methods, had a period of rapid growth and application. That period ended about 20 years ago, and since that time NAA and nuclear techniques have maintained a steady but unspectacular place in analytical research, development and service.

Nuclear techniques were at one time seen to be sophisticated and expensive techniques. The latter is probably still true, but there are many more sophisticated analytical techniques available today—techniques that can determine species, not just elements. But even now NAA can provide extremely sensitive low level determination for many elements, and thus continues to play a large role in many environmental studies. And let us be frank: those of us who were in at the beginning of the so-called atomic age have been our own best/worst enemies: every few weeks another estimate is made public concerning what it will cost to clean up old uranium mill sites, old uranium processing plant, waste dumps, decommissioned reactors, etc. All these will be grist for the radiochemical analysis mill. We can be assured that nuclear analytical chemists will be grinding out results for many years to come—to

Table 6.  
Methods used in 133 "most-cited" analytical  
chemistry papers

Rank	Topic	% of total
1.	Spectroscopy and spectrometry	44.8
2.	Chromatography	36.8
3.	Immunoanalysis	13.8
4.	Nuclear analysis	3.4
5.	Electroanalysis	1.2

Table 7.  
Emerging specialty "hot spot" clusters  
(Analytical Chemistry and Instrumental Techniques)

- Chemically Modified Polymer Electrodes
- Pollution of Aquatic Environments
- Atomic Fluorescence Spectrometry
- Sulphur Compounds in the Atmosphere
- Field Desorption Mass Spectrometry
- Techniques of Photoacoustic Spectroscopy
- Mass Spectrometry
- Atmospheric Chemistry: Air Pollution
- Analytical Electrochemistry: Methodology and Application of Dynamic Techniques
- Continuous-Flow Injection Analysis

satisfy public pressure groups of for no other reason. That is our legacy to you younger analytical chemists, like it or not!

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# Life Begins at 40

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## ABSTRACT

*The role of the New Brunswick Laboratory and its contributions to the U.S. Government over its 40 years of operation are traced from the perspective of DOE Headquarters.*

In deference to NBL's 40th Anniversary, I've titled my talk "Life Begins at 40," after the movie of the same name that some of your older folks will recall. I think if we've been impressed with the forty years of accomplishments of the laboratory, looking ahead to the next forty, I think we can say, "You ain't seen nothing yet."

The National Bureau of Standards, (NBS), now the National Institute of Standards and Technology, in 1948, playing the role of a surrogate mother, spawned the nucleus of the New Brunswick Laboratory (NBL) at New Brunswick, NJ. The AEC-operated Laboratory was established under the direction of Dr. Clement J. Rodden, NBS, to provide official assay analysis of samples of material procured or produced for AEC. This continued as a major effort of the Laboratory until January 1959 when the analysis of plutonium sample for safeguards purposes was added to its repertoire.

During this early history of the Laboratory, which was under the jurisdiction of the Oak Ridge Operations Office, its safeguards role was very limited. Primarily, independent safeguards analyses were performed only for the facilities within the ORO complex; Y-12, K-25, ORNL, Paducah and Portsmouth. It was not until the workload for the Division of Production and Materials Management began to diminish markedly that safeguards samples from facilities under the other AEC field offices began to be accepted by the Laboratory. This trend continued and in July 1971, programmatic responsibility for NBL was transferred from the Division of Production and Materials Management to the Division of Nuclear Materials Security.

During this time, as a result of environmental concerns, the AEC requested a staff evaluation of moving the plutonium analysis work out of the New Brunswick, N.J. area, to be followed later by the entire Laboratory. The Laboratory was opened originally in 1949 on a five acre site

in a relatively isolated part of the New Brunswick township. At the time of the decision to move the Laboratory, the buildup of industry and traffic in the immediate area had increased significantly. In fact, a restaurant diner had located immediately across the street from the Laboratory. Subsequently, the plutonium operations were terminated in 1972 at NBL and arrangements were made for Argonne National Laboratory (ANL) to provide the interim plutonium analytical services under the watchful monitoring eye of AEC-NBL to certify the accuracy and reliability of sample analyses by ANL.

In planning the relocation of the Laboratory, a number of AEC sites were visited and evaluated. These included ANL, NBL, BNWL, LASL and ORNL. As I recall, some of the criteria favoring the final selection of the ANL site was its expanse of 1,500 acres, its handling of large quantities of nuclear materials and it had facilities required for the expanded activities of the safeguards Laboratory. Also, under serious review was the question of possible regulatory administration of the Laboratory which would provide safeguards and other analytical services for both the regulatory and general manager operations. The then projected growth of the commercial power industry and the anticipated growth of IAEA inspections lent serious considerations to a Regulatory administration. In fact, another consideration favoring the ANL site was the location of the International Airport at Chicago to accommodate direct foreign flights by IAEA, and the central US location of ANL. In May 1973, the final decision by the Regulating group was, however, to continue to obtain analytical services from a General Manager administered operation. One factor in that decision may have been the fact that the General Manager had an operating and construction budget already in place and could better handle the costs associated with the move and construction of the new Laboratory. As a result of these actions, following the move of the plutonium operations in 1974, plans were made to move the uranium operations and NBL staff to ANL in 1977.

In 1971, the Laboratory came under the direction of Dr. Carleton Bingham who continues in that capacity today.



"Bing" was well aware of the NBL's leadership in the development of advanced measurement methods for nuclear materials; its supply to NBS of the first uranium metal samples for standard reference materials, its preparation of beryllium standards for government and industry, the preparation and characterization of the first plutonium compound—plutonium sulfate tetrahydrate, for use by the NBS as standard reference materials for plutonium assay and isotopic abundance measurements. What Bing had not been made aware of, probably intentionally, was the harassment the Laboratory had been undergoing from a series of continuing AEC internal studies and evaluations aimed at determining the fate of the Laboratory, but couched in such reassuring terms as "The Future of NBL." Even these reviews were often overridden by or interspersed with OMB evaluation known as "A-76" studies. These studies required the Office of Safeguards and Security, in conjunction with the Laboratory, to conceive and support a convincing argument that it was more cost-effective to continue operating the Laboratory as a Federally-operated facility versus "going private." Even Bing's coming aboard did not end this travail. Being primarily a service industry, NBL suffers from a well-known characteristic of a service-related industry that the apparent value of a service diminishes rapidly after the service has been performed.

What is not well known are some of NBL's very significant contributions to the nuclear industry. Under the AEC's Industrial Participation Program in the early 1960s, the NBL was called upon to take a lead responsibility in evaluating the prospective commercial uranium scrap recovery capabilities to analyze diverse uranium solutions. This was essential to the program in order to establish the correct financial responsibility of the scrap reprocessor. I remember well the consternation of the involved NBL staff when the first results were received of the industries' analysis of the "unknown" samples. To say that most of the results were in "left-field" would be an understatement. However, NBL nurtured and worked hand in glove with the industrial participants to raise their capabilities to acceptable levels.

Another important activity involved a nuclear fuel fabricator whose inventory verification by the AEC indicated a substantial inventory difference (ID). One of the suspect causes was a storehouse, known as the "Blue Room," of over 735 used non-combustible air filters which had been removed from the plant over an eight-year period, containing somewhat arbitrarily assigned plant values of U-235. To aid in the nondestructive assay of these filters, the NBL developed a series of calibration standards which provided a basis for establishing their U-235 content. This effort, and NBL's analysis of many inventory samples enabled the AEC to establish the plant's inventory and the inventory difference for which the company was financially responsible. Similar experiences resulted at other commercial facilities because of NBL's involvement and acceptability in the nuclear community. These experiences provided much of the impetus for the AEC's abandonment of its "financial responsibility" policy which gave way to precise regulatory safeguards requirements.

In reviewing NBL's history, other attributes stand out. One is the quality of staff and recognition of that quality by others. In reviewing the annals of nuclear analytical chemistry, one is overwhelmed by the number of widely accepted publications sponsored and developed at NBL. Another is their authorship and contributions to nuclear analytical reference books and texts. If one looks at the many standards committees, national and international, e.g., INMM, ANS, ANSI, ASTM, etc., one finds a very substantial involvement by NBL staff. Last, but not least, travels across the US, and indeed around the world, many NBL alumni are found in highly responsible positions throughout the nuclear community. It is these activities that attest to the great respect in which the NBL staff, its leaders and "NBL" itself are held.

To sum it up—NBL has given the government an outstanding return on its investment.

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Samuel C.T. McDowell received his B.S. in chemical engineering from the University of West Virginia, and his M.S. and Ph.D. in physical chemistry from the University of Delaware. For 10 years he worked in the private sector as an analytical chemist. He joined the AEC in 1957 and subsequently managed and directed the Safeguards and Security R&D program, the support program for the IAEA, and the MC&A activities for all domestic and international interests of the U.S. Government. Since his retirement from DOE in 1985, he has been with Lamb Associates, where he is currently Director of Safeguards.

# Challenges of Tomorrow ... Chemistry

■  
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■

## ABSTRACT

*Nuclear Materials are going to play an increasing role in concerns regarding proliferation and international affair, with an increased demand for clean electric power, and in environmental and health and safety issues. Challenges range from detecting a singles species in a sea of others at molar ratios of  $10^{-12}$ , or smaller, to a knowledge of the fundamental physical chemistry (e.g., thermodynamics, activity coefficients, etc., of a two phase system, containing about 40 materials, at 500°C) for the lanthanide and actinide elements produced during reactor operation. Other concerns are identified and discussed.*

Let me say that my excursion into the future is going to be purposefully flawed and I'm going to take a modest look backwards and use some of what I think we've seen as a guide. I also am going to talk from the standpoint of chemistry, not analytical chemistry, and I would assume that the analytical folks will see their niche and their ubiquitous nature fairly clearly. I will make some comments about analytical chemistry specifically, at least as I see it.

Well, having disclaimed all decent precision and no accuracy whatever, I am perfectly free to speculate, as you might expect from anybody who says, "This is what we're going to do tomorrow."

I'm going to divide the world into three parts. There are broad topics of science and technology with which each of us is interested, or familiar, or involved in. They're going to hold our attention. They will hold the attention of the young ones that are coming along. I think it's worthwhile identifying those broad topics. The second level of division is the focus that a technical person, a chemist or an analytical chemist, would bring to that subject, that broad topic. And then finally, I think it's worthwhile mentioning some specific technical details of chemistry that should be a focus of laboratory work or theoretical work.

The broad topics we can simply enumerate. Nuclear materials are going to play an increasing role in the concerns on proliferation, the concerns and activities in international affairs that deal with treaties, and treaty verification. Nuclear materials are going to play an increasing role in the general discomfort that people have with the presence of highly enriched fissile material in the hands of the irresponsible. Nuclear materials, therefore, are going to be looked at from the international standpoint, largely based on the weapons history of nuclear materials, as least as we've been discussing it.

Another very broad topic is the obvious amount of continuing demand for energy. That's largely translated, in our case, as our interest in electric power, and I would submit to you that reactors are going to continue to be built. They're going to continue to be operated. They're going to continue to be cleaned, refurbished and decommissioned. Nuclear materials end up playing an important role in all those and the analytical chemical chemist is going to have his/her hands full trying to devise ways to keep the bureaucrats reasonably content.

I don't think that this most recent last two weeks' confusion about low temperature fusion is going to change anything in the reactor business, and I hope you won't be too affected by all the things you read in the various papers, including such scientific journals as Wall Street Journal. Along with the nuclear reactor, and sometimes a less than Utopian view of our international relations, will come the continued need to process materials.

I see no obvious reason to discontinue the production of weapons-related material unless and until some drastic things happen in the international scene, which we as chemists are obviously not qualified to discuss, but do anyway. Nuclear materials are going to have to be processed for fuel, they're going to have to be processed for waste management reasons, and I'll touch on that a little later. We're going to have to clean up a few things and the good Secretary of Energy has inherited a gargantuan job which he's pretending to at least attack to some extent.

All this processing, as some of you I'm sure understand, has got to basically come in the form of separation science and technology, so another one of the broad topics that I'm going to talk about is processing in the area of separation science and technology as far as nuclear materials are concerned.

There are two other broad topics that I want to lump together. They have to be, however, specifically identified because they probably represent the largest challenges that we will have, or have right now, in the area of chemistry and specifically in the area of chemistry of nuclear materials. They deal with environmental issues and the health and safety issues. Those of you who are involved in the bureaucracy of the Department, I'm sure, just based on the weight of paper that's crossing your desk. Those issues have become extremely important, and in some cases, for very good reasons.

Let's talk about the technical focus that a chemist, rather than a political scientist or physicist or whatever, would bring to this kind of thing. And let me walk down the same set of broad topics and talk about the chemistry focus. The proliferation issue, the verification of treaties, those are challenges in the area of nuclear material detection. Detection of not only the elements, but in many cases people are asking detection of specific compounds. Furthermore, they're talking about specific compounds at concentrations that are so low that they're basically impossible to even think about. At least they have been thus far. If someone is trying to find an extremely small amount of tritium in a large sea of hydrogen deuterium, where the ratio of those two is something in the order of  $10^{13}$  or  $10^{15}$ , you begin to appreciate what kind of analytical challenges you have facing you. Those will have to be addressed in some fashion or another as standard methods probably will not do the job. Furthermore, if you're trying to find a nuclear warhead that's buried in 14 different missiles that you can get at only from a thousand yards and someone says you really need to have a pretty positive identification of that warhead or that particular missile shroud, the challenge that you have there I think people are working on, but I think have a bit of a way to go yet.

The production of nuclear power in more specific detail then, demands that we might have to think about new fuels, and I'll talk a little bit about that later. We certainly may have to think about new materials of construction and while that generally is left to the metallurgists or the mechanical engineer, it isn't quite the subject that's left to these folks. There are some important chemistries I'll talk about a little later, which are involved in both new fuels, as well as material construction. Remember please that, at this stage of the game we tend to push materials to pretty much their limits of both chemistry and physical properties, and then we wonder why we don't have a good understanding of, for example, stress corrosion crack propagation at long times, under what appear to be fairly severe conditions, where one would think one ought to be able to understand the mechanism, but the fact is we don't.

Kinetics mechanisms involving these nuclear materials in various fashions, both in metals and in oxides for exam-

ple, are going to become extremely important. They are not easy fields to work on as anybody who has dealt in those can attest.

We go to processing. Processing was one of my broad topics. Let's go a little bit more specific and see what kind of chemistries we're talking about.

We're talking about conversion chemistries, separation, purification and waste management. We will, I believe, see an increasing requirement on the recycle of all streams in all processes. And that's not true only for the oil industry or the plastics industry. It's going to suddenly be true in our business. There are major attempts currently being made within the complex to see whether or not you can recycle reagents or whether you can avoid waste streams that represent 50 percent or more of your throughput. In short, processing is going to take a significant amount of effort on our part. We're going to have to devise new processes to take the place of old ones that didn't seem to do the job.

In the environmental issue and the health issue domain, it's pretty easy to say, "Well obviously, the problems that the chemist faces there are effluent control and detection. Detection of trace materials, far downwind from the stack or whatever, is clearly the most important issue."

Well, my contention is that that's much too narrow a view. I think we need to include in the area of environmental issues, as far as the chemist is concerned, and detection, things like the determination of biological pathways of radioactive materials, and you may wonder why I bring biology into an area where most of us are probably inorganic, physical or analytical chemists. But the biological pathway folks have analytical problems that won't quit, and we're going to be continually subjected to guesses as to what the impact of some of the materials are. Those guess tend to be destructive to the system more than they tend to be useful. We also point out that dose determination both implied and explicit are an analytical problem of this sort. The transport of material in the atmosphere has gotten more and more attention ever, since Chernobyl blew a bit of material out of the stack. At the moment we're focusing our attention on nuclear materials, but that's clearly a broad-based subject and we can learn something from the folks that have to worry about dioxins and PCBs and chlorinated hydrocarbons that move in the groundwater. But they also have an opportunity to learn something from us on these techniques.

Let me see whether I can maybe touch on a couple of areas and then make some comments about the important role of physical chemist, chemical physicist in this whole domain. But again I've divided the world into three parts, macro-chemistry, milli-chemistry and micro-chemistry, you probably don't recognize the middle one but you can easily figure out what it is. The macro-chemistry is the kind of thing that we've classically been doing for years. You can see the amount of material you're dealing with, you can weigh it on a reasonable balance, and you can measure it without having to use fantastic techniques. Let me illustrate, however, how dumb we are in the area of macro-chemistry as far as nuclear materials are concerned. Let me remind you the here at Argonne there is a major

activity in the fast reactor business called the IFR, the Integral Fast Reactor. This is not a plug, this is simply a litany of some of the problems that we've had doing some processing for the Fast Reactor. To give you a little background, this reactor uses a uranium-plutonium-zirconium alloy, a metallic alloy as a fuel. The integral part of this title is derived from the way we handle the processing. The fuel cycle in effect looks like this, the spent fuel comes out of the reactor, is cooled for a fairly short time, moves into the adjacent connected shielded cell and is processed by a fairly low DF (decontamination factor) process. If we get a DF of over 100 overall we think we're doing all right. We don't really need to have a high DF process. The Purex folks have a different goal. In case of a fast reactor it doesn't make a difference. We do have to reconstitute the fuel however, at the right density.

We isolate uranium-plutonium, contaminated mostly with various kinds of fission products, but we isolate them as metal. We cast fuel from that metal, throw in some additional zirconium to make up the right composition in the alloy, and that's basically the fuel cycle. All that is handled within a stone's throw of the original reactor, and we use EBR-II in Idaho and the fuel cycle facility there essentially as our model. And, I don't know, Bill Sovereign, the distance between the reactor and the processing cell? It can't be more than 200 yards, I would guess—integral in the real sense.

In our fuel cycle we make sure that the fuel, which is always radioactive, never leaves the confines of the reactor fuel processing cell. So much for the fuel cycle.

The process itself that we've been fussing with can be most simply described as an electrochemistry process dealing with liquid metals and fuel solids operating at about 500 degrees centigrade. We dissolve the fuel in cadmium, we then take most of the uranium off by electrorefining it from the cadmium through a salt, to a solid cathode, and then we readjust voltages and concentrations and we take the plutonium off, together with some of the rest of the uranium and a bunch of fission products into a liquid cadmium pool, distill off the cadmium from that pool and we reconstitute the plutonium metal. On the surface that sounds fairly straightforward. Let me, however, remind you that the stuff we use as feed is a composite of three major elements and 35 minor elements, and then some other junk that's been thrown in because the fabrication hasn't been very clean; and so we end up with not only with metal but we also end up with a few oxides, nitrides and miscellaneous junk. When you try to make the model for this thing, to see whether or not you can predict what is actually going to happen, you are suddenly faced with trying to do a chemical and electrochemical modeling at 500 degrees and a two-phase system containing about 40 different materials, most of them as metals, sometimes as oxides. For that, as you can readily imagine, you need some decent thermodynamic data. We had some decent thermodynamic data, not very much. It was surprising to us that in just focusing our attention on uranium, neptunium, plutonium, americium, curium—normal actinide elements—that you are thinking about, we had very little data in the way of activity coefficients of

these materials as chlorides in the salt. We had some data. Argonne did a lot of this work in the 1960s and the early 1970s. We had some data available for what happens in cadmium solutions. But if you ask did we have enough to do systematics, to be able to predict reasonably well what might happen in some of those solutions, the answer was not very much. Some of our guesses were poor. We were surprisingly lucky in many areas and we managed, in fact, to put together a reasonable process. That was not necessarily true because we had a great deal of information. Fundamental data simply weren't there.

Well, that simply points out that there are lots of things that we need to learn in such macro-systems where we're working in bulk concentrations. We're talking solutions in chloride salts, where the plutonium content may be five atom percent. It's not trivial, we're talking substantial concentrations. Chemistry of the three valence states of zirconium, for example .. yes, three valence states of zirconium in this mess, basically, was uncertain and still is uncertain, and we're gradually trying to unravel it.

Activity coefficients of rare earths that have both valence 2 and 3 were simply unknown and we had no good mechanism for predicting them, except a pair of dice against the wall, and that's not a very good way to run a processing model. So I give you, as part of the challenge into macro-chemistry for example, thermodynamics. We had to know something about kinetics. We had to know something about complex formation in this particular system.

I could also cite you some examples out of the program that we happen to be running in a Truex facility, which is an aqueous system, runs at normal temperatures, and you think, "Well, this is simply an extraction process. It doesn't look a whole lot different to an engineer than the Purex process," until you ask, "Well, what do you know about the activity coefficients of nitric acid in the system?" You don't. You have to determine it. It happens to have not only tributyl phosphate in the nitric acid solvent, but it also happens to have CMPO. But that's immaterial. The fact is, we really don't have a good handle to predict, on a systematic basis, what to expect of plutonium-uranium distribution coefficients in that system.

So there are fairly large uncharted areas, and I wouldn't want those of us who've been fussing around in chemistry for 30 years to get too complacent about having done all the work and we can now go home.

Isotope separation these days for uranium is done by an AVLIS process in which lasers are used to ionized uranium vapor. The process itself is under some reasonable control, it's not really a chemistry process, it turns out to be largely a physics process. But you have to make a conversion from yellowcake to metal, because metal is the feed for that process. Converting uranium oxide to metal has been done 40 years ago by Mallinckrodt. The process didn't work very well, and it wasn't used—it wasn't necessary. When the folks who did this at down at Oak Ridge decided maybe they needed to revise it and make it a little more efficient, they went to the literature because they were needing some simple solubility data on uranium oxides in certain kinds of salts. They weren't there. Now, after all

the fussing that we've done, collectively and individually, with uranium and plutonium and all the other nuclear materials with that we deal with, one would have thought that the uranium oxide solubilities in a few salts would have been, at least, predictable. The answer is, it isn't very predictable, and we really don't have a good handle on what goes on in fluoride and chloride salts. So they had to go out and dig it out. Well, that's something that's obviously going to get done, but that's simply another example of where we really don't have a good handle on the systematics of nuclear materials in various kinds of media.

Well, I could go on in that area. We've recently, for example, looked at the question of how do we recover plutonium oxide out of scrap and residue, of which there is a fair amount floating around the complex, in order to put it back into the system. This seems like a not only worthwhile exercise, but clearly various parts of the DOE complex have assigned a very high priority to that, for a number of reasons, not in the least of which is the production reactors which are having a bit of a problem. Well, the refractory nature of plutonium oxide is well defined, I don't need to tell any of you what that's all about. Our own, somewhat provincial, answer to this problem, is to jack up the temperature and work in liquid metals and a few salts. You say, plutonium dioxide is not the most stable oxide in the world, therefore we ought to be able reduce this to the metal in some fashion, but for that you need to have a reasonable idea of thermodynamics and activity coefficients of the products in solution. Fine, that's not very hard to get for plutonium, although, again, that's a little tricky to determine how good those numbers are. But the  $\text{PuO}_2$  that's part of the scrap and recycle operation is dirty, I mean that's precisely why it's not being used. It's very dirty. It has maybe 14, 15, 16 other elements in it. When you then ask how do those other elements behave in the fused solid-liquid metal system that we were using to reduce  $\text{PuO}_2$  to the metal, and specifically, are there any interactions between plutonium and those other elements in a metallic solution, and what do we know about the activity coefficient or distribution between fused solids and liquid metals, we found the literature is empty. We obtained some interesting results, surprises, I think they're called, which we eventually worked our way through once we realized that certain avenues that we were trying to push simply wouldn't work. But it would have been nice to be able to predict that based on the amount of effort that people have expended in this business.

So much for macro-chemistry. What do we have to do in macro-chemistry? We've got to look at thermodynamics. We really ought to have a better idea of some of the phase studies, especially in immiscible systems. We need to do something about electrochemistry and complexing systems where we really don't have a good idea what the actual voltages are that we should use. In non-aqueous chemistry, actinides have been largely neglected as far as we can tell, but I'll make some other comments on actinides later.

Let me pass through milli-chemistry. That happens to be, I think, the area where analytical folks probably have

the biggest role to play. They worry, and they should worry, about knowing something about redox reactions, at the modest and low concentrations, particularly with impurities that come along with some of the reagents that some of these folks use, and one member of the audience has regaled me with stories that last almost forever, as they did yesterday, about the fact that some of the nonsense in the literature may be due to the fact that people either aren't reading the literature or haven't determined some of the important nuances of what they're doing.

Photochemistry and complexation in the milli-chemistry range is important and it would be nice to be able to unravel those before we do an analysis and find out that we can't get the kind of exchange that we thought we would get.

But let me move over to micro-chemistry, which is where the real analytical problems are, and where we are really almost blind, I think. The intense societal interest that has developed relatively lately on anything that has to do with life, I think, begins to impinge on us fairly heavily. We're beginning to pay a great deal of attention on those things which, in the eyes of the Delaney Amendment, for example, become essentially nonmeasurable by normal techniques. We begin to worry about possible or real or imagined contamination of groundwater by ... and you can fill in the blank. We begin to be very interested in the lower end of the dose/effect relationship and begin to try and see whether we can determine from the very small body burdens that some folks carry that there is any effect. The 109 mice of Weinberg notwithstanding. We have been subject to a significant amount of regulations that deal with air sampling, and find that air sampling techniques are simply not very good from the standpoint of matching what we used to call the maximum permissible body burden. The ability for example, at very low concentrations, to directly detect the valance state of plutonium at  $10^{-8}$  or  $9$  or  $10$  or  $11$  molar ... directly detect, not by inference—is nil. We've been fussing with a thing called the laser photoacoustic spectrometry in our shop. Down below  $10^{-8}$ , it's not very good. It's not bad, but it's not very good, if you really wanted to get a direct measurement. What's been done in the past has been indirect, that is we based it on chemistry that we think we understand. Let me comment on that a little later.

The analytical chemist finds that stability of a solution sometimes is difficult to define and is certainly not very clear. The isotopic exchange of spiked analytical samples suddenly goes to zero for some reason or another which he or she cannot fathom. There are kinds of gremlins that appeared, concentrations, in what I called the micro-chemistry range. There are no gremlins in this world, that's because we don't understand the system, and we really need to do that. Let me give you some examples.

We commonly purify laboratory distilled water or deionized water by a series of organic resins and filters. And if you ask, "What do we know about the micro-chemistry of plutonium with organic materials? What kind of idea do we have on complexation?" The answer is nil.

That's a little bit too strong and I'm perfectly well aware of the fact that it isn't quite nil, but for my purposes here, I

submit to you that you really don't have a very good idea of what happens at  $10^{-10}$ , or 11 or 12 molar, when you introduce a reagent whose impurities you think you have driven to zero. Most of the time, very often in fact, this laboratory distilled water is one of the major culprits in being unable to determine why it is that you suddenly can't seem to extract plutonium from here to there. But laboratory distilled water is not the only problem. We tend to take bottles off the shelf or order them very carefully or order what we call super pure reagents, and we tend to take on faith what it says on the label. We hardly ever look to see what else might be in there, and again I want to go back to the organics, because they happen to be important in a number of areas. We really don't know very much about the organics that are present in reagent grade—pick your poison—sodium chloride. We have no idea what comes out of plastic bottles that contaminates whatever it is we happen to be interested in at the moment. We also therefore don't know how to handle the problem of where does plutonium go in groundwater. Even if we thought we could analyze groundwater for the concentrations at very low levels of the various organics that are present in all reasonable ground water.

At the micro-level, what I call the micro-level, we are really fairly blind, as we operate pretty much as though we were dealing with macro-chemistry, where if we lose one part in  $10^5$ , it doesn't make a lot of difference. But if you don't have one part in  $10^5$ , or you may only have a part per billion, then it does make a lot of difference, and I don't think in the nuclear material area we have yet learned that some of those topics need to be at least looked at in some fashion. Notice I'm not telling you how to do this for the future. I don't have the slightest idea how you go about identifying compounds. You talk to the hydrologist and you say, "Well, tell me what humic acid really is that floats around most of our aquifers," and he or she will refer you to the nearest textbook in which you will find humic acid is a generic name for a lot of different things. How do you unravel the chemistry of a lot of different things? That's a problem which I leave to the student for an exercise.

Let me simply begin to close in. I think we need to have, in the case of analytical work, some idea, for example, to get away from complex chemistry, whether, somebody using ion chromatographs with multiple stages in the very short column, whether that actually separates isotopes in the event that you're interested in knowing something about the isotopic composition. The chance that you get isotopic selectivity in multi-stage operations of any kind, is almost 100 percent. I don't think that people pay much attention to that, when they hand a isotopic ratio to the guy who asks for the analysis. The are people who are looking at this for a number of reasons, and it's becoming reasonably clear that any multi-stage operation is suspect as far as isotopics is concerned.

I've already mentioned that we need to have a little better look on contaminants, both in our distilled water and our reagents. The ASTM method for total organics in distilled water is a very precise thing. What you do is take a drop of permanganate solution and you throw it into a li-

ter of water and you wait. If you can still see the color of the permanganate after a 30-minute time, then everything is okay. That hardly represents what I would call dealing with the problem with a scalpel. It sounds more like a shotgun to me. Furthermore, you've also ruined that particular batch of distilled water, and you really don't know what's next.

I think it's important to know how many halogenated materials ooze out of the plastic containers in which we mostly get some of our reagents. Nominally, the containers are supposed to be inert, but we don't know whether or not, at low concentrations the halogenation of our reagents contributes to the volatility loss, at low concentration, from plastics if we heat material.

What I'm saying is not that the analytical chemist has difficulties, you folks already know that. What I'm saying to the chemist is we need to know a little bit more about the micro-chemistry of the things what we think we're really pretty sure of. Well, let me make one other set of comments, and close. I'm sure that you've noticed by now that I'm talking generally classical chemistry, and that is, we're talking about kinetics and mechanisms and ordinary complexation. But there is a very large field where the analytical chemist has perhaps the greatest opportunity, and that's the interface between physics and chemistry. There are few things that make elements and compounds unique, that come out of the nuclear portion of the business, and as a consequence the things that we tend to deal with, radioactivity for example, are really not much use in this area, except perhaps where you have spectra that are so clean that you don't have to worry about interferences. But you do have the possibility of looking at electronic contributions to selectivity and uniqueness, and it seems to me that the energy level of the electron, both as it exists in the particular element or compound, or after you've kick the system and you fire one out and you look at it, probably represents the most obvious way to reduce your background, increase your selectivity and be able to get at very low concentrations of specific identified materials.

There are number of other areas in which chemical research, I think, is necessary. I tend to focus in on the laser because it has two attributes that I think are interesting: 1) it has a very short line; and 2) it has an enormous linear energy transfer, where you can disrupt selectively, depending on how you do it, the things you want to disrupt and then see what kind of analyses you have as products.

The future generation of chemists, I think, is going to have to learn why the early pioneers were, in fact, pioneers in our business, and how they were able to accomplish what they were able to accomplish. There were a lot of folks that worked in the Manhattan District, some of them are perhaps here. A lot of them worked here. These were the folks that labored in micro-chemistry. They lost materials on beaker walls, they were plagued by unexplained low material balances. They were not unique, obviously. They had no computers. They had no fast electronics for multi-channel analyzers. Their multi-channel analyzers consisted of them doing single-channel analysis by hand. They made their own micro-balances. They made their own micro-pipettes. They determined crystal

structures and reaction products on quantities and material that you could barely see with a microscope. But, nevertheless, they were able to produce seminal results. They still are valid today.

I think it's perfectly fitting that this conference, at least, salutes these folks. And I hope that in the next 40 years our chemistry, with whatever prodding we have, will be as innovative and productive as the last ones.

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# Mass Spectrometry

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## ABSTRACT

*The limiting factor to the absolute accuracy of isotopic measurements is no longer instrumentation hardware. Greater understanding and control of the chemistry of sample purification, gravimetric blending of separated isotopes, filament loading, and the physico-chemical processes occurring at the high-temperature filament will be necessary before the advantages of robotic sample preparation and filament loading and automated analysis can be attained. Such improved understanding is an essential precursor to controlling and reducing the uncertainty in isotopic ratio measurements to one part in  $10^5$ .*

My colleagues who spoke yesterday on mass spectrometry had the easy tasks. Hind sight is always 20/20 and discussing the present is fairly easy if you keep up with the current literature. I am not sure what great sin I committed to warrant being tasked with predicting the future. However, I have learned that good quality crystal ball polishing compound is difficult to obtain. I am sure that many of you have crystal balls that may show a different picture than mine. Therefore, the discussions that follow this presentation should prove to be far more interesting and entertaining than my talk.

For the purpose of this discussion, I am going to divide mass spectrometry into two broad areas: instrumental and chemical. By instrumental, I refer only to the mechanical and electrical equipment involved in mass spectrometric measurement. The chemical area is much more complicated and diverse. It includes chemical dissolution of the sample, chemical separation and physical purification of the element of interest, the chemical and physical processes that occur during the procedures necessary to introduce the sample into the mass spectrometer, and of great importance, the physical chemistry that occurs during the ionization process.

In the 1960s, the limiting factor in the accuracy of absolute isotopic abundance measurements was clearly the instrumentation. The chemical methodology in terms of chemical purification, assay and gravimetric mixing of separated isotopes had evolved to a point where isotopic

mixes of known isotopic composition could be prepared with accuracies of a few parts in  $10^4$ . Instrumentation was limited to basically vacuum tube technology with its inherent slowness and lack of linearity relative to modern electronics. If one examines the data on absolute isotopic abundance measurements between 1960 and the present, a definite pattern emerges. Until the early 1970s, instrumentation was a major source of error; by the mid 1970s instrumental and chemical components were about equal. Since then, the instrumentation has improved at a rate that only the most liberal of science fiction writers could have predicted. Advances in the electronics industry are still accelerating at an exponential rate; I do not anticipate a change in this trend, and the resulting spin-off will be improved mass spectrometric instrumentation. I do not foresee instrumentation capabilities as being a limitation to future nuclear mass spectrometric needs, however there are definite direction which should be pursued.

This explosive development in the sophistication of instrumentation, however, is a double edged sword; improved accuracy has been at the expense of serviceability. In the good old days, a mass spectroscopist was expected to repair his own equipment. This for the most part is no longer true, and the situation can only get worse as electronics get smaller and more sophisticated. Even factory representatives, like modern auto mechanics, have become parts changers rather than repair persons. The end result will be greatly increased operating costs due to expensive but necessary maintenance contracts and repair parts.

At this point I see the future course of mass spectrometric instrumentation approaching a fork in the road, two separate paths or goals but still maintaining interaction between the two paths. One path is the requirement to pursue the highest quality of measurement accuracy and precision for primary nuclear standard materials. History supports the fact the relationship between improved accuracy and required effort is, in the language of chemical kinetics, a first order equation, with measurement improvement being plotted linearly and time and money being logarithmic in order to produce a straight line graph.



This path, regardless of the required time and expense is necessary to maintain a measurement base that exceeds, by at least an order of magnitude, the user needs. The second path, which is the major challenge for the future, is the development of mass spectrometric instrumentation that will provide rapid and cost effective measurements sufficient for the user's needs. This instrumentation package is, in various stages, either available, being developed, or just around the corner. The challenge is to mold together various developing technologies into an accurate, rapid cost effective and preferably mobile, mass spectrometric system tailored specifically to the needs of the nuclear community.

Reliable, rapid and cost effective will be the key words for routine measurements in the nuclear industry in the future. Improvements in the thermal ionization quadrupole mass spectrometer (Thermoquad) in recent years indicate a very strong potential for this instrument's use in routine nuclear measurements. Its size and portability, relative to magnetic sector instruments, will allow on site measurements, thus reducing the turn around time between sample collection and data availability. This approach is being investigated in both Europe and the United States and shows promise. The newly developing technique of "total sample burn" using extremely small samples is also well suited to the thermoquad. The total burn technique has the advantage of reducing errors from non-control of isotopic fractionation during the measurement process and also reducing operator exposure to radiation due to the small sample size required for analysis. Increased cost effectiveness will also involve the automated chemical manipulation that is currently evolving within the robotics industry. Microwave sample dissolution, although still in the experimental stages, shows promise for greatly decreased sample preparation time and is amenable to robotic control. The advancement and priorities of technology development by industry is governed by economics. Although we know that we are important, to be honest, nuclear mass spectrometry is a very small slice out the instrumental economic pie. However, I see strong support from our scientific colleagues in the environmental and health related areas, who comprise a much larger slice of the pie. The mass spectrometric package for the routine measurements that I have described is ideally suited to the future needs in trace element analyses relating to the health and environmental sectors of society. I feel that the nuclear industry can easily piggy back onto this emerging expertise, which should accelerate rapidly during the next decade.

As I indicated earlier, the chemical aspects of mass spectrometry are the most complicated part of the system. Initially I had planned to devote a considerable portion of this presentation to this aspect of the subject. However, after more careful thought, I realized that I could talk all morning and only hit the tip of the iceberg. Due to time limitations, I will concentrate on what I feel are the major concerns for the future. Most areas of chemical improvement, such as separations methodology and assay procedures, will naturally evolve from other areas of analytical chemistry. Thus, our major concerns are those

areas unique to mass spectrometry, and their impact on improved nuclear measurements. The major limitation in the present accuracy of thermal ionization mass spectrometric measurements is the ability to control the inherent isotopic fractionation process that occurs during sample ionization. Initially, the lighter isotopes are preferentially ionized, resulting in a measured light to heavy isotope ratio that is greater than the true value. As the analysis proceeds, the ratio decreases and reaches the true value when approximately 2/3 of the sample is consumed. Making measurements at the true value point is not a practical approach. The reasonable, and generally used approach, is to control the rate of fractionation, collect data on a precise time schedule and correct for systematic bias with samples of known isotopic composition, analyzed under identical conditions. The control of these parameters is limited by our knowledge of the complex physical chemistry that occurs on the filament and in the ionization region around the filament. Although numerous papers and theories have been published on this subject, this critical portion of the mass spectrometric process remains, to a great extent, a "black box." Additional advances in the accuracy of thermal ionization mass spectrometry will require extensive additional research into the mechanisms of the ionization process. Although this work is best suited to major research laboratories, and the knowledge gained is most directly applicable to the certification of primary nuclear reference materials, the application to improved routine measurements is obvious.

This brings me to the second, and in the near future, most critical need for improved mass spectrometric measurements in the nuclear community. I could sum it up with one word—education. However, I will elaborate. Although we do not fully understand the mechanisms of thermal ionization, there are several scientists in the world that have reasonable working knowledge of the processes involved and the consequences resulting from not controlling the processes. Several of these scientists are in the audience today. We have all lectured and published in this area, but I get the feeling that we have just been talking to each other. I have only been closely associated with the nuclear community for a short time, but my observations are that much of the available knowledge on the control of isotopic fractionation and other sources of systematic error have not been transferred to the technicians who are making the actual measurements. The blame for this situation must be shared; research scientists have not reached the audience that is in greatest need of the knowledge, and administrators have not required the skills and/or encouraged the self-motivation needed to keep abreast with current developments in the field. Improvements in instrumentation and computerization will continue, but improvements in the quality of measurements, at least during the next decade will be limited by the experience and theoretical knowledge of humans who still must make the final decisions on the quality of each step in the measurement process. As automation takes over many of the human tasks, it becomes more important for the human supervisor to fully understand both the physical and theoretical aspects of the measurement pro-

cess. Computers will always be capable of producing very precise wrong numbers! It will be a long time before they will be able to replace human experience and "gut instinct."

I will conclude this presentation by gazing into my crystal ball to see the state of nuclear mass spectrometry in the year 2001. I see a van pulling up to a nuclear site. Two men get out, collect several samples and take them back to the van. They hand the samples to a robot. The robot is going to dissolve the samples in a microwave oven, chemically separate the nuclear material with ion exchange, load the appropriate column fractions onto mass spectrometer filaments, place the filaments into a multi-sample turret and then into a quadrupole mass spectrometer. The men are getting into a car and driving into town. The men are now in a bar having a beer and watching a football game (it looks like the Washington Redskins versus the Chicago Bears). The game is over and the men return to the van to find all of the samples analyzed and the data neatly printed out and FAXed back to the headquarters.

I picked the year 2001 for a reason based on personal experiences of my life. I moved out of a college dormitory just before co-ed dorms became popular. I got married just before it became socially acceptable to live with someone without getting married first. Since I am eligible to retire from the government in the year 2000, the year 2001 seems about right for mass spectroscopists to be paid high salaries to drink beer, watch football games and let automation do all their work for them.

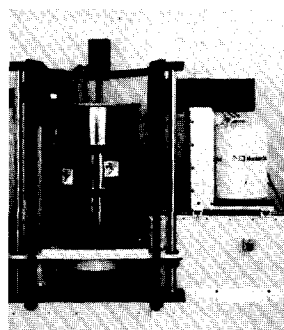
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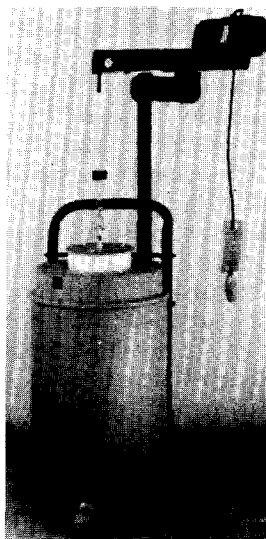
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# Measurements and Material Accounting

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## ABSTRACT

*The DOE role for NBL in safeguarding nuclear material into the 21st century is discussed. Development of measurement technology and reference materials supporting requirements of SDI, SIS, AVLIS, pyrochemical reprocessing, fusion, waste storage, Plant Modernization Program, and improved tritium accounting are some of the suggested examples.*

## INTRODUCTION

There is an expression that, "The past gives us experience and memories; the present gives us challenges and opportunities; the future gives us vision and hope." It is challenges and opportunities, and the vision and hope that I plan to discuss today in our celebration of the 40th anniversary of the New Brunswick Laboratory and to honor its contributions to our country's nuclear energy programs in the areas of measurement science and material accounting.

NBL, over the years, has served well as the U.S. Government's Nuclear Materials Measurements Laboratory. It has continued to set the example for the development of material standards and as an unrivalled center of excellence for nuclear material measurements. This is due, in no small part, to its high caliber staffing, dedicated management, and innovative, farsighted approach to problem solving. We recognize that knowledge is important but perhaps, as Einstein said, "Imagination is more important than the knowledge."

## BACKGROUND

NBL's *entre'* as a full-fledged internationally recognized safeguards laboratory occurred when it took responsibility for the Safeguards Analytical Laboratory Evaluation (SALE) Program in 1976. This program, under NBL's direction, grew from one involving DOE laboratories to one of international scope and participation. As a result of funding constraints and increased safeguards priorities at DOE facilities, the program was redirected in 1984 as Safeguards Measurement Evaluation (SME) Program to more effectively serve the DOE community. The database, col-

lected from over 50 laboratories worldwide, provided perhaps one of the largest known critically evaluated and reliable measurement data bases of nuclear analytical capabilities and identified the need for new analytical techniques and new certified reference materials. These endeavors, coupled with the interagency agreement to move the then National Bureau of Standards' (NBS) program for nuclear materials to NBL in July, 1981, went far in establishing NBL as a national and international center of excellence for standard methods and reference materials in the chemical and isotopic analyses of nuclear materials.

Building on its broad base of technology and expert experience, NBL has progressed and excelled in many allied and sometimes diverse areas in pacing the advances and innovations of the other nuclear sciences. An example of this diversity was NBL's demonstration in 1984 of the use of a Plutonium Air Transport Container (PAT-2) for transporting plutonium safeguards samples to the IAEA. NBL also completed and made available its design and fabrication details of a markedly improved coulometer for plutonium measurement. A major but often overlooked contribution of NBL is its transfer of technology to others. This transfer takes many forms, including:

- Technical papers on NBL development and improvement of methods of analysis of nuclear materials.
- Evaluation of the continuing performance of laboratories engaged in the measurement of nuclear materials. This is a two-way street for technology transfer. NBL may transfer its best technology to the laboratories or may find a better technology that the NBL can use or improve upon.
- Field support and on-site technical assistance to the DOE facilities. Being on-site, this approach is probably one of the more effective and efficient means of transfer, essentially on a person-to-person basis.
- Preparation, characterization, certification and distribution of nuclear reference materials. Technology transfer here involves a strong interaction and exchange between the parties whether it be for preparation, characterization or treatment of the derived data for the certification.

- Training of personnel (Government, IAEA and private industry) in specialized techniques. Training, of course, is one of the more commonly practiced and effective forms of technology transfer.

NBL's efforts have contributed significantly to the evolution of many improvements in safeguards, provided a basis for evaluation and projection of the future role and state of nuclear materials safeguards on both the national and the international levels.

To the extent that advanced planning is possible, what are some of the challenges of tomorrow for NBL in the area of nuclear materials measurement and accountability?

## CHALLENGES AND FUTURE DIRECTIONS

The Office of Safeguards and Security, other domestic nuclear programs, and the international nuclear community all rely, and will continue to rely, on NBL for leadership in the nuclear material measurement technologies, reference methods and materials and, perhaps most importantly, the initiation of new ideas. The safeguarding of nuclear material will continue in importance and present new and exciting challenges as the nuclear technology progresses and, hopefully, as peaceful utilization of nuclear materials increases. The many advances in applications of nuclear materials, such as the various medical uses, research for better understanding of nuclear structure, effects on materials from neutronic reactions, all enhance and enrich our lives. The increasing danger of the greenhouse effect from burning fossil fuels should soon convince a skeptical public of the urgent need for nuclear fueled power reactors and assurances that they can be operated safely.

As we look to the future, DOE continues to emphasize the need for enhanced capability to mitigate the spectrum of threats to DOE facilities and to improve the effectiveness of international safeguards. Our planning strategy includes assessment of near-term and potential future threats, with the aim of investing in improvement efforts that maintain acceptably low levels of risk and the minimize the cost of implementing safeguards and security systems. High quality measurements and accountability are required to reduce risks associated with potential special nuclear material (SNM) diversion hidden by falsification of data such as understating input, overstating output or misrepresenting current inventory. Improved materials accounting, better measurement techniques and measurement control programs are necessary to help address these concerns by providing site-specific material balances that are well-characterized and documented in terms of measurement capability and validated with reference standards. Creation of valid standards for the increasing use of nondestructive assay (NDA) is a real technical challenge. NDA instruments are usually calibrated by measuring the response from a synthetic standard containing a known amount of nuclear material, or by selecting a subset of representative containers for careful analysis by wet chemistry. There is a need for better understanding and use of reference materials for NDA measurements. An alternative that needs further exploration is to determine the calibration function or measurement basis from first principles. For example, the principal attribute measured

in calorimetric assay, heat, is related directly to plutonium content and the standard is related directly to the national measurement system. Until such time as NDA standards represent first principles, uncertainties caused by calibration errors, nonrepresentative standards or improper operating procedures will be difficult to estimate or reduce. These are important safeguards concerns where they are major contributors to shipper-receiver or inventory differences.

As federal employees with expert technical knowledge of plant operations, NBL should play a major role in providing meaningful insight and recommendations to the DOE safeguards program. The DOE program requires increased coordination with outlay program offices, field offices and Environment, Safety and Health (ES&H). The development of preconceptual safeguards and security designs are necessary to influence and provide timely performance expectations and cost-effectiveness for new DOE facilities and processes. Measurement technology and standards for materials that are produced or used in new DOE programs, such as Strategic Defense Initiative (SDI), Special Isotope Separation (SIS) and Atomic Vapor Laser Isotope Separation (AVLIS), pyrochemical processes, fusion and waste storage will be needed from NBL. Strict nuclear materials controls and monitoring of DOE operations under highly visible conditions and increased volume of nuclear material from arms reduction may also require involvement from the Laboratory.

The Plant Modernization Plan will require replacement of most major DOE facilities, presumably by the year 2010. OSS will require support from NBL to help:

- tailor instruments to address specific facility applications; although measurement problems may be nominally the same in different facilities, differences in the process, local radiation backgrounds, etc., usually preclude use of "off-the-shelf" instruments;
- incorporate rapidly increasing electronic and computer capability that will improve measurement performance and reduce dependence on operator's skills;
- address new, or as yet unsolved measurement problems; for example, those associated with laser isotope separation of uranium and plutonium, and hard to dissolve materials, such as sand-slag-crucible residues;
- improve techniques for determining nuclear material retained as holdup in piping, vessels, gloveboxes and filters; and
- address tritium accountability and new large-scale tritium handling facilities, including the new tritium facility to be built in the future. If these materials are to be safeguarded effectively, development of an improved measurement technology will be required because there are few usable isotopic signatures.

DOE Order 5633.3, "Material Control and Accountability," and its associated guides, dictate new performance requirements which should be attainable by the state-of-the-practice measurement capabilities throughout the complex. OSS will require support from NBL, through the Laboratory's measurement development and measurement evaluation programs, to assist facilities in acquiring expanded measurement control programs which are easy

to substantiate by DOE Inspectors. Measurements and measurement control programs are vital to the materials accounting subsystem. The principal index for meeting the objectives is the sensitivity and reliability of gauging the true status of material balances involving material flows, material transfers, inventories, and process holdup. A strict measurement control program is necessary to ensure the accurate calibration of the measurement systems and reliability and reproducibility of the measurements. Among other things, a high-quality measurement control program permits monitoring the relative accuracy between input and output measurements—the limiting factor being the uncertainties in fundamental constants, that is, the relative biases between reference standards and methods used for measurement. Emphasis must be placed on obtaining adequate and accurate key measurement points to reduce such biases.

As the Committee on Material Control and Accounting of the National Academy of Sciences pointed out in its 1988 report, "Material Control and Accounting in the Department of Energy's Nuclear Fuel Complex," few facilities are performing materials accounting as well as needed, and facilities are not in all cases taking advantage of currently available technology. Most operational materials accounting systems are basically computerized book-keeping systems, and inventory difference and control limit calculations, as well as data and decision analyses, are not an integral part of most systems. The gap between available technology and use must be bridged. An expanded program of operational test, evaluation and demonstration is needed. Testing and demonstrating systems for the neutralization of insider-assisted theft or diversion of SNM are technical areas in which on-site test and evaluation efforts need to be directed, including systems for the recognition of statistically based inventory difference control limits, shipper-receiver measurement differences, advanced accountability (computer-bases and near-real-time capability) systems and accountability systems for new processes.

## CONCLUSION

NBL must remain in the forefront of measurement technology by continuing: (a) to maintain and operate a nuclear materials measurement standards laboratory for the quality assurance of nuclear material measurements; (b) to provide on-site support for calibration and evaluation, and to provide recommendations for improvements of MC&A systems for DOE facilities; and, (c) its service as technical extension of OSS in the area of nuclear measurement technology. The direction for nuclear material accounting improvements and upgrades at DOE facilities are ultimately driven by the need for quality and credibility. We are always concerned with how well the system is working and the technical possibilities for improvement.

To address these concerns, the trend is toward the following objectives:

- understanding of the causes of inventory differences on an MBA-by-MBA basis;
- demonstrable programs for the systematic reduction

of inventory differences to the point of diminishing returns; and

- expanded measurement control concepts and programs for all terms of material balance.

NBL has operated with national and international renown for many years. The present and future challenges are many. NBL, with its high caliber staffing and management, has been established as a national asset and national treasure. With such continued dedication, foresight and imagination, I believe NBL can indeed face the future with 20-20 vision and high hopes.

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Glenn A. Hammond received his B.S. in chemistry from East Tennessee State University. He joined the AEC in 1956 as a Technical Intern in the Production Division, Oak Ridge Operations Office. He was assigned to AEC Headquarters in 1961. Since that time, he has held various technical positions involving nuclear material safeguards for AEC/ERDA/DOE. He is currently the Director of the DOE Division of Safeguards, Office of Safeguards and Security.

# Chemometrics/On-Line Measurements

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## ABSTRACT

*The possible future of on-line analytical-quality measurements for improved process control and more timely safeguards measurements is examined in the light of a current project at Savannah River. A measurement system involving a fiber-optic spectrophotometer and the application of mathematical techniques called "chemometrics" is described.*

I've been given the task of looking ahead at how we can make analytical-quality measurements, nearer to the process—on-line. It's a very difficult problem, actually. In order to look at some of the concepts that, I think, need to be addressed, and how possible solutions can be arrived at, using some of the new mathematical techniques that are lumped together, and called chemometrics, I'd like to look at one particular measurement system that I'm intimately familiar with, and that's a fiber-optic spectrophotometer that we've developed at Savannah River, to be used on liquid-process streams. And, by looking at this I hope that we can glean some of the problems, and possible solutions that we can get for on-line measurements

Well, of course, the reason that we want to make measurements on line, to get the high quality measurements closer to the process, is so that we could make the measurements faster, and get the information in a more timely fashion so that we could know whether it's good information or bad information, and know what we need to do in the process, and our ability to know where our nuclear materials are in the process. If you think about it, the closer and closer we get to measuring the nuclear material as it's transferred, the closer material accountancy becomes to material control.

In order to sell it to the process people, however, you also have to tell them, and show to them, how these measurements are going to help them run their process more efficiently, more safely. They are very interested in reducing their radiation exposure via having to pull samples less often. On line analysis, of course, will never eliminate the need to pull samples, because almost all techniques that you will put on line are secondary type techniques, and

will always need to be correlated back to more fundamental measurement principals and standards.

These on-line measurements can lower facility operating costs, principally by reducing the amounts of waste. For instance, around ion exchange columns, you can significantly reduce the amount of liquid waste produced, if you know exactly when the materials you are trying to elute are coming off the column, and when you have got most, or a sufficiently large quantity of the material off the column.

We've also noticed that, in the process of developing the on-line measurement systems, there have been spin-offs. Bill Jacobsen's crew at the Savannah River Plant Laboratory, with which we have worked closely to try to develop the techniques and to demonstrate their accuracy, precision, sensitivity requirements, have picked up on the techniques, and are now using them in the Laboratory. Certainly, if these techniques are good on-line, they can be even better in the laboratory, to help improve the efficiency of the laboratory and to help increase the awareness of these techniques in the plant.

When you talk to the plant people, and ask them what they want to see, in an analyzer, they just have very few specifications, actually. When you go to them and say, you want to sell them an on-line analyzer to measure their chemical concentrations, they say, "Fine, but, it's always got to give me the right number, and when I want the number, it's got to work. It's got to be easy enough to install so that anybody with a twelve inch crescent wrench, and who knows where the electrical plug is, he can do it ... and I don't want to cut any lines when I install it either, no radioactive lines. It can't get in the way of anything I'm doing now, and I don't want to know how it works. I don't. All I want to know is the number out." We had a discussion yesterday about significant digits. They may be to the point where they understand that only two or three digits are significant, primarily because that's all the machine will give them, but they don't necessarily understand when you give them, but they don't necessarily understand when you give them a range of accuracy, or an estimated uncertainty in the number, that's foreign to them.

And they also like it to cost about five dollars an analysis point. But, it depends, if they can see the value in what you're trying to analyze, if they can see the value to them, they negotiate on these points somewhat.

We developed a system around a diode-array absorption spectrophotometer. We were impressed with a particular Hewlett Packard machine that was developed for the laboratory about four years ago, with its extremely high precision. And we noticed that it would probably be good for an on-line type analyzer because it had no moving parts, that it was extremely fast, as well as high precision. We've had about a hundred man-years of operating experience with these spectrophotometers in the laboratory, and have only had about two or three failures, which were fixed in matters of minutes. Excellent, excellent machine to try to develop an on-line analyzer for. This is something that they could install and drop wrenches on, and so forth.

The trouble was, it's difficult to install flow cells in the line. You have to cut pipes. It's not particularly cost-effective to be putting one of these analyzers in every place that you want to put one, and it is an electronic piece of equipment that you wouldn't necessarily want to put in a high radiation field, or in a radiation environment. So Dave Van Hare and Bill Prather in our laboratory developed a fiber optic system in order to funnel the light from the light source that's located in a non-radioactive environment, through fiber optics to a process cell, or a cell in a hot laboratory, and back to the instrument that's in the cold. Now, we have, also developed ways to multiplex, one instrument and one lamp source to, maybe up to ten different sample positions. This makes it very, very easy to install in a process. They are rugged, extremely reliable, and allow you to operate at remote distances. Now, this 100 meter limit here is for uranium, which is in the near ultraviolet, about 350 nanometers. If you want to do plutonium three, which is out around 650 nanometers, we can go kilometers over fiber optics.

The chemometric data analysis is to get around the persistent problem that the absorption spectra depend so sensitively on the matrix that they're in. We'll get into more of the chemometrics later. Right now I just want to talk about hardware.

This is a photograph of the instrument here. You can see the diode-array spectrophotometer at the bottom. The computer system that controls the spectrophotometer and the process samplers is above it, and we're using a high-stability xenon arc-lamp as the source. The fiber optic multiplexer is shown over here, outside of the instrument where we can look at it.

This is a system schematic. It shows you all of the parts. The xenon arc-lamp illuminates a single fiber which goes to the multiplexer. The multiplexer then selects one fiber that you're going to analyze. On every instrument that you install you have to have a reference fiber, or a reference cell, so that you can tell how your instrument's doing, what's the lamp source looking like. It's always good to have an in-line standard, so that you can test the software, or you can test the whole system to find out whether it's giving you the correct numbers. It's good to change that standard out every couple of days, using different ma-

trix materials and so forth, to make sure that the instrument is working properly. And, up to ten different process cells, in addition to the standard and reference cell.

The light that is selected travels through the cell, and is partially absorbed by the material in the cell. The light returns to the diode array spectrophotometer through another fiber. Information from the spectrophotometer, the spectra, are transferred to a computer, which crunches the numbers, and hopefully produces a good, accurate number, from the highly precise data.

The multiplexer is extremely simple. This is one of Bill Prather's designs. We had originally tried to make much more complicated devices, but didn't need them, as it turned out. We kept telling Bill that something as simple as this wouldn't work, and that's exactly what you need to tell Bill, in order to make him do something. Light from the light source will come in this fiber. You see some of the light jumping the gap there. Out to the process. In the process, some of the light is absorbed. It comes back, and you can see it, a small jump there. And this is the end of the spectrometer, to analyze.

This particular one has twelve positions that we can monitor—ten process and the reference and the standard. Travel time from one end of the stage to the other end of the stage is about two seconds, and it's under computer control. Reproducibility of it is around two microns, which is far more than we need, because we're using 600 micron diameter fibers. Light loss across each junction is around one-and-one-half dB, so the total for that multiplexer is a three dB loss.

Out in the process, we wanted a lens window material that would be extremely easy to install, so we based it on standard compression-type fittings. The lens is just a quartz rod with a hemispherical surface ground on one end. It costs about twelve dollars apiece from Atlantic Industrial Optical. That is press-fit, either with a Teflon sleeve or epoxy, into a standard Swage-lock barrel. The fiber optic, then is held at the focal point of that lens, and the light comes out collimated. I have another lens just like it on the other end of the cell, to receive the collimated light and refocus it back to the fiber.

So, anywhere that you can put a Swage-lock fitting, we can put in one of these flow cells, and get fairly good results. We were rather pleased with the reproducibility of these compression-type fittings. Of course, the amount of signal that you get out of an absorption experiment depends on the path-length, and we have found that these path-length are reproducible on the order of a tenth of a percent, which is pretty good for an off-the-shelf item.

This shows some of these cells, located in an ion-exchange prototype facility in SRL. Here is one of the flow cells, with the other flow cell. We're monitoring the feed and effluent of uranium onto an ion exchange column. These cells are located in a sample loop because it is necessary occasionally to flush these cells with water to make sure that you still have a good understanding of what is the absorption of the fiber optic in the cell itself. And it's also necessary to check for buildup of films on these lenses, but more about that later.

This is the type of cell that you'd use in a hot cell, or

where the standard or reference material is located.

Now, again, we had to put these in our process. Our particular samplers that we use in our radiochemical separations plants, at SRP, use an air-lift-type sampler. Whenever a process was built, 30 years ago, and rightly so, we did not want any pumps in the sampling lines, because we didn't want to pressurize any of the radioactive lines. So, we blow air through an air jet, create a vacuum, and try to suck the sample up through the sampling loop. Unfortunately, there is about 35 feet of difference between the top of the tank and the sampling loop, and that creates problems for vacuums. So, in order to lift it up that far we had to bleed in some air, at the top of the tank, and what you get circulating up through your sample cell, and back down, is something like an old coffeepot percolating. You get a slug of liquid, followed by a column of air, and then another slug of liquid and a column of air, slug of liquid and a column of air. If the vial here is quite small, why sometimes they'd open it up and find that there was nothing in the vial, because you'd stop the sample when you had a slug of air in it. But, that's the way it's been working for 30 years, and it works reasonably well. There has always been a persistent, nagging question of how well we are sampling these tanks, especially with high-density solution. Again, these are things that you can only answer by pulling multiple samples and analyzing them, over and over again.

There are essentially three valves that control this sampler. To automate that, with our fiber optic system, we simply replaced the needle-block assembly with a fiber optic interface—a five-minute operation. The air jet, and all the sampling pipeline are exactly the same. replaced the three valves with automated valves, so that we could control the operation of the sampler from the control room computer, automatically.

This is the picture of one of the process cells. This is a sampling bottle. The air and the liquid slugs are jetted down into this split tube probe. They then go up the other side of the split tube probe and are jetted down into this blank tee. When there's a slug of solution, it comes down and mixes with the solution that's already there. When there's air, it does not disturb the inside of the solution very much. So we're able to get decent absorption data on that. The residence time of solution in this cell is about two-and-one-half seconds under normal operating conditions in our test facility.

This is a photograph of an actual sampler that we've automated out in the canyon process, the sixteen-eight sampler. This particular sampler samples the tank from which we feed uranium to one of the separation banks. Light, then, that's been absorbed in these cells, is then fed back to the diode array absorption spectrometer.

This is a photograph of the diode array absorption spectrometer where we've popped off the lens that used to be in front of the split and simply replaced it with a standard SMA fiber optic connector. The spectrometer itself is about as big as your two fists. The diode array is behind this plate, there.

Now, the spectrometer is capable of producing precise spectral data. The precision is on the order of two hun-

dredths of a percent ... two sigma. Very, very precise ... incredibly precise. Unfortunately, as you well know, the actinides, when you change the strength of the complexing reagent with the actinides, they change their spectra drastically. So, we could reproduce any one of those curves, these are all the same uranyl concentration. I could reproduce any one of those curves to 0.2 percent, and they'd be, as we heard before, always wrong, if I didn't know how to reduce the data. That's where the chemometrics is necessary. Because, in an on-line system, I can't do very much chemistry. It's too hard to get rid of the waste products, too difficult for the engineers who are running the process to be bothered, going out and filling up bins, or buckets of reagents. They don't understand it, they don't want to understand it. In order to get around the sample preparation, we have to do some mathematics. We're essentially replacing sample pretreatment, post-measurement. Using the chemometrics, we can take data like that, and produce calibration curves similar to this. What we have here are four different uranyl concentrations, each at different nitrate levels. We're able to predict, given any one of those spectra, and no other information, very, very accurately, what is the uranium concentration. Now the standards that I used in this model probably aren't much better than one percent, especially down here at the lower concentrations. It's quite good.

Trying to do the best we could with uranyl, I obtained some standards from a General Electric commercial plant in Wilmington, North Carolina. Bob Parnell did this work for me, and the standards were certified to be a quarter of a percent, one sigma accuracy. We were able to reproduce that data, well, not exactly that data. We were able to reproduce samples run from those spectra to do better than 0.34 percent, two sigma accuracy.

Plutonium three is not nearly so bad as uranium, but it too, has some matrix effect. Plutonium four is much worse, more like uranyl. It just wanders all over the place. But the chemometrics is able to pull it out. Now, of course, what's going on here is we're forming different plutonium and different uranyl, nitrate-complexes. The mathematics is sorting those complexes out, in its own special way. Now, I cannot predict, from chemometrics, exactly how much uranyl dinitrate is there. But that doesn't matter. All I'm really concerned about is, how much is the sum of all of the different nitrate-complexes, and that's what chemometrics can do for me.

There are calibration curves for the plutonium III. Notice a couple of points that are off the mark here, and one for plutonium IV. Now, the samples that were off the mark in plutonium IV are now showing up over here. What happened was, I used the same data set to find out how well my model was built. When they told me that this particular sample had all plutonium III in it, well, I'm afraid they lied to me, and I was able to tell them, that they'd lied to me, because that sample that was supposed to have all plutonium III in it, when they turned up low over there, they were turning up high over here. And, in fact, if I can overlay this just right, by the same amount ... see that? So, total plutonium was predicted quite accurately—better than one percent.



So, what is this chemometrics that allows us, in some cases, to predict very, very accurate results without having to do any chemical pretreatment? My definition is that it's just a methodology. It's a bunch of tools that you use to take a lot of data, and reduce it down to something that's useful. Tools that you might use: multiple linear regression, classical least squares, principal component, partial least squares, there are more. You make a couple of assumptions whenever you use any of these models. What you have to do is present it with all of the data that you think that method will ever encounter. Now, that's a big problem. But in on-line work, it's not so hard, because, darn it, in a process, you're supposed to know, the engineers are supposed to know what they are doing. They're supposed to have some idea what is the range under which their process operates. Now if it gets out of control, which can happen, my models can break down. But as we'll see in a few minutes, chemometrics allows you, at this point, it allows you to determine that you have interference. It doesn't allow you to determine how bad the interference is, but at least it flags it and says, "There is something here that I have not seen before."

There are new techniques on the horizon, however, and under certain conditions, they will be able to tell you how bad is the interference, and actually correct for an interference that it has never seen before.

The other major assumption is that the thing you're trying to predict, say concentration here, is linear in the data that you're going to present it. By linear, I mean that if you supply it functions, for instance, you could make this a polynomial, and if this is pressure, and pressure squared, and pressure cubed, the coefficients A, B, and C are still linear. You just have to supply it with, what is the function, then. What chemometrics does then, given the information that you want to predict, say concentrations of some standards, and what functions you want to do your data, it will then find the A's, the B's and the C's that best predict what is your concentration.

Benefits we get out of it are, of course, the higher accuracy. We can determine if there are unknown effects, in interference, and we can correct for interferences, one we know what they are.

Now before you actually do a model, there are some thing that you can do to your data to have a better shot at making a model. For instance, you can reduce interferences and artifacts in your data by trying to discriminate the signal that you want from background—background subtraction. Derivatives often do a good job in UV visible spectrophotometry for removing baselines. Now again, since I have this diode array spectrophotometer and the whole spectrum is collected, say, in a tenth of a second, it's very, very easy to do background subtractions or derivatives. The noise on the spectrophotometer is phenomenally good.

There are scaling functions that you can use, for instance in chromatographic data, if your peaks aren't coming out all at exactly the same time, if you have a marker compound in there and you know that this one should come out at 10.2 seconds, or 10.2 minutes, you can scale your data to make those peaks come out in the right place.

There are other functions that you can use. Peak integration, for instance, often does a good job reducing noise. To reduce noise in you data, Fourier transforms. You should only use the channels in spectra, for instance, that have information in them. If it's just noise, don't use them in your calibration. That just makes sense, but often, chemometricians who are more statisticians than chemists will just use data that may not have anything in it.

Whenever you do a data treatment, of course, your criterion is that you're improving the correlation between the data that you have, and what you're trying to predict.

There are various types of calibration models. I call them one-step and two-step models. Multiple linear regression is a one-step model. I have some concentrations, and I have some data, and I just say, "Relate those data that I have to my concentrations, in this linear fashion. I have the X's and the Y's. Now find me the C's."

This is limited to about 20 different X's there, the reason being that I have to invert a matrix, and a twenty-by-twenty matrix is getting kind of large. The time isn't too bad, but you begin to get some roundoff errors, especially when you're trying to do work around less than a tenth of a percent—precision work.

To get around this  $N=20$ , and we actually gain more capability, we go to a two-step process, where I will take the unknown spectrum that I have, or, to build the model, my calibration spectra, and "decompose" it into different components. Now, if I'm doing curve-fitting, for instance, and I have iron III, and uranyl and yellow dye, or something like that, I just give it the spectra of the iron III and the yellow dye, and the uranyl, and I can decompose the sample spectrum that I'm given into how much iron III there is, and how much uranyl there is, and how much yellow dye there is. I can then predict the concentration that I want from these components using multiple linear regressions. So essentially, I've taken a spectrum that may have a couple-hundred points, or a couple-thousand point in it, and reduced it to a number that's relatively small, because there typically aren't more than 10 or 20 different points in a sample. Especially, if you have to come up with the components, then you're really limited.

Classical least squares is one of these two-step processes. There are really two types of least squares. If you can come up with the pure components, or you know what are the pure components in your standards, classical least squares can come up with the spectra of those pure components, and then you can decompose any unknowns into those. The advantage being that, what you're left with when you're done decomposing is the residual, and if that residual is large, then you've got something else in there that you don't know about. It's a big flag—not in your model.

There is another way you can do it. If you don't know the pure components, but for instance, do know the total uranium or the total plutonium, you can give it several different spectra. You can give it a low uranium-nitrato, and a high uranium-nitrato, and one in the middle say. And it'll say, "Fit those three, and tell me how much total uranium is in there." That's very, very similar to how your eye works. You can see frequencies of all different colors,

and they are decomposed into three components of the rhodopsin dyes in your eye. Your brain, then, takes the signal levels of each three components, and reintegrates it, and you get your 256 million colors. Very, very similar to how this works.

Principal component regression analysis is very similar to classical least squares, in that it is trying to find components, then relate those components to a concentration. But, with principal component regression, you don't need to know so much about what components are in there. The only thing you need to know is, what is the concentration of the thing you're trying to predict. The way it works, it'll compute a weighted average of everything. First guess is always just the average, and if that doesn't work well enough, then it'll guess the average of the residuals, and keep going until it can explain everything that you want it to explain. For instance, with that uranyl spectra that I showed you, that family of curves, this is the first guess of a principal component regression, and it looks suspiciously like the average of all those components. The second principal component, since it can't predict the uranium of each of those standards, with that one, is the weighted average of the residuals. Now that disturbs a lot of people, because the signal's going negative on an absorption spectrum, but there are spectra that are the negative of the average. And after all, all I'm really after is, what combinations of these things I can get to predict my total uranium.

Partial least squares is extremely similar to principal component, where all I'm doing is taking averages. There are different ways of taking averages. This "weighted" word right there, is a "weasel word." There are about a million different ways to weight your averages. They will give you different results ... not much different, but they're still different, which is why you have to be careful. I've written a program, SRL-NVA, which is available to any of you in DOE or DOE contractors, it uses all these techniques, and helps you out. Often it will do an extremely good job, predicting what are the concentrations. But that doesn't mean a darn thing. You don't know whether it's good or not until you've tested it on data that you did not use to build the model. Once you've tested it though, and have assured yourself that you're within the range of the model, the results that I have found, have been very, very good.

A little bit more, then, about how to tell whether your data is good or not, from the residuals. This is how you tell, for instance, if your cells are coated with a material. It's extremely easy. That is the residual that you find after all of the uranium has been removed mathematically, when your cell is coated. You see just a beautiful interference pattern due to a seven-and-a-half-micron thick layer. The more you flush it with water, you see that the fringe pattern doesn't change very much, so we're probably not reducing the thickness of that film. All we're doing is changing the index of refraction of it, getting it closer and closer to water. You can easily tell if your sampler is flowing ... That's the pattern we get on these air-lift samplers, as it's flowing. You can see the slugs come through there, and you can actually do a Fourier analysis on that

quite rapidly, to determine how well your sample is flowing.

We can determine the residuals from spectra. Here is a uranyl spectrum. When I add quinoline yellow to it, the results, to my eye, look very much like uranyl, but the computer is picking out the residuals very readily. Any residual ratio that's over two is suspect, and when the residual ratio get over six, all alarms should go off. So by the time I get a two-and-a-half percent error, the residual ratio's already six times above the alarm point.

We have put this on-line in the Savannah River Plant, to monitor various tanks around the mixer-settler bank. The tight data that we get out of it is extremely good, and provides a lot of information, more to the processing people than they were able to get before. A blowup of the second half of the curve, looking like that, shows you what is the mixing time in that tank, of the higher concentration heel, with the material that I just batch in. We can then see that they batched in another quantity, into that tank, of slightly higher concentration. The accuracy on those, is around a quarter of a percent.

In summary, you can develop on-line instruments that are reliable, simple and accurate. They can be automated, but it is absolutely necessary to make an analytical measurement to be able to program your knowledge of how the system should look in the computer. That's the difference between a process measurement and an analytical measurement in my respect. If you can't sit there and tell from a spectrum whether you've got a problem or not, then you can't make an analytical measurement on-line with it. You haven't got a chance.

Patrick E. O'Rourke received his B.S., M.S., and Ph.D. in physics from the Georgia Institute of Technology. He is currently a Staff Physicist at the Savannah River Laboratory where his assignments have included electron beam microanalysis, x-ray spectroscopy, optical microscopy, image processing, UV-VIS-NIR spectrophotometry, fiber-optics, and chemometric data analysis.

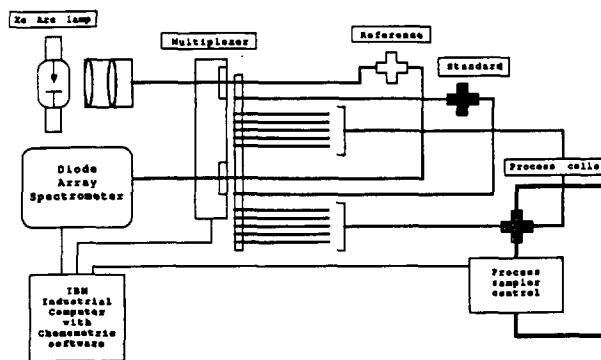


Figure 1. Fiber-Optic Spectrophotometer Schematic

Figures continued on pages 90-94.

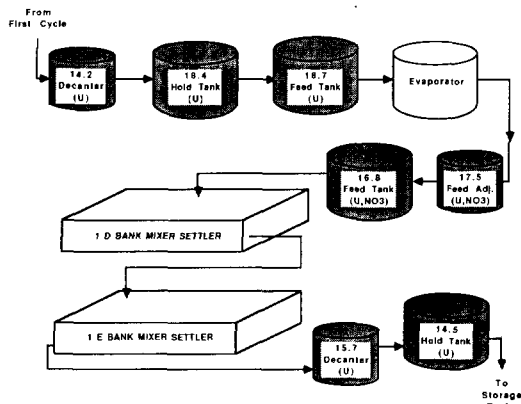


Figure 2. Second Uranium Cycle Process

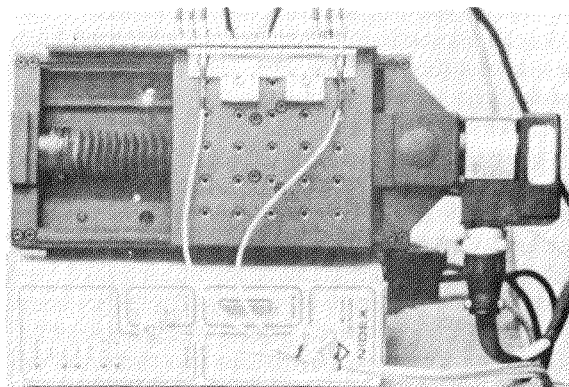


Figure 3. Fiber-Optic Multiplexer

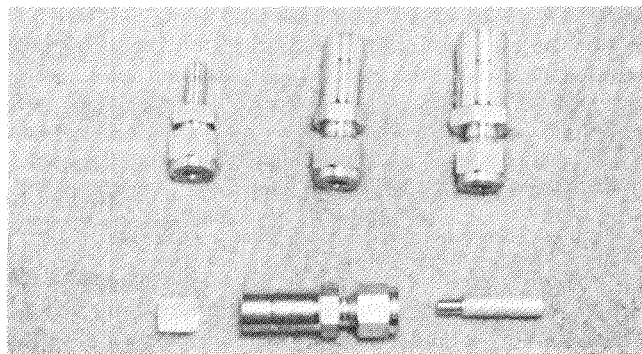


Figure 4. Lens Mounting in Swagelok™ Reducer

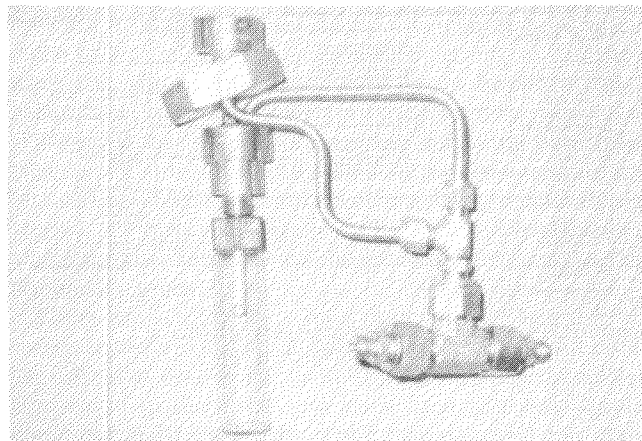


Figure 5. Sampler Interface Containing Sample Probe

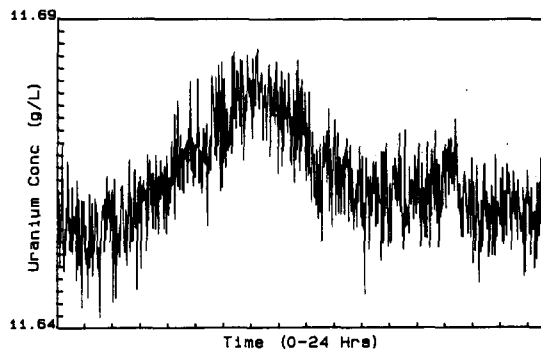


Figure 6. Uranyl Concentration of Inline Standard

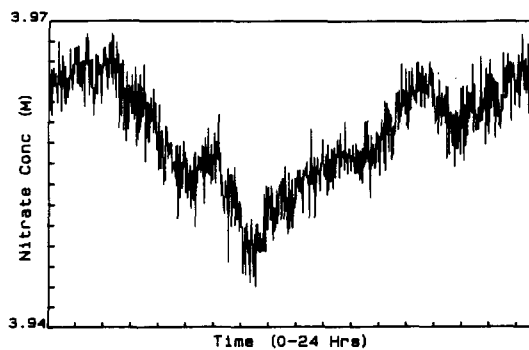


Figure 7. Nitrate Concentration of Inline Standard

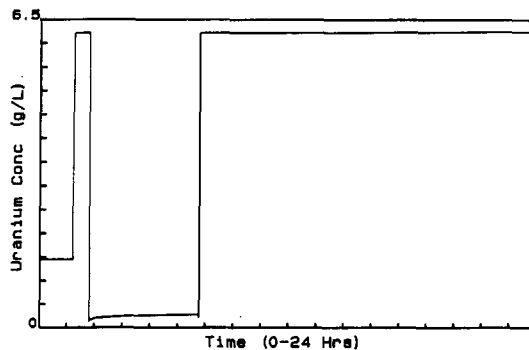


Figure 8. Uranyl Concentration of Product Hold Tank

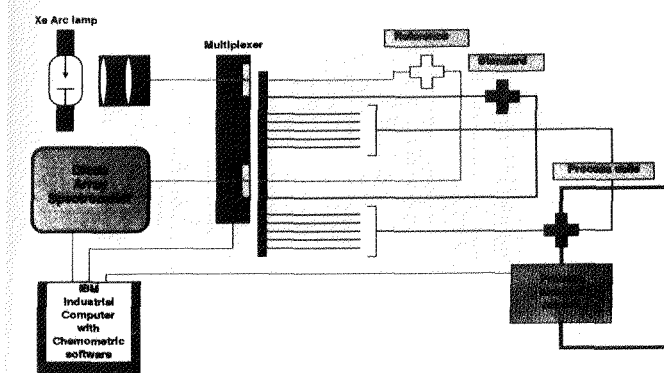
**Application of Chemometrics to Nuclear Fuel Reprocessing**

By  
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## Chemometrics

CHEMOMETRICS is the STUDY of METHODS to  
REDUCE large quantities of non-specific DATA to  
concise and useful INFORMATION

## Fiber-optic Spectrophotometer Schematic



## INCENTIVES

- ▶ Better use of multi-parameter data
- ▶ Improved Accuracy
  - Reduce effects from interferences
  - Account for known matrix effects
- ▶ Ability to "teach" instruments
  - Determine instrument stability
  - Evaluate quality of sample
  - Recognize uncalibrated effects

## Chemometric Tools

- ▶ Computer graphics
- ▶ Data Processing
  - Linear Transforms - FFT, Derivative, etc.
  - Apriori Transforms
- ▶ Regression Analyses
  - Multiple Linear Regression (MLR)
  - Classical Least Squares Curve Fitting (CLS)
  - Principal Component Regression (PCR)
  - Partial Least Squares Regression (PLS)

## Data Processing

GOAL : To improve correlation between  
DATA and INFORMATION

- ▶ ENHANCE SIGNALS
  - Fast Fourier Transforms
  - Derivatives
  - Data Scaling
- ▶ IMPROVE PRECISION
  - Smoothing
  - Integration
  - Axis Scaling

## Regression Analysis

GOAL : To build models which predict  
INFORMATION from DATA

- ▶ BUILD MODEL FROM CALIBRATION SAMPLES
  - Samples span operating range
  - Data collected from samples
  - Information from analysis of samples
- ▶ TWO TYPES of MODELS
  - One Step - Data ==> Information
  - Two Step - Data ==> Reduced Data
  - Reduced Data ==> Information

## Regression Analysis 1

- ▶ SINGLE STEP MODEL (MLR)

$$Y = (A_1 * X_1) + (A_2 * X_2) + \dots + (A_n * X_n)$$

Find A's from set of known X's and Y's

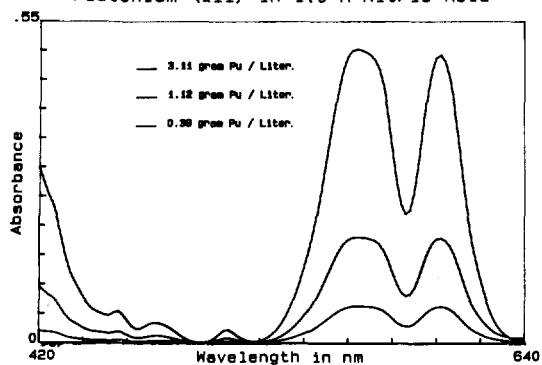
Example 1.

$$X_1 = \text{Abs}(410), X_2 = \text{Abs}(416), X_3 = \text{Abs}(425)$$

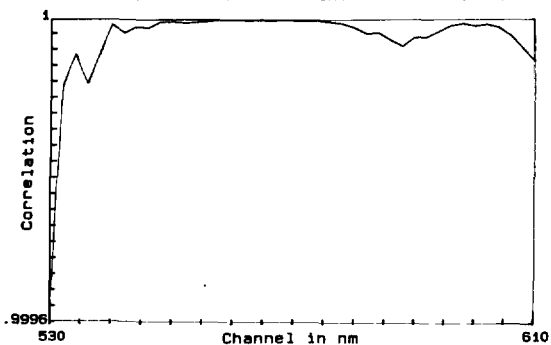
Example 2.

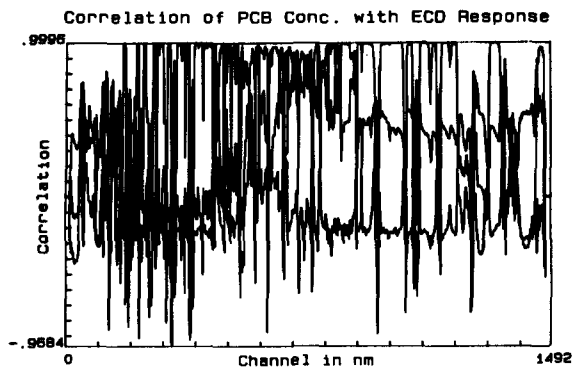
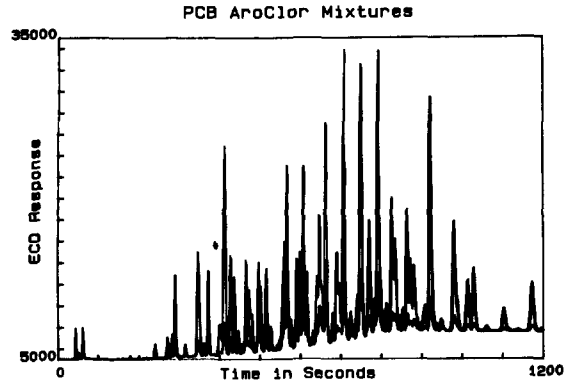
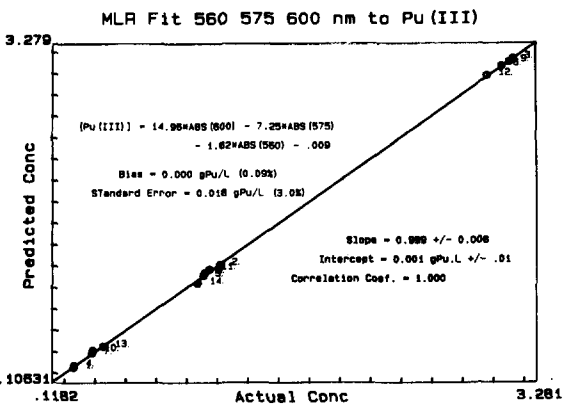
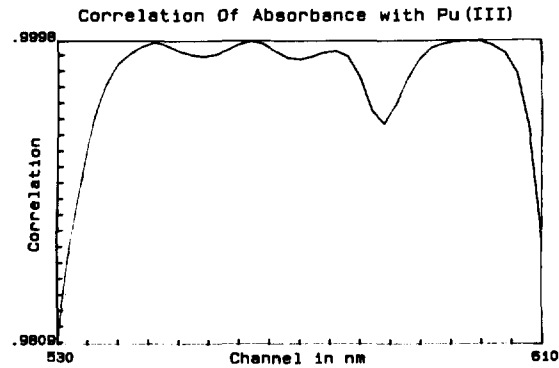
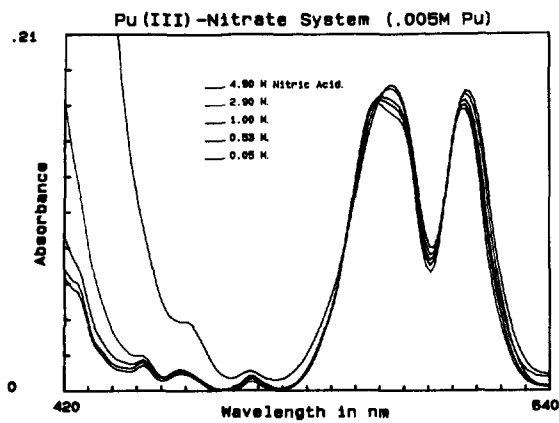
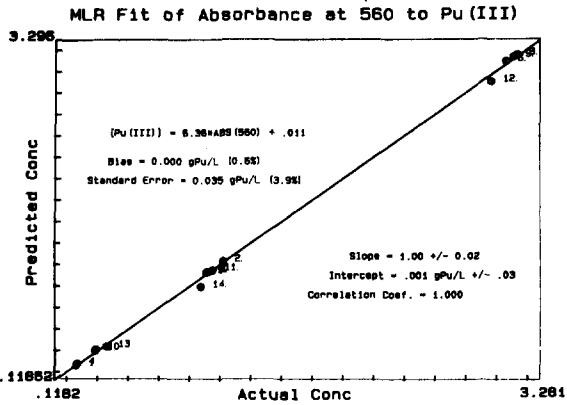
$$X_1 = \text{Density}, X_2 = (\text{Density})^2, X_3 = (\text{Density})^3$$

Plutonium (III) in 1.0 M Nitric Acid



Correlation of Absorbance with Pu (III)





**Regression Analysis 2**

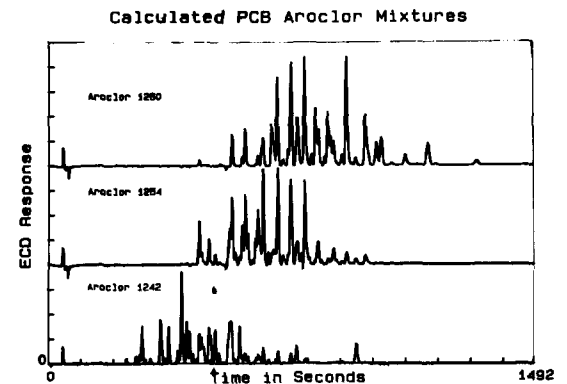
► DUAL STEP MODELS (CLS), (PCR), (PLS)

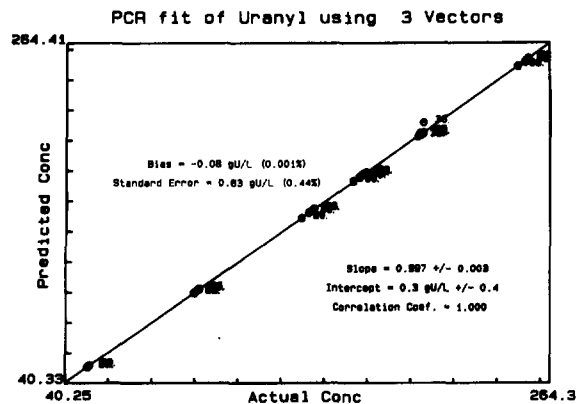
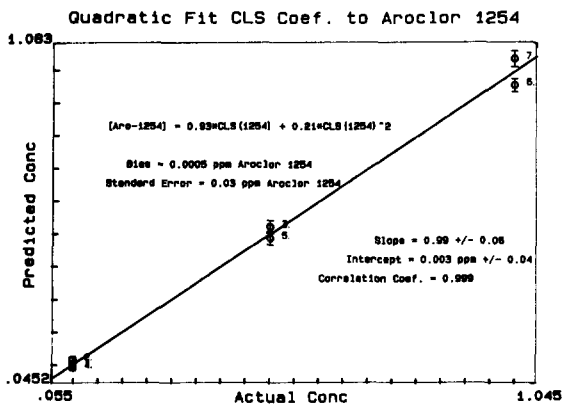
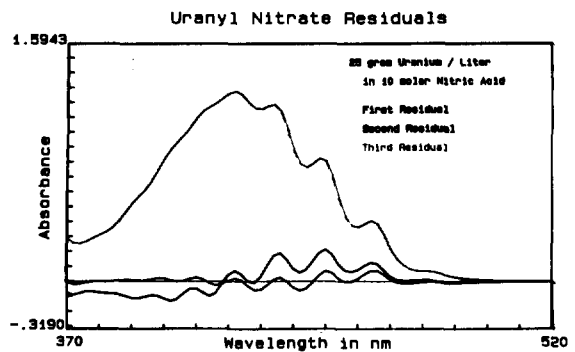
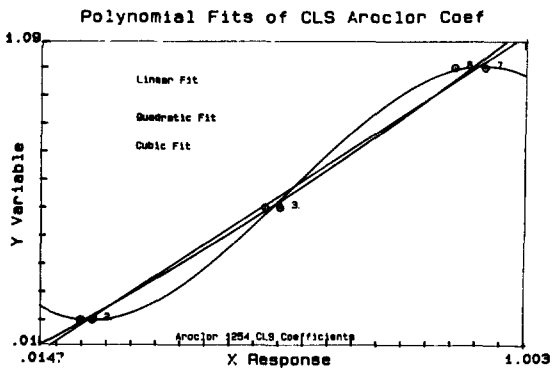
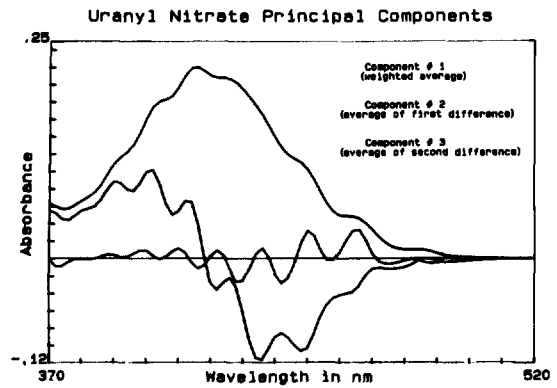
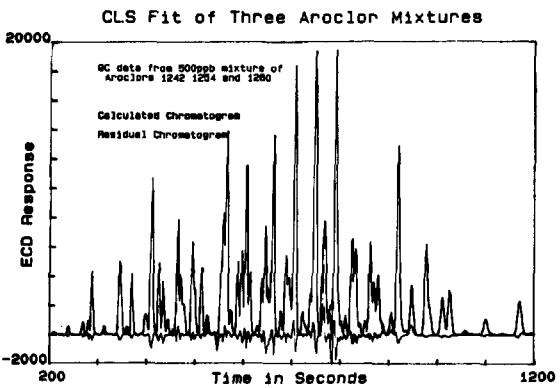
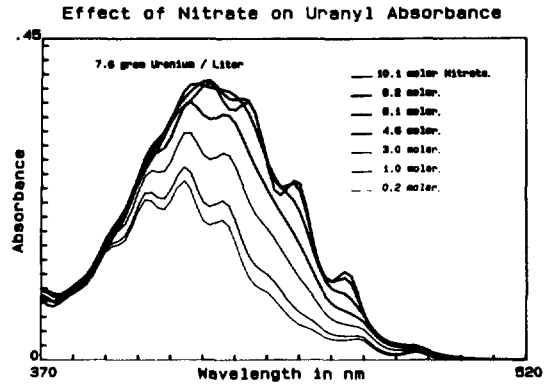
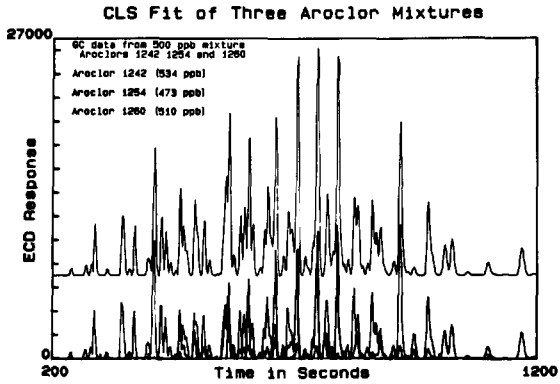
$$\bar{X} = (E_1 * \bar{V}_1) + (E_2 * \bar{V}_2) + \dots + (E_n * \bar{V}_n)$$

Find components V and likeness E from data X

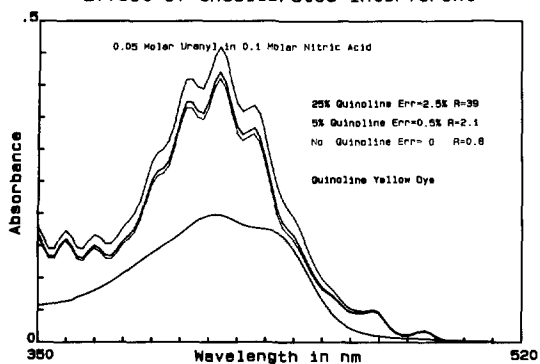
$$Y = (A_1 * E_1) + (A_2 * E_2) + \dots + (A_n * E_n)$$

Find A's from set of E's (above) and known Y's

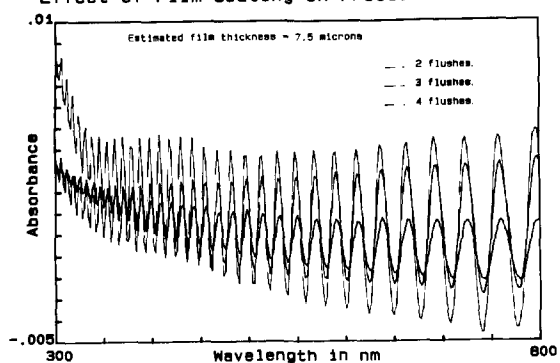




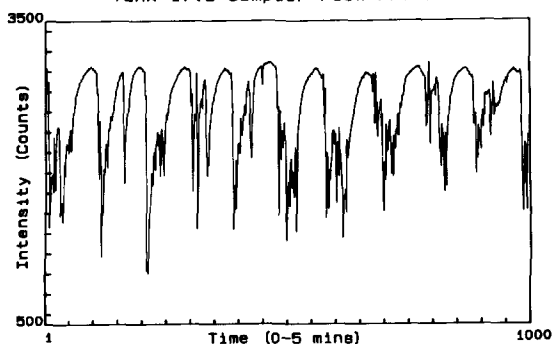
Effect of UnCalibrated Interferent



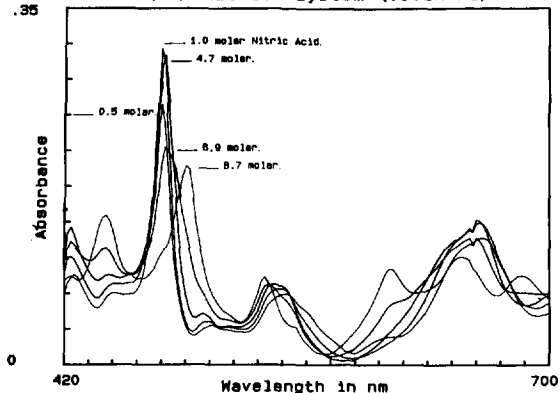
Effect of Film Coating on Process Flow Cells



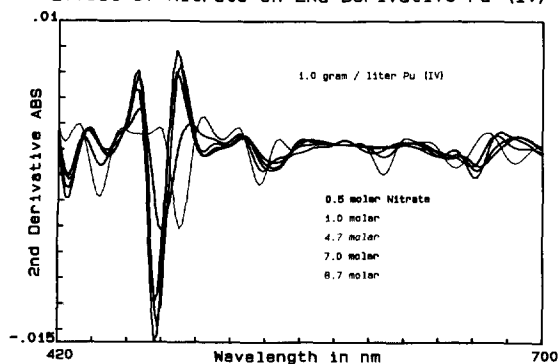
Tank 17.5 Sampler Flow Profile



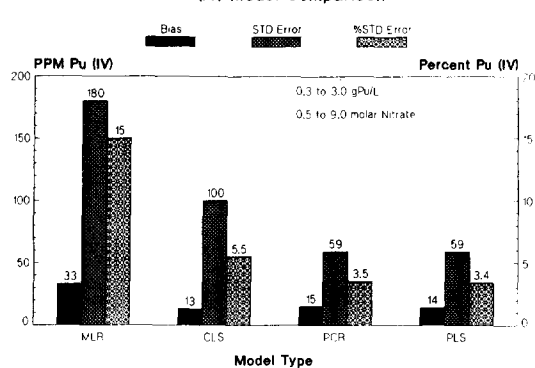
Pu (IV) -Nitrate System (.005M Pu)



Effect of Nitrate on 2nd Derivative Pu (IV)



Pu (IV) Model Comparison



### SUMMARY

- ▶ Chemometrics Improves Accuracy
  - Reduces interferences
  - Accounts for matrix effects
- ▶ Chemometrics Reduces Errors
  - Simplifies sample preparation
  - Detects instrument malfunctions
  - Evaluates sample quality
  - Recognizes uncalibrated effects

### FUTURE CHEMOMETRICS

- ▶ Generalized Rank Annihilation
  - corrects for unknown interferences
- ▶ Generalized Standard Addition
  - multi-element techniques
- ▶ Non-linear Modeling
  - neural network simulations
- ▶ Chemical Component Analysis
  - chemical-principal components

# Laser Applications

■  
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■

## ABSTRACT

The breadth of current applications of laser technology is described as a basis for extrapolating to their future application in such activities as AVLIS, SIS, ICP-MS, and RIMS.

My task is to look into the future of laser applications to nuclear materials, with particular emphasis on safeguards. I thought that it might be interesting to look at the many ways lasers are used today, about 25 or 26 years after the laser was introduced. These span applications as diverse as material processing and medicine. We have laser printers, optical memories, bar code scanners (very useful safeguards), and lasers in entertainment. When I got to the hotel yesterday, I turned on the television and watched Mayor Daley's victory celebration, which included a laser light show! When my wife returned from a visit to Disney World, she mentioned that one of the highlights of her visit was the laser light show at the end of the evening. As a scientist, I am, to a certain extent, upset at this frivolous use of laser technology ... But I am apparently in the minority.

Laser applications run the gamut from the scanner at the end of the line at the supermarket to some rather exotic lasers used for such applications as laser-induced nuclear fusion. Lawrence Livermore National Laboratory has constructed the Nova laser, perhaps the most powerful laser in the world, for fusion work. It is interesting to think, that should the news out of the University of Utah be accurate, we could replace the Nova laser with a bank of Die-Hard batteries! In any case, the Nova laser is an incredible achievement, that will have many interesting uses.

Lasers have been around now for about 25 years, and there are many interesting scientific applications that take advantage of the laser's unique qualities. Lasers have been used in combination with mass spectroscopy, for example, to derive very interesting spatial information. In this example (Figure 1), a pulsed neodymium-YAG laser by Bob Conzemius and Harry Svec at the Ames Laboratory to measure the distribution of material at a weld joint. The laser was tightly focused on the material and then rastered

across the joint. The power densities achieved with this laser ( $10^8$  to  $10^{10}$  watts/cc) is sufficient to generate ions from virtually all materials and these ions can be fed into a spectrometer for mass analysis. The success of this application is simply dependent upon the high powers that can be achieved with pulsed laser sources and the ability to focus lasers to very small spot sizes.

Another such application of particular relevance to the nuclear community is provided by some recent work from Los Alamos National Laboratory. Kremers has focused the light from a neodymium-YAG laser to a small spot on the surface of a liquid containing uranium. This experiment could be accomplished with flowing liquids in processing facilities. The laser pulse creates a spark at the surface of the solution [I defy anyone to describe the processes in the interaction region at the power densities achieved by this laser!] This laser-induced plasma emits light that can be

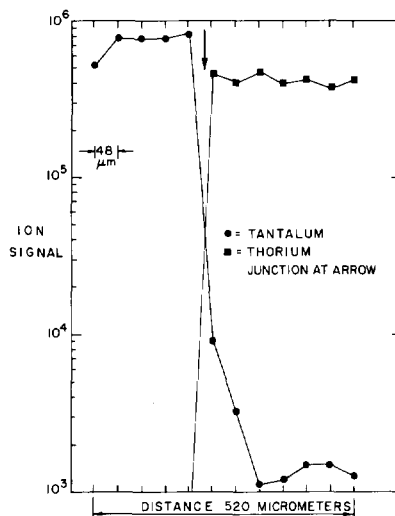


Figure 1. Scan of tantalum-thorium weld junction. (Reprinted with permission from, "Scanning Laser Mass Spectrometer Milliprobe," by R.J. Conzemius and H.J. Svec, *Analytical Chemistry*, Vol. 50, Page 1854, November 1978. Copyright 1978 American Chemical Society.)



spectrally analyzed to determine the concentrations of solution components. Kremers and co-workers have been able to monitor U concentrations from a few tenths to a couple of hundred grams per liter with very good precision (about 1 or 2%) for such an on-line instrument. One laser quality that is revealed by this LANL application is that lasers can be used for remote investigations of materials. As Pat showed us a moment ago, you can send light through optical fibers for hundreds of meters and avoid working in or near high radiation-dose areas. That's a very important quality of lasers for nuclear applications.

There is another quality of laser sources that is intrinsically more interesting to the chemist and the spectroscopist. Laser sources are available with different output wavelengths and these in turn can be changed by frequency-doubling, Raman shifting, and wave mixing to cover the wavelength range from the vacuum ultraviolet to the infrared. Lasers can also be used to stimulate emission from organic dyes and the resultant "dye lasers" are continuously tunable over wide wavelength ranges.

Introducing tunability to laser sources makes them ideal for probing atomic structure via electronic spectroscopy. Electrons in materials have very characteristic energy level separations and, by choosing the energy of a laser source to equal the energy difference between an appropriate pair of energy levels, the material can be induced to absorb light. The electron absorption spectrum of an element is very specific to that element and can be used to identify the presence and quantitate the amount of the element present. Over 100 years ago, Kirchoff and Bunsen used this analytical property to determine a new element, Cesium, by recognizing that the electronic spectrum of a cesium-containing mineral could not be understood on the basis of any previously analyzed elemental spectrum.

Yesterday, John McCown was telling me about a woman who protested to a DOE regulator that the DOE was negligent in not tagging its wastes for easy identification. She said (approximately), "You people should be ashamed. Why can't you color, and give an odor to some of those materials that you emit from nuclear power plants, so that we can detect them more easily. You know, if plutonium had a characteristic color or odor, people would know to go into their cellars at the appropriate times!" Well, if that DOE regulator has been a spectroscopist, he could have said, "Plutonium does have characteristic colors due to its electron level spacings, but you need a much more selective detector than your eye to pick it out from all the other materials that come out of the stack."

In a very simple electron-energy diagram there are two things to note. First, one can cause discrete absorption of laser light at certain selected frequencies. Second, if an element is struck with the right combination of photons, it can be driven into the ionization continuum ... or, that is, ionized. Light can be used to selectively ionize materials. That's very important for sensitive detection because you can create ions selectively and then detect the ions on an almost zero-intensity background. The ions and electrons that are created by ionization can also be collected for detection with far greater efficiency than can, say, fluorescence from an excited atom.

This laser ionization technique has been used by a group at Oak Ridge National Laboratory to address a persistent problem in mass spectroscopy: isobaric interferences. Even with a high-resolution mass spectrometer, it is very difficult to determine whether the signal at mass = 238.xxx is due to uranium-238 or plutonium-238. With resonance ionization mass spectroscopy (RIMS), as practiced by Donohogue and others at ORNL, laser light is tuned to be equal in energy ("resonant") with a plutonium electronic transition to selectively ionize Pu, or to assist the ionization of Pu relative to U. Thus, the ionization signal at mass = 238 from Pu can be distinguished from that of U, resolving an isobaric interference. That is a very neat way of using the electronic absorption properties of Pu to alleviate a problem in mass spectroscopy.

It turns out that the electronic absorption spectra of the actinides are complicated by two additional phenomena. The first, isotopic splitting, refers to an isotope-dependent energy change that can lead to a fine structure in electronic spectra. For example, Figure 2 shows the electronic emission from a mixture of U isotopes excited by an inductively coupled plasma source. The three peaks, each characteristic of one isotope, are easily resolved. This observation implies that, if a laser is tuned to an absorption line that has resolvable isotopic splitting (not all lines do) only one isotope will become electronically excited. Thus, it would be possible to selectively ionize one isotope and separate it from a mixture of isotopes ... thus we can enrich materials via selective laser absorption. We will return to this in a moment. The second phenomenon complicating the electronic absorption of the actinides is "hyperfine splitting," which refers to an energy-level splitting produced by a coupling of the nuclear and electronic spins. Since the nuclear spin of even-mass, even atomic number nuclei, such as U-238 and Pu-240 is 0, these effects are only important for species such as U-235, Np-237, and Pu-239. Fortunately, it is usually possible to select electronic transitions for which this effect is small relative to the isotopic splitting. [For example, a close examination of Fig. 2 would reveal that the U-235 component is broader than either the U-236 or U-238 component. How-

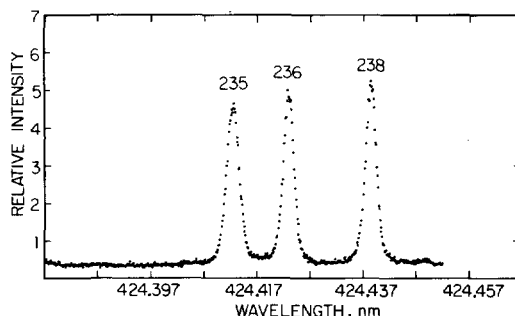


Figure 2. Resolution of isotopic splitting of U emission line near 424.37 nm. (Reproduced with permission, VCH Publishers, Inc., from *Inductively Coupled Plasma in Analytical Atomic Spectrometry*, Edited by A. Montaser and D.W. Golightly, 1987; "High-Resolution in Plasma Spectrometry," by M.C. Edelson, Chapter 7.)

ever, the effect is small compared to the isotopic splitting and it does not lead to undue complications.]

The most important proposed application of lasers to the nuclear industry is for laser isotope separation and is referred to by the acronym AVLIS (atomic vapor laser isotope separation) in the English-speaking world and as SILVA in France. AVLIS was first proposed in 1971, by a Soviet scientist, and by 1973 a U.S. patent covering the use of AVLIS for the separation of U isotopes was filed by scientists from the United States. In 1985, the DOE announced that future U enrichment facilities would rely on AVLIS technology in preference to gaseous diffusion or gas centrifuge technology.

What would an AVLIS facility look like? First, it would contain a materials conversion section to prepare feed material for laser isotope separation, the laser isotope separation instrumentation, and, finally, a section for converting product materials to a form suitable for storage, shipping, or conversion to a final product form. The laser isotope separation (LIS) process is accomplished in the gas phase at low pressures. Generally speaking, the material to be enriched is volatilized and the vapor-phase materials are collimated by slit-shaped orifices. The collimated beam is then irradiated by powerful "process" lasers leading to isotopically-selective photoionization. The isotopes that are ionized at a given facility will depend on the economics of the process. For example, at an AVLIS facility for U enrichment, the process lasers will be tuned to a U-235 resonance to produce U-235 ions that can be separated from the more numerous, electrically neutral U-238 materials in the vapor. In a facility designed for Pu-239 materials (AVLIS for Pu enrichment is referred to as SIS for special isotope separation ... the incorporation of Plutonium into the acronym could lead to unfortunate results!) the process laser would be tuned to the non-Pu-239 isotopes, which would be less numerous than the Pu-239 isotope, and the neutral Pu-239 would be collected.

The world has taken note of the DOE decision to pursue AVLIS for enrichment. Figure 3 represents the result of a recent literature survey on publications about U and/or Pu enrichment via LIS. I apologize to Bill Lyons for not correcting the numbers of publications with "impact" parameters, but what is of most interest in this figure to me is the large number of nations showing an interest in AVLIS technology. The Japanese have successfully interested industry in AVLIS R&D and the Hitachi Company alone has more than 60 people working on this technology. It is apparent from Figure 3 that Japan is working very hard on AVLIS; it is also fairly apparent that the technology to do AVLIS is fairly widespread throughout the world. It is interesting to contemplate the proliferation consequences of this new laser-based technology.

I am particularly interested in investigating the applications of tunable lasers to the safeguarding of nuclear materials. We are now trying to develop optical methods for monitoring AVLIS, that is, for on-line monitoring of the actual LIS process. Why should optical spectroscopy be successful for LIS monitoring? All the conditions required for precise high-resolution spectroscopy ... low pressure, collimated material beams, high atomic density ... are in-

herent to the AVLIS process. If AVLIS is successful for isotopic enrichment it should be amenable to optical monitoring ... it's a natural.

Our first experiments have utilized europium as a surrogate material. Natural europium is quite nice to work with in the sense that only two isotopes occur naturally and the natural isotopic abundance is roughly 50% Eu-151 and 50% Eu-153. Europium can absorb light produced by a dye laser operating with rhodamine 6G dye, and, as everyone who has ever worked with dye lasers will attest, you work with non-rhodamine dyes at your own peril!

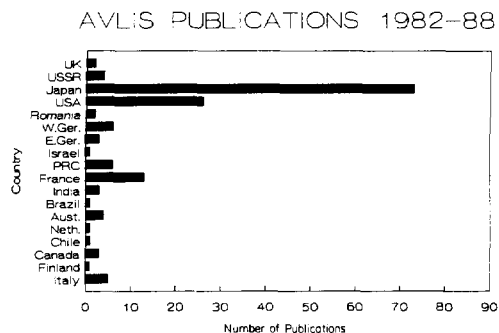


Figure 3. Results of literature search (STN International; Chemical Abstracts Data Base) combining (Laser and Isotope) with (Uran? or Plut?). Figure shows number of citations by country of author for 1982-1988.

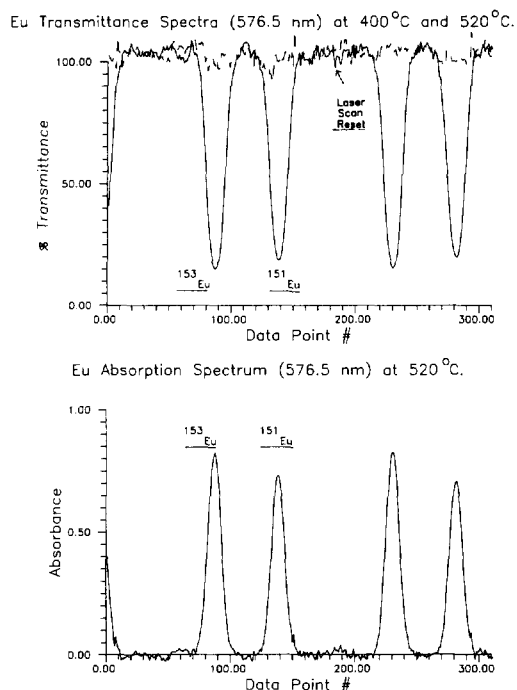


Figure 4. Transmittance and absorption spectra of vapor-phase Eu in a heat-pipe oven. Each spectrum shows two replicate spectral scans. The upper spectrum compares the transmittance at 400 C, where there is little Eu in the vapor phase, and at 520 C where there is appreciable absorption. (Reprinted from, "Progress in the Development of a Spectroscopic Method for the Quantitative Assay of Actinides within a Gaseous Flow-Stream," by Kevin P. Carney and M.C. Edelson, Ames Laboratory Report IS-4976, issued December 1988.)

Eu Absorption Spectra (576.5nm) at 580°C and 560°C.  
(Superposition of Three Consecutive Spectra)

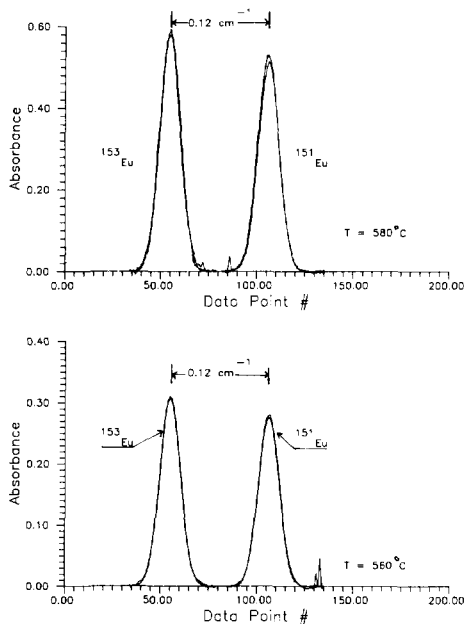


Figure 5. Superposition of three Eu absorption spectra at 580 C and at 560 C. The precision [RSD] of absorption measurements was 1.5% for the 580 C data set and < 1% for the 560 C data set. Ratio of peak absorbances for Eu isotopes results in Eu isotope ratio [natural abundance sample] of 52.68% Eu-153, 47.32% Eu-151 (560 C data set), which is within 0.5% of reference value. [Reprinted from, "Progress in the Development of a Spectroscopic Method for the Quantitative Assay of Actinides within a Gaseous Flow-Stream," by Kevin P. Carney and M.C. Edelson, Ames Laboratory Report IS-4976, issued December 1988.

Figure 4 contains a transmission spectrum of Eu in the gas phase. The Eu was heated in a commercial heat-pipe oven, so we haven't simulated a functioning LIS system here. This is a static mixture of Eu isotopes in the gas phase, not the dynamic environment of an AVLIS facility. Note that at 520°C, where there is an appreciable Eu vapor pressure in the cell, there are nicely resolved Eu-151/Eu153 absorption maxima. This Eu transition has no resolvable hyperfine splitting, which simplifies the analyses. Figure 5 shows the superposition of two sets of three absorption spectra taken at 560°C and 580°C. You have to be very close to the screen to see the very small differences in the peak absorptions of the three replicates in each set and there is an occasional pulse due to noise (these spectra are untreated). The precision in absorption data is better than 1%.

We've done similar measurements with a highly enriched Eu sample, obtained from Oak Ridge National Laboratory, that was about 98.8% Eu-153 isotope. Figure 6 shows the transmission spectrum from such a sample. Even in this sample the Eu-151 absorption is evident. The major element is determined with better than 0.5% precision, but the minor isotope is not done quite as well. We are still at an early stage in this work and we think that it

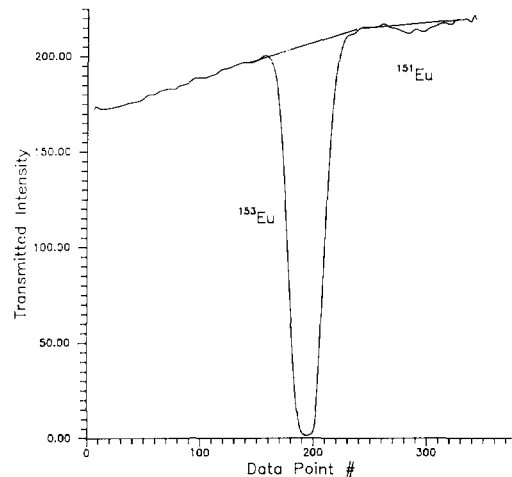


Figure 6. Transmission spectrum at 576.5 nm of enriched Eu sample (Eu - 153 = 98.76%, Eu - 151 = 1.24%). Sample was prepared as a 1:2 mixture [alloy] with Yb. The positions of light absorption by the two Eu isotopes are noted. (Transmitted intensity data was treated with a 9-point Savitsky-Golay smoothing function.)

has promise for use as a monitor for the separation stage in an AVLIS or SIS facility.

I wanted to finish with two references taken from a volume published as a tribute to laser pioneer, Arthur Schawlow, who continues to be at the forefront of laser spectroscopy and innovative laser applications. Schawlow had a sign posted on his door in the late 1960's that had a graphic illustration of a battery of laser weapons for use in a Strategic Defense Initiative context. The sign was titled, "The Incredible Laser." At the bottom of the sign, in small print, it said, "For credible lasers, see inside."

The second application was a demonstration of novel lasing media. Schawlow's group was able to dissolve sodium fluorescein dyes in gelatin, and use a pulsed nitrogen laser to induce lasing in the dye. Thus, Schawlow had produced the world's first edible laser. You may not think that this has very great application, but I think of it as the forerunner of the "light lunch."

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Martin C. Edelson received his B.S. and his M.S. from the City College of New York and his Ph.D. in physical chemistry from the University of Oregon. After post doctoral work in laser spectroscopy, he joined the Ames Laboratory of Iowa State University in 1978. From then until the present, he continued to develop the application of high-resolution techniques to ICP spectroscopy.

# Education and Training

■  
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■

## ABSTRACT

*The ability of this country to move forward into and have an impact on the nuclear technology of the 21st century will be dependent upon the availability of well-trained scientists in many subfields and an informed public. The number of nuclear-trained faculty is an indicator of the means for producing nuclear scientists. The currently experienced decline in nuclear faculty is resulting in decreases in graduate students in nuclear fields and a decrease at the undergraduate level of "nuclear awareness." An apparent shortfall between supply and demand is identified.*

## INTRODUCTION

I'd like to spend a few moments today, reviewing the present status of education in nuclear radiochemistry, nuclear engineering, and then try to see what we know about the probably future demands and how that matches what we may expect in terms of future supply. As Jim Warf has already indicated, we are faced with sea of ignorance. I hope our knowledge of what we need is not as ignorant as the public's knowledge of what is happening.

The culmination of the Manhattan Project was an explosion of interest in nuclear science. The brightest and bold-student students entered this field as it was the new, exciting frontier. New elements, new particles, new isotopes, new applications and new theories seemed to be a matter of daily occurrence. Physics and chemistry departments as well as schools of engineering added new faculty and courses. Nuclear energy was just over the horizon and the electricity it would produce would be too cheap to bother monitoring. Society looked forward with enthusiasm to the rich rewards of a nuclear future.

Perhaps it is fitting at this time to review the reality as contrasted to those early dreams. The periodic table has been extended to 109 elements and the catalog of new elementary particles has provided us an unexpected model of the nature of matter—from the subnuclear to the astronomical end of the scale. The new field of nuclear medicine has grown to where 10 percent of all hospital patients in the United States now receive some type of treatment

using this technology. Activation analysis has opened new vistas in archaeology, ecology, forensic science, geology and many other areas. Radioactive tracers led to a flood of discoveries in biology and chemistry. TMI demonstrated that despite technical misjudgments, U.S. nuclear reactors were not a significant danger to the public even in a fuel meltdown. The discovery of the Oklo natural reactor provided the evidence the geological disposal of nuclear waste was a safe method of permanent disposal. In summary, the past four decades have witnessed the fulfillment of much of the promise and we are benefitting in countless ways from nuclear science.

Unfortunately, while this is a valid assessment, it would be rather misleading to say that society has retained its early enthusiasm in nuclear science. No new nuclear plants are planned and activists seek to close those in operation. The waste problem is thought to be insoluble and radioactivity is more feared than praised. The purpose of this paper is to assess how this public view is reflected in education. We need well trained scientists in many nuclear subfields, so a legitimate concern is whether the supply and demand for these scientists are in balance and, if so, will they continue to be? If they are not, how bad is the problem and what can be done about it?

## CHEMISTS IN NUCLEAR AREAS

In February, 1988, a Workshop was held in Washington at the National Academy of Sciences. The U.S. Department of Energy, the National Institutes of Health and the Electric Power Research Institute funded this effort whose subject was "Training Requirements for Chemists in Nuclear Medicine, Nuclear Industry and Related Areas." Much of the subsequent data and discussion is drawn from the report of that workshop.

Education depends on an adequate number of faculty. Table 1 records the decline in the number of nuclear faculty in Ph.D-granting departments of chemistry in the United States. The decline in numbers extended over all nuclear research areas and, overall, was about 40 percent for the nine-year span. An area of science generally thrives best when there is more than a single faculty member in

that general area in the same institution. In 1963, 14 chemistry departments had more than two members in nuclear research; by 1978 this had grown to 32, but by 1987 only 20 departments still had two or more faculty involved in nuclear research. The 40 departments with a single nuclear faculty member in 1978 had shrunk to 25 by 1987.

The numbers and types of courses presently offered are shown in table 2. The 42 Ph.D.-granting departments represent less than 20 percent of graduate level departments while the 75 undergraduate-only departments teaching such courses are perhaps five percent of the total. This indicates very little exposure of chemistry undergraduates to nuclear science. A survey of college and university freshman chemistry courses by the Educational Testing Service reported that an average of only 2.3 percent of the courses is devoted to nuclear topics<sup>2</sup>. Radioactive decay and half-life are not covered in 10 percent of the courses,

Table 1  
Faculty by Research Area and Age

	Primary		Interests Secondary		Avg. Age <sup>a</sup>	
	1987	1978	1987	1978	1987	1978
1. Fundamental Nuclear Chemistry	34	38	7	12	50	47
2. Chem. of Radioactive Elements	4	11	8	18	60	52
3. Analytical Applications	33	45	20	30	49	48
4. Nuclear Probes for Chemical Studies	6	27	9	10	51	47
5. Tracer Techniques and Labelled Compounds	23	59	11	28	49	47
6. Nuclear Medicine and Radiopharmaceutical Chem.	8		5		49	
Totals 1987	108	180	60	98	50	48
Average Age						

<sup>a</sup> Average age tabulated according to faculty member's primary interest.

Table 2  
Number of Nuclear and Radiochemistry Courses

Course Level <sup>a</sup>	Ph.D. Departments (42)	
	With Lab	Without Lab
Lower Level UG	1	0
Upper Level UG	8	11
UG and G	5	8
G only	10	23
Total Courses	24	42
	Non-Ph.D. Departments (75)	
Lower Level UG	4	4
Upper Level UG	40	14
UG and G	7	5
G only	5	12
Total Courses	56	35

<sup>a</sup> UG - Undergraduate  
Grad - Graduate

nuclear stability and nuclear reactions are neglected in 20 percent, and only 15 percent of the courses discuss radioactive elements. With such scant coverage, the lack of student interest in preparing for careers in this field is not surprising. Even the minimal treatment is often negative—for example, a recent freshman level text which provides unusual coverage (25 of 850 pages) of nuclear science devotes four of these pages to the topic "Arguments Against the Use of Nuclear Energy"<sup>3</sup>.

This lack of exposure is reflected in the level of student interest. In 1960 there were about 215 chemistry graduate students in nuclear/radiochemistry research while, at present, the number seems to be about half of that and among the latter, the number of non-U.S. students has increased significantly.

### NUCLEAR ENGINEERING

The situation in education in nuclear engineering is rather similar.<sup>4,5</sup> In the 1960s, there were 70 departments of nuclear engineering. This has decreased to 42 at present and is predicted to decline to 25 within five years. The decrease in faculty and courses parallels the termination of

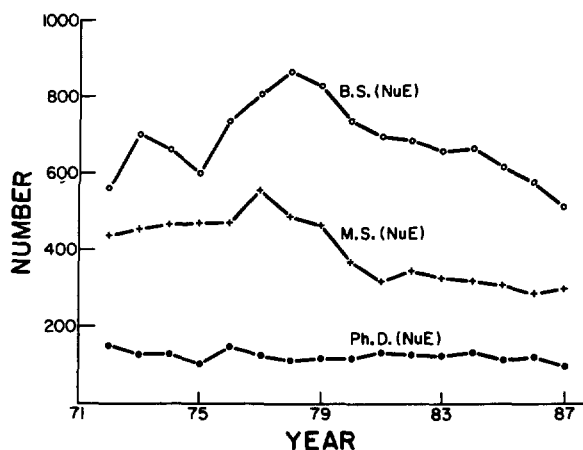


Figure 1. Number of degrees awarded annually in nuclear engineering (data from U.S. D.O.E.).

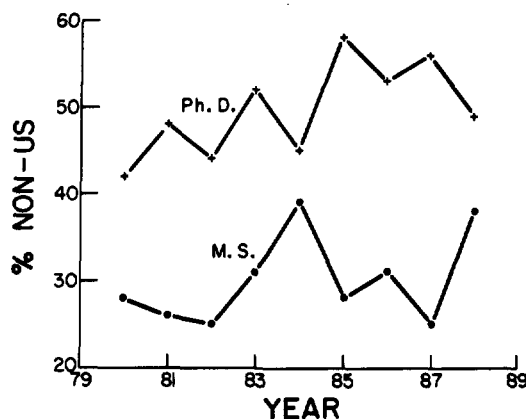


Figure 2. Percentage of M.S. and Ph.D. degrees awarded annually to foreign nationals (data from U.S. D.O.E.).

majors programs. The student population has remained higher than might be expected as reflected in the degrees awarded over the last 15 years (Figure 1). However, these statistics are somewhat misleading when we include consideration of the foreign nationals component shown in Figure 2. The majority of the non-U.S. M.S. degree recipients return to their country while many of the Ph.D. recipients remain in the United States.

### SUPPLY VERSUS DEMAND

These data are alarming only if they indicate an imbalance at present or predict one for the future. The NAS Workshop defined a number of areas which depend on scientists trained in nuclear and radiochemistry:

1. Health care, including nuclear medicine, the radiopharmaceutical industry, and radioactive tracer studies in the ethical drug industry.
2. National security, specifically the nuclear weapons program.
3. Nuclear energy, which currently provides 17 percent of U.S. electric power.
4. Nuclear waste isolation, an important issue even if all nuclear power plants were to be shut down immediately, because there is a 40-year accumulation of waste from the defense and power plants.
5. Monitoring and management of the environment.
6. Fundamental nuclear science, including chemical effects of nuclear transformations.

Table 3  
Number of Staff Members at National Laboratories Using Radiochemical Techniques

Area of Study Requiring Knowledge of Nuclear and Radiochemistry	Nuclear and Radiochemistry Staff with Advanced Degrees
1. Basic Research	100-200 (20%)
2. Analytical Chemistry	200-300 (35%)
3. Process Applications Research and Development	100 (15%)
4. Health-Related Applications	50-100 (10%)
5. Environmental Applications	25- 50 (5%)
6. Nuclear Weapons Application	100 (15%)
<b>TOTAL</b>	<b>575-880 (100%)</b>

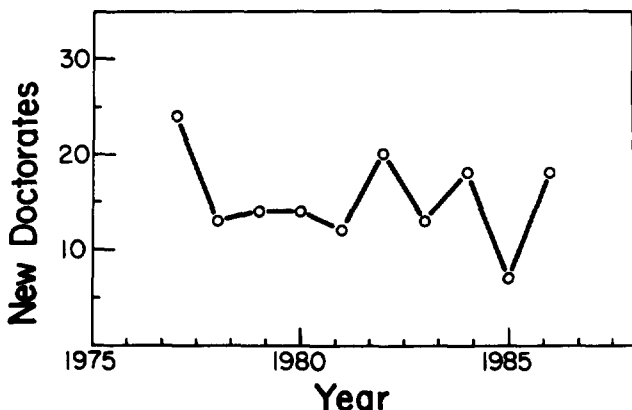


Figure 3. Number of Ph.D. degrees in nuclear chemistry awarded annually (data from the National Research Council).

It is estimated that the relevant staff in the DOE laboratories will remain constant (575 to 850). The number in basic research and nuclear weapons applications may decrease while that in process research and development and in health and environmental areas is likely to increase. This conclusions are summarized in Table 3. Based on a five percent annual rate of turnover, the workshop estimated an annual new need of 10-20 Ph.D. and 20-40 B.S. staff in the total DOE complex. This Ph.D. estimate matches closely the present Ph.D. graduation rate in nuclear and radiochemistry (Figure 3).

Table 4 presents the estimates of needs in the general area of nuclear medicine. In addition, approximately 2200 personnel with one to two semesters of training in radiochemistry are presently serving as supervisors, managers, and senior technologists. A five percent annual turnover would mean a need, annually, for new highly trained scientists or six to 12, and over 100 with some training in nuclear science if there is no growth in this area.

It is more difficult to estimate future needs in the nuclear industry as it depends strongly on the scenario chosen. In the absence of any well-defined national policy on energy, any scenario is questionable. The projections of the Workshop for the need for radiochemists are given in Table 5 and are based on a conservative estimate (no new plants). This does not include estimates of Department of Defense needs (e.g., in the nuclear Navy). The employment of nuclear engineers for 1983, 1985 and 1987 is shown in Table 6<sup>4</sup> to reflect the trends. At the B.S./M.S.

Table 4  
Need for Ph.D. and M.S. Scientists with Training in Nuclear and Radiochemistry

	1988	1993
<b>Medical Centers</b>		
Imaging and related fields	15	40
Nuclear pharmacy	10	30
<b>Industry</b>		
Radiopharmaceutical manufacture	40	60
Ethical drugs	40	80
Radioimmunoassay	5	5
<b>Universities and National Laboratories</b>	10	10
<b>TOTAL</b>	<b>120</b>	<b>225</b>

Table 5  
Radiochemists Needed in Nuclear Power Industry: 10-Year Projection (1987-1997)

	Current Filled Positions	Current Vacancies	Needed for Growth	Replacements	Total Hiring Requirements
Chemical Engineers	305 (0.3) <sup>*</sup>	12	3	88	103
Chemists	261 (0.3) <sup>*</sup>	22	8	136	166
Chemistry Technicians	1,538 (1.7) <sup>*</sup>	65	49	492	606

\* As a percent of total work force.

Table 6  
Nuclear Engineers Employment

	1983	1985	1987
Fuel Cycle & Waste Management	340	210	520
Reactor & Facilities Design, Engineering & Production	1,460	3,790	5,400
Reactor Operation & Maintenance	2,050	2,660	3,700
Utility Employees	1,740	2,030	2,040
Nonutility Employees	310	630	1,660
Nuclear Energy Related Research	860	690	740
Weapons Development & Production	220	310	320
Government	910	860	920
Other	1,380	950	310

Source: U.S. Department of Energy

level, it is estimated that there is about a 35 percent discrepancy between supply and demand of engineers in nuclear energy related jobs while at the Ph.D. level the shortfall is about 20 percent.

## THE FUTURE

Considering these data, what can we expect for the future? Some, and, perhaps a major, revival of nuclear power is probable. Nuclear medicine, even at a constant usage will be expected to serve a growing and aging population. Nuclear waste disposal and reclamation of contaminated DOE sites will become a major industry. By contrast, present trends suggest that there will be essentially no academic training available within a decade in nuclear and radiochemistry and only slightly more in nuclear engineering. The Workshop recommended that the appropriate Federal agencies establish a system of Young Investigator Awards for new faculty entering this field. Training grants and post-doctoral fellowships were also recommended as a further means to maintain an appropriate number of academic centers of excellence in nuclear science and engineering. NSF has programs of this nature but they are intended to cover all academic science. It would seem that the Department of Energy must assume the responsibility to establish such programs in the nuclear field.

All the news is not bad. For a few years, the Division of Nuclear Chemistry and Technology of the American Chemical Society through DOE funding and with the full support and cooperation of the Committee on Nuclear and Radiochemistry of the Board on Chemical Sciences and Technology, NAS-NRC, has sponsored a Summer School in Nuclear Chemistry at San Jose State University. About 12 to 15 selected undergraduate students have attended each year and almost 50 percent have subsequently entered graduate school in some area of nuclear science. The success of the San Jose school has led to the establishment, under the same auspices, of a Summer School on the East Coast at Brookhaven National Laboratory. Since these schools can introduce nuclear science to 25 to 30 undergraduate students a year, this is only a beginning.

Nuclear and radiochemists in industry, in national laboratories and in universities must join in common cause to

see that this area of science which is so important to our national good in so many ways does not wither and die. We must counter the adverse press about nuclear matters and show students that this area of science still offers exciting and rewarding careers.

The preparation of this paper was supported in part by a Grant from the U.S. DOE Division of Chemical Sciences.

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Gregory R. Choppin received his B.S. from Loyola University (New Orleans) and his Ph.D. from the University of Texas, Austin. From 1953 to 1956 he was with the Lawrence Radiation Laboratory. He joined the chemistry faculty of Florida State University, where he has been a Professor since 1963. He has published and lectured extensively on nuclear-related subjects. He was a member of the National Academy of Science task group that recently reported to DOE on the status of MC&A.

**Statistical Methods For Nuclear Material Management**

Edited by W. Michael Bowen and Carl A. Bennett, Nuclear Regulatory Commission, NUREG/CR-4604, 1988.

xxii + 1000 pages.

**Training Manual on Statistical Methods for Nuclear Material Management**

John L. Jaech. U.S. Nuclear Regulatory Commission, NUREG/CR-4605, April 1988.

The preface of *Statistical Methods* describes the origin and purpose of these books: "Since 1973, the standard manual of statistical analysis methods for nuclear material management has been a book by John L. Jaech, *Statistical Methods of Nuclear Material Control* ... In 1981, the Office of Standards Development of the U.S. Nuclear Regulatory Commission ... contracted with Pacific Northwest Laboratory ... to prepare a new reference manual and a training manual for guidance in the application of statistical methods in nuclear material management. The reference manual was to be complete enough to serve as a single source, ... provide abundant examples of practical applications ... and explain the principles and rationale ... This book and the companion training manual written by Jaech are the result of this effort."

The *Training Manual* was written by a single author while *Statistical Methods* (the text) was written by eleven authors including the editors. Most of the 11 contributed to two or more chapters, and most of the 17 chapters had two or more contributors. The result of this multiple authorship is some unevenness in style and notation, some gaps and some overlap. At times it seems that different authors have somewhat different purposes.

Although the authors did not attempt a single source text, they do provide a good overview of the role of statistics in nuclear material management. The editors express the hope

that this text contains "enough basic statistical methodology to (enable the user to) handle many routine applications and to recognize those situations where professional statistical assistance is needed." They state that "this book ... is not always a substitute for professional statistical advice." This is sound advice; there is much valuable information in the text, but it is not always easily accessible, comprehensive or current. There are numerous references to other texts for further explanations, but few of these are references to material published in the last five years.

The word "management" in the title is not meant to imply that these books were written for managers. The text and manual are written for nuclear material management practitioners (NMMPs). These are "scientists and engineers ... who produce and evaluate nuclear material accounting data, and ... those ... who develop and administer accountability requirements ..." The NMMP appears to include everyone who is involved in accounting for nuclear material. The books assume that the reader is familiar with advanced algebra, some elementary calculus and, in a few sections, matrix algebra. Little, if any, statistical background is assumed. However, a reader without a good statistical background will find self-study difficult.

*Statistical Methods* is a text book, a reference, not a "how-to-do-it" book. The text is designed to be used with the *Training Manual* in a course. To meet this need, the DOE sponsors a series of three short courses on the text and manual. These courses can supplement the text material by providing detail, more complete explanations and current developments. For further information on the courses, contact Dr. J. Rivers, Safeguards Division, U.S. Department of Energy, Washington, D.C. 20545.

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The text has two parts. The first part, Chapters 1 through 12 (618 pages), provides statistical background needed for nuclear material accountability, as well as brief introductions to simulation and decision theory. There are many insightful discussions and numerous worked examples applied to the nuclear industry. Coverage of some topics is too brief, and reference to other sources will be necessary. Chapters 13 through 17 comprise the second part (304 pages). These chapters cover applications to specific problems in nuclear material accounting. As in the first part, some of the discussion is necessarily brief and reference to other sources is required. There are 59 pages of statistical tables and an index of 13 pages. Neither a glossary nor symbols list is provided.

The chapter headings of the first 12 chapters are 1. Data Description and Display, 2. Probability, 3. Estimation, 4. Hypothesis Testing, 5. Analysis of Variance, 6. Regression Analysis, 7. Experimental Design, 8. Statistical Sampling of Finite Populations, 9. Nonparametric Methods, 10. Simultaneous Inference and Detection of Outliers, 11. Simulation, and 12. Elements of Decision Theory. In each of these chapters there are many valuable discussions, but in some there are omissions which are bothersome. Examples of these omissions follow.

The concept of relative standard deviation is used throughout the text in the context of relative errors, yet is not defined. There are not explicit formulas for the mean and variance of a product or quotient of random variables. Only a first order Taylor series approximation for the mean and variance of a general function of  $n$  random variables is given. (Thus the expectation of a function is the function of the expectations.) The formula (3.14) for the variance of the sample variance from a normal distribution is given but apparently never used in the text. There is no warning that the so-called computational for-

mula for the sample variance (p. 105) can be disastrous for computing. Little encouragement is given to plot data or to check randomness, independence, or distributional assumptions. Normal probability plots are mentioned but neither described nor referenced.

Practical advice on sample sizes needed to determine control limits for control charts is lacking. Three pages are devoted to discussing control chart V-masks but there is no discussion of supplementary runs tests, other cusum tests or moving averages.

Two further comments on Part 1. The notation in Chapter 8 on sampling conflicts with the notation in the rest of the book. This is noted in the chapter introduction but not satisfactorily explained. Also, the discussion in Chapter 11 on simulation models and their (potential) role in nuclear material management is worth noting. A major portion of this chapter (21 pages) is devoted to random number generation. While this may be excessive, it does make interesting reading. The example on percentile estimation by a simulation of only 5,000 trials produces estimates with five significant digits! To leave a reader with the impression that these five digits are meaningful is a disservice.

The second part of the text, Chapters 13-17, covers nuclear material accounting. These chapters are well written in general and the NMMP will benefit greatly if he/she at least reads the explanatory sections and studies the examples. These chapters will be reviewed individually.

Chapter 13. Nuclear Material Accounting. This Chapter gives a good overview of the material transactions in a nuclear facility and how the accounting system tracks these activities. The two appendices "The Accounting System" and "Measurement Systems" add to the importance of this chapter. This chapter should be required reading.

The section on shipments (p. 641) mentions the DOE/NRC Form 741 but fails to note that this form requires Limits of Error (LE). The text gives no explicit advice on the LE calculation. How will the NMMP who computes the LE of a shipment total as the addition in quadrature of the item LEs know that this is usually incorrect?

The omission of item sampling from the section on Physical Inventories (13A.6) is unfortunate. In section 13B.6, the text confuses random and representative samples by implying that random samples are necessarily representative. Some discussion on the need to take adequate bulk sample sizes to better ensure obtaining a representative sample would have been useful.

Chapter 14. Modeling Measurement Variability. The chapter gives a detailed description of "the basic statistical concepts involved in modeling and estimating the effect of the presence of measurement error on accounting results." The appendix applies these ideas to the "measurement process for determining the input to a scrap recovery operation." Sections 14.0 through perhaps 14.2.1 are easily comprehended. Following the detail in the remainder of the chapter is simply painful. I doubt if many NMMPs will be willing to work through the material. Section 14.3.4, Variance of the Variance Estimator, is conceptually valuable but, like formula 3.14 referred to above, apparently never applied. Thus, the reader doesn't know how much faith to put in the 212 kg value obtained at the end of Example 14.6.

Some of the error variances given in the example on p. 706 have four significant digits for the constant and random effects components. Numbers such as these are ordinarily very difficult to obtain. It would be interesting to know the uncertainty on these values.

Chapter 15. Estimating and Controlling Measurement Variability.

This chapter presents some techniques for obtaining estimates of measurement error uncertainties. Included are sections on calibration, measurement control and repeated measurement. This latter section covers multiple measurements on the same and different instruments. The example in the measurement control section determines control limits from data collected in a 10-day time period. This is usually too short a time period to capture the variability needed for the limits. Inclusion of the uncertainty of the standards in the control limits is a questionable practice. The calibration procedures presented give a good overview of the topic.

Chapter 16. Evaluation of Accounting Results. Covered in this chapter are the inventory difference (ID) equation and application of various techniques from Part 1 to the evaluation of the variance of the ID. The effects of measurement errors and correlation among terms are considered.

Chapter 17. Verification of Accounting Data. An overview of the process of verifying stated amounts of nuclear material is presented here. Sampling techniques, attribute and verification measurements and inferences about the inventory are discussed. The "difference statistic" is also covered.

Tables. (59 pages) There is a set of 28 very useful tables. The binomial table covers probability of occurrence from 0.05 to 0.95 by steps of 0.05 and  $n$  from 1 to 20, the F tables give critical value for 6 values of  $p$  from 0.5 to 0.995. Other tables have similar useful detail. An omission which might be noticed by a NMMP is that there are no plots of binomial confidence limits.

Index. (13 pages) The index is a major disappointment in a book intended as a reference. It is very difficult to use. Some topics, like sample size, verification measurement and fixed effects, are not included; some topics misplaced. Sample

covariance is under "s" while sample correlation is under "c." Variance formulas are under "Taylor Series Approximations." There are a large collection of references under "test for," "testing," "testing for," "tests" and "test of." Will a NMMP think to look under each or any of these for a test of normality? (It's under "tests for normality.") A major omission is that there is no entry for "sample sizes." The text has numerous formulas and valuable discussions on sample sizes but they can be hard to find.

The Training Manual contains problems for all chapter except Chapter 12. (Problems in that chapter were deemed to be too complex and beyond the scope of the manual.)

Unfortunately, problems on control charts are also omitted. Detailed solutions for all problems are included. The problems and solutions are generally easy to follow. There are, however, a fair number of typographical and calculational errors and the answers to a few problems are incorrect. The terminology in the manual is not always consistent with that of the text (see Chapter 14).

A word on terminology is necessary. The text attempts to use conventional statistical terminology and avoid terms such as precision and accuracy, limit of error, reproducibility and repeatability, systematic error, and long-term and short-term systematic error. Though these terms are the subject of some contro-

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versy, and perhaps because they are so, they should have been discussed. The authors could have explained why they don't recommend the terms and that if used, they must be defined carefully and used accordingly. The NMMP will be looking to this book for an explanation of these and other terms and will not find it.

Likewise, a NMMP expecting straightforward guidance in setting up and maintaining a measurement control program, computing limits of error, determining inventory difference control limits, or reporting random and systematic errors will be disappointed. The ingredients for doing these are mostly in the text but they can be hard to find. This may discourage use. The NMMP should also be aware that the text examples and manual problems are directed more toward production facilities than other facilities.

The text succeeds in giving the flavor of many applications but does not succeed in describing the difficult of getting estimates or models. The time and effort required to build these models or obtain estimates is not addressed. More emphasis should have been put on the approximate nature of models. It has been said that "All models are wrong; some models are useful." The text seems to imply that an error term or process can be modeled to any degree desired, that estimation and modeling are easily accomplished, and that there is such a thing as the variance of the measurement. Unfortunately, this is often not the case. Models of error terms in processes are approximations at best. Measurements taken on an autocycle run have different variance than those taken over a week, a month, a year. The context is important. One should not estimate the components of variance for operators, for day of the week, etc. unless the estimates are meaningful and contribute to the problem solution. If the error or process models are only approximations and the uncertainties

on the estimates of the error variances large, perhaps a less detailed model is appropriate.

In spite of the above criticisms, there is much to praise here. The text contains a wealth of information and much practical advice. These volumes coupled with the DOE short courses can serve to increase the understanding of the proper use of statistical techniques in nuclear material accountability. This can serve as a unifying device among the nuclear facilities.

*Reviewed by*  
*Lawrence A. Bruckner, Ph.D.*  
*Los Alamos National Laboratory*  
*Los Alamos, New Mexico*

## Posts Vacant in the IAEA

The Department of State, the U.S. Arms Control and Disarmament Agency and the Department of Energy have initiated a program to improve recruitment of U.S. nationals for employment in the IAEA.

In an effort to support this program, *JNMM* will publish IAEA vacancies.

### *Department of Administration*

*Division: Languages Section: Chinese Translation Position: Head of Section Grade: P-5 Vacancy #89/070 Opened: 26 Sep 1989 Closing: 26 Jan 1990*

*Division: Languages Section: Arabic Translation Position: Reviser Grade: P-4 Vacancy #89/073 Opened: 26 Sep 1989 Closing: 26 Jan 1990*

*Division: External Relations Section: Conference Service Position: Conference Service Administrator Grade: P-3 Vacancy #80/066 Opened: 5 Sep 1989 Closing: 5 Jan 1990*

*Division: Languages Section: French Translation Position: Reviser Grade: P-4 Vacancy #89/060 Opened: 5 Sep 1989 Closing: 5 Jan 1990*

*Division: Budget and Finance Section: Operations, Field Accounts and Commercial Claims Unit Position: Unit Head Grade: P-3 Vacancy #89/059 Opened: 22 Aug 1989 Closing: 22 Dec 1989*

### *Department of Nuclear Energy and Safety*

*Division: Scientific and Technical Information Section: INIS Position: Head, INIS Section Grade: P-5 Vacancy #89/071 Opened: 26 Sep 1989 Closing: 26 Jan 1990*

*Division: Nuclear Safety Section: Radiation Safety Service Position: Radiation Protection Services Specialist Grade: P-5 Vacancy #89/072 Opened: 26 Sep 1989 Closing: 26 Jan 1990*

*Division: Nuclear Fuel Cycle Section: Waste Management Position: Nuclear/Chemical Engineer Grade: P-4 Vacancy #89/068 Opened: 19 Sep 1989 Closing: 19 Jan 1990*

*Division: Scientific and Technical Information Position: Director Grade: D-1 Vacancy #89/065 Opened: 12 Sep 1989 Closing: 12 Jan 1990*

*Division: Nuclear Safety Section: Engineering Safety Position: Reactor Accident Prevention Specialist Grade: P-4 Vacancy #89/064 Opened: 5 Sep 1989 Closing: 5 Jan 1990*

### *Department of Research and Isotopes*

*Division: Agency's Laboratories, Seibersdorf Section: Agriculture Laboratory Position: Research Entomologist Grade: P-4 Vacancy #89/069 Opened: 26 Sep 1989 Closing: 26 Jan 1990*

*Division: International Centre for Theoretical Physics, Trieste Section: Scientific Information Services Unit Position: Scientific Information Officer Grade: P-3 Vacancy #89/074 Opened: 26 Sep 1989 Closing: 26 Jan 1990*

*Division:* Agency's Laboratories, Seibersdorf  
*Section:* Agricultural Laboratory, Soil Science  
*Unit Position:* Soil Scientist *Grade:* P-1 *Vacancy* #89/075 *Opened:* 26 Sep 1989 *Closing:* 26 Jan 1990

*Division:* Life Sciences *Section:* Applied Radiation Biology and Radiotherapy *Position:* Radiation Biologist *Grade:* P-4 *Vacancy* #89/061 *Opened:* 5 Sep 1989 *Closing:* 5 Jan 1990

*Division:* Agency's Laboratories *Section:* Chemistry Unit *Position:* Environmental Radiochemist *Grade:* P-2 *Vacancy* #89/062 *Opened:* 5 Sep 1989 *Closing:* 5 Jan 1990

#### Department of Safeguards

*Division:* Operations A *Section:* OA3 *Position:* Group Leader *Grade:* P-5 *Vacancy* #89/063 *Opened:* 5 Sep 1989 *Closing:* 5 Jan 1990

*Division:* Operations *Position:* Nuclear Safeguards Inspector *Grade:* P-3 [several positions] *Vacancy* #89/SGO-3 *Opened:* 25 April 1989 *Closing:* Continuous recruitment until 31 Dec 1989.

*Division:* Operations *Position:* Nuclear Safeguards Inspector *Grade:* P-4 [several positions] *Vacancy* #89/SGO-4 *Opened:* 25 April 1989 *Closing:* Continuous recruitment until 31 Dec 1989.

#### How to Apply

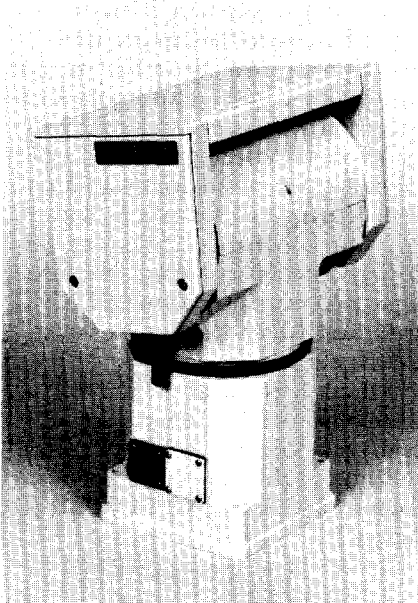
Applications must include a vacancy notice number, and should be mailed to the United States Mission to the International Atomic Energy Agency, Kundmangasse 21, 1030 Vienna, Austria (Attention Ronald Bartell). After U.S. Government endorsement is given, the Mission will forward the application to the Division of Personnel at the IAEA.

U.S. Candidates must also send a photocopy of the original application to: (for positions in the Department of Safeguards) P.O. Box 650, Brookhaven National Laboratory, Upton, NY 11973, (for all other positions) IO/T/SCT, Rm. 5336, Department of State, Washington, D.C. 20520.

For more information contact Mr. W. Porter, Department of Energy, (202) 586-8253, FTS 586-8253. Potential applicants should leave their name, address, and position in which they are interested. DOE will then forward a package of information on the IAEA and the position for which they applied.

## "Omni-Trak" Pan Tilt Series

Javelin Electronics has unveiled its "Omni-Trak™" Pan/Tilt series with the introduction of two full-featured units designed to provide unbeatable performance in most indoor or outdoor security applications. One of the advanced new Pan/Tilt drives (model JPT-2420ACU) is designed for complete compatibility with Javelin's new "Omni II™" modular Security Management Systems. It offers the world's first built-in Accessory Control Unit, eliminating the need for a separate ACU.



Models JPT-2420 and JPT-2420ACU are versatile medium-duty Pan/Tilt units that are compatible with most popular camera/lens combinations. Built in the USA by Javelin, both have been engineered to be totally weatherproof and will not allow the intrusion of moisture even when mounted outdoors in an upside-down position.

The JPT-2420 is compatible with a variety of industry-standard control equipment for manual or autopan operation. The JPT-2420ACU accepts operating commands from Javelin Omni II microprocessor/computer based control systems via industry standard RS-232 communication.

Both the JPT-2420 and JPT-2420ACU can meet most motion requirements, and feature quiet, dependable operation. The units will also accept all Javelin camera housings.

For more information contact Javelin Electronics at 213/327-7440.

## ASTM Safeguards Applications Subcommittee

Participants are needed for a subcommittee on safeguards applications, sponsored by ASTM standards-writing Committee C-26 on Nuclear Fuel Cycle.

Subcommittee C26.12 is developing standard guides for using metal detectors to detect handguns and radiation shielding materials at DOE (Department of Energy) and NRC (Nuclear Regulatory Commission) licensed facilities. The subcommittee will also continue ongoing development of guides for SNM (Special Nuclear Material) monitor in-plant testing and calibration at the meeting.

For more information contact Ann Gibbs, Westinghouse Savannah River Company, Building 707C, Aiken, SC 29808, 803/557-9092 or Kathie Schaaf, ASTM, 1916 Race Street, Philadelphia, PA 19103-1187, 215/299-5526. The next meeting of the subcommittee will take place during the January 21-25, 1990 standards development meetings of Committee C-26 in Las Vegas, Nev.

Committee C-26 is one of 134 ASTM technical standards-writing committees. Organized in 1898, ASTM (American Society for Testing and Materials) is one of the largest voluntary standards development systems in the world.

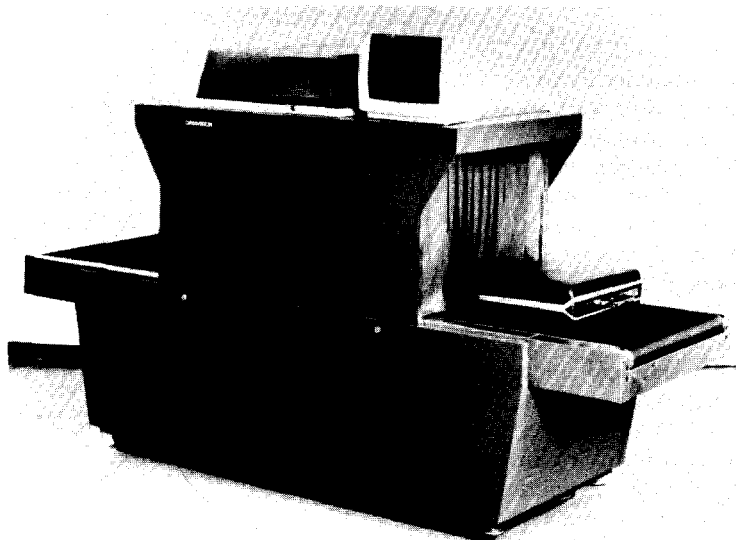
## Dynagraphy Security Screening

Scan-Tech Security, L.P., announces Dynagraphy, a revolutionary new technology for security screening.

Dynagraphy combines advanced image processing, unique x-ray configuration and ergonomic system design for unequaled detection capability for weapons, narcotics, explosives and other dangerous items.

Scan-Tech has designed sophisticated new conveyerized security systems incorporating Dynagraphy—the Dynavision 900 Series. Dynavision 900 offers the new Dynagraphy technology, and features unavailable on other systems such as a 15-position image enhancement slide switch, true edge enhancement and automatic zoom. The Dynavision 900 electronics are PC controlled; its multi-function membrane panel eliminates switch and bulb malfunctions, and “function centralization” provides that a lower number of components performs a higher number of functions.

The new Dynavision 900 X-ray Security System: Dynagraphy technology, unique standard features, and designed-in reliability. For more information contact Scan-Tech Security at 234 Industrial Parkway, Northvale, New Jersey 07647 or call (201) 784-1400.



## Breakthrough in Fingerprinting

A Los Alamos National Laboratory scientist has achieved a remarkable breakthrough in the century-old identification technique of fingerprinting.

George Saunders of the Lab's Cell Biology Group, working closely with the U.S. Secret Service's Forensic Services Division, adapted an immunological-chemistry technique that stains proteins to sort and quantify them, and used commonly available reagents to develop and enhance latent fingerprints.

The technique has proven effective on a variety of surfaces, some of which have never had fingerprints developed on them. Saunders' method uses gold to adhere to the protein present in secretions left by the finger when something is touched.

The Los Alamos method has been tested successfully on porous and non-porous materials, including plastic, paper, metal and glass. The technique also works for palm and footprints, which also leave characteristic marks.

“I think it is one of the top five developments in the fingerprint field,” said John Piper, deputy agent in charge of the U.S. Secret Service's Technical Security Division in Washington, D.C.

“It's the only method that works on the adhesive side of tape, for example,” said Piper.

Saunders' method led to the arrest of a criminal suspect for the first time in March. Palm prints were developed on a blank government check that had been stolen from a military facility in Pennsylvania.

Saunders' technique involves using “colloidal gold,” a buffer solution of citric acid containing tiny particles of gold. The fingerprint is washed in this mixture for about 30 minutes—depending on the type of surface—and then bathed in a silver solution.

The gold is attracted to the protein in the fingerprint through an electrical charge and an image begins to emerge. The silver then enhances the image by filling in around the gold, making the gold particles bigger and highlighting the fingerprint features.

The prints also can be transferred from surfaces to thin nitrocellulose membranes, which are cotton-like polymers, and then developed.

Saunders' method has worked are tape, computer floppy disks, credit cards, bullet cartridges, wet and dry paper, glass and some styrofoam, among others.

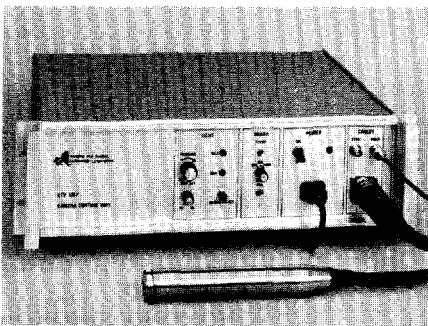
The technique, for which a patent has been applied, was developed last December. It was first revealed publicly at an International Association of Identification Educational Conference in June and is currently being used by both the U.S. Secret Service and the FBI.

## Color Inspection Now Available for Harsh Environments

Imaging and Sensing Technology Corp. (ISTC) introduces a Solid State Miniature Color Inspection Camera that operates both in air and water and tolerates low levels of radiation.

The ETV-1257 CCD Miniature Color Inspection Camera can tolerate a Gamma dose rate up to 1000 R/hr and a cumulative radiation dose of more than 104R.

The light weight CCD camera head measures only 6.8" (173mm) in length and 1.25" (32mm) in diameter,



making it easier to maneuver than larger inspection camera heads. The ETV-1257 camera head has both remote control iris and optical focus. A wide range of viewing accessories are also available.

The ETV-1257 is designed for inspection applications that range from reactor vessel inspection to geotechnical inspection. Color resolution is 360 TV lines horizontal and 350 TV lines vertical. A complete product bulletin detailing all features, accessories and options is available from ISTC.

ISTC supplies miniature TV inspection systems for a variety of applications ranging from reactor vessel inspection, pipe inspection, maintenance, fuel inspection, fueling support operations, and geotechnical inspections. Call ISTC for more information about the miniature TV inspection system at 607/796-3372 or FAX 607/796-3279.

## Improved Resolution of Germanium Detectors

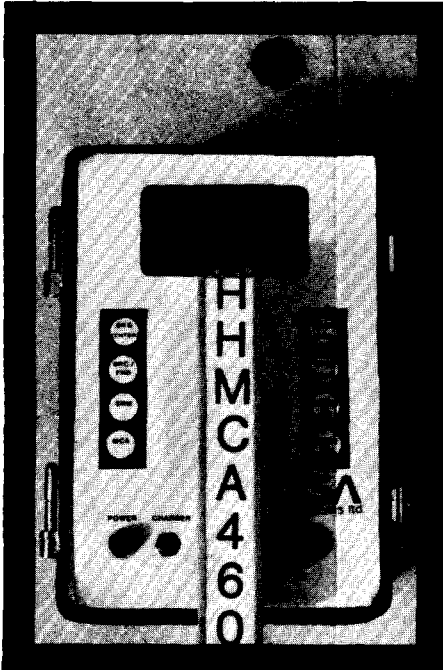
EG&G ORTEC announced that it is no longer necessary to accept the energy resolution of a germanium detector as it stands! The new Model 675 Ge Resolution Enhancer electronically eliminates the unfavorable effects of majority-carrier trapping in germanium gamma-ray spectrometers. This dramatically improves the energy resolution in all of the following cases: charge trapping (as a result of the Ge crystal's properties) in N-type detectors, charge trapping (as a result of neutron damage) in P-type detectors, and ballistic deficit effects (when using short shaping time constants for high counting rates) in P- and N-type detectors.

The Model 675 makes corrections on every pulse received, with none being discarded; therefore, the resolu-

tion improvement is made without any loss of detector efficiency.

A data sheet from EG&G ORTEC gives examples of the improvement in performance experience on a variety of Ge detectors with relative efficiencies ranging from 14 to 77%. Copies of recently published technical papers on the new technique are also available on request.

Call the HOTLINE, 800-251-9750, or the local EG&G ORTEC representative for more information.



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All this in a light hand-held instrument that is tough, sensitive, and easy to use. The HHMCA-460 uses a 1" x 2" NaI detector and "intelligent" micro-processor-based digital electronics. You can further expand its capabilities by using the built-in RS-232C output to save data to the TSA Printer or a PC, and by adding the optional gamma or neutron probes. Rechargeable batteries give up to 10 hours continuous use.

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January 17-19, 1990

**Spent Fuel Management Seminar VII**, Loew's L'Enfant Plaza, Washington, D.C., USA *Sponsor*: Technical Working Group on Waste Management of the Institute of Nuclear Materials Management *Contact*: Barbara Scott, INMM Headquarters, 60 Revere Drive, Suite 500, Northbrook, IL 60062 USA, (708) 480-9573.

April 8-12, 1990

High Level Radioactive Waste Management, Caesar's Palace, Las Vegas, Nevada, USA *Sponsor*: American Nuclear Society *et al.* *Contact*: American Society of Civil Engineers (212) 705-7543.

June 4-7, 1990

Emerging Technologies For Hazardous Waste Treatment, Atlantic City, NJ USA *Sponsor*: American Chemical Society *Contact*: Dr. D. William Tedder (404) 894-2856.

June 10-15, 1990

ANS Annual Meeting, Opryland Hotel, Nashville, TN *Sponsor*: American Nuclear Society *Contact*: General Chair Donald P. Trauger, Oak Ridge National Laboratory, P.O. Box 2008, Oak Ridge, TN USA 37831.

*The events listed in this calendar were provided by Institute members or taken from widely available public listings. We urge INMM members, especially those from countries outside the United States, to send notices of other meetings, workshops or courses to INMM headquarters.*

## LEADERSHIP OPPORTUNITIES IN NUCLEAR TECHNOLOGY

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**NUCLEAR MATERIALS CONTROL AND ACCOUNTABILITY SPECIALIST-** A highly technical position in which the successful candidate will evaluate and exercise the nuclear materials control and accountability systems of DOE facilities. Requirements include at least five years of practical experience in the design and utilization of such systems; willingness to travel extensively; and demonstrated ability to communicate effectively and tactfully in high pressure situations. Candidates having CPA certification are preferred.

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