Re-designing a TSI FMAG 1520 for the production of monodisperse uranium-oxide microparticles. A status report.

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Abstract

For the analysis of individual micrometer- and sub-micrometer-sized particles collected on swipe samples by International Atomic Energy Agency (IAEA) safeguards inspectors during in-field verification, well-defined microparticulate reference materials are requested by IAEA for quality control measures. In this context, an aerosol-based approach to produce U_3O_8 microparticulate reference materials is implemented in the laboratories of the Forschungszentrum Jülich. Since 2020 the Safeguards Laboratory at Forschungszentrum Jülich has been first and to date only qualified member of IAEA's NetWork of Analytical Laboratories (NWAL) for the provision of microparticle reference materials for particle analysis in nuclear safeguards. The centrepiece for the production of these uranium oxide-based microparticles is a modified aerosol generator, TSI VOAG 3450 (Vibration Orifice Aerosol Generator), which was acquired in 2012. Unfavourably, TSI has ceased the production of the VOAG and will soon also cease servicing and procuring spare parts. Therefore, and because of the extension of the chemical composition of the microparticles to include more complex systems e.g., Pu doped uranium oxide, a new aerosol generator, the TSI FMAG 1520 (Flow Focussing Monodisperse Aerosol Generator), was purchased. In order to produce particles of comparable quality (like VOAG) and to build up on existing experience, the original setup of FMAG needs to be significantly modified. The redesign has to meet a number of requirements: (1) it has to fit into a glove box, (2) all steps of a particle production such as cleaning or replacement of parts has to be easily performed in a glove box environment. In addition, the redesign allows to bring in the experience made with the VOAG to enable a wider variation of the process. An overview of the status of the redesign of the TSI-FMAG and first results will be presented.

1. Introduction

The IAEA has an increasing demand for micrometre-sized uranium oxide-based reference particles. These particles are used by the IAEA and its connected NetWork of Analytical Laboratories (NWAL) for machine calibration, method development and proficiency testing [1]. Up to date only a few laboratories can supply the NWAL with these materials, namely Forschungszentrum Jülich (FZJ, Germany), which is recently the only qualified NWAL member for the provision of microparticulate reference materials for particle analysis in nuclear safeguards, Savannah River National Laboratory (SRNL, USA), Pacific Northwest National Laboratory (PNNL, USA), and Institut de Chimie Séparative de Marcoule (ICSM, France). From these laboratories FZJ and SRNL are producing uranium oxide-based microparticles using aerosol-based methods.

The development of the methodology to produce microparticulate reference materials at FZJ was started in 2012 using a modified TSI VOAG 3450 (Vibration Orifice Aerosol Generator) [2-5]. Unfavourably, TSI has ceased the production of the VOAG and will soon also cease servicing and procuring spare parts. Therefore, and because of the extension of the chemical composition of the microparticles to more complex systems e.g., Pu doped uranium oxide [6-8], and to be able to meet the demand for new advanced reference materials e.g., for nuclear forensics and age dating and the research and development required for this purpose, a new aerosol generator, the TSI FMAG 1520 (Flow Focussing Monodisperse Aerosol Generator, see figure 1a) was purchased.

2. Redesign of TSI FMAG 1520

The initial aerosol generator setup at FZJ using the TSI VOAG 3450 was based on the original TSI setup, where the aerosol jet was shot from the bottom up into a drying column. At the top of the drying column the produced microparticles were then driven through a tube furnace by the airstream, heated and deposited on a substrate or a filter [2, 3]. Due to the gravitational loss of particles and the resulting poor yield, this setup was intensively optimised. These modifications ended up with the currently used design, where the aerosol generator of the VOAG was placed upside down and the aerosol is moved through the drying column, the aerosol heater (pressurized air heater, Dekati Ltd., Finland), and a subsequent cooling track by an air stream. The particles are finally collected on a substrate placed in an inertial impactor. This leads to an enormous improvement of yield and monodispersity [4, 5].

In order to produce particles of comparable quality to those produced in the VOAG setup at FZJ and to build up on existing experience, the original setup of FMAG (see figure 1a) was significantly modified according to the experiences gained during the design of the VOAG-based setup at FZJ. Additional changes were made to enable a broader range of the process parameters i.e., temperature by the installation of two furnaces which are connected in line and are individually controllable. Finally, care was taken to ensure that the handling of the system was made as simple as possible, for example by using gas-tight quick couplings of the gas tubes to simplify the cleaning process and replacement of parts, as it is planned to operate the system in a glove box (see figure 1b) and c)).

The synthesis of uranium oxide-based microparticles with the used TSI FMAG setup begins with the generation of an aerosol droplet jet in the aerosol generator assembly from a uranium nitrate bearing solution as precursor. This jet passes through the drying column to evaporate the solvent (50% H_2O/ 50% ethanol mixture) and dried uranium nitrate particles can, driven by an airstream, pass the two aerosol heaters, where the nitrate is decomposed, and uranium oxide particles are formed and sintered. In the subsequently attached cooling column, the airstream

loaded with particles is cooled down to room temperature and the particles were collected on a freely selectable substrate installed within an inertial impactor (see figure 1b) and c)). An optical particle sizer (TSI OPS 3330) is located behind the cooling track and taps a small fraction from the air stream. This allows online monitoring of the quantity and size of the produced particles.

The size, monodispersity and to some extend the structure of the synthesised microparticles can be controlled by the change of the following process parameters:

- Concentration of uranium nitrate solution
- Feeding rate of the solution
- Frequency of the HF-generator of the aerosol generator
- Dilution air (air stream in drying column)
- Focussing air (airflow within the aerosol generator assembly)
- Temperature in both aerosol heaters
- Collection time

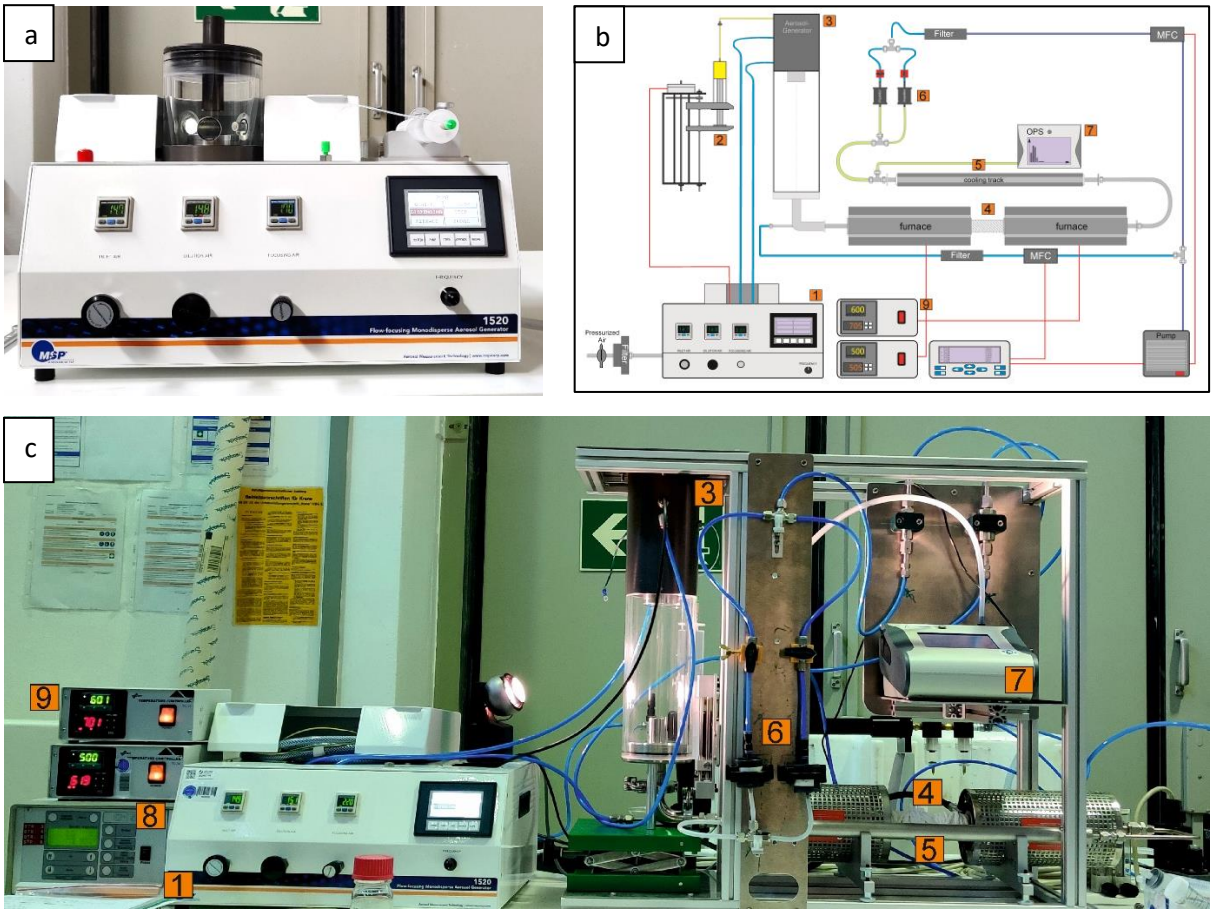

***Figure 1**: a) Photograph of the original FMAG 1520 setup; b) scematic drawing of the redesign. The setup consists of 1) electronics and controller, 2) syringe pump, 3) aerosolgenerator assembly with attached drying column, 4) furnaces, 5) cooling track, 6) vaccum impactors, 7) optical particle sizer (TSI OPS 3330), 8) gas mass flow controller, 9) furnace controller; c) photograph of modified TSI FMAG setup. The numbering corresponds to that of 1b, except 2 which is not visible on this photograph.*

3. Results

To test the function of the modified setup, first experiments were performed as “cold” particle productions using neodymium nitrate solutions as precursor. Figure 2a) shows a quartz substrate which was placed in an inertial impactor after 1 hour of particle collection time. The extremely high yield is obvious. A spot of collected microparticles is visible with the naked eye as light

blue dot in the centre of the substrate demonstrating the high yield archivable with the new FMAG setup.

Figure 2 b), c), and d) show SEM images of the first experiments using a uranyl nitrate precursor for the production of microparticles. The experimental parameter can be found in table 1.

***Table 1**: Experimental parameters of production of first uranium oxide particles.*

	Figure 2b	Figure 2c	Figure 2d
U conc. (µg/mL)	120	240	240
Feeding rate (mL/h)	5	6	6
Frequency (kHz)	70	120	240
Dilution air (L/min)	15	15	15
Focussing air (psi)	2.75	2.84	2.84
Temperature f1/f2* (°C)	500/500	500/500	500/500
Collection time (min)	20	20	20

*f1/f2 = temperature furnace 1 and temperature furnace 2.

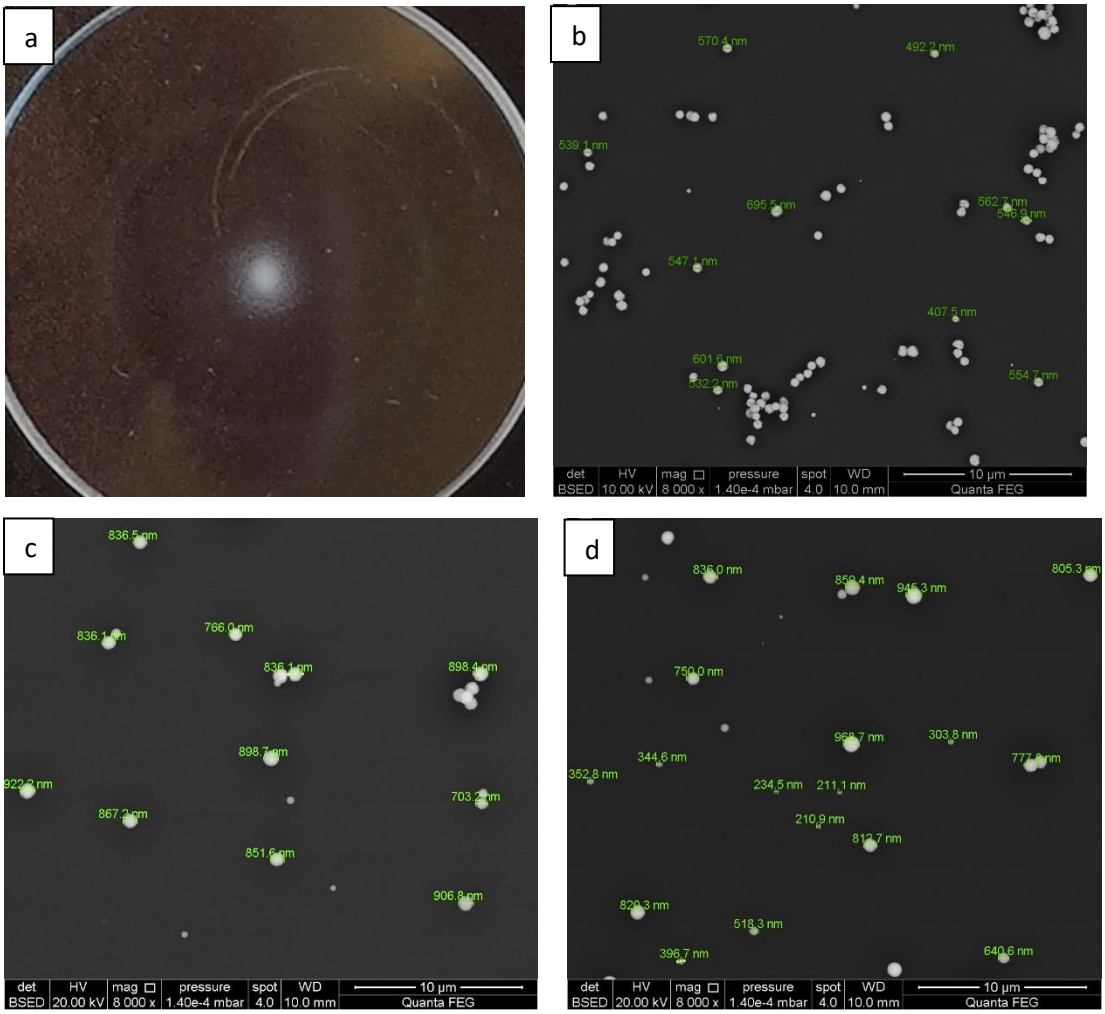

***Figure 2**: a) Photograph of quartz substrate after 1 h of collection time in a "cold" test using a neodynium nitrate solution as precursor. The large amount of collected particles are visible with the naked eye as light blue dot in the centre of the substrate; b) - d). SEM images of the particles of the first microparticle production with a uranyl nitrate solution as precursor. The parameters of the experiments are shown in table 1.*

Figure 2b) show uranium-oxide particles of a round shape with a size distribution between 400 and 600 nm. In addition some, so called satellite particles of ~ 100 nm are visible.

The increase of uranium concentration of the precursor and frequency in the experiment as shown in figure 2c) leads to bigger particles compared to those in figure 2b). The size distribution is in the range of 750 to 900 nm. Satellite particles of ~ 200 nm are evident.

The particle size distribution shown in figure 2d) is poorly monodisperse. Unexpetvively the further increase of the frequency did not result in smaller particles than in figure 2c). It results in particles with a wide size distribution between 350 and 950 nm and many additional small sattelite particles instead.

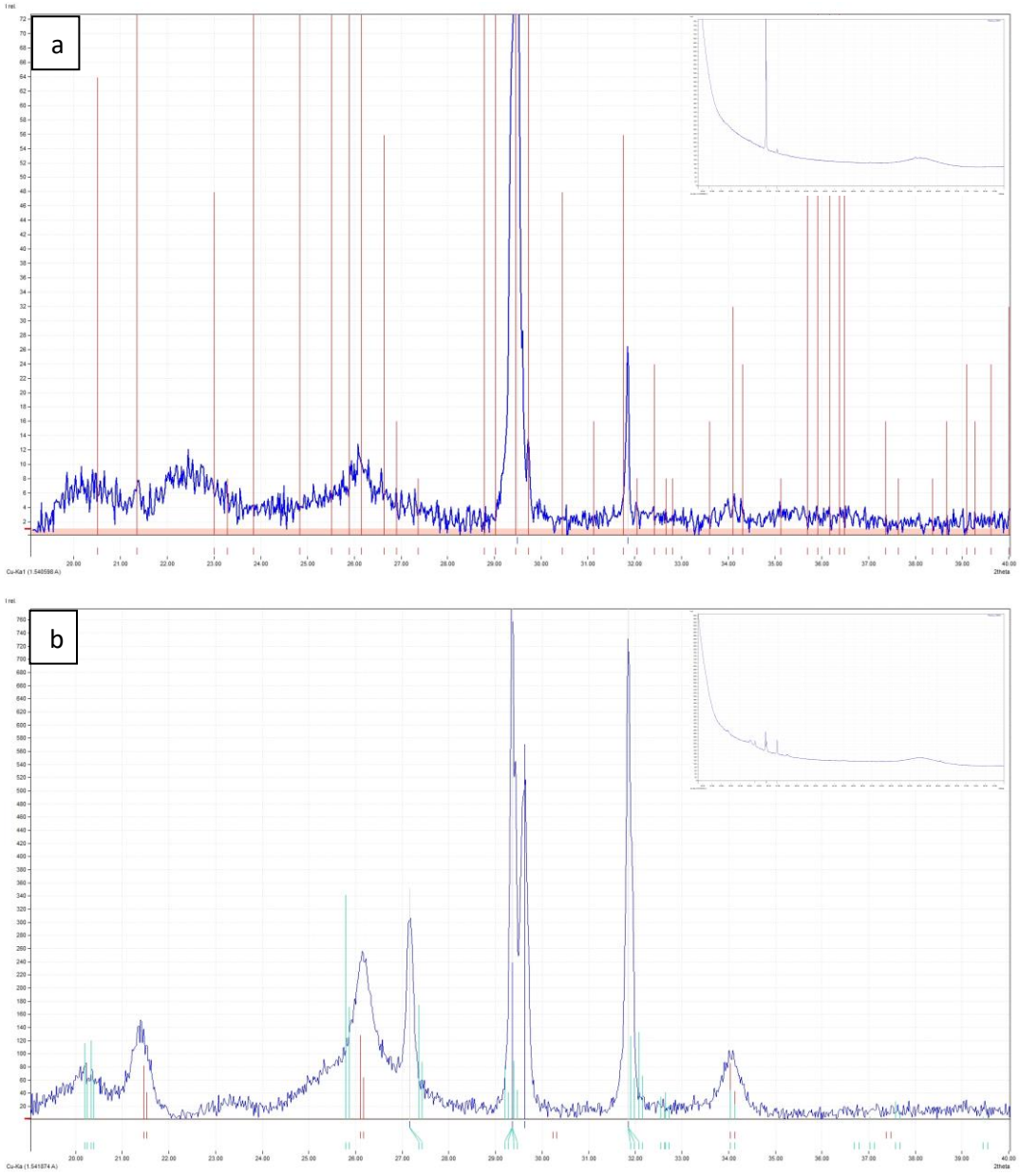

Figure 3*: a) XRD pattern after background correction of uranium oxide microparticles produced with a temperature of 500 °C in both furnaces. Amorphous and a monoclinic UO_3 (entry number: 00-031-1418) was identified as phase. In the upper right corner the original pattern is shown; b) XRD pattern after background correction of uranium oxide microparticles produced with a temperature of 500 °C in the first and 600 °C in the second furnace. Orthorhombic UO_3 (green, entry number 00-031-1431) and orthorhomic U_3O_8 (red, number: 00-074-0562) were identified as phases. In the upper right corner the original pattern is shown.*

The high yield of the new TSI FMAG setup at FZJ allows to use standard in-house equipment for structural analysis such as X-ray diffraction (XRD) of the produced microparticles. For that, the particles must be transferred from the substrate, where the particles were collected on, to a special zero background sample holder for XRD measurments. This is done by producing ethanolic particle suspension [9].

Figure 3a) and b) show the XRD-pattern of samples where the microparticles were produced with different temperatures. The measurements were made on a Bruker D4 from 15 to 80° 2Θ with 20 seconds counting time per step with a step width of 0.02° 2Θ and a fixed divergence slit of 1°. For better visibility the background is substracted in the main figures and only the range between 19 and 40° 2Θ is plotted. In both figures the original XRD pattern is shown the upper right corner.

In figure 3a) both furnaces were set to 500 °C. It is visible that the sample has a very low crystanilltiy. An amorphous and a monoclinic UO_3 phase (entry number: 00-031-1418) could be identified.

Obviously the crystanillity of the phases in figure 3b is higher than in figure 3a. Here the first furnace was set to 500 °C whereas the second furnace was set to 600 °C. This leads to the formation of two phases, an orthorhombic UO_3 phase (entry number 00-031-1431) and an orthorhombic U_3O_8 phase (entry number: 00-074-0562).

In both samples only spherical uranium microparticles and no debris of broken particles were found. This is a good indication that the two-step temperature treatment does not cause the particles to break.

4. Conclusions

The first results of the re-design of the TSI FMAG for the production of uranium oxide-based microparticles are very promising. The two staged furnace allows a more flexible handling of the temperature e.g., to react on different precursor compositions or to tune the crystal structure of the microparticles. Especially the high yield of microparticles collected on a substrate allows the possibility to perform analysis with in-house analytical devices like X-ray diffraction. Obviously more work have to be invested to get a more monodisperse particle size distribution.

5. Acknowledgements

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