

DEVELOPMENT OF METHODS FOR ISOTOPIC ANALYSIS OF URANIUM CONTAINING PARTICLES

Interim report on Task FIN A 1318 of the Finnish
Support Programme to IAEA Safeguards

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VTT Processes

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Summary

In the IAEA Support Program Task 00/SAL-005 the methods for separation of uranium containing particles by fission track-etch technique and development of SIMS method for the analysis of uranium containing particles have been reported previously in STUK-YTO-TR 188 (2002). In this report the use of track-etch method for separating particles from swipe samples for the measurement of isotope ratio are described. First part of this report describes the separation of the particles and their analysis by ICP-MS and the second part the use of SIMS for the analysis of uranium particles.

TRACK-ETCH METHOD FOR EXTRACTING URANIUM CONTAINING PARTICLES FROM SWIPES AND THEIR ANALYSIS WITH ICP-MS

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VTT Processes

Abstract

Track-etch method was developed at VTT to identify uranium containing particles of interest from swipe material. The extracted uranium containing particles were analysed with ICP-MS after track-etch analysis. This procedure was used for testing the separation and analysis of uranium containing particles from the IAEA filter samples 8250...8252 and from paper filter samples with NIST Standard Reference Materials of the uranium oxide se-

ries having nominal $n(^{235}\text{U})/n(^{238}\text{U})$ of 0.03 and 0.25. The analysed particles from the IAEA reference samples were very small ($< 1\mu\text{m}$). Unfortunately highly enriched particles were not among the picked up and analysed samples due to lack of time for sample handling. The results from the NIST samples were satisfactory when analysed with ICP-MS.

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1 Introduction

Track-etch method was developed at VTT for extracting uranium containing particles from swipe material. Sample preparation was performed by ashing the filter samples and collecting the ashing residue in Collodion. The mixture was spread on Makrofol detectors, where it formed a thin film. Irradiation was carried out in Triga Mk II reactor in Otaniemi. After etching the detectors the fis-

sion tracks could be examined under a microscope and the particles were picked up for the analysis with ICP-MS.

The method was tested with IAEA cotton swipe quality control samples 8250...8252 and filter samples with NIST uranium oxide standard reference material with known isotopic ratio of $^{235}\text{U}/^{238}\text{U}$.

2 Experimental

The track-etch method has been described in STUK-report [1]. Some changes had to be done anyway because the picking up of the particles did not succeed in an expected way.

The procedure to separate the particles from the Collodion film was changed because micromanipulator needles with acetone did not work satisfactorily. The acetone drop became easily too large and the track-etch print and the particle could not be seen because of the milky color in Collodion due to acetone. Besides it was difficult to dissolve the Collodion with the particle in acetone quickly enough to be drawn into the needle.

The Collodion piece with the uranium particle was cut out from the Collodion film with a razor knife. The visit to the Safer Laboratories in California gave good ideas how to proceed [2]. The film

was made thinner to make the cutting of the film easier. The ashing residue is mixed with a mixture of Collodion and ethanol in ratio one to ten. This sample is spread out to the Makrofol sheets so that about ten drops of solution is spread on each Makrofol. After a couple of hours a thicker Collodion mixture (1 to 1) is spread on the sheets and left to dry up over the night.

The separation of the thinner Collodion film from the Makrofol sheet is difficult with a razor. The film was separated easily from the Makrofol with hot water.

This procedure was used in order to separate the uranium particles from the IAEA filter samples 8250...8252 and from NIST Standard Reference Materials of the uranium oxide series having nominal $n(^{235}\text{U})/n(^{238}\text{U})$ of 0.03 and 0.25.

3 Analysis of swipe samples

3.1 Sample preparation

3.1.1 IAEA Reference Samples 8250, 8251 and 8252

The cloth swipes were divided into eight parts and two of them were placed in quartz crucibles in the clean room. They were ashed in 800 °C. The residue was ultrasonerated with 1 ml of ethanol for six minutes. Collodion was added so that Collodion to ethanol was one to ten. Then the ultrasoneration was continued for 3 minutes. The mixture was pipetted to Makrofol sheets. Each of the four sheets had about 12 drops. The next day Collodion in ethanol-mixture (1:1) was added to cover the sheets as a thick layer and were left to dry up overnight.

The sheets were irradiated for one hour in the neutron flux $1.2 \cdot 10^{12} \text{ cm}^{-2} \text{ s}^{-1}$ of the Triga Mark II reactor in Otaniemi, Espoo. The Collodion film was separated from the Makrofol in hot water after marking the specimens. The Makrofol was etched in 6.5 M KOH for 15 min and glued to the microscope slides.

The particles in the Collodion film were cut off with a razor knife under the magnification of 100. The Collodion film in this procedure was much thinner than in the original and the particles could not be detected by focusing because the track-etch marks in the Makrofol were disturbing.

The Collodion pieces were picked up into 0.5 ml polyethylene vials. The vial was filled with acetone to dissolve the Collodion. Acetone was evaporated so much that 250 μl of 5% HNO_3 could be added. The rest of the acetone was evaporated under an infrared lamp. Three samples (IAEA 8250) containing natural uranium particles and five samples (IAEA 8252) containing NU/LEU/HEU particles were analysed with ICP-MS. The track-etch prints of one particle and the Collodion piece containing the particle is shown in the Figure 1. The magnification is 200. According to the measurements made with a copper grid (Agar Scientific square 75 mesh grid) the diameter of the track-etch circle is 35 μm (Figure 2). Samples from 8251 filters with NU/LEU particles were not analysed before the results were obtained from the other samples and seen if they are worth analysing.

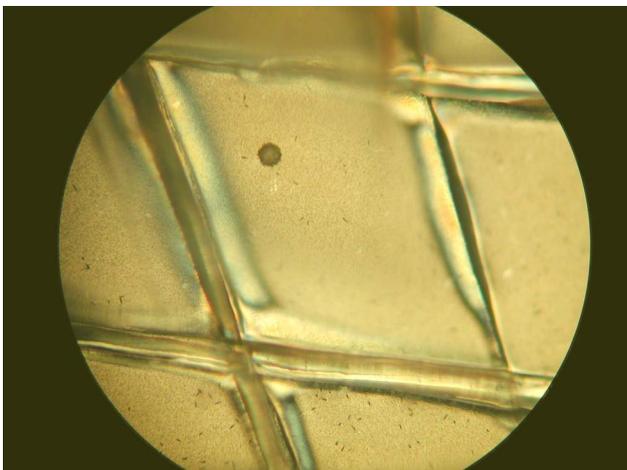


Figure 1. IAEA sample 4 (IAEA 8252), Collodion piece cut for the analysis, 200 \times magnification.



Figure 2. Track-etch print of the U-particle, IAEA sample 4, 500 \times magnification.

3.1.2 NIST Standard Reference Materials of the uranium oxide series

NIST Standard Reference Materials of the uranium oxide series having nominal $n(^{235}\text{U})/n(^{238}\text{U})$ of 0.03 and 0.25 were used to prepare spiked filter paper samples [1]. The spiked filter papers were ashed in 800°C in quartz crucibles and the track-etch samples were prepared as above. Seven samples were prepared for the ICP-MS -analysis.

In Figures 3 and 4 are shown the track-etch prints of U-particles having the isotopic ratios 0.25 and 0.03. The prints differ quite clearly from each other. Thus a highly enriched U-particle could be separated from others but requires anyway more practice to give reliable results.

3.2 ICP-MS analysis

The analysis of separated particles by using an ICP-MS (VG Plasma Quad 2+) with quadrupole mass separator was studied. The small amount of sample solution with low uranium concentration makes the task specially demanding. The use of microconcentric nebulizer (Cetac MCN-100) is obligatory. By using the natural uptake the sample flow rate is 50 $\mu\text{l}/\text{min}$. In this work sample volume 250 μl was enough for 3 parallel measurements for each sample.

The mass spectrum of the nitric acid used for dissolution of particles is free from uranium (Fig-

ure 5). The reagent blank containing acetone and acid (Figure 6) has a clear mass peak 238 and also some extra counts on mass 232 from acetone.

The spectra of separated particles (Figures 7–10) show a rather poor statistics. The three parallel measurements of 3 pg particle of 20% enriched uranium (NIST) gave isotopic ratio 0.22 ± 0.04 and a bigger particle, 7.5 pg of the same enrichment give 0.28 ± 0.06 isotope ratio 235/238 when given value is 0.25125. The analysed 3% enriched particles were bigger, 21 and 38 pg and isotope ratios calculated from three parallel measurements were 0.016 ± 0.006 and 0.028 ± 0.001 and given value 0.03143. The small amount of counts in 235 peak is the limiting factor in the analysis. The track-etch prints of the 21 pg particle is shown in Figure 4. The theoretical size of the analysed particles varied from $<1 \mu\text{m}$ (3 pg) to $2 \mu\text{m}$ (38 pg). The low background in the mass peak 235, only <5 counts/s, makes it possible to separate rather small particles with different enrichment from each others. For natural uranium, the total amount of uranium in the analysis should be at least 200–250 pg for the isotope ratio measurement. According to these measurements the precision of $\pm 10\%$ could be possible in that case. The theoretical diameter of the particle is about $4 \mu\text{m}$.



Figure 3. Track-etch prints of a U-oxide particle, ($^{235}\text{U}/^{238}\text{U}$ 0,25), NIST sample 3, 500 \times magnification.

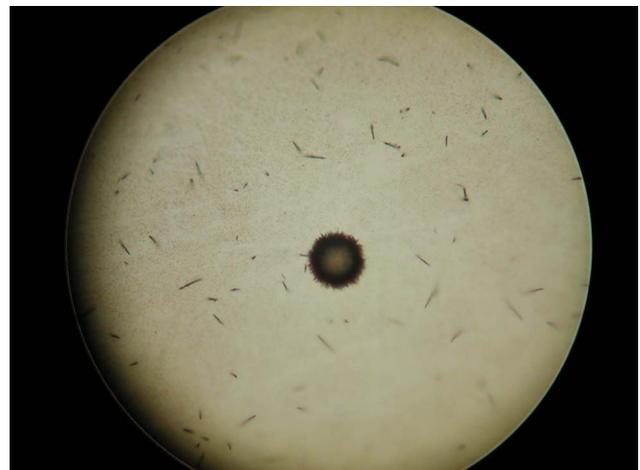


Figure 4. Track-etch prints of a U-oxide particle, ($^{235}\text{U}/^{238}\text{U}$ 0,03), NIST sample 4, 500 \times magnification.

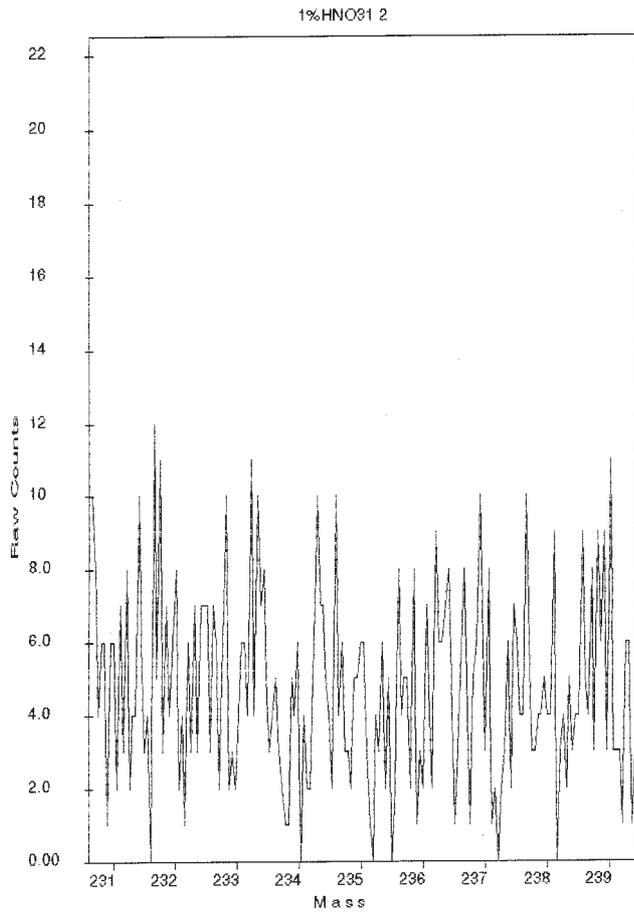


Figure 5. Mass spectrum of nitric acid used for sample preparation.

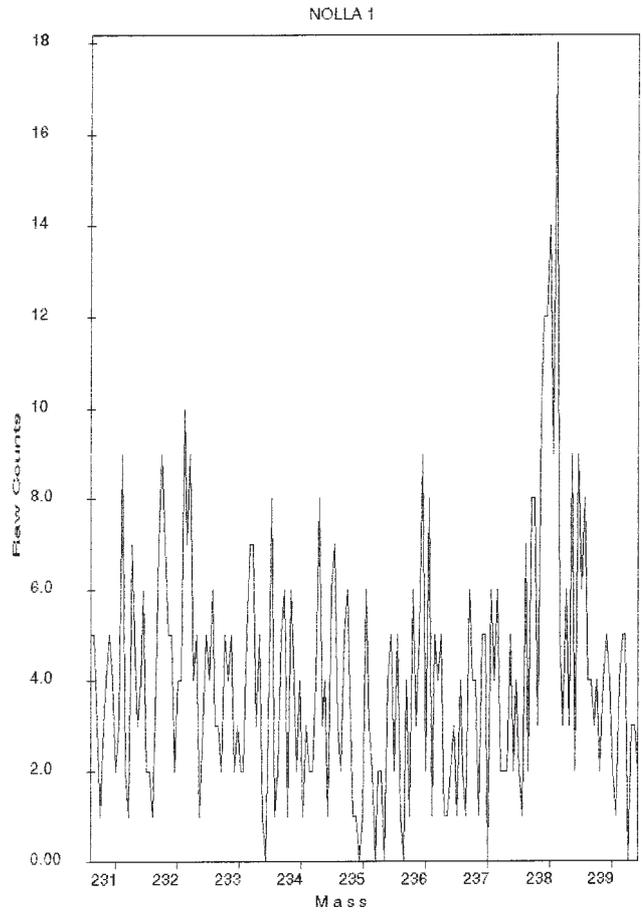


Figure 6. Mass spectrum of reagent blank.

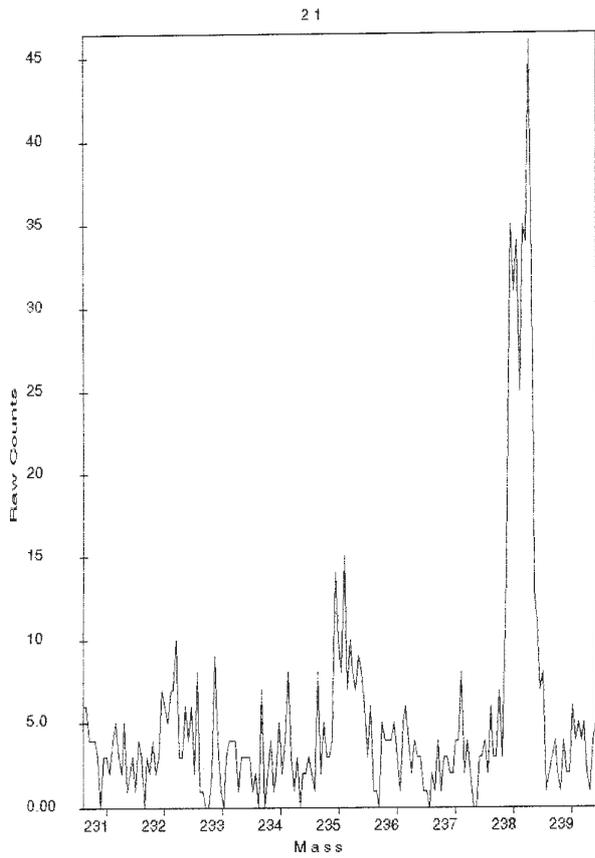


Figure 7. Mass spectrum of a 3 pg particle of 20% enriched uranium.

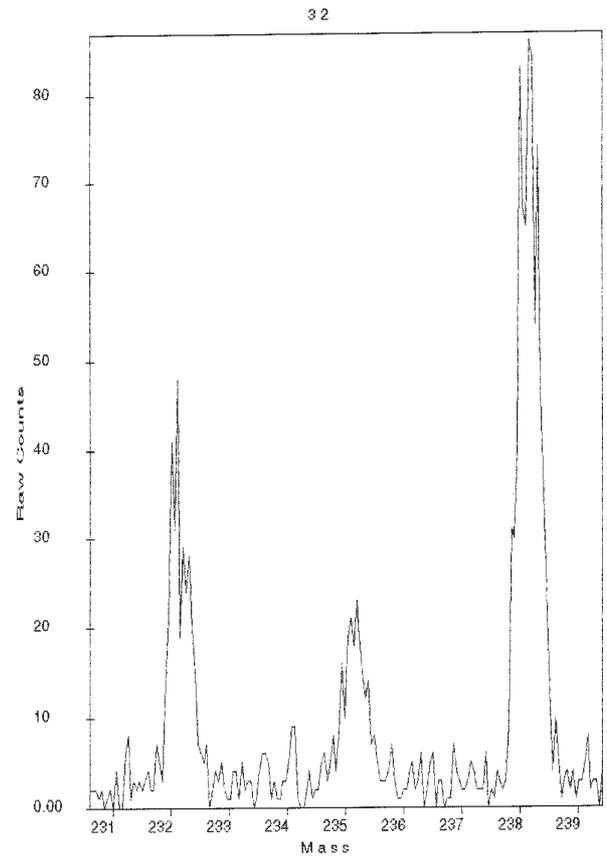


Figure 8. 7.5 pg particle of 20% enriched uranium.

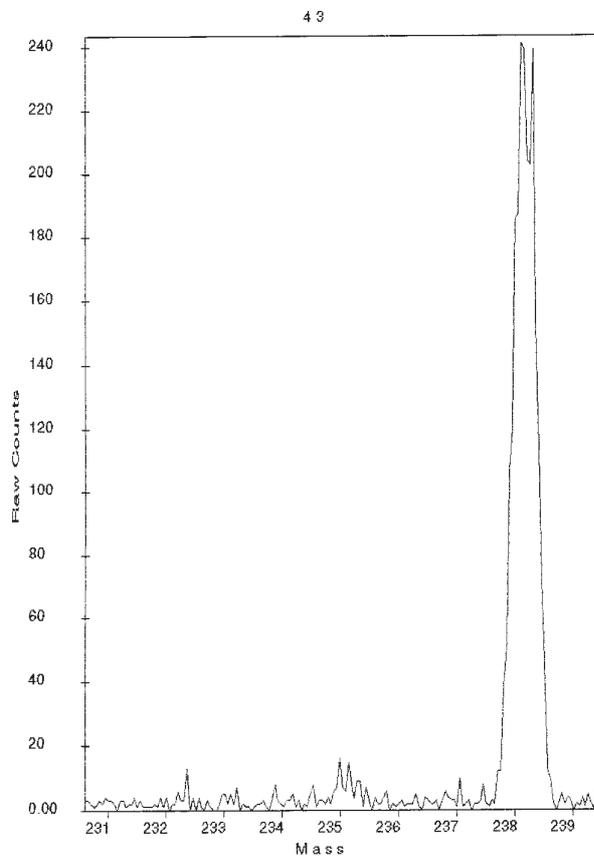


Figure 9. Mass spectrum of a 21 pg particle of 3% enriched uranium.

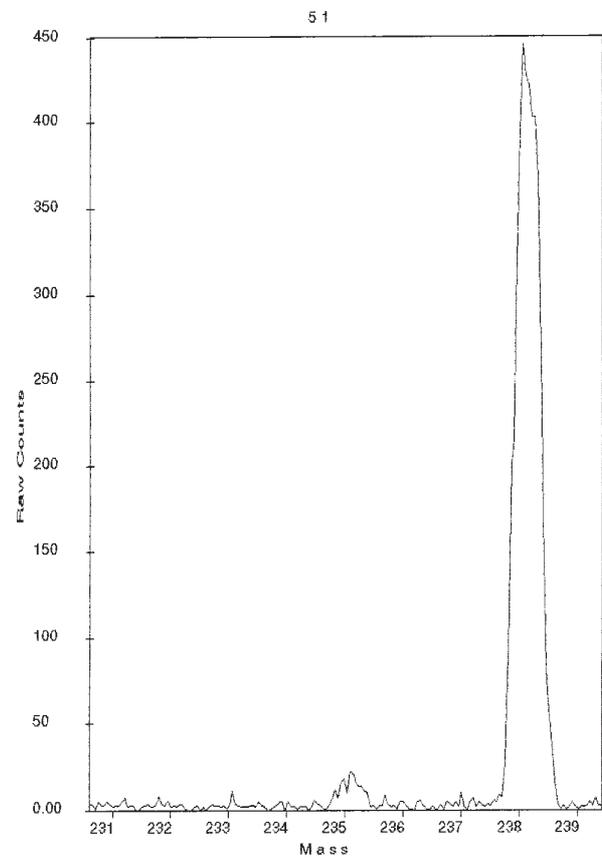


Figure 10. 38 pg particle of 3% enriched uranium.

4 Conclusions

The developed track-etch method for picking up U-particles from swipe samples has been proved to work out. The method could anyway be further developed for better prediction of the size of the particles according to their track-etch prints. Practice is needed also to differentiate enriched uranium particles from natural uranium particles.

The particles in the IAEA samples were very small ($<1\mu\text{m}$) and unfortunately highly enriched

particles were not among the picked up particles due to limited time for sample handling.

The analysis of the NIST samples proved that the method can be used to separate the enriched U-particles from the natural ones and analyse the $^{235}/^{238}$ uranium isotope ratio supposing that the minimum particle size is $4\mu\text{m}$ for natural uranium particle.

References

1. Lipponen M, Lehto S. Development of a track-etch method for extracting uranium containing particles from swipes. Development of a SIMS method for isotopic analysis of uranium containing particles. Report on Task FIN A 1318 of the Finnish Support Programme to IAEA Safeguards. STUK-YTO-TR 188, STUK Finland, July 2002, 10+12p.
2. Myers B. Personal communication, Schafer Vallecitos Laboratory, California, USA

SIMS ANALYSIS OF URANIUM CONTAINING PARTICLES

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Abstract

A SIMS method developed at VTT for uranium containing particles has been applied to characterise quality control samples of the International Atomic Energy Agency (IAEA) as well as two samples of the 2001 round robin exercise organised by the Institute for Transuranium Elements (ITU) and the IAEA. The IAEA control samples were scanned to find uranium containing particles. Most particles were very small ($< 1 \mu\text{m}$) and were sputtered off before they could be analysed. Only few were big enough for isotopic analysis which yielded natural $n(^{235}\text{U})/n(^{238}\text{U})$ ratios. No enriched particles were found in any of the samples even

though they were known to be present, demonstrating inadequate efficiency of sample preparation and manual search in a limited time. The $n(^{235}\text{U})/n(^{238}\text{U})$ measured for particles in the round robin samples are in good agreement with known values (2–3% bias). Secondary ion image cross sections gave apparent particle sizes comparable to reference values. To improve the sensitivity of the method for analysis of the very small particles, oxygen bleeding was employed but no enhancing effect was observed, probably because uranium particles tend to be oxides.

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1 Introduction

The SIMS method developed at VTT for measuring the $n(^{235}\text{U})/n(^{238}\text{U})$ in uranium containing particles [1] has now been applied to the round robin samples of the Institute for Transuranium Elements (ITU) and the International Atomic Energy Agency (IAEA). Also quality control samples of IAEA of the 8250-series with particles of known composition on a cotton swipe were analysed to test the method.

Due to better sensitivity it is more common to

use oxygen primary bombardment for the uranium analysis than gallium used at VTT. Even though large particles and highly enriched particles can be analysed fairly easily, the sensitivity of the method should be improved to allow for a more reliable isotopic analysis of small particles with low enrichment. Therefore, the possible enhancement of secondary ion yields by oxygen flooding was studied.

2 Experimental

2.1 SIMS measurement parameters and data treatment

The Ga⁺ ion source of the VG IX70S double focusing magnet sector instrument was operated with an energy of 22 keV giving a bombardment energy of 16 keV. The primary ion current was 500 pA as measured with a Faraday cup in sample position. The secondary ion currents were detected with a Channeltron operated in ion counting mode. Due to small size of particles, the energy slit was set to 180 eV (open). The resolution ($m/\Delta m$) at mass 238 was set to 200. An offset of 40 eV was used when possible. The vacuum in the sample chamber during analysis was typically $3 \cdot 10^{-7}$ Pa.

The secondary ion images were recorded while rastering the primary beam over the selected area using a 30 s/60 s frame time for the selected field. The lateral scale was calibrated with a copper grid of 1500 mesh and 5 μm wire width. Isotopic analysis of a selected particle was performed in depth profiling mode. The rastered area for individual particle analysis was approximately 13 μm \times 13 μm , and the analysed area was restricted to cover the area of the chosen particle by electronic gating (20, 10 or 5%). The ion currents of ²³⁵U and ²³⁸U were sequentially measured for 1 s with a 300 ms delay between channels and were recorded until the particle was almost consumed.

The isotope ratios were calculated using the intensities measured during one cycle. The isotope ratio in an individual particle is then the average

of cycle ratios. The isotope ratio given for a sample is the average of ratios determined in at least eight particles. The uncertainty on sample values is the standard deviation of the ratios of individual particles. This describes the repeatability of measurement (precision under repeatability conditions). All uncertainties are given as 1 s values and should be multiplied by a factor of 2 to reach the 95% probability level. Dead time corrections were not applied, nor were the data corrected for channel measuring time.

NBS U200 uranium oxide powder deposited on a gunshot residue stub (Tri-tech Inc.) and IAEA SR-54 on adhesive carbon disk (Agar Scientific Ltd.) were used as monitor samples.

2.2 Sample preparation

The IAEA control swipe samples were prepared in two ways. Eight parts of the swipes were cut to smaller pieces and ultrasonerated for 15 minutes in ethanol to extract the particles. 400 μL portions were pipetted on carbon sheet discs of 10 mm diameter mounted on 12.5 mm diameter (0.5") aluminium SEM specimen pin stubs. One sample was prepared on a carbon planchet by depositing 400 μL of the ultrasonerated aliquot. Eight of control swipes were also ashed at 800 °C and the residue was dispersed into ethanol. 50 μL of the dispersion was then pipetted on a carbon sheet disc.

3 Results

3.1 Round robin samples

The two round robin samples containing uranium oxide particles were analysed for particle size (imaging) and the $n(^{235}\text{U})/n(^{238}\text{U})$. In the previous study[1], where the SIMS instrument sensitivity parameters, relevant to the detection of efficiency for small uranium oxide particles were to be determined, the data obtained for U500 K was inconsistent with the given information on the sample. The U500 K was reanalysed at ITU and then again at VTT. The new results of VTT show that the average diameter of the particles is 1.2 μm ($n=21$)

(Figure 1) whereas according to scanning electron microscopy analysis at ITU the majority of particles were between 1 and 1.5 μm . Also the particles of sample C8 were smaller than estimated in the previous study, now giving an average of 1.9 μm ($n=15$) (Figure 2). Average diameter calculated for sample C8 using the mean volumes given in the round robin evaluation report was 2.5 μm . The problem earlier was attributed to bad focusing of the ion gun that after realignment was solved. A clear reason for the high sensitivity of the previous measurements could not be found.

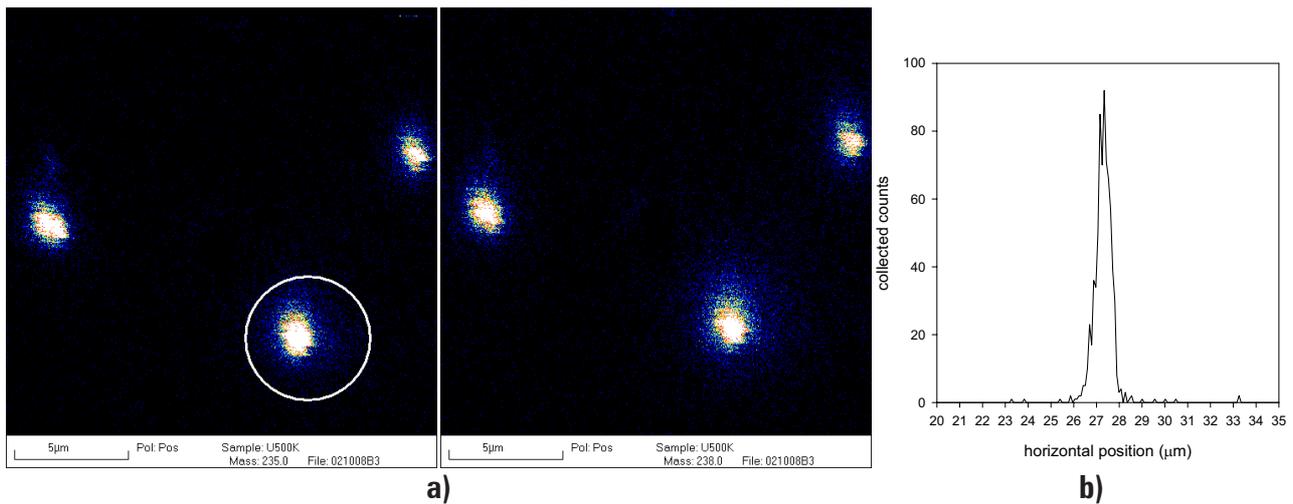


Figure 1. a) $^{235}\text{U}^+$ and $^{238}\text{U}^+$ secondary ion images of uranium oxide particles in a round robin sample U500 K. **b)** Cross section analysis of the particle indicated.

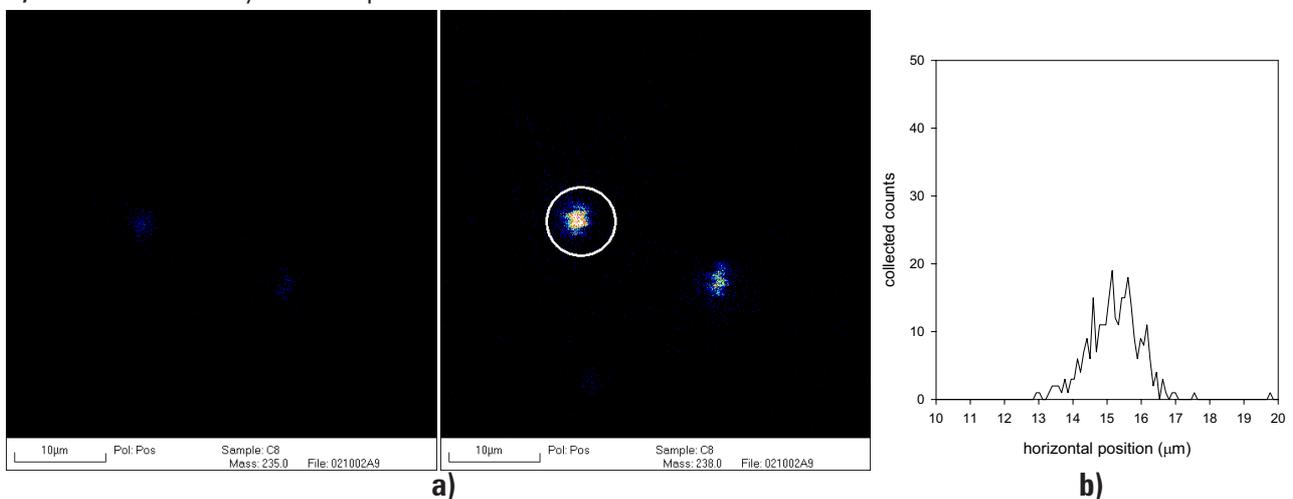


Figure 2. a) $^{235}\text{U}^+$ and $^{238}\text{U}^+$ secondary ion images of uranium oxide particles in a round robin sample C8. **b)** Cross section analysis of the particle indicated.

Table I. Isotope ratios $n(^{235}\text{U})/n(^{238}\text{U})$ in particles of analysed samples. Uncertainties are 1 s and given in the brackets applying to the last two digits.

	C8	U500 K	NBS U200	Nat U_3O_8 (SR-54)
reference value	0.038 42 (3.7 w%)	0.999 70 (71)* RSD 0.0007	0.251 26 (13)* RSD 0.0005	0.007 2 0.007 23 (20) **
SIMS	0.039 3 (16) RSD 0.040	1.028 (17) RSD 0.016	0.256 5 (54) RSD 0.021	0.007 67 (37) RSD 0.048
SIMS bias	2.3 %	2.8 %	2.1 %	6.5 %
bias/u	0.8 %	0.9 %	0.7 %	2.2 %

* certified value by TIMS

** measured with ICP-MS at VTT; 1s uncertainty

The measured isotope ratios are given in Table I. In accordance to earlier measurements, the monitor samples have a positive bias of 2–7%. The ratios determined for the round robin samples deviate by 2–3% of the known values. 1s uncertainties are below 5% for all samples.

3.2 IAEA quality control samples

Samples prepared from IAEA control swipes were scanned with SIMS to find the uranium containing particles. Track-etch analysis of the control

samples showed plenty of tracks but originating from small particles of diameters under 1 μm . This observation is in good agreement with the SIMS results. On all samples uranium was found but apparently the particles were too small to be detected as particles (< 1 μm) and were consumed while scanning with the ion beam. Of each control sample a couple of micron size particles were found, though (Figures 3 and 4). Their $^{235}\text{U}^+$ ion current was barely detectable while the $^{238}\text{U}^+$ signal was 130...17000 s^{-1} meaning that all found

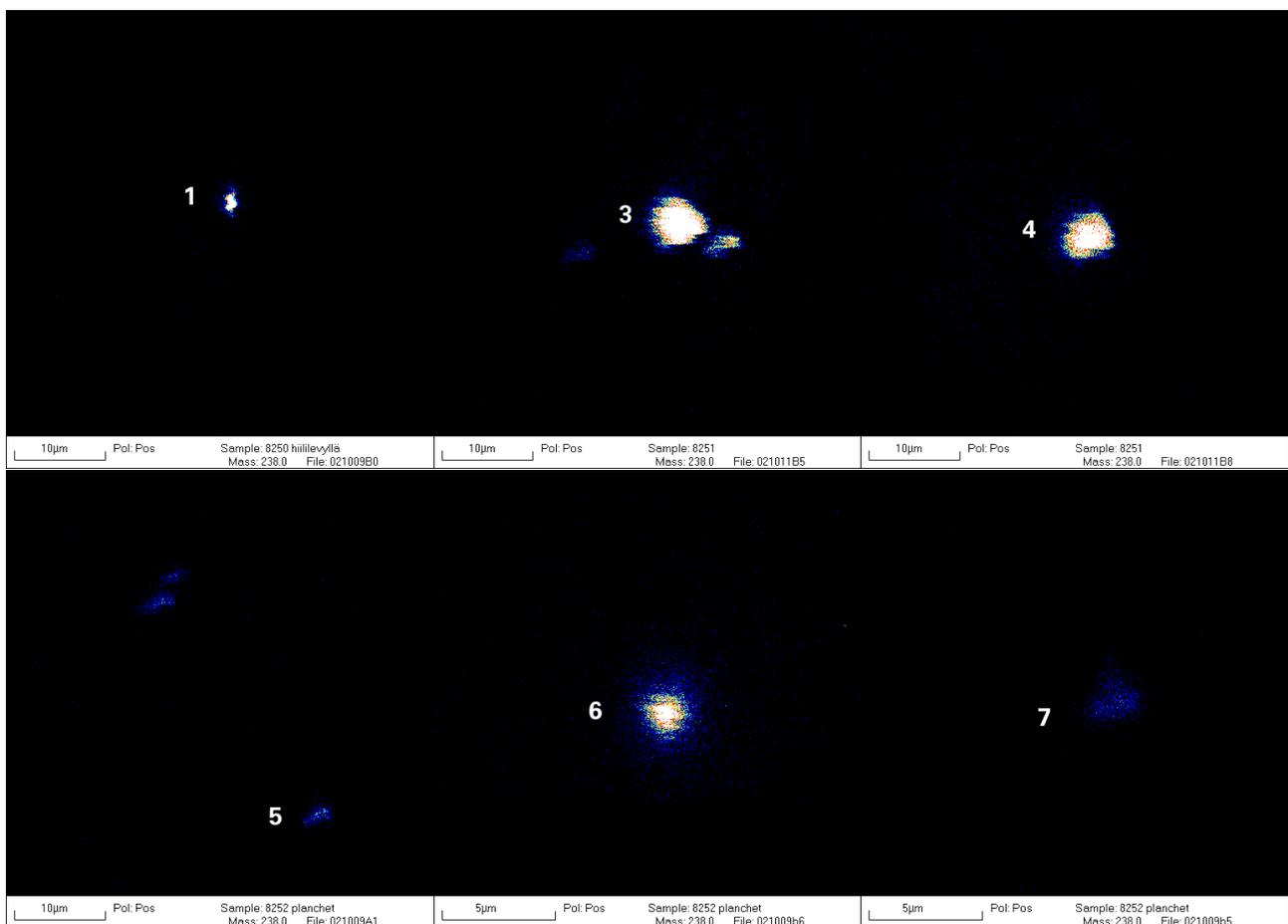
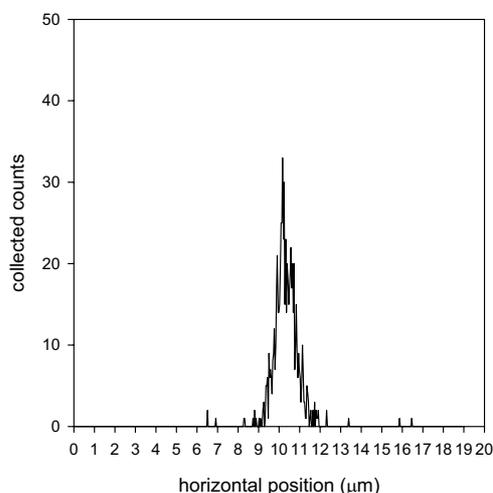


Figure 3. $^{238}\text{U}^+$ secondary ion images of uranium containing particles found in IAEA control samples.

Table II. Isotope ratios $n(^{235}\text{U})/n(^{238}\text{U})$ in particles of IAEA control samples. Uncertainties are 1s and given in the brackets applying to the last two digits.

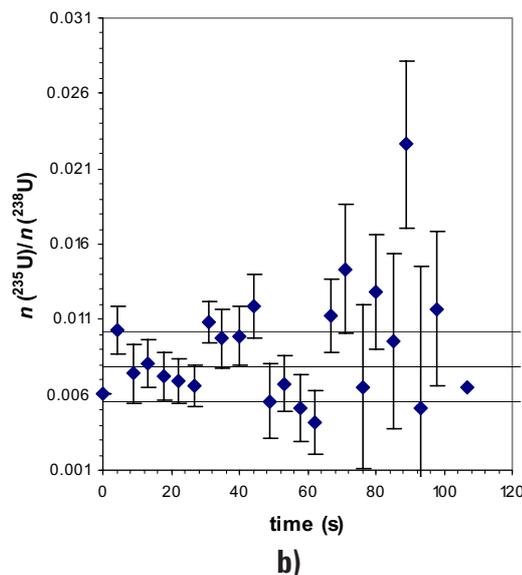
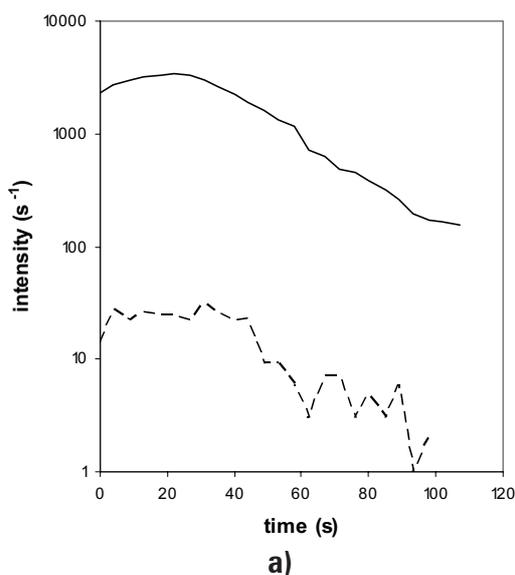
sample	particle no. in Figure 3	$n(^{235}\text{U})/n(^{238}\text{U})$	apparent particle size (μm)	maximum $^{238}\text{U}^+$ intensity (s^{-1})	no. of data points for isotope ratio determination
8250 NU*	1	0.007 9 (23) RSD 0.29	1	3000	14
		0.011 8 (43) RSD 0.36	<1	130	3
8251 NU+LEU*	3	0.007 13 (79) RSD 0.11	3.5	17000	46
		0.007 9 (10) RSD 0.13	3.5	15000	47
8252 NU+LEU+HEU*	5	0.010 5 (46) RSD 0.44	1.5	400	9
		0.008 7 (38) RSD 0.44	1.5	900	9

* NU—natural isotopic composition, LEU—low enrichment of ^{235}U , HEU—high enrichment of ^{235}U (>20%) (IAEA Consultants' Group Meeting in 1998)

**Figure 4.** Cross section analysis of a particle in sample 8252 (no. 6 in Figure 3).

particles were of natural isotopic composition (Figure 5 and Table II). No enriched particles were found in any of the samples even though they were known to be present, demonstrating inadequate efficiency of sample preparation and the manual SIMS search in a limited time. Not all the subsamples were scanned and those that were analysed were not scanned thoroughly, the work being limited by the available time and lack of automated scanning system.

In addition to samples prepared for SIMS, analysis of a particle extracted from a track-etch plate was attempted. The measurement was hindered by the collodion layer covering the particle that could not be removed.

**Figure 5.** a) $^{235}\text{U}^+$ (dashed line) and $^{238}\text{U}^+$ (solid line) secondary ion intensities vs. sputtering time in a particle of 8250 and b) $n(^{235}\text{U})/n(^{238}\text{U})$ vs. sputtering time. The uncertainties on individual points are based on Poisson statistics. The solid lines indicate the average and 1s spread of the points included in ratio calculation (0–40 s).

3.3 Oxygen flooding

Oxygen flooding has been successfully used for example to stabilise the ion signals of the outer layers of silicon samples where the presence of an oxide layer gives rise to a significant change in sensitivity of many of the impurity metals measured. Therefore, bringing oxygen to the surface of a uranium containing particle sample while using the gallium ion source for actual analysis may enhance the sensitivity. To test this the round robin sample SRR C8 was analysed with and without oxygen flooding. The ion current of $^{238}\text{U}^+$ in a particle of SRR C8 was measured at first at normal operating pressure of $3 \cdot 10^{-7}$ Pa and the measurement was continued at an elevated oxygen pressure of $5 \cdot 10^{-4}$ Pa. No change was observed (Figure 6).

It is not surprising that no enhancement effect was observed in the case of an uranium oxide particle. It is felt however, that in the case of unknown samples flushing the sample surface with oxygen before analysis may be advantageous if uranium is not in oxide form. Additional isobaric

interferences, charging effects or damage of the substrate surface were not observed.

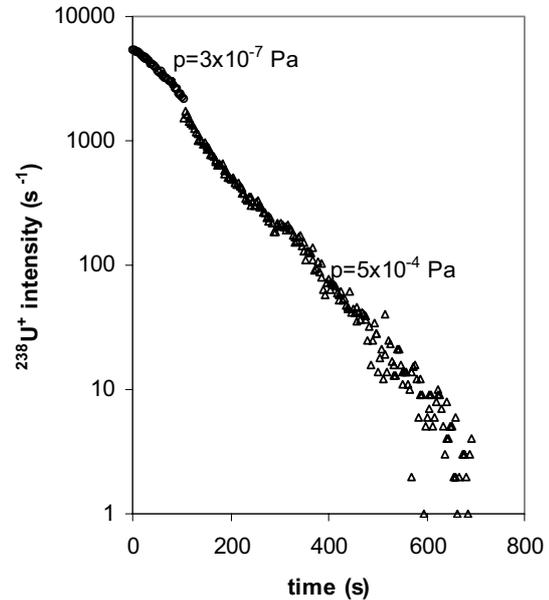


Figure 6. $^{238}\text{U}^+$ intensity measured for a particle of SRR C8 under primary ion bombardment first without (o) and then with oxygen flooding (Δ).

4 Conclusions

The analysis of round robin samples and the IAEA control samples has shown that 1 μm particles containing uranium can be detected and the $n(^{235}\text{U})/n(^{238}\text{U})$ exceeding 1% enrichment reliably determined by using the SIMS method of VTT. The $n(^{235}\text{U})/n(^{238}\text{U})$ measured for particles in the round robin samples are in good agreement with known values (2–3% bias) and the secondary ion image cross sections gave apparent particle sizes comparable to reference values determined by scanning electron microscopy. Particles containing natural uranium were found in the IAEA quality control samples but due to inadequate efficiency of sample preparation and manual search in a limited

time no enriched particles could be found even though they were known to be present. The efficiency of analysis of enriched particles could be improved by combining the track-etch method and SIMS, if collodion was dissolved and the particle revealed from under.

To improve the sensitivity of the method for analysis of the very small particles, oxygen bleeding was employed but no enhancing effect was observed. Oxygen flooding does not enhance the sensitivity of oxidised particles but did not cause additional interferences either. It is considered a useful precaution to flush sample surfaces with oxygen before analysis.

Reference

1. Lipponen M, Lehto S. Development of a track-etch method for extracting uranium containing particles from swipes. Development of a SIMS method for isotopic analysis of uranium containing particles. Report on Task FIN A 1318 of the Finnish Support Programme to IAEA Safeguards. STUK-YTO-TR 188, STUK Finland, July 2002, 10+12p.