

DEVELOPMENT OF A TRACK-ETCH METHOD FOR EXTRACTING URANIUM CONTAINING PARTICLES FROM SWIPES

Maija Lipponen

DEVELOPMENT OF A SIMS METHOD FOR ISOTOPIC ANALYSIS OF URANIUM CONTAINING PARTICLES

Sari Lehto

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Abstract

The first part of the report describes the development of a track-etch method for identification of uranium containing particles extracted from swipe samples. Uranium oxide spiked samples were ashed and the residue was collected in a Collodion solution. The mixture was spread on Makrofol solid state nuclear detectors which were irradiated with neutrons in the TRIGA Mk II reactor in Otaniemi. The etched detectors were examined under a polarising microscope to locate the fission tracks and the uranium containing particles in the Collodion film. Picking of the particles was tried out by dissolving the Collodion film surrounding an identified particle with acetone and using a micro injector to extract it and to place it in a vial for subsequent isotopic analysis by inductively coupled plasma mass spectrometry (ICP-MS).

The second part of the report describes a secondary ion mass spectrometric (SIMS) method for measuring the $n(^{235}\text{U})/n(^{238}\text{U})$ in uranium containing particles with the VG IX70S secondary ion mass spectrometer at VTT. The method was validated with four of the NIST uranium oxide Standard Reference Materials having nominal $n(^{235}\text{U})/n(^{238}\text{U})$ of 0.005, 0.03, 0.25 and 1. In addition, the $n(^{235}\text{U})/n(^{238}\text{U})$ in the IAEA SR54 and in a depleted uranium oxide powder from STUK were determined and compared to values measured by ICP-MS. The accuracy of the measured isotope ratios was 2–5% and the repeatability of the ratios in particles sized 3–10 μm in diameter ranged from 0.01 (RSD) for the 1:1 ratio up to 0.16 (RSD) for the small ratios (0.0072 of $^{\text{Nat}}\text{U}$). Participation in the sensitivity round robin organised by the Institute for Transuranium Elements and the IAEA is also shortly dealt with.

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1 Introduction

Track-etch methods are used to identify uranium containing particles of interest for further isotopic analysis by thermal ionisation mass spectrometry. In general, the procedure consists of extracting particles from swipe material by ultrasoneration, collecting of particles in a Collodion film or similar on a solid state nuclear detector and irradiation with neutrons, followed by examination of etched neutron induced fission tracks on the detector, and locating and picking of particles under a microscope. The most common etchable solid state nuclear detectors are CR-39 (polyallyldiglycol carbonate, $C_{12}H_{18}O_7$), Lexan and Makrofol (bisphenol-A

polycarbonates, $C_{16}H_{14}O_3$), which are insensitive to light charged particles, X-rays and gamma rays. Various ways to prepare the detector and to locate the particles of interest have been described.

The method developed at VTT used Makrofol as detector. Particles were collected in Collodion and the mixture was spread on the detector to form a thin film. Irradiation was carried out in a Triga Mk II reactor in Otaniemi.

Sample preparation was performed by ashing uranium oxide spiked filter papers and cotton cloth.

2 Experimental

Preliminary experiments on the sensitivity of CR39 and Makrofol detectors showed that the U-particles caused clearly noticeable marks in both materials. The tracks in Makrofol were considerably bigger and more evident. Therefore, Makrofol was chosen to be used as the track-etch detector.

The test samples were swipe materials spiked with uranium oxide powder.

2.1 Sample preparation

Two materials were used to simulate swipes: ashless filter paper and 5 cm × 5 cm pieces of cotton cloth.

Spiked samples were prepared from powders of the IAEA SR-54 (^{Nat}U) and U030 and U200 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. An aliquot of the sample powder suspended in ethanol was pipetted on the swipe.

2.1.1 Ashing of swipes

The spiked swipes were placed into quartz crucibles and heated up in three hours to 800°C in a Nabertherm furnace. The sample was kept at 800°C for four hours before cooling down. The filter paper samples left no visible traces of residue but small white bits, probably due to TiO₂ used as pigment, could be seen at the bottom of the bowls where the cotton cloth was ashed.

2.1.2 Preparation of track-etch samples

Two types of Collodion solutions were prepared from flexible Collodion (Acros Organics), one for collecting the ashing residue and one for preparation of a thin film on the nuclear detector sheet.

Collodion I	160 mL flexible Collodion 56 mL diethylether 24 mL ethanol
Collodion II	30 mL Collodion I 70 mL ethanol

The ashing residue was removed from the bowl using Collodion I. The sample was ultrasonerated for 5 min in 1 mL of Collodion II and immediately after that the mixture was pipetted on 2.4 cm × 4.0 cm Makrofol detector sheets. On each sheet an area of 1 cm × 2 cm was covered. After the first layer had dried up, half a milliliter of Collodion I was spread on each Makrofol sheet on an area about half a centimeter larger than the first film. This was repeated three more times to form a film thick enough to be removed from the Makrofol after the irradiation.

2.1.3 Irradiation and chemical etching

The Makrofol covered with the Collodion films were wrapped in plastic foil and inserted in irradiation capsules, two in each.

The capsules were irradiated in the thermal flux of $1.2 \cdot 10^{-12} \text{ cm}^{-2} \text{ s}^{-1}$ in the research reactor Triga Mk II (Otaniemi, Espoo) for one hour.

To better reveal the neutron induced fission tracks in the Makrofol, the detector sheets were etched in 6.5 M KOH for 20 min at 60°C in a thermostatic water bath. Before chemical etching, the Collodion film was removed with a razor knife. To locate the particles the Collodion film has to be replaced later exactly in its former position on the Makrofol. Therefore, placing marks were made on the Makrofol with a special tool (Figures 1 and 2) before removing the Collodion film. The marks



Figure 1. Marking tool.

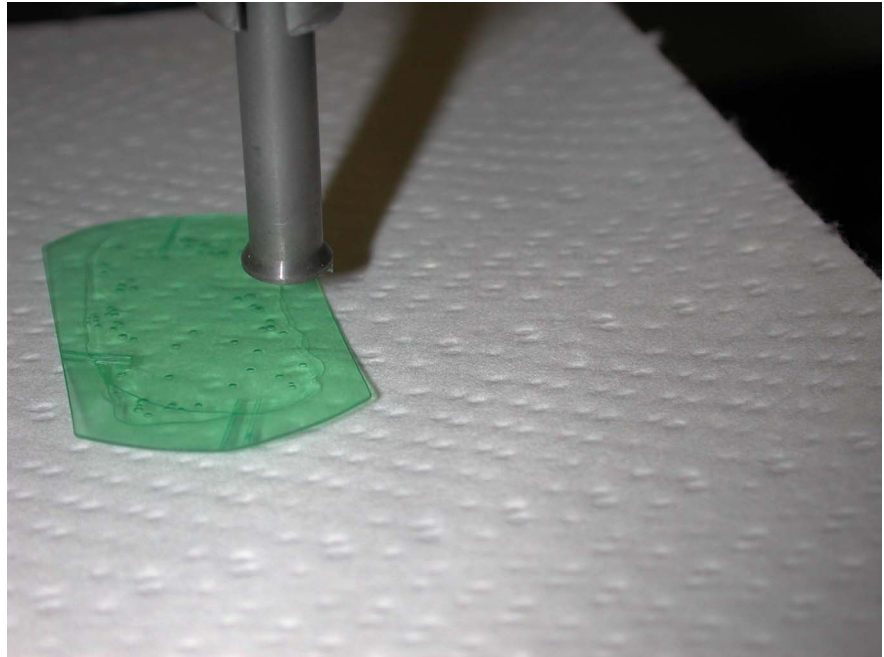


Figure 2. Marking the Collodion film on Makrofol.

were made outside the area, where the particles were expected to be.

After etching the detectors were rinsed carefully with water and left to dry. In the process of irradiation and etching the Makrofol sheets become opaque in colour.

2.1.4 Preparation of slide samples for microscopic inspection

The etched Makrofol were glued onto microscope glass slides with Loctite's Glass Attak and the identification code was written on the slide (Figure 4). The Makrofol sheet was pressed under a weight because it must be flat for the inspection with a microscope. The Collodion film may be adjusted in place at this time or after the inspection of the fission tracks.

2.2 The microscope

For the inspection of etched detectors and picking the particles, a polarising microscope NIKON ECLIPSE E600POL equipped with micromanipulators was used (Figures 5–7).

The microscope has a revolver type objective changer and five objectives. Manipulation is possible with the magnifications of 40, 100, 200 and 500. The particles and tracks can be examined with a magnification of 1000. A high precision rotating stage helps the examination of the sample.



Figure 3. Irradiated Makrofol detectors before etching.



Figure 4. Etched Makrofol glued on microscope slides.

For precise micromanipulation of the particles hydraulic fine manipulators with two micro injectors are connected to the microscope. The operating range of manipulators by joystick is at maximum a 2 mm-diameter circle on the X–Y plane and the minimum graduated scale is 2.5 μm . The microin-

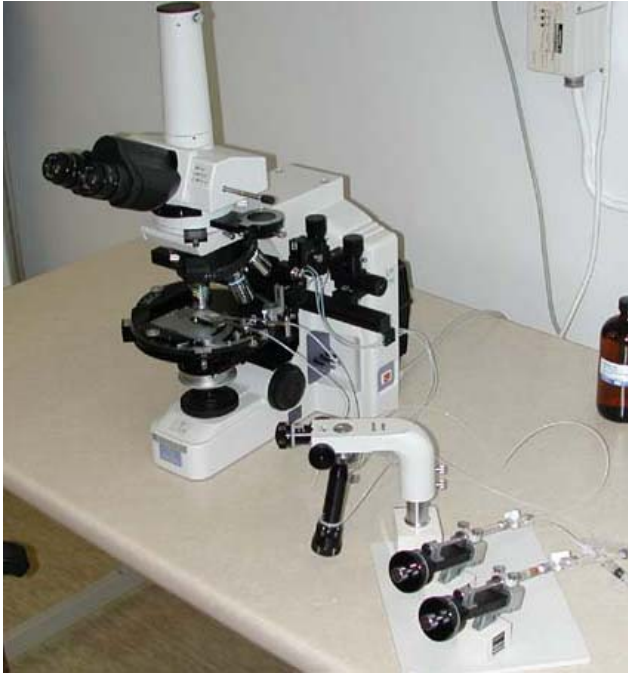


Figure 5. The polarising microscope NIKON ECLIPSE E600POL with micromanipulators.

jectors are NIKON/NARISHIGE IM-16. A minimum graduation of the control knob is 1 μm and one rotation of the control knob is 250 μm . The microsyringe capacity is 800 μL .

The microscope is also equipped with a Nikon COOLPIX 990 digital camera which is connected to a colour monitor to view working with the microscope, and to a PC to save images for further handling.



Figure 6. Microinjectors.



Figure 7. The colour monitor helps working with the microscope.

2.3 Locating uranium particles

The irradiated and etched Makrofol are first examined with the microscope using the 100× magnification. Under this magnification the fission tracks can be seen and the sheet can be quickly scanned. After preliminary examination single fission tracks are looked for first with the 200× and then with the 500× magnification. The coordinates in the rotation disk table of the microscope with 500× magnification are written down so that the track can be found easily later. Besides, the switch-over to 1000× magnification is sometimes difficult and the track might get lost.

When all interesting tracks on the Makrofol detector have been found the Collodion film is replaced on it. With a magnification of 40 the placing marks both on the Makrofol and the Collodion film are seen in the monitor. These are set on each other and all other marks on the sample are checked as well. For example, in Figure 8 the marks in Collodion and Makrofol are upon each other. The end of the marks is seen as arch-like lines in the Makrofol, which is a harder material. In Figure 9 the lines are seen clearly.

When the adjustment is done a drop of Collodion I is pipetted onto each corner of the Collodion-Makrofol. It is allowed to dry for one minute and then the microscope slide is set under a weight to press the Collodion sheet flat into the Makrofol. The Collodion sheet is very thin and light and would easily move off its place if the microscopic slide were moved earlier.

The sample slide is placed back onto the microscope table and the coordinates of the fission tracks are searched under 500× magnification. Focusing very slowly from the level of the Makrofol to the Collodion surface the particle can be found. It is probably somewhat apart from the fission track since the marks on the Collodion film and Makrofol do not exactly meet due to shifting

between the magnifications of 40 and 500 for placing and inspection of particles, respectively.

Some etched fission tracks and the respective particles are presented in Figures 10 and 11.

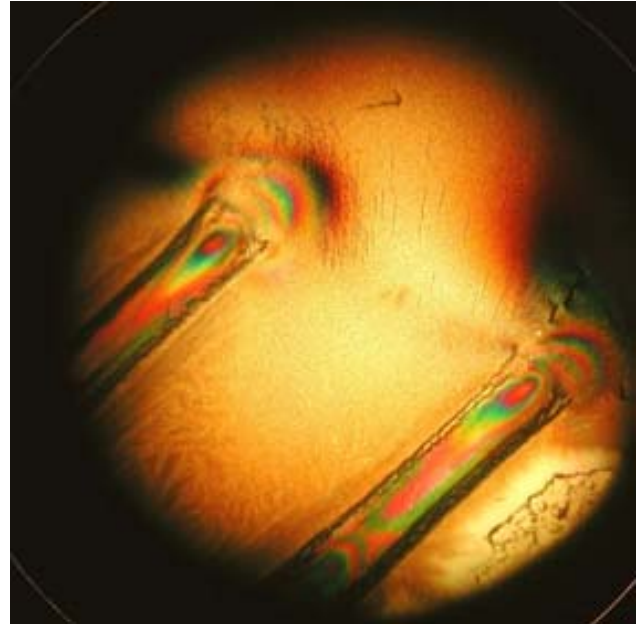


Figure 8. Two marking prints, 40× magnification.

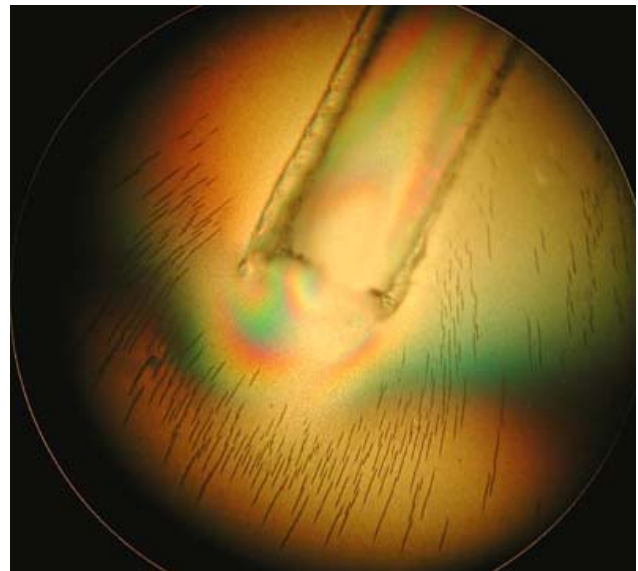


Figure 9. Marking print, 100× magnification.

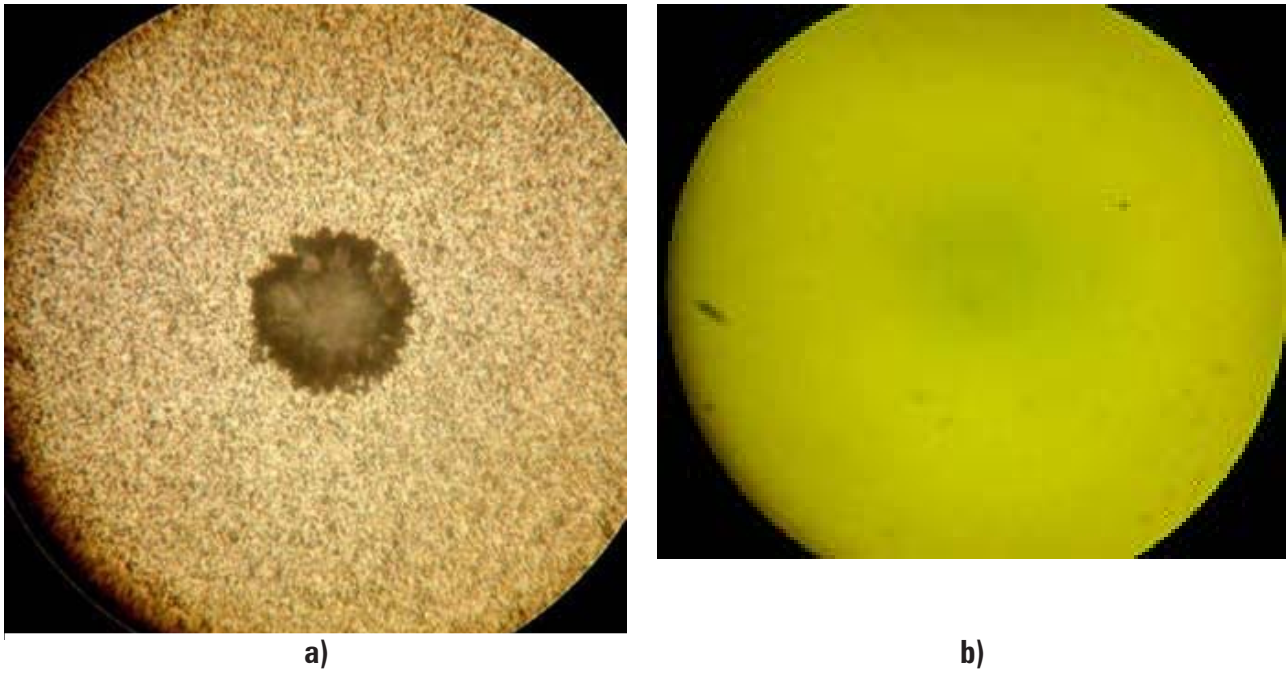


Figure 10. The etched fission track (a) and the particle (b) of a NBS U030 sample under 500× magnification.

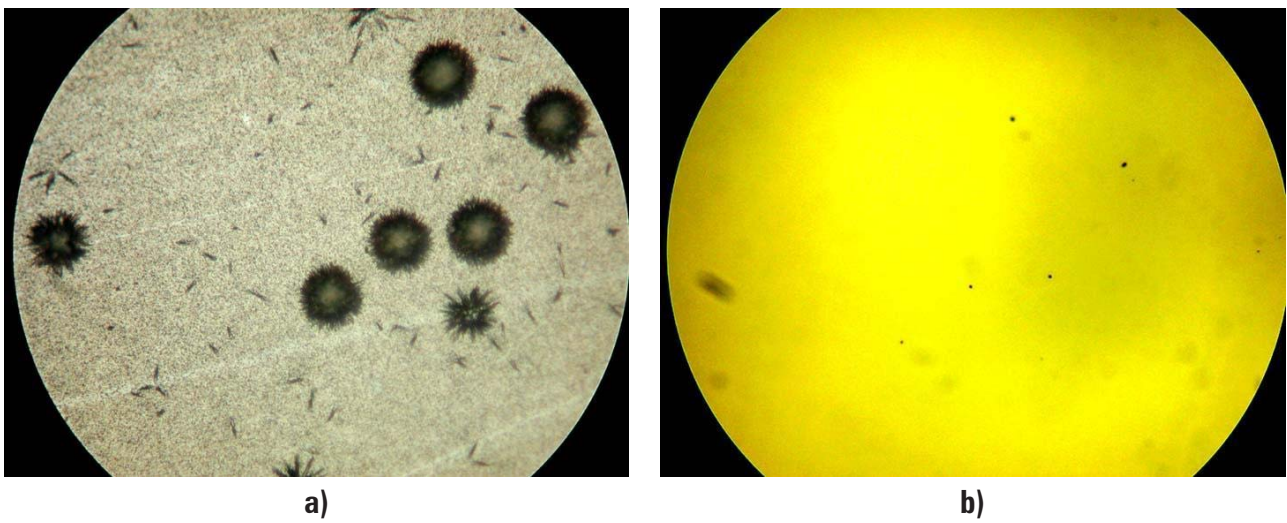


Figure 11. Fission tracks (a) and particles (b) of a NBS U030 sample under 500× magnification.

2.4 Picking the particle

Once an interesting particle has been found, it would be picked for further treatment. Picking the particle was foreseen to be effected by dissolving the Collodion films around the particle and picking it with a glass capillary to be transferred to a digestion vial. Therefore, one of the glass capillaries of the micromanipulator has been filled with acetone which would be applied to soften the Collodion film. The other capillary would be used to suck the particle off the film. The microinjectors have been tested with transfer tips with an inner diameter of 0.015 mm, see Figure 12, where the tip is imaged under magnification 200 \times .

So far, attempts to pick a particle this way have not been succesfull for many reasons. Learning to move the capillaries under the microscope still needs more practice. The capillaries must be han-

dled very gently because they break down easily. The microscope must be focused to the picking capillary, which must lie under the capillary with acetone. More practise will surely give the desired result.



Figure 12. The tip of a capillary under 200 \times magnification.

3 Future prospects

Training on particle picking will continue. First some capillaries with larger tip will be used and later the micro capillaries for picking the individual particles from the sample film. If this will not for some reason succeed other ways of picking the particles will be tested.

After refining the method of particle picking transfer of particles into a vial for digestion and ICP-MS analysis will be tried out. The whole procedure will be tested with control swipes from IAEA.

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1 Introduction

Today secondary ion mass spectrometry (SIMS) is considered a routine technique for nuclear safeguards analysis. It is mainly used to determine the isotopic composition of uranium in uranium containing particles but also to solve other nuclear forensic analysis problems¹⁻⁶.

Most of the laboratories involved in the International Atomic Energy Agency (IAEA) Network of Analytical Laboratories (NWAL) perform the measurements in much the same way. A Cameca instrument is used, often equipped with a Peak-Search analysis program of Charles and Evans, or a similar in-house software. Oxygen primary ions are used, the data is acquired in microscope mode as ion images with a resistive anode encoder (RAE), or in microprobe mode when a focussed microbeam is available. Particles down to one micron size can be analysed. Typically, an accuracy of < 1% and a precision at 10⁻² RSD level on the

measured isotope ratios are reached.

This report describes a method for measuring the $n(^{235}\text{U})/n(^{238}\text{U})$ with the VG IX70S secondary ion mass spectrometer at VTT. The method employs gallium primary ion bombardment and the instrument is operated in microprobe mode. The method was validated with four of the NIST Standard Reference Materials uranium oxide series having nominal $n(^{235}\text{U})/n(^{238}\text{U})$ of 0.005, 0.03, 0.25 and 1. In addition, the $n(^{235}\text{U})/n(^{238}\text{U})$ in the IAEA SR54 and in a depleted uranium oxide powder from STUK were determined and compared to values measured by inductively coupled plasma mass spectrometry (ICP-MS).

Participation in the sensitivity round robin organised by the Institute for Transuranium Elements (ITU) and the IAEA is also shortly dealt with.

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 6. Rüdener, F., Kuno, Y., Hedberg, P.M., Vogt, S., Kohl, M., Pichlmayer, F., *idem*.

2 Experimental

2.1 Sample preparation

NBS U-series powder samples were ultrasonerated for 1 h in deionised water to break down the clusters of particles. For substrate loading the sample was later resuspended in ethanol and 50 μL portions were pipetted on double sided adhesive carbon discs of 12 mm diameter mounted on 12.5 mm diameter (0.5") aluminium SEM specimen pin stubs, both from Agar Scientific Ltd. A few samples were prepared by collecting particles dispersed on a flat surface directly on the carbon tab. One sample of NBS U200 was deposited on a gunshot residue stub of Tri-tech Inc., provided by D. Simons from NIST.

2.2 Secondary ion mass spectrometry

Measurements were carried out with a VG IX70S double focusing magnet sector instrument. The instrument operates in microprobe mode and is equipped with a duoplasmatron (O_2^+ , Xe^+ , Ar^+), cesium ion gun and a gallium (liquid metal) ion source. The secondary ion currents are detected with a Channeltron operated in ion counting mode. The primary ion current is measured with a Faraday cup in sample position. The data acquisition interface and software were developed and built in co-operation with Technische Universiteit Delft. The vacuum in the sample chamber during analysis is $< 10^{-7}$ Pa.

2.2.1 Measuring parameters

SIMS analysis of uranium containing particles was performed using the gallium ion source which produces a finely focused primary ion beam for imaging (1–3 μm). The ion source was operated with an energy of 22 keV giving a bombardment energy of 16 keV and the ion current was 500 pA. The energy slit was set to 30 eV and resolution ($m/\Delta m$) at mass 238 to 200. An offset of 10 or 40 eV was used.

Typically, the secondary ion images were recorded while rastering the primary beam over an area of 100 $\mu\text{m} \times 100 \mu\text{m}$ using a 60 s frame time for a field. The lateral scale was calibrated with a copper grid of 1500 mesh and 6 μm wire width.

Isotopic analysis of a selected particle was performed in depth profiling mode. The rastered area for individual particle analysis was approximately 25 $\mu\text{m} \times 25 \mu\text{m}$, and the analysed area was restricted to cover the area of the chosen particle by electronic gating (50, 20, 10, 5 or 2 %). The ion currents of ^{235}U and ^{238}U were sequentially measured for 1 s with a 300 ms delay between channels and were recorded for a total time of 300–700 s (70–160 cycles). One example of the resulting 'depth profile' is shown in Figure 1. To detect possible interferences caused mainly by ions formed of the primary ion species (e.g. Ga_3C_2^+ or Ga_3OC^+) also the ion currents at m/z 233 and 234 were monitored.

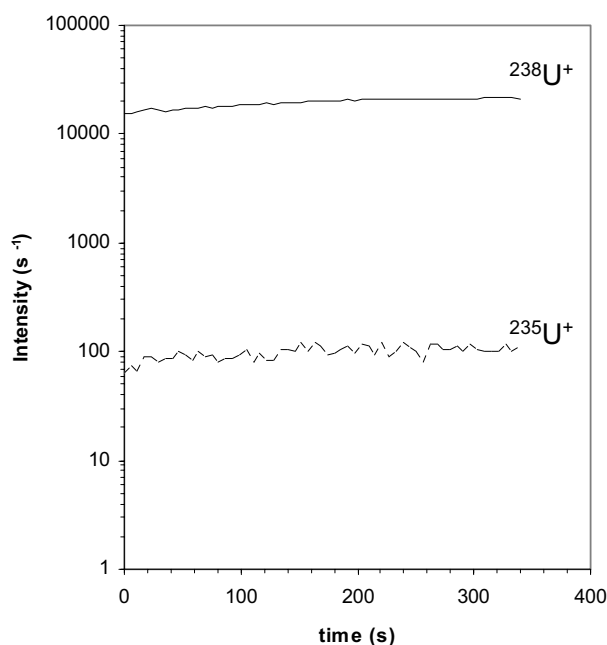


Figure 1. $^{235}\text{U}^+$ (dashed line) and $^{238}\text{U}^+$ (solid line) secondary ion intensities vs. sputtering time in a particle of NBS U005 powder.

Table I. Interferences from Ga containing ion species. Isotope patterns (% I_{max}).

m/z	207	209	211	213	219	220	221	222	223	224	225	226	227	229
Ga_3^+	50.2	100	66.4	14.6										
Ga_3C^+					50.2	0.5	100	1.1	66.4	0.6	14.6	0.2		
Ga_3O^+									50.2		100		66.5	14.8
m/z	231	232	233	234	235	236	237	238	239	240	241	242	243	245
Ga_3C_2^+	50.2	1.1	100	2.2	66.4	1.3	14.6	0.2						
Ga_3CO^+					50.2	0.5	100	1.1	66.5	0.6	14.8	0.2		
Ga_3O_2^+									50.1		100		66.7	14.9

2.2.2 Background contribution from substrate

The mass spectra of the adhesive carbon disc substrate revealed isobaric interferences on the mass range relevant for uranium isotope ratio determination. The isobars are formed of the primary ion gallium and carbon of the substrate. Other possi-

ble interferences would be combinations of gallium, carbon and oxygen.

The isotope patterns of possible gallium, carbon and/or oxygen are collected in Table I. Comparing the measured mass spectra of Figures 2 and 3 with the data of Table I, patterns of Ga_3^+ ,

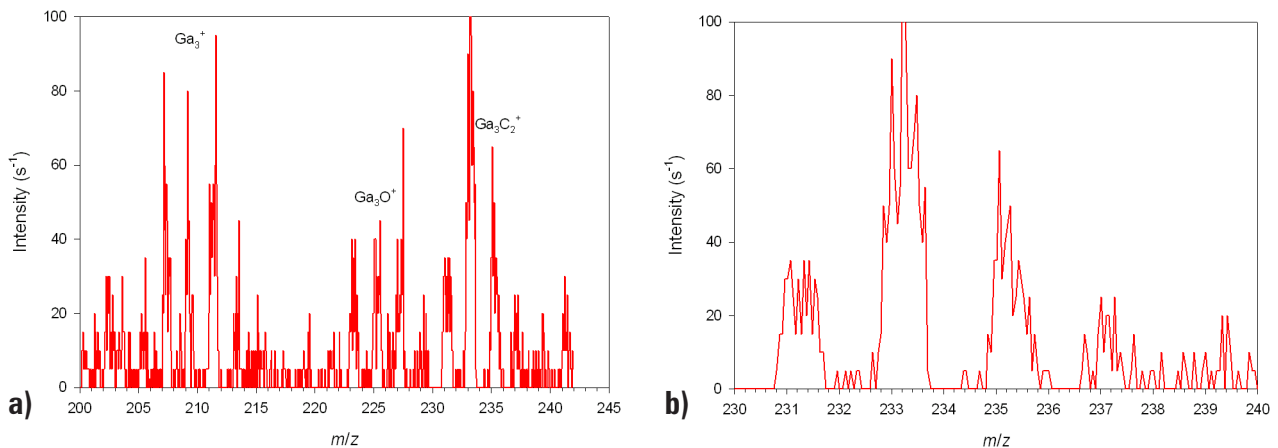


Figure 2. Secondary ion mass spectra of a carbon adhesive disc substrate. a) Mass range 200–245 b) mass range 230–240.

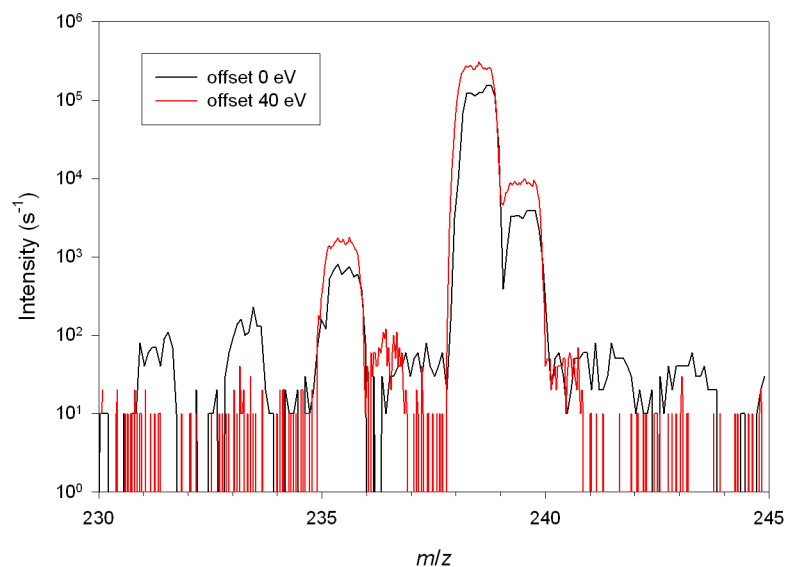


Figure 3. Secondary ion mass spectra of a NBS U005 sample on a carbon adhesive disc substrate with and without offset. Offset of 40 eV suppresses molecular ions of gallium and carbon.

Ga_3O^+ and Ga_3C_2^+ can be identified. Interference on the uranium peaks is most serious on mass 235 where the isobar can be identified to originate from Ga_3C_2^+ species. Applying an offset of 40 eV eliminates the isobar, as is seen in the mass spectrum of a NBS U005 sample in Figure 3, and the effectiveness of the offset can be monitored by including masses 233 and 234 in the measurement scheme. Failure to suppress the molecular interference would mostly disturb determination of low enrichment ratios, or measuring low intensities at a level of a few hundred counts.

2.2.3 Data treatment

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.

Dead time corrections were not applied (see below), nor were the data corrected for channel measuring time.

The data presented in this report carries uncertainties as follows:

- 1) The uncertainty of the measured ratio of each individual particle (see Figure 4) is the standard deviation of the ratios of ^{235}U and ^{238}U ion currents measured during one cycle. The uncertainty of each point on the curve was deduced from Poisson statistics on the measured intensities.
- 2) 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).
- 3) All uncertainties are given as 1s values and should be multiplied by a factor of 2 to reach the 95% probability level.

2.2.4 Dead time

For determination of the dead time of detection system the isotope ratio $n(^{235}\text{U})/n(^{238}\text{U})$ was recorded as a function of intensity I of the major isotope. The counting system was found to respond best to a cumulative model of dead time

$$I_m = I e^{-\tau I} \quad (1)$$

where I_m is the measured intensity, I the true intensity and τ the dead time.

Assuming the true intensity of ^{238}U was rightly obtained from the intensity of ^{235}U by applying the natural isotope ratio in the uranium foil sample, the dead time was determined from the slope of the $\ln R_{\text{measured}} \text{ vs. } I(^{238}\text{U})_{\text{corrected}} - I(^{235}\text{U})$ curve. Fitting the data of measured ^{238}U intensity in the range of 8 000–500 000 s^{-1} , yielded a dead time of 400 ns. To effectively correct for dead time effects on even higher count rates 500 ns should be used as illustrated in Figure 5 where the original and corrected ratio data *vs.* $I(^{238}\text{U})$ are displayed. Since the uranium intensities measured on particles were below 100 000 s^{-1} the dead time correction would not be significant and was in general not applied. Ignoring the effects of dead time, however, can induce an additional 5% increase on the measured isotope ratios and also affects precision. If a correction was applied, the following approximation was used

$$I = I_m / (1 - I_m \tau) \quad (2).$$

The major source of the large dead time has been identified in the rate meter of the detection system.

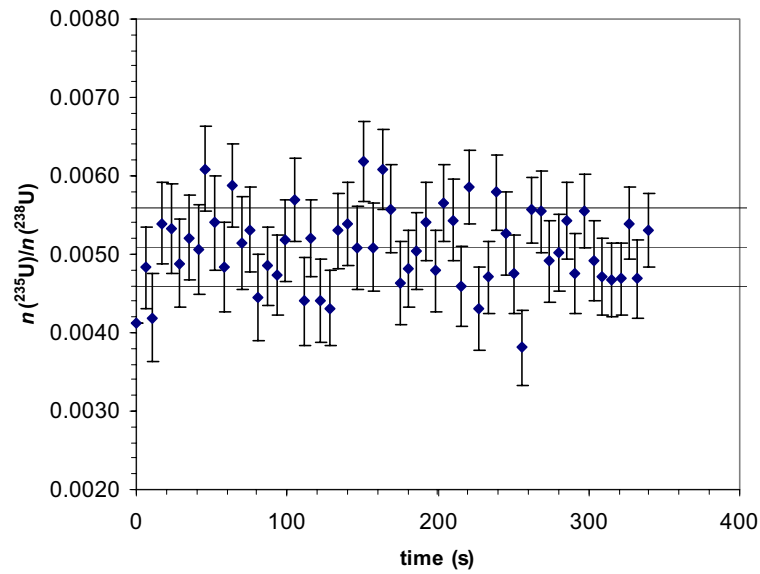


Figure 4. $n(^{235}\text{U})/n(^{238}\text{U})$ vs. sputtering time in a particle of NBS U005 powder. The uncertainties on individual points are based on Poisson statistics. The solid lines indicate the total average and 1s spread.

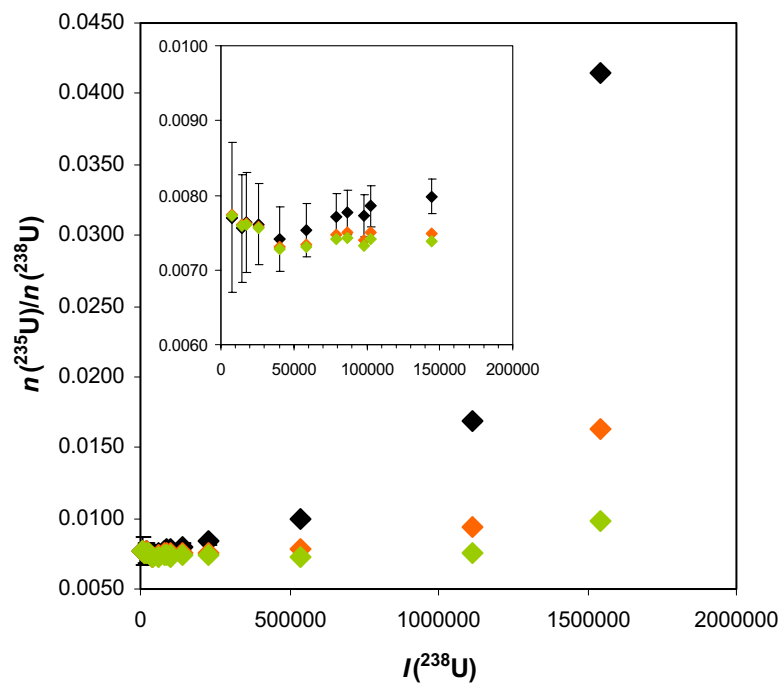


Figure 5. Measured and corrected $n(^{235}\text{U})/n(^{238}\text{U})$ vs. $I(^{238}\text{U})$. (\blacklozenge) $\tau = 0$, (\blacklozenge) $\tau = 400$ ns and (\blacklozenge) $\tau = 500$ ns. Error bars indicate 1s uncertainty.

3 Results

The lateral resolution achieved with the gallium ion gun allows to image uranium oxide particles of 5–10 μm diameter without difficulty. Typical secondary ion maps of $^{235}\text{U}^+$ and $^{238}\text{U}^+$ of Figure 6 show particles smaller than 10 μm in diameter and details of 1–2 μm can be distinguished. The diameter of a particle can be determined from the cross section analysis of image (insert in Figure 6).

The measured $n(^{235}\text{U})/n(^{238}\text{U})$ in four NBS (NIST) U-series reference materials, in IAEA SR54 uranium oxide and in one depleted oxide sample are given in Table II. Comparison with reference values, given in the same Table, shows biases of SIMS results from 2 to 5%, or 0.7–1.7% deviation per mass unit. The mass bias can be caused by fractionation in the instrument (sputtering or mass dependence of SEM detection) or

by background contribution that was not properly corrected for. In the case of 1:1 ratio the measured bias is in accordance with the values reported in literature for this type of mass spectrometer. Since the bias per mass unit is most pronounced for the lower enrichments it is probable that the background caused by Ga primary ions disturbs the measurement of small ion currents. However, the uncertainty of the bias measurement is largest as well, see Figure 7, and the inaccuracy of the results of lower enrichment materials cannot be assigned to background interference only. Also, the background was monitored by measuring 233 and 234 that would reveal interference by Ga containing species, and was found to be negligible.

When analysing real samples other isobars can be present. Monitoring the background of m/z 233

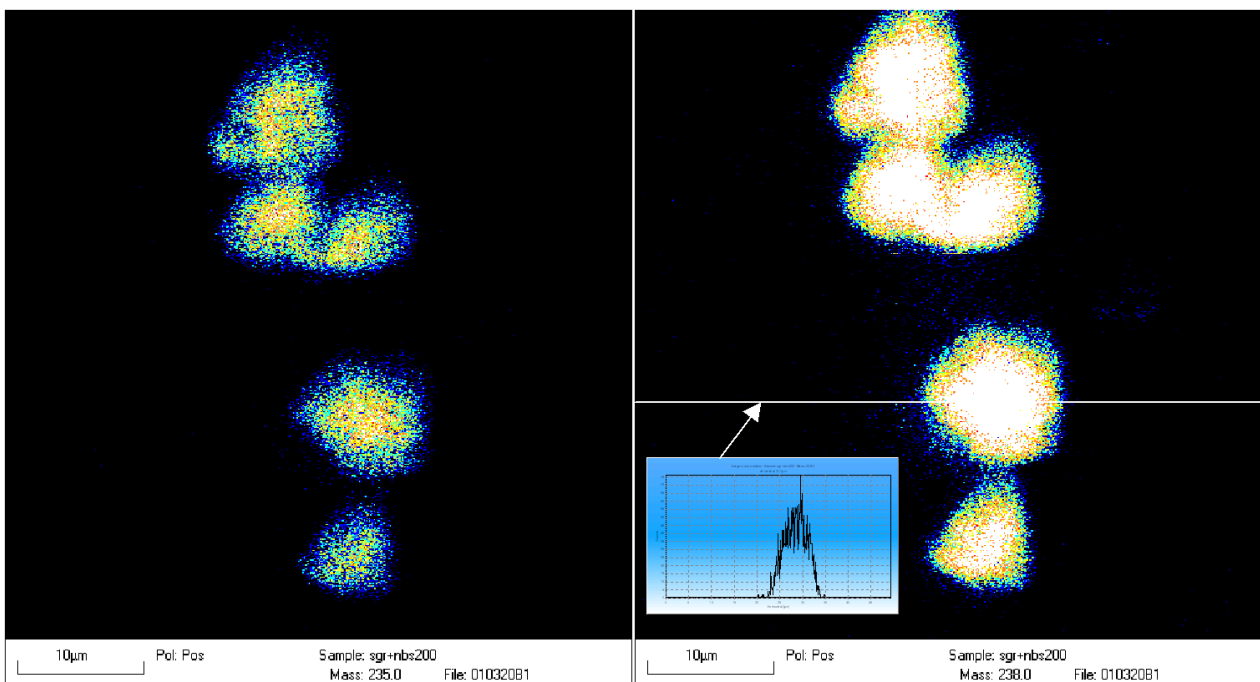


Figure 6. $^{235}\text{U}^+$ and $^{238}\text{U}^+$ secondary ion images of uranium oxide particles in a sample of NBS U200 powder. Insert depicts a cross section analysis of image.

Table II. Isotope ratios $n(^{235}\text{U})/n(^{238}\text{U})$ in particles of NBS U-series standard reference material powders, IAEA SR-54 and an uranium oxide sample from STUK. Uncertainties are 1s and given in the brackets applying to the last two digits.

	NBS U005	NBS U030	NBS U200	NBS U500	NatU_3O_8 (SR-54)	Uranium oxide powder from STUK
certified by TIMS (or*)	0.0049194 (25) RSD 0.0005	0.031430 (16) RSD 0.0005	0.25126 (13) RSD 0.0005	0.99970 (71) RSD 0.0007	0.0072 0.00723 (20)*	0.00399 (18)* RSD 0.045
SIMS	0.00502 (81) RSD 0.16	0.03255 (42) RSD 0.013	0.2582 (14) RSD 0.0053	1.0214 (95) RSD 0.0093	0.00755 (19) RSD 0.025	0.00419 (10) RSD 0.025
SIMS bias	2.0%	3.6%	2.8%	2.2%	4.9%	5.0%
bias/u	0.67%	1.2%	0.93%	0.73%	1.6%	1.7%

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

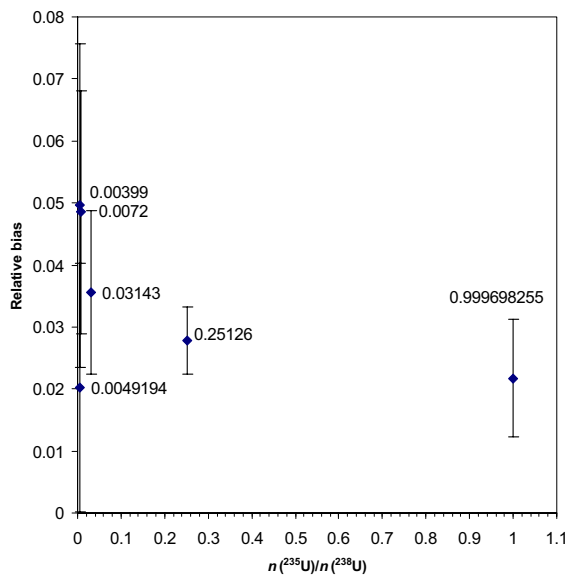


Figure 7. SIMS bias when using an offset of 40 eV and a resolution 300 ($m/\Delta m$). Uncertainty is the standard deviation of biases of ratios of individual particles.

and ^{234}U may not be sufficient to give an indication of an interference in the measurement. This is a more general problem though, and the mass spectrum of a particle showing an unexpected isotope ratio should always be examined more carefully to verify the result.

The repeatability of the measured isotope ratios in particles sized 3–10 μm in diameter ranges from 0.01 (RSD) for the 1:1 ratio up to 0.16 (RSD) for the small ratios (0.0072 of NatU). In the case of low enrichments the precision is mostly limited by counting statistics. Other important components are fluctuation of the primary ion beam, the electronics and the magnet. The repeatabilities obtained are typical for this instrument. The reproducibility of ratios remains to be assessed.

Differences in sample preparation or the type of the adhesive carbon disk did not alter the measured isotope ratios.

4 Participation in a sensitivity round robin study

The laboratory participated in a round robin study organised by ITU and IAEA where the SIMS instrument sensitivity parameters, relevant to the detection of efficiency small uranium oxide particles were to be determined. Practical sensitivity was determined by recording the $^{238}\text{U}^+$ secondary ion current from a U foil. Useful yield was determined by recording the total $^{238}\text{U}^+$ secondary ion intensity of a particle or a cluster of particles until it was fully consumed by sputtering. The particle samples were provided on carbon planchets marked SRR C8 and U500 K.

4.1 Experimental conditions

For the determination of practical sensitivity the $^{238}\text{U}^+$ secondary ion current from a U foil was measured using 1 nA 16 keV Ga^+ primary ion beam. The bombarded area was $94\ \mu\text{m} \times 94\ \mu\text{m}$. For the determination of useful yield the ion current was set to 1–2 nA. Bombarded area was $24\ \mu\text{m} \times 24\ \mu\text{m}$ or $13\ \mu\text{m} \times 13\ \mu\text{m}$ and was further limited to include one particle only by electronic gating. The total ion current was measured in 30 particles in each sample provided. The background signal caused by the carbon planchet was much stronger than what is usually measured in the adhesive tabs. Therefore, the background was deducted from total ion current data.

4.2 Results

As most other laboratories employ a Cameca instrument and oxygen primary bombardment for analysis of uranium, it is very interesting to see how the VTT method compares to others. Based on commonly known differences observed in the sensitivity obtained by using oxygen and gallium primary bombardment, one would expect to find using oxygen bombardment much superior to using gallium.

However, the preliminary evaluation of the

round robin study (December 2001) showed that on the basis of measurements on the uranium foil the sensitivity of the VTT instrument would be approximately five times higher than of the Cameca instruments using oxygen primary bombardment. This is not quite true though, since the operating parameters used at VTT give rise to yield enhancement effects. Changing measuring parameters to eliminate the effects of residual gas deposition on the bombarded surface is restricted by the ion gun operation and detection capability using a SEM. Therefore, the practical sensitivity value does not give a realistic view of the true sensitivity of the instrument, nor should it be compared to the practical sensitivity obtained by the Cameca instruments.

Similarly, the VTT data on U500 K gives a useful yield that agrees unexpectedly well with those of other laboratories and is most likely incorrect. A possible reason for the good result can be found in the particle size determination. The given average particle size was around $1\ \mu\text{m}$ but the sizes of particles in the recorded images range from 3 to $10\ \mu\text{m}$, see Figure 8. It is likely that the particles have formed large clusters and the measured intensity data is a sum of several particles. This could explain the suspiciously good result. On the other hand, it is not clear why the individual particles cannot be distinguished in the ion maps.

A more realistic measure of the available sensitivity is the useful yield of $2 \cdot 10^{-5}$ determined for sample SRR C8, which was more than one order of magnitude smaller than the useful yields of the most sensitive instruments. This is in accordance to knowledge of secondary ion yields obtained using the two ion sources. Also, the average diameter of SRR C8 particles was given to be $3.6\ \mu\text{m}$ and the diameters of particles in Figure 9 correspond well to the given data.

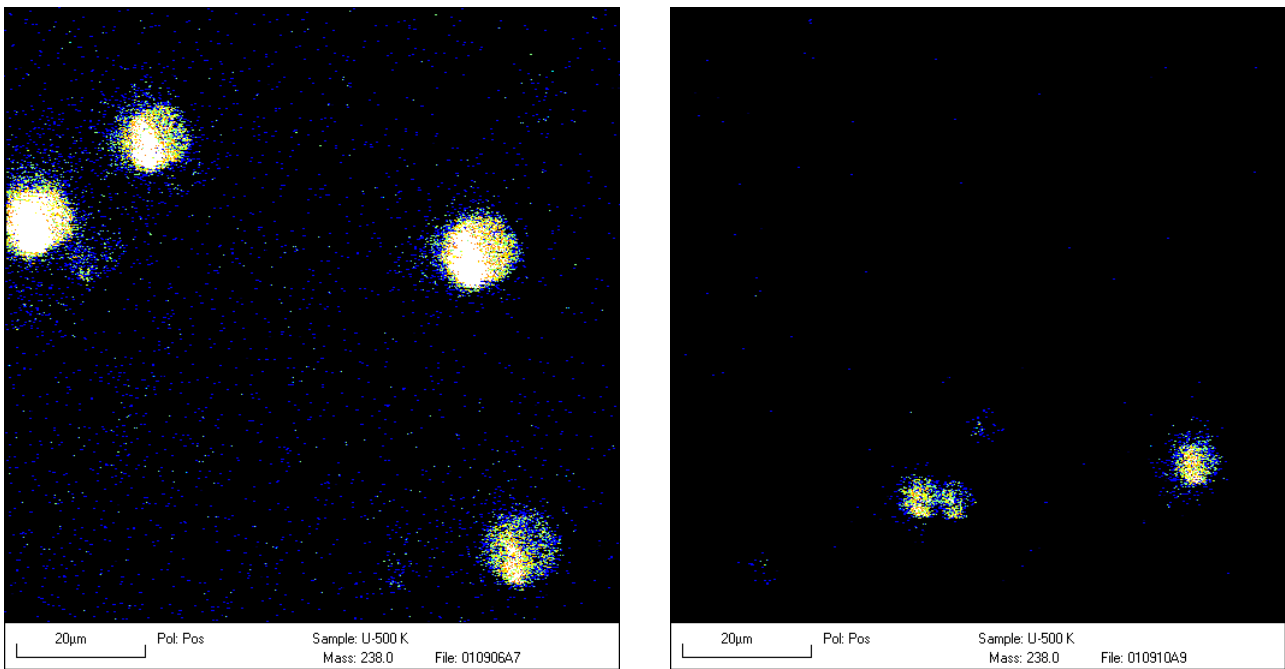


Figure 8. $^{238}\text{U}^+$ secondary ion images of the round robin sample U500 K.

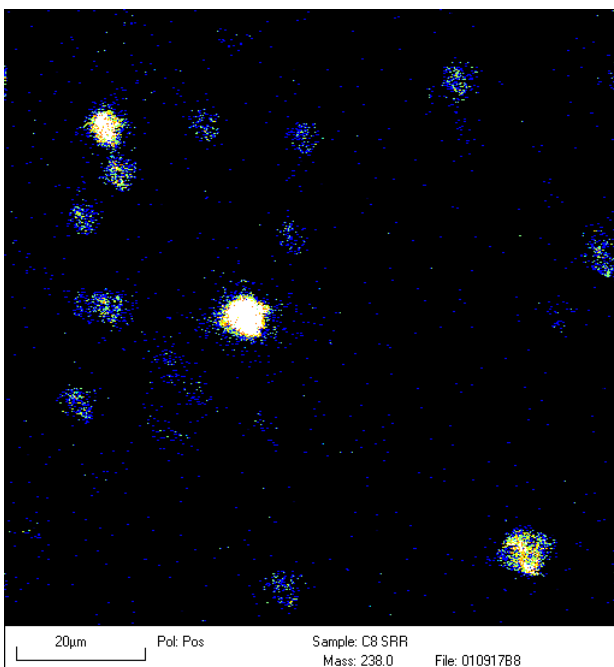


Figure 9. $^{238}\text{U}^+$ secondary ion image of the round robin sample SRR C8.

5 Future prospects

Due to better sensitivity it is more common to use oxygen primary bombardment for the uranium analysis than gallium. Since the SIMS instrument of VTT does not have a microfocussed oxygen source and the instrument does not operate in microscope mode, the full potential of SIMS in the analysis of uranium containing particles cannot be exploited. Even though large particles and highly enriched particles can be analysed fairly easily, the sensitivity of the method needs to 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 bleeding will be studied. Bringing oxygen to the sample surface while using the gallium ion source for actual analysis could solve the prob-

lem of low sensitivity. On the other hand it may cause difficult isobaric interferences, charging effects and damage the substrate surface.

In addition to studies on the enhancement of sensitivity, the work will continue by analysing real swipe samples and testing sample preparation methods and different substrates for SIMS. The possibility of isotope ratio determination from secondary ion images and automation of measurement will be assessed. Other activities in the SIMS laboratory that coincide with the needs of uranium analysis include plans for modifying the detection system to decrease the dead time of the channeltron and installing encoders on the manipulator motors to record absolute coordinates of the sample holder.