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

Final report on Task FIN A1318 of the Finnish Support Programme to IAEA Safeguards

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VTT Processes

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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 has been used earlier for testing the separation and analysis of uranium containing particles. In this work it was used to identify U-doped glass particles in IAEA reference samples to find out the reliability of the procedure.

Contents

1 Introduction

Track-etch method was developed at VTT for extracting uranium containing particles from swipe material. Sample preparation was performed earlier by ashing the filter samples and collecting the ashing residue in Collodion [1,2]. The IAEA glass reference samples were extracted with ultrasonification from the cotton pieces and after the separation mixed with 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 fission tracks could be examined under a microscope and the particles were picked up and dissolved for the analysis with ICP-MS.

2 Experimental

The track-etch method has been described in previous STUK-reports of the task [1,2].

3 Analysis of IAEA Glass Particle Reference Samples

The analysis of the IAEA Glass Particle Reference Samples was started in May 2003. The five cotton pieces (10×10 cm) were packed in double plastic bags, each of which had a code number (Table I).

Table I. Sample codes.

Sample	Outer plastic bag	Inner plastic bag
1	20177-01-02	1-2
2	20177-02-01	4-1
3	20177-03-01	5-1
4	20177-04-01	7-1
5	20177-05-01	9-1

3.1 Sample preparation

The samples were cut off the cotton swipes in the clean room. A strip of 2 cm was further cut for two pieces and these pieces (2×5 cm) were placed in tubes with 7 ml of ethanol. The samples in ethanol were ultrasonerated for 3 minutes. The samples were centrifuged for 15 min with 1500 rpm and ethanol was removed carefully with a pipette. Collodion was added so that Collodion to ethanol was one to ten. 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 1.2×10^{12} $cm^{-2}s^{-1}$ 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 Makrofols were etched in 6,5 M KOH for 15 min and glued to the microscope slides. The collodion films were placed back on the Makrofol sheet according to the marks.

The particles in the Collodion film were cut off with a razor knife under the magnification of 100. 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 under an infrared lamp and 7 drops of conc.HNO_3 was added to burn the residue of possible organic material. After the evaporation of HNO_3 the glass pearls were dissolved in five drops of conc. HF, which was evaporated. The same was repeated with five drops of HNO_3. Then 150 µl of 5% HNO3 could be added and the sample analysed with ICP-MS.

3.2 ICP-MS-analysis

The analysis of the separated particles was performed by an ICP-MS (VG Plasma Quad 2+) with quadrupole mass separator. The small amount of sample solution with low uranium concentration makes the use of microconcentric nebulizer (Cetac MCN-100) obligatory. By using the natural uptake the sample volume 150 µl was enough for 3 parallel measurements for each sample.

The results of the analysed particles are presented in the Tables II…VI with the standard deviation of three parallel measurements. No bias correction was made in the isotope ratio measurement. The ^{238}U standard was measured in each sample series to calculate the total amount of uranium in the particles. The particles were chosen both according to their track-etch print and the size of the particle. Some of the results have been left out from the list because the ^{235}U-concentration of the particle was below the detection limit. Usually the particles and the track-etch prints were both detectable. In the case were the track-etch print was big but the particle could not be seen the analysed U-ratio was high. This was the case in two particles in the sample 2 (Figures 1 and 2).

Table II. Sample 1 (20177-01-02, 1-2).

Particle code	tot. U pg	d µm* calculated	d µm measured	$^{235}U/^{238}U$	Stdev
111203/1	73.2	12	12	0.042	0.001
111203/3	5.5	4.7		0.040	0.002
111203/6	47.3	9.7		0.051	0.001
111203/7	27.7	8.1		0.0441	0.0004
111203/4	191	15		0.261	0.001
111203/5	15.8	6.7		0.410	0.012
120504/5	919	26		0.0075	0.0001
120504/7	246	17		0.0075	0.0003
120504/8	253	17		0.0128	0.0002
120504/9	124	13		0.0072	0.0003
140604/62	15.7	6.7	9.1	0.020	0.001
140604/69	291	18		0.011	0.0004
140604/70	4.28	4.3	14	0.089	0.008
140604/71	46.7	9.63		0.0422	0.0002
140604/72	169	15		0.0045	0.0003
150604/75	88.3	12	16	0.0294	0.0008

Table III. Sample 2 (20177-02-01, 4-1).

Particle code	tot. U pg	d µm* calculated	d µm measured	$^{235}U/^{238}U$	Stdev
140604/53	13.8	6.4	14	0.035	0.004
140604/54	10.8	5.9		0.039	0.004
140604/56	6.94	5.1	11	0.040	0.005
140604/57	3.70	4.1		0.431	0.026
140604/60	19.0	7.1		0.041	0.004
150604/78	5.75	4.8	11	0.525	0.039
150604/80	110	13	31	0.043	0.001
150604/81	14.1	6.5	11	0.043	0.002
150604/84	26.1	7.9	17	0.041	0.001

Table IV. Sample 3 (20177-03-01, 5-1).

Particle code	tot. U pg	d µm* calculated	d µm measured	$^{235}U/^{238}U$	Stdev
111203/8	11.4	6.0		0.045	0.006
111203/9U	30.8	8.4		0.043	0.001
111203/11	7.00	5.1		0.045	0.002
140504/26	58.7	10	19	0.044	0.002
140504/27	3.86	4.2	16	0.055	0.003
140504/28U	6.87	5.1		0.042	0.002
140504/29	26.3	8.0	15	0.044	0.007

* calculated from the total counts of uranium in ICP-MS measurement

Table V. Sample 4 (20177-04-01, 7-1).

Particle code	tot. U pg	d µm* calculated	d µm measured	$^{235}U/^{238}U$	Stdev
140504/33	348	18	20	0.0074	0.0002
140504/37	148	14	7.9	0.0084	0.0003
140504/38	381	19	11	0.0073	0.0001
140504/41U	486	21	4.5	0.0074	0.0002
140504/39	11.3	6.0		0.042	0.002
140504/32U	6.80	5.1	6.8	0.038	0.003
140504/34U	19.3	7.2	9.2	0.038	0.001
140504/35U	9.00	5.6	9.1	0.041	0.002

Table VI. Sample 5 (20177-05-01, 9-1).

Particle code	tot. U pg	d µm* calculated	d µm measured	$^{235}U/^{238}U$	Stdev
140504/43	96.4	12	23	0.0077	0.0006
140504/44	2.75	3.8	5.7	0.037	0.002
140504/45	46.9	9.6	14	0.0064	0.0001
140504/48	2.90	3.8	5.7	0.045	0.004
140504/49	50.2	9.9	14	0.043	0.001
140504/42U	29.1	8.2	16	0.043	0.001

* calculated from the total counts of uranium in ICP-MS measurement

The amount of uranium in particles was calculated by comparing with the standard solution. To calculate the diameter, the particles were assumed to be spherical 5% U_3O_8 in glass matrix with the density of 2. The comparison with the micrographs shows, that the size of the particles was in most cases bigger than that calculated from the uranium content. It is also unknown, if we were able to dissolve all uranium from the particles.

In some cases the big particle gave just few counts for ^{238}U. Probably the dissolution of the glass particle was only partly succesful. The biggest particle among the picked up ones (Figure 3) gave an isotope ratio of 0.029. The isotope ratio 0.04 was found in some particles in all of the samples. A typical track-etch print and glass particle with this isotope ratio is shown in Figure 4.

The precision of three parallel measurements of 235/238 ratio was <10% in those cases where the number of counts for each isotope was over the detection limit (3 sigma). The total time used for measuring the isotope ratio in one sample was less than 10 min.

The results in the tables were sent to IAEA, because the isotopic ratios of the glass particles were unknown to us at the time of the analyses. The weight ratios of the particles in the 5 samples are presented in the Table VII. The HEU particles have the isotopic ratio ($^{235}U/^{238}U$) 0.546 and the LEU particles 0.0433.

Table VII. The weight ratios of the glass particles containing different enrichment factors.

Sample number	Weight ratios of particles in samples
1	HEU:LEU 1:10 and no NU
2	HEU:LEU 1:110 and no NU
3	HEU:LEU 1:1010 and no NU
4	HEU:LEU:NU 1:1:220
5	HEU:LEU:NU 1:10:1110

In samples 2 and 3 we found particles that match quite well with the expected ratios, but sample 1 has contamination of NU particles. This contamination probably originates from the laboratory. The ratio of HEU and LEU particles in the samples is good. The analysed particles in the samples 4 and 5 do not reflect the expected ratio but the particle size differences between the standards could lead to quite different particle number ratios. Therefore the results are quite satisfactory.

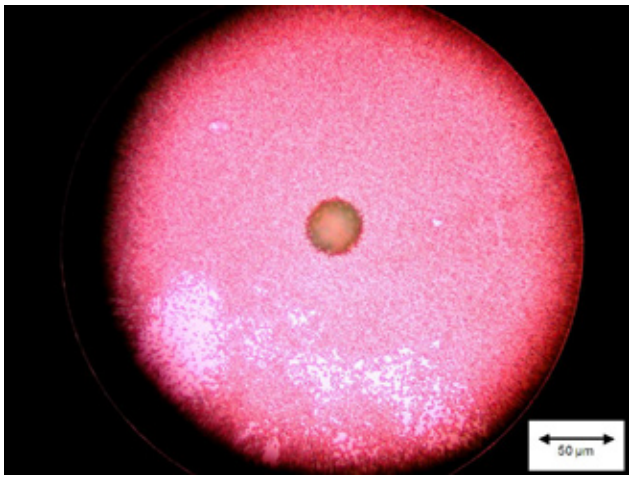

Figure 1. Track-etch print of the particle 140604/57 in sample 2.

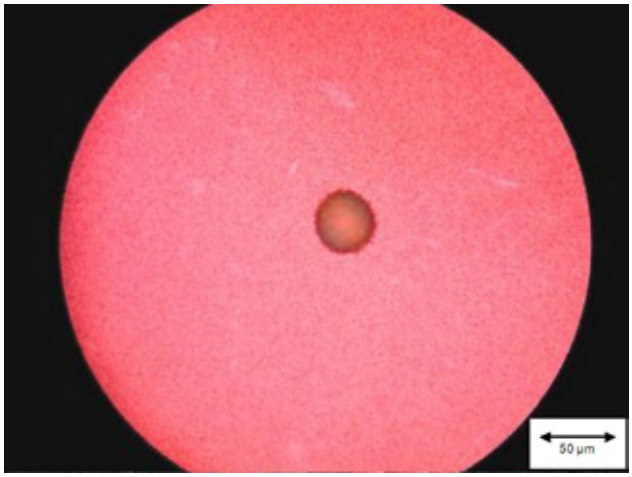

Figure 2. Track-etch print of the particle 150604/78 in sample 2.

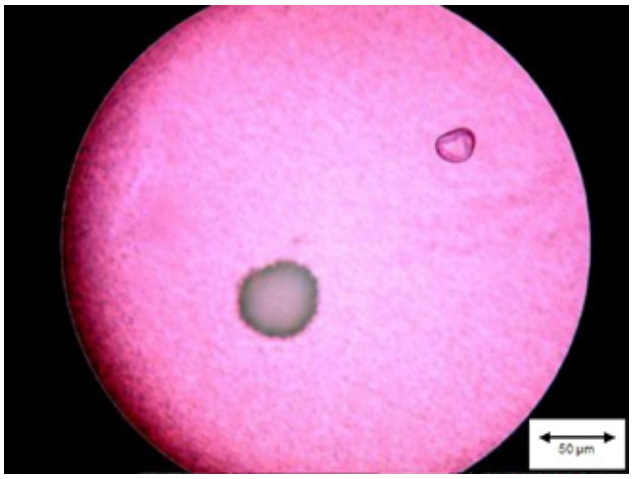

Figure 3. Track-etch print and particle 150604/75 in sample 1.

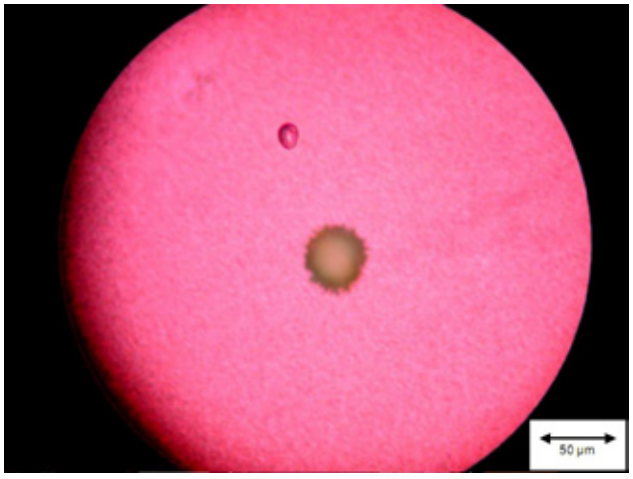

Figure 4. Track-etch print and the particle 140604/60 in sample 2.

4 Conclusions

With the precision reached with quadrupole ICP-MS it is possible to separate particles of NU, LEU and HU. The need for more experience in particle separation is obvious. The NU contamination in the samples can be avoided by performing the sample preparation and dissolution of separated particles in a clean room. Also the microscopic work including cutting of the Collodion film should be done in a cleaner environment than in normal laboratory. The results are anyway encouraging and when more particles from each sample were analysed it is possible that the isotopic ratios would be nearer the expected ones.

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] Lehto, S., Lipponen, M., Zilliacus, R., 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, STUK-YTO-TR 200, STUK Finland, August 2003.