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A. Kuchkin, V. Stebelkov, K. Zhizhin, C. Lierse von Gostomski, C. Kardinal, A. H. J. Tan, B. K. Pong, E. Loi, E. Keegan, A. Gaffney, R. Williams, M. Kristo

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Names of the authors:A. Kuchkin[1], V. Stebelkov[1], K. Zhizhin[1], Ch. Lierse von Gostomski[2], Ch. Kardinal[2], A. H. J. Tan[3], B. K. Pong[3], E. Loi[4], E. Keegan[4],Michael J Kristo[5], M. Totland[6], I. Dimayuga[6], M. Wallenius[7]

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Affiliations and addresses of the authors:

[1]Laboratory for Microparticle Analysis,
117218 Bolshaya Cheremushkinskaya, 25, Moscow, Russia

[2]Radiochemistry Munich, Technical University of Munich,
D-85748Garching, Germany

[3]DSO National Laboratories,
20 Science Park Drive, Singapore

[4] Australian Nuclear Science and Technology Organisation
Locked Bag 2001, Kirrawee, NSW 2232, Australia

[5] Lawrence Livermore National Laboratory,
P.O. Box 808, Livermore, CA 94551-0808;

[6]Canadian Nuclear Laboratories,
286 PlantRoad, ChalkRiver, Ontario,Canada K0J1J0

[7]European Commission, Joint Research Centre,

P.O. Box 2340, 76125 Karlsruhe, Germany

E-mail address of the corresponding author: v.stebelkov@lma.su

CONTRIBUTION OF BULK MASS SPECTROMETRYISOTOPIC ANALYSIS TO CHARACTERIZATION OF MATERIALS IN THE FRAMEWORK OF CMX-4

A. Kuchkin[1], V. Stebelkov[1], K. Zhizhin[1], Ch. Lierse von Gostomski[2], Ch. Kardinal[2], A. H. J. Tan[3], B. K. Pong[3], E. Loi[4], E. Keegan[4], Michael J. Kristo[5], M. Totland[6], I. Dimayuga[6], M. Wallenius[7]

[1]*Laboratory for Microparticle Analysis,*
117218 BolshayaCheremushkinskaya, 25,Moscow, Russia

[2]*Radiochemistry Munich,Technical University of Munich,*
D-85748 Garching, Germany

[3]*DSO National Laboratories,*
20 Science Park Drive, Singapore

[4] *Australian Nuclear Science and Technology Organisation*
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[5] *Lawrence Livermore National Laboratory,*
P.O. Box 808, Livermore, CA 94551-0808

[6]*Canadian Nuclear Laboratories,*
286 PlantRoad, ChalkRiver, Ontario, Canada K0J1J0

[7]*European Commission, Joint Research Centre,*

P.O. Box 2340, 76125 Karlsruhe, Germany

Abstract

Seven laboratories used the results of bulk uranium isotopic analysis by either Inductively Coupled Plasma Mass Spectrometry (ICP-MS) or Thermal Ionization Mass Spectrometry (TIMS) for characterization of the samples in the Nuclear Forensic International Technical Working Group (ITWG) fourth international collaborative material exercise, CMX-4. Comparison of measured isotopic compositions of uranium in the samples is implemented for identifying any differences or similarities between the samples. These compositions are collated also with the data about the products of three hypothetical facilities for the conclusions about possible origins of the measured materials. The role of isotopic analyses in real similar investigations is determined. Several imperfections of carrying out of ICP-MS or TIMS analysis in CMX-4 are noted.

Keywords: Isotopic composition of uranium, inductively coupled plasma mass spectrometry, ICP-MS, Thermal ionization mass spectrometry, TIMS, CMX-4, nuclear forensics.

Introduction

The purpose of bulk isotope ratio mass spectrometric (e.g., ICP-MS and TIMS) analyses, as well as of any other measurements that were performed in the framework of CMX-4, was to obtain forensically meaningful information to answer questions formulated by the investigating authority in the scenario of Exercise.. Unlike secondary ion mass spectrometry, these bulk analytical methods are not designed to reveal any heterogeneity in composition at the microstructural level. The measured uranium isotope ratios are the average of the sample volume prepared. But differences in measured uranium isotopic composition between samples allow conclusions about different origins of materials to be made.

At the same time, similarities between the sample uranium isotopic compositions leave open the possibility of the linkage of origins. Such concurrences, especially when supported by other analytical results, allow the development of a hypothesis about the same origin and processing history of samples. Comparison of measured isotopic compositions of uranium with technical specifications on the facility's products can suggest the possibility of manufacturing of questioned materials at these facilities.

ICP-MS and TIMS are widespread in analytical practice. TIMS is characterized by highest precision for bulk mass spectrometric techniques. ICP-MS is characterized in the whole by a little bit smaller precision, but in addition ICP-MS is characterized by very high rapidity of analysis. Characteristics of the results of isotopic analysis of uranium in different samples by using these two methods are well known [1, 2, 3, 4, 5]. Despite the methods being destructive, only negligible quantity, several milligrams or less, of materials are necessary for determination of isotopic compositions of uranium. For many years, these methods have been recommended for characterization of materials during nuclear forensics examinations [6].

Experimental

Five laboratories, referred to as Rembrandt, Renoir, Matisse, Van Gogh and Monet, performed uranium isotopic analysis on the CMX-4 samples by using ICP-MS. These laboratories have different ICP-MS instruments, different levels of expertise and use different analytical and sample preparation techniques. Two laboratories, referred as Buonarroti and Manet, performed the isotopic analysis by TIMS, and also used different instruments and sample preparation techniques and have different levels of expertise.

Instrumentation

Monet used a Nu Plasma HR, a used a multi-collector double focusing magnetic sector ICP mass spectrometer; Renoir and Matisse both used an ELEMENT 2, a single collector double focusing magnetic sector mass spectrometer. Rembrandt used a Varian 820, a quadrupole mass spectrometer, and Van Gogh used an Agilent 7700, also a quadrupole mass spectrometer. Manet used a Finnigan MAT 262 TIMS, while Buonarroti used a Finnigan MAT 261 TIMS. Some of instruments characteristics as well as some of measurements parameters are presented in Table 1.

Table 1. Instrument characteristics and measurements parameters used by laboratories

Laboratory code	Instrument	Detection system	Resolution, M/ΔM	Spray system type/filament	Flow rate, μL/min
Rembrandt	Varian 820	DDEM	0.8 amuat 10% peakheight	Micromistlow flow Nebulizer	400
Renoir	ELEMENT 2	- " -	300	PFA micro flow nebulizer	50
Matisse	ELEMENT 2	- " -	300	Micromistlow flow Nebulizer	50
Van Gogh	Agilent 7700	- " -	300	Nebulizer	80 … 100
Monet	Nu Plasma HR	Faraday/ DDEM	350	Aridus II desolvating nebulizer	50
Buonarroti	Finnigan MAT 261	Faraday/EM	400	W/Re	N/A
Manet	Finnigan MAT 262	- " -	> 500	Zone-refined Re	N/A

N/A – TIMS is not characterized by flow rate;
W/Re – Buonarroti use tungsten as an evaporation filament and rhenium as an ionization one.

As Nu Plasma HR is a multi-collector instrument, the ion currents of all uranium isotopes of interest are measured simultaneously. For the CMX-4 measurements, two Faraday cups and three DDEM were used as detectors; ^{238}U and ^{235}U ion currents were measured on Faraday detectors, whereas the ions for minor uranium isotopes, i.e. ^{236}U, ^{234}U, and ^{233}U were measured on ion counters. Because all ion currents are measured simultaneously, the analytical uncertainty associated with variation in the ion beam intensity is minimized. Therefore, multi-collector double focusing magnetic sector instruments generally provide more precise isotope ratio measurements than single-collector instruments.

The ICP mass spectrometers ELEMENT 2, Varian 820 and Agilent 7700 use only one collector for ion current measurements during the analysis. All measurements using ELEMENT 2 were implemented in "peak-jumping" mode, and $^{234}U^{+}$, $^{235}U^{+}$, $^{236}U^{+}$ (Renoir measured $^{236}U^{+}$, but Matisse did not) and $^{238}U^{+}$ species were collected sequentially on the same detection system, a discrete dynode electrons multiplier (DDEM). This detector enables the quantification of both minor and major isotopes in a single analysis across a dynamic range of 10^{9}.

Routine mass scanning is performed by a sector field ICP-MS using the combination of magnetic field and electric field jumps. But the ELEMENT 2 has the capability to scan an additional 30% higher from the mass, which is determined by a fixed magnetic field, by decreasing the acceleration voltage. This property of ELEMENT 2 instrument allows maintenance of a constant magnetic field and variation

only of the acceleration voltage during isotopic analysis of uranium, resulting in the fastest mass scanning.

Quadrupole instruments provide continuous mass spectra from starting mass point in the analysis up to finishing mass point. Scanning of masses is carried out by changing the frequency of the RF generator. The measurements made using quadrupole instruments can also be carried out in peak jumping mode, jumping between masses of interest to reduce measurement time. A DDEM is used as a detection system in both quadrupole instruments (Varian 820 andAgilent 7700) which were used for CMX-4 measurements.

The thermal ionization mass spectrometers MAT 261 and MAT 262 are also multi-collector instruments having a combination of Faraday cup detectors as well as one or more ion counting electron multipliers. The ion beam to one of the electron multipliers passes through a retarding potential quadrupole (RPQ) providing superior resolution. Manet utilized simultaneous measurement of masses 235 and 238 on the Faraday cups and peak hopping on the RPQ/EM for the minor abundant isotopes at mass 234 and 236. Buonarroti measured all U isotopes simultaneously by Faraday cups using total evaporation method.

Sample preparation

All three CMX-4 samples were delivered into each participating laboratory in the solid state: powder (sample ID ES 1) and typical fuel pellets (sample IDs ES 2 and ES 3). Fragments of pellets were delivered to one laboratory. As all laboratories used liquid sample introduction for ICP-MS analysis or dried solutions for TIMS, the main stage of sample preparation was dissolving of weighed portions of samples. All laboratories dissolved weighed portions in concentrated 8 M or 6 M nitric acid under heating. The criterion for complete dissolution of the weighed sub-samples was the absence of a visible precipitate.

After complete dissolution, the preparations were diluted to required concentrations by using (2 … 5)% nitric acid prepared from high-purity concentrated nitric acids. The dilution factor was determined by the mass of sub-sampled portions and by the range of allowable concentration of the solution to be analyzed. Both Manet and Buonarroti diluted the solutions to approximately 100 µL/mL and loaded approximately 1 µL (or ~100 ng sample) onto a rhenium or tungsten filaments, respectively, for sample introduction.

Three laboratories performed additional sample preparation operations. Rembrandt cleaned both pellets before their dissolution. Firstly the pellets were washed in ethanol, followed by distillated water, 3% nitric acid, distillated water again and air dried. Van Gogh obtained light brown solutions from the dissolution of weighed portions and therefore diluted these solutions 300-fold up to the discoloration.

Monet purified the sample solutions prior to analysis using UTEVA selective extraction resin (Eichrom Technologies, Inc.): the samples were dissolved in 0.5 mL 4 M nitric acid and loaded on 1.0 mL UTEVA resin beds in Poly-Prep columns (Bio-Rad Laboratories). The resin was washed with 4.5 mL 4 M nitric acid, 1.5 mL 9 M hydrochloric acid, and 4 mL 5 M hydrochloric acid to remove matrix elements, while the uranium remained sorbed to the resin. The uranium was subsequently eluted in 6.5 mL 0.1 M hydrochloric acid. Eluents containing uranium were dried down and dissolved in 100 µL concentrated nitric acid and dried. This process was repeated, and then samples were dissolved in 3 mL 2% nitric acid for Nu Plasma HR analysis.

Some laboratories had prepared replicate dissolutions from each sample material for determination of uranium isotopic composition. For example, Rembrandt prepared

two and Matisse three replicate dissolutions. Manet dissolved and analysed small portions for a quick determination, followed by dissolution of larger sample sizes for multiple analyses including repeat mass spectrometric analysis.

Reagent-blanks were prepared and analysed for a correct background correction on the uranium content, i.e. correction for uranium from reagents used in the sample dissolutions. All sample preparation steps were carried out in accordance with the procedures developed in individual laboratories to avoid cross contamination between samples (e.g. use of glove-bags or glove-boxes, new sampling tools for each sample).

The amounts of sample materials, which were used for preparations in different laboratories, are presented in table 2.

Table 2. Material amounts, which were used for preparations

Laboratory code	Weighed parts masses, mg		
	ES 1	ES 2	ES 3
Rembrandt	146.1; 76.8	254.7; 175.5	302.5; 132.4
Renoir	123.8	124.9	125.8
Matisse	5.3; 7.2; 6.1	6.5; 5.9; 6.8	7.1; 5.9; 6.7
Van Gogh	2.2	3.5	6.1
Monet	592	664	637
Buonnarroti	2498.4	1222.3	1640.8
Manet	4.27; 1233.9	283.2; 714.3	252.2; 837.5

It can be seen that very different amounts of materials, from units of milligrams up to hundreds of milligrams were utilized by different laboratories for analyzed sample preparations.

Measurements

Analyses of the CMX-4 samples were performed in accordance with the quality control system of each laboratory. Reference materials were analysed for the instruments calibration as well as for the quality control (QC) purposes. For example, Rembrandt used CRM U-010 for instrument mass bias correction, and CRM U-100 and CRM U-500 as check samples. Monet used CRM U-010 for mass bias correction and the determination of relative detector gain factors. Matisse used internal reference solutions of natural and depleted (concentration of ^{235}U ~ 0.3%) uranium with concentration from 0.1 ppb to 2.0 ppb for detector dead time correction. These reference solutions were prepared using multi-element standard solutions: HIGH-Purity STANDARDS ICP-MS-68A for natural uranium samples and Merck 15474 for depleted uranium samples. Manet utilized CRM-020 to determine the TIMS mass fractionation factor and CRM-112A for additional sample preparation quality control. Buonarroti used IRMM-185 for quality control. No standard was required for fractionation correction as total evaporation method was applied.

Blank-preparations were analysed for the cross-contamination control as well as for determination of background ion currents.

Results and discussion

The results of analyses are summarised in Table 3.

Table 3. Isotopic composition of uranium in samples.

Laboratory code	Concentration of isotopes, % at.							
	^{234}U	σ	^{235}U	σ	^{236}U	σ	^{238}U	σ
ES 1								
Rembrandt	0.025	0.002	2.91	0.04	0.00186	0.00005	97.09	0.04
Renoir	0.0253	0.0002	2.95	0.02	0.00257	0.00002	97.0	0.6
Matisse	0.0211	0.0004	2.98	0.04	Not measured		97.00	0.04
Van Gogh	Not determined		2.96	0.3	Not determined			
Monet	0.024520	0.000084	2.8937	0.0030	0.001802	0.000014	97.080	0.014
Buonarroti	0.02465	0.00073	2.8950	0.0023	0.00195	0.00019	97.0784	0.0037
Manet	0.02429	0.00023	2.9003	0.0022	0.001818	0.000025	97.0736	0.0016
ES 2								
Rembrandt	0.020	0.002	2.21	0.03	< 0.00005*		97.77	0.04
Renoir	0.01943	0.00012	2.249	0.013	0.00064	0.00001	97.7	0.7
Matisse	0.0165	0.0003	2.25	0.02	Not measured		97.74	0.02
Van Gogh	0.0178	N/d	2.0	0.1	< 0.0055*		97.9	0.2
Monet	0.018802	0.000065	2.1979	0.0023	0.000085	0.000007	97.783	0.014
Buonarroti	0.01883	0.00056	2.1970	0.0018	< 0.001*		97.7842	0.0037
Manet	0.01864	0.00018	2.1998	0.0016	0.0000190	0.0000011	97.7815	0.0016
ES 3								
Rembrandt	0.024	0.002	2.89	0.04	0.00188	0.00005	97.10	0.04
Renoir	0.0252	0.0002	2.95	0.02	0.00256	0.00013	97.0	0.8
Matisse	0.0203	0.0002	2.98	0.02	Not measured		97.01	0.02
Van Gogh	Not determined							
Monet	0.024533	0.000084	2.8936	0.0030	0.001808	0.000016	97.080	0.014
Buonarroti	0.02495	0.00074	2.8953	0.0023	0.00182	0.00018	97.0780	0.0037
Manet	0.02425	0.00023	2.9011	0.0022	0.001808	0.000020	97.0728	0.0016

N/d – not determined. Uncertainties represent the 95% confidence interval.

* – the value of the detection limit

Presented data show that six laboratories demonstrated the coincidence of measured isotopic compositions of uranium in samples ES 1 and ES 3 (all uranium isotopes agreed within uncertainties) and significant difference of uranium isotopic composition of ES 2 from that of ES 1 and ES 3. The seventh laboratory did not analyze the sample ES 3, but demonstrated significant difference of uranium isotopic composition of ES 2 from that of ES 1. These results could support the conclusion that materials of ES 1 and ES 3 are similar despite ES 1 is a powder and ES 3 is a pellet. That is they may have been manufactured in the same plant, same technological site, and even they may be originated from the same batch of the product. However neither ICP-MS nor TIMS is an all-embracing analytical method, therefore additional analyses using complementary techniques can confirm or disprove this outlet.

ES 2 material is conclusively dissimilar compared to ES 1 and ES 3. ICP-MS and TIMS results are enough for such conclusion and additional measurements for confirmation of this outlet are not necessary.

Some differences in the uranium isotopic results obtained by different laboratories demonstrate the different qualities of measurement techniques. Analysis of these differences allows improvement in analytical techniques in several laboratories, which participated in the CMX-4. Moreover such analysis can be useful for other laboratories, which are going to participate in such measurements in the future.

The multi-collector instruments, utilized by Buonarroti, Monet, and Manet demonstrated the high precision isotopic measurements possible, which although not required in this exercise to provide confidence in drawing conclusions, may be valuable if distinctions between only slightly different materials are required. Obviously these three laboratories obtained most precise results of analyses. Measured concentrations of ^{235}U as well as ^{234}U in replicates of all three samples differ only in the third meaningful figure. Measured concentrations of ^{236}U in ES 1 samples differ in the second meaningful figure, in ES 3 samples they differ in the third meaningful figure, although differences in the results of ^{236}U measurements in ES 2 are more significant.

But differencesin the results of all different laboratories are not crucial for the conclusion about principal possibilities of the method for obtaining forensically meaningful information. Moreover concentrations of ^{235}U as well as of ^{234}U measured in materials of the samples at least by five laboratories virtually coincide within the errors of measurements.

Three laboratories, including one laboratory which used single collector instrument, detected ^{236}U in all three samples. These results demonstrated that all three CMX-4 materials contain irradiated uranium, although the ^{236}U abundance in ES 2 is distinctly lower than in ES 1 and ES 3. These results also showed that ^{236}U can be detected by ICP-MS and TIMS at abundance levels down to the $(10^{-3} \ldots 10^{-4})$% range if the most perfect mass spectrometer is used for measurements.

It should be noted also that very important characteristic of forensic examination is rapidity. The rapid provision of investigators with relevant information facilitates to solve the crime hot on the hills. Renoir implemented complete and very precise ICP-MS isotopic analysis of uranium in all three samples within the 24 hour timeframe, demonstrating high rapidity and accuracy of the technique utilizing only negligible amount of the material evidence.

Conclusions

The results of determination of uranium isotopic composition in samples of CMX-4 by using ICP-MS and TIMS contributed significantly to their characterization. The best analysis results provide more forensically meaningful information. These results reveal the presence of irradiated uranium in all samples (common signature). Practically all results determine also the similarity between materials of ES 1 and ES 3 on the one hand and significant difference of ES 2 material on another. It means that ES 1 and ES 3 could be prepared from one batch of materials, while ES 2 was prepared from another one.

The results demonstrated that such material characterization can be carried out in the first stage of investigation within 24 hours. At the same time the accuracy and precision of the ICP-MS and TIMS measurements are better than that of other rapid, first of all radiometric, methods. Measurements of uranium isotopes concentrations with uncertainties smaller than 1% can provide more confident conclusions about differences or concurrences of materials content, about possible origin of materials.

Rapidity of ICP-MS and relative to radiometric methods rapidity of TIMS together with negligibly small amounts of utilized sample materials, only several milligrams or less, allow this method to be used justifiably in the first stage of investigation of incidents with actual scenarios similar to the CMX-4 scenario.

Such precise results during the first stage of investigation, when the versions of the crime incident are only formulated, are very important for the prosecution. They allow the limitation of the set of versions, which should be developed by prosecution, eliminating those which do not correspond with the accurate and precise results of ICP-MS and TIMS measurements.

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