Informativeness of microparticle analysis for Nuclear Forensics

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Abstract. Different nuclear security events, investigation of which can require microparticle analysis, are considered. Capabilities of analytical techniques are reviewed. There is demonstrated that analysis of microparticles with sizes down to 0.5 μm provides investigation with information about nuclear materials detained out of regulatory control, route of this material transfer, people, which were involved to illicit trafficking.

1. Introduction

Investigation of microparticles can be useful for nuclear forensics goals in several cases. First of all these are the cases, when some unknown material is out of regulatory control, but it is not seized. Nevertheless trace amounts of this material can be found on the surfaces of different objects, which contacted with material, and these trace amounts may be the only source of information about material. Such objects can be empty container, wrapping material, worktop, special instruments, etc. In such cases completeness and accuracy of information about material depends on the number and sizes of microparticles had been detected as well as on the involved analytical capabilities. But in any case any information is better than nothing.

If material is seized, but the route of material transfer and involved persons are not established, analysis of environmental samples from suspicious areas, analysis of clothing and other belongings of suspicious people can clarify both: areas, on which some operations with material were processed, and people, who were involved.

The objectives of this paper are indication of such kinds of incidents and demonstration of the possibilities of corresponding analytical methods.

2. Nuclear forensics tasks, which need microparticles analysis

Analysis of individual microparticles can provide the prosecution with following useful information concerning the investigation of incident:

- Determination of characteristics of nuclear or other radioactive material out of regulatory control, when material is not seized, but some trace amounts of material are found anywhere, including crime scene. Such determination is relevant during investigation of incidents with deliberate or accidental dispersion of such unknown material as well as incidents with disappearance of material;
- Determination of the transfer route of material, which is found out of regulatory control, as well as possible sites of processing, people and items, which could be involved in illicit trafficking and hidden activity;
- Indicating real manufacturer of the seized material, if the same materials could be produced by different manufacturers. Trace amounts of other materials inherent to real manufacturer can indicate it in such cases;
- Determination of characteristics of nuclear and other radioactive materials found out of regulatory control in the form of mixture of powders of different materials.

Despite of some diversity of these tasks from the prosecution point of view, all of them are decided on the base of determining of not so many characteristics of particles. Morphological characteristics: shapes, sizes and surface structures, elemental composition (including impurities), isotopic composition of uranium and plutonium in particles and content of specific isotopes (for example, isotopes-chronographs) – these are the characteristics, which can be determined in the result of particle analysis. But determination of these characteristics allows to characterize materials with some accuracy.

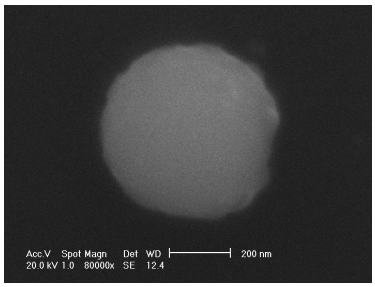
3. Determination of the material characteristics

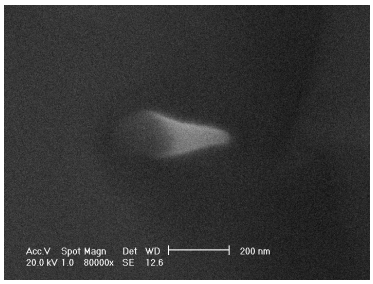
The results of microparticles analyses allow to determine the composition of materials as well as to decide some tasks, which are connected with determination of the age of materials.

3.1. Determination of isotopic compositions of uranium and plutonium

Isotopic compositions of uranium and plutonium determine designation and, in some cases, manufacturer of nuclear material. Thermal ionization mass spectrometry (TIMS) and secondary ion mass spectrometry, using large geometry mass spectrometer Cameca IMS-1280 (LG-SIMS), provide most accurate isotopic analysis of uranium and plutonium in particles. Accuracy of measurements by means of these two methods is approximately the same [1]. Of course it depends on the amount of uranium and/or plutonium in particle that is on the size of particle and on real density of uranium and/or plutonium in particle.

Most reliable results of TIMS analyses are provided by AFTAC laboratory [2]. LG-SIMS analyses are provided by several laboratories – members of IAEA network of analytical laboratories [3]. On the fig. 1 image of spherical UO_2 particle before LG-SIMS analysis and image of the residue of that particle after analysis are shown.





Reference values:

$n(^{235}U)/n(^{238}U) = 0{,}007\,043\,9 \pm 0{,}000\,003\,5$

$n(^{234}U)/n(^{238}U) = 0{,}000\,049\,817 \pm 0{,}000\,000\,048$

Measurements results:

$n(^{235}U)/n(^{238}U) = 0{,}007\,04 \pm 0{,}000\,05$

$n(^{234}U)/n(^{238}U) = 0{,}000\,053\,0 \pm 0{,}000\,004\,2$

FIG. 1. Uranium particle before (left) and residue of particle after (right) LG-SIMS analysis. Reference and measured values of isotope ratios are presented under pictures.

Diameter of initial particle is about 0.6 µm. Reference and measured isotope ratios presented on this figure also, they characterize the accuracy of measurement. Comparison of reference and measured values of uranium isotopes ratios allows to conclude, that approximately 7 fg of uranium-235 in that particle was measured with relative error less than 1%, and

approximately 0.05 fg of uranium-234 – with relative error less than 10%. Analyses of other similar particles confirmed that relative errors less than 1% for uranium-235 and less than 10% for uranium-234 are typical for particles with diameters dawn to 0.5 µm.
Approximately the same results are obtained for analysis of plutonium particles. Unlike the almost regular spherical uranium particle, which is shown on the fig. 1, investigated plutonium particles had not so regular shape. Therefore the sputtered amounts of plutonium in particles are estimated more roughly, than in uranium particle on fig. 1. But several plutonium particles were analyzed, and the trend has been determined. The dependence of uncertainties of measured content of plutonium isotopes on the value of the content is illustrated on fig. 2.

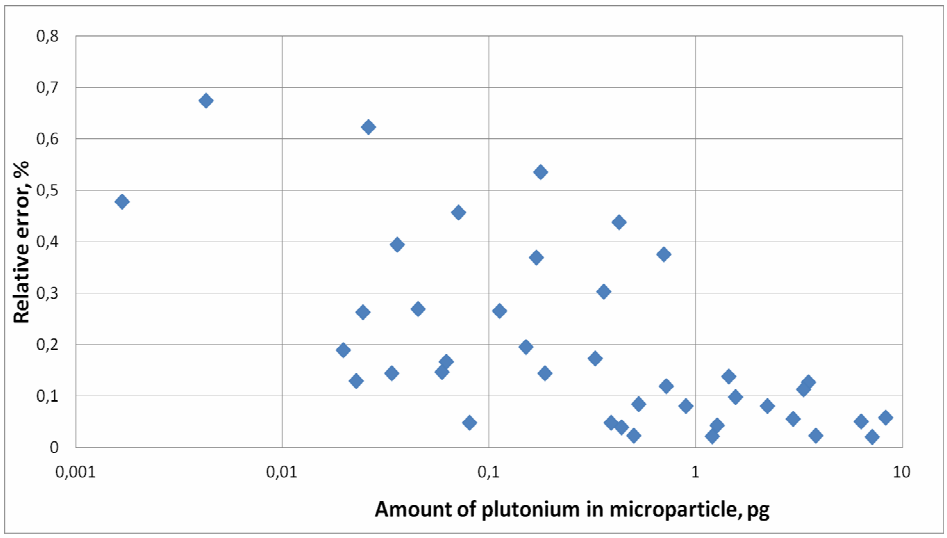


FIG. 2. Uncertainties of the results of measurement of the amount of plutonium in microparticles.

Deviations of relative errors for the same indicated amounts of plutonium in particles can be explained by complex shape, by different and not dense inner structure and accordingly by difficulty of estimation of sputtered amount of plutonium. Nevertheless the results for uranium and for plutonium particles are consistent with each other.

3.2. Determination of elemental composition of materials

Elemental composition (including impurities) of nuclear and other radioactive materials can carry information about its designation. Some impurities can also disclose information about row materials and processing technologies. If the particles are the fragments of some material, elemental composition of particles and material are the same. In this case elemental composition of particles provides useful information for prosecution.

Elemental composition of the particles can be determined by using energy dispersive or wavelength dispersive X-rays detectors practically together with morphology investigation by means of scanning electron microscope. Detection limits of weight concentration are (0.2 … 0.5)% for different chemical elements and for measurements by using more productive energy dispersive detectors [4]. Using wavelength dispersive X-rays detectors can decrease detection limits approximately on the order of magnitude [5].

Accuracy of measurements of elemental concentrations depends first of all on concentration value for particles with sizes more than (2 … 3) µm. If the analyzed particle is smaller than volume of X-ray excitation, accuracy depends also on the size and density of particle. As a

rule the measuring by using energy dispersive detectors provide relative errors of element concentrations in particles with irregular surface about 100% if concentration is smaller than 1%, and up to 10% for concentrations about 50%.

But last time the using of modern electron microscopes, equipped by productive EDX detector and inbuilt ion beam, allow to use more effective low energy electron beams and preparation of the particle surface for more accurate X-ray analysis. Cutting of some part of particle and smoothing of the analyzed surface in combination with using of low energy electron beam decrease the relative errors of measurement several times. Illustration of this fact can be found in papers [6, 7]. Fig. 3 shows UO_2 typical particle with rough surface (left) and similar UO_2 particle after preparation of the surface for more accurate analysis (right).

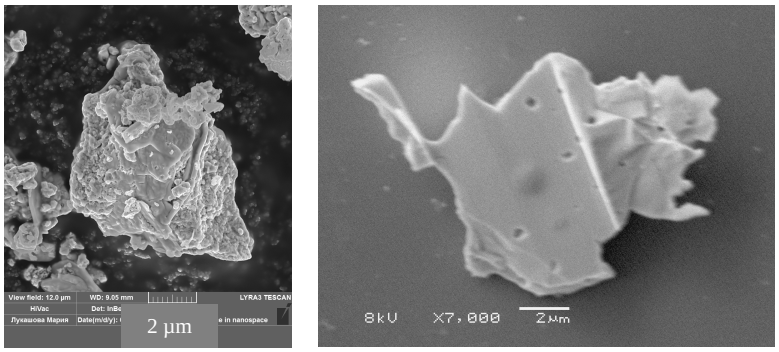


FIG. 3. Particle without influence of ion beam (left) and particle with truncated top (right).

Four successive measurements of concentration of uranium were implemented for each particle. These four analyses of each particle differed by the orientation of particle relative EDX detector – after each measurement the planchet with particle was rotated onto 90º. X-rays were collected from the same part of surface for each particle. Relative deviation of measured concentration for left particle was about 6%, for right particle with prepared surface – 3 times smaller.

3.3. Deciding of some tasks for age determination

It is known, that the age of uranium materials can be determined undoubtedly by using ICP MS techniques [8]. But such determination will be correct only if one nuclear or one other radioactive material is presented in analyzed sample and no isotope-chronograph presents in background particles of sample in significant quantities.

For particle analysis, which can be implemented by using SIMS, these restrictions are not valid. Practically the particle always characterizes only one material and does not contain background isotopes-chronographs. But determination of the age based on the result of measuring of the ratio of the contents of thorium-230 and uranium-234 – isotopes of different chemical elements. Difference of coefficients of ionization of uranium and thorium and dependence of these coefficients on composition of particle does not allow to use this method directly for determination of the age.

Nevertheless SIMS is very useful for dating of uranium materials, especially if the sample can contain small amounts of materials. In this case analysis of different fragments of materials by SIMS (particles) can confirm or not confirm the result, had been obtained by ICP MS. SIMS possibilities for the solution of the age task can be estimated with help of the fig. 4, which shows the particle of uranyl-nitrate before analysis and residue of this particle after sputtering.

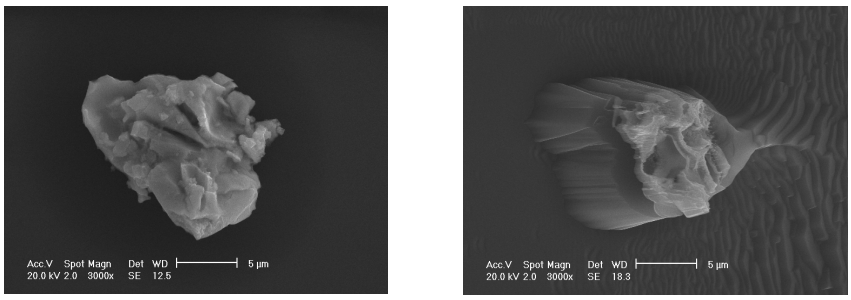


FIG. 4. Uranium particle before (left) and residue of particle after (right) LG-SIMS analysis. Ages, measured by ICP MS and LG-SIMS are presented under pictures.

The ratio of ion currents of thorium-230 and uranium-234, measured in the result of analysis is $(1.72 \pm 0.37)\times10^{-5}$. The particle contained approximately 300 pg of uranium before sputtering. Age of material during analysis was (1.66 ± 0.05) years, uranium was enriched up to 4% on uranium-235. It means that if the age of uranium, which is enriched up to 4% on uranium-235, is approximately one and half years, analysis of uranium particle with effective diameter about 8 µm can provide uncertainty of measurements about 20%.

If all detected and analyzed particles will have the same ratio of ion currents of isotopes of thorium-230 and uranium-234 within the errors, the result of ISP MS is correct. Moreover, SIMS analysis of some relatively large particles can provide smaller uncertainties than uncertainty had been provided by ICP MS. In this case SIMS will improve the ICP MS result.

If particles will be characterized by different ratios of ion currents, the ages of materials of these particles are different also and the result of ICP MS can not be related to any of presented materials. But in this case the ages of different materials can be still estimated if the different particles have the same elemental composition. The “age”, which had been determined by ICP MS, can be correlated with the average ratio of ion currents of thorium-230 and uranium-234, which had been determined by SIMS for all analyzed particles. This correlation determines the ratio of coefficients of ionization of uranium and thorium, which should be the same for all particles with same elemental composition. Of course additional investigation of particles should be implemented in this case for confirmation of sameness of elemental composition of particles. Such investigation for example can be implemented by SEM-EPMA.

If different particles are characterized by different ages and different elemental compositions, ICP MS result is senseless. In spite of this fact some age estimations can be implemented for different particles in this case also. But information about the ratios of ionization coefficients for thorium and uranium should be provided from anywhere. It can be provided by the previous investigations as well as by the results of special measurements, which can be organized especially for the purpose of concrete crime investigation. Particles with elemental compositions identical to elemental compositions of particles in sample, which have to be investigated, should be manufactured from the material with known age. Results of the analysis of these particles allow to calculate the ionization coefficient ratios, lake it was done in the work [9].

4. Determination of morphology characteristics

Morphological characteristics of nuclear materials particles are intensively investigating from 1990th seeing IAEA Safeguards goals. Corresponding tasks practically look like forensics

tasks but without a court of low. Main purpose of the development of morphology investigation was determination of correspondence between the kind of operations with nuclear materials and sizes, shapes and surface structure of industrial dust particles, and accordingly determination of industrial dust features, which could facilitate identifying of the kind of nuclear activity. Industrial dusts of different enterprises were investigated, and particles with specific morphology characteristics were determined for each kind of enterprise.

Scanning electron microscopy is used for morphology analysis. The determination of morphology details with sizes down to 0.1 µm on the surface and on the perimeter of microparticles is possible. The paper [10] shows that the results of particle morphology investigation allow to distinguish industrial dust of enrichment plants, fuel fabrication facilities and reprocessing plants. Fig. 5 presents three particles; each of them is typical only for one of these enterprises.

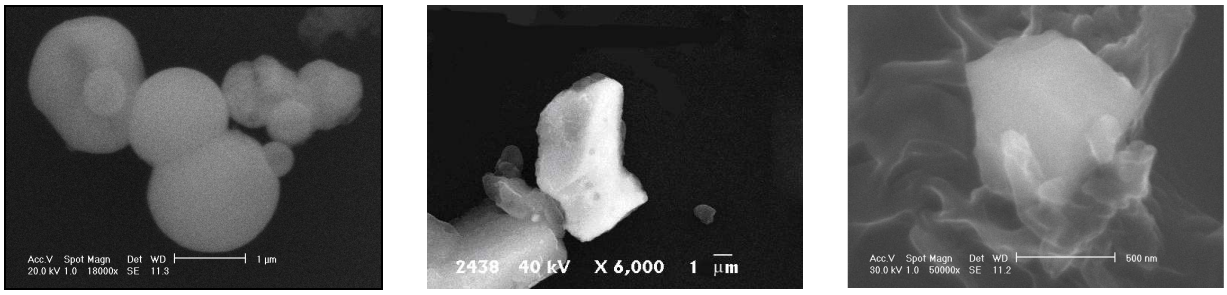


FIG. 5. Particles typical for enrichment plants (a), fuel fabrication facilities (b) and reprocessing plants (c).

Accordingly detection of any of these particles indicates the presence of industrial dust of corresponding enterprise. Signatures, which can distinguish industrial dust of different kinds of enrichment plants: centrifuge plants and diffusion plants, are considered in the paper [11]. Detection of particles with typical morphology allows to characterize the kind of facility, which can be concerned to the illicit trafficking of nuclear material, or kind of operations with stolen unknown material.

It is necessary to highlight, that differences of morphology characteristics are caused by different mechanisms of particle formation. Therefore the study of morphology characteristics of particles, detected on the site of deliberate or accidental dispersion of nuclear or other radioactive material can provide the prosecution with information about the method of dispersion and accordingly possible consequences of the incident.

5. Conclusions

5.1. Individual microparticles of nuclear or another radioactive materials can be only source of information about such material out of regulatory control, when material is not seized, but its trace amounts are found on the surfaces of some objects.
5.2. The particles of material, which is seized, but was out of regulatory control, can be source of information about the route of illicit trafficking and involved persons.
5.3. Analyses of particles with sizes at least down to 0.5 µm can provide the prosecution with useful information.
5.4. The advanced equipment and corresponding techniques are extremely important for obtaining of maximum useful information from analysis of microparticles.

REFERENCES

[1] K. Vilece. NWAL and Mass Spectrometry Particle Technique Comparison for Safeguards Samples. Environmental Samples Particle Analysis Technical Meeting, IAEA, Vienna, 2013
[2] Ch. Brennan, L. Henry. Air Force Technical Applications Centre. Support to the IAEA. IAEA Consultants Group Meeting, IAEA, Vienna, 2007
[3] M. Humphrey. Particle NWAL Status. . Environmental Samples Particle Analysis Technical Meeting, IAEA, Vienna, 2013
[4] Goldstein, J. I., et al., Scanning Electron Microscopy and X-ray Microanalysis, 2nd ed., Plenum Press, New York, 1992
[5] Wavelength Dispersive X-ray Microanalysis. OIA/011/B/0502, Oxford Instruments Analytical Limited, 2002.
[6] V.G. Dyukov, E.N. Evstaf'eva, V.A. Stebelkov, A.A. Tatarintsev, V.V. Khoroshilov "X-ray microanalysis of uranium dioxide particles with a low electron beam energy" Bulletin of the Russian academy of sciences: Physics, 2014, v.78, №9 in print
[7] V.G. Dyukov, V.V. Khoroshilov, V.B. Mityukhlyaev, V.A. Stebelkov. "Increasing of the EPMA accuracy for microparticles by means of smoothing of its surface by using ion beam" Bulletin of the Russian academy of sciences: Physics, 2015, v.79 (in print)
[8] Z. Varga, G. Surranyi. Production date determination of uranium-oxide materials by inductively coupled plasma mass spectrometry// Analytica Chimica Acta 599 - 2007. – p.p. 16 … 23
[9] G. Tamborini, N. Niagolova, Yl. Ranebo, M. Betti. Uranium Age Determination by SIMS: Determination of Th/U Relative Sensitivity Factor, IAEA Consultants Group Meeting, IAEA, Vienna, 2005
[10] V. Stebelkov. Informativeness of Morfology Analysis of Uranium Microparticles from Industrial Dust at Nuclear Plants. Proceedings of International Conference GLOBAL 2005 "Nuclear Systems for Future Generation and Global Sustainability", October 9-13, 2005, Tsukuba, Japan. Proceedings, Paper No. 084
[11] V. Stebelkov, V. Khoroshilov, Yu. Stebelkov. Occurrence of Particles with Morphology Characteristics Which Are Typical for Certain Kinds of Nuclear Activity. Symposium on International Safeguards. Vienna, 2010. Proceedings, IAEA-CN-184/82