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Tracing nuclear fuel: Monitoring and characterization of low-level radiocontaminations by laser mass spectrometry in bulk materials and environmental nanoparticles

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Summary. — For the determination of lowest level radiocontaminations from anthropogenic sources, the use of mass spectrometric methods often is a favourable approach. For many long-lived α- and β-emitters, mass spectrometry can significantly outperform conventional radiometric detection technology with respect to sensitivity, selectivity and significance. In these cases, the quantification of atom numbers of individual radioisotopes in a sample not only excels decay counting and prevents potential interferences, but can deliver robust additional information on elemental composition, spatial distribution on a microscopic or macroscopic scale and on the origin of a contamination. These data are highly relevant for counteractions, control and forensics. Elemental selective laser mass spectrometry, applied either on bulk material or for depth profiling, surface layer mapping or non-destructive hot particle inspection, today has achieved maturity to serve as routine technique for numerous applications in the fields of radioecology and radiation protection.

1. – Introduction

Even smallest radioactive contaminations from anthropogenic sources in the environment today are of highest concern for the responsible authority, the public and for decision makers. They cause fear and rejection among the population, no matter whether originating from facilities related to nuclear energy, nuclear medicine, military use or unclear sources. While in case of an emergency, the determination of radiation from short lived radioisotopes, *i.e.*, fission and activation products, their localization and removal is paramount, the lowest level determination of long lived α- and β-emitters is of high concern in regard to long term hazards in permanently affected regions, *e.g.*, in the vicinity of nuclear weapon test sites, in the vicinity of shut-down or operating nuclear facilities, as well as around existing intermediate storage sites or planned long-term repositories. The

task also includes the characterisation of numerous undeclared depositions of radioactive materials worldwide as well as cases of nuclear forensics related to terrorism or crime.

Aside of measuring overall radiation levels, which characterizes total activities and deposited amount, the specific aspects of elemental and isotopic composition, spatial macroscopic and microscopic distribution on surfaces and depth profiles, the size and composition of hot particles as well as migration and speciation of a radioisotope in an environmental compartment are of major relevance. These parameters disclose origin, age, chemical history and bonding, as well as physical constitution or stability of radioisotopes complexes. Theses are of concern to consider means of action, protection and decontamination, but are frequently no accessible by standard techniques.

As example for nuclear fuel disseminated released into the environment, *i.e.*, as hot particles or in strongly-diluted solution, it is crucial to identify the reactor type, the nuclear fuel composition and to consider circumstances and the reasons for the release. In case of particle emission, these data must be obtained from smallest fragments of typically only few μm diameter. For dissolved or adsorbed activities similarly very low contaminations in small sample sizes must be analysed on the basis of minimized chemical separation or pre-treatment to prevent the risk of introducing artefacts.

Since the very beginning of the nuclear age and the introduction of the term nuclear energy as early as 1899, ascribed to Friedrich Ernst Geitel [1-3], a contemporary of Henry Becquerel and the couple Pierre and Marie Curie, the non-radiometric technique of mass spectrometry (MS) has strongly contributed to detect, quantify and analyze radioactive contaminations in environmental and technical samples. On one side, MS is by far more extensive (and expensive) than simple and robust gas-filled devices like Geiger-Müller counters, which can detect all three kinds of nuclear radiation, *i.e.*, α-, β- and γ-radiation, with reasonable sensitivity, or the less sensitive but energy-resolving proportional counters, solid state detectors or scintillator techniques. Radiometric detection limits (LOD) as low as 100 μBq per sample are reported even for α- and β-emitters, limited only by unavoidable detector background or natural activities. This correspons to about 10^8 atoms/sample for the longest lived isotopes.

In respect to the simple or even energetically resolved counting of decay processes, there are a number of advantages of mass spectrometric quantification of individual atomic ingredients in a sample. These include

- a considerably higher sensitivity, achieved in the determination of long lived radioisotopes, which exhibit only a very limited number of disintegrations in a reasonable measuring time,

- the prevention of spectral interferences of energetically similar decay processes from different nuclides,

- the precise analysis of spatial distributions of contaminations.

The latter becomes possible by using direct approaches of MS, *e.g.*, by ion beam sputtering or laser ablation. On the other hand, MS in general suffers from strong isobaric interferences, which would, *e.g.*, prevent mass spectrometric quantification of ^{238}Pu or ^{241}Am in contaminations from nuclear facilities due to the overwhelming surplus of the isobars ^{238}U or ^{241}Pu, respectively. This latter drawback can be prevented by designing either the ionization or alternatively the detection as sophisticated element-selective process, which is the case for resonance ionization mass spectrometry (RIMS) by multi step laser ionization or for accelerator mass spectrometry (AMS) by combining an initial

formation of negative ions, stripping towards positive ions and isobar selective detection, respectively. Both techniques today are in use for specifically sensitive and selective determination of ultra-trace amounts of anthropogenic as well as natural radioisotopes originating from the nuclear fuel cycle or from other sources [4-6].

2. – Resonance ionization mass spectrometry in nuclear application fields

Bulk analysis. – Mainz University hosts the research reactor facility TRIGA Mark II as one of the last operating reactors remaining in Germany after the 2011 resolution on complete phase-out of nuclear energy. Since as early as 1982, complementing reactor based neutron activation analysis, laser based techniques of analytical mass spectrometry were investigated and advanced as a novel key technology for ultra-sensitive and selective determination of radiocontaminations, initialy with particular focus on plutonium content [4]. The implemented concept was based upon suggestions by the groups around the two pioneers in the field of resonance ionization mass spectrometry (RIMS) of atoms, V.S. Letokhov and S. Hurst, which are presented in detail in [7, 8]. Their ideas were also adopted and further developed at that time at various other research laboratories worldwide performing ultra-trace determination of various rare radionuclides [9-13].

At Mainz the development was brought to operational readiness addressing the quantification of Pu as key isotope in the radioactive threat as well as in the public awareness soon after [14]. In the development strongest emphasis was placed upon the aspects of sensitivity, selectivity and significance of the obtained data, the latter regarding specifically the precision of isotope ratios and the absence of isobaric or unspecific interferences. Following optimization and refinement of the technique, primarily on the side of the filament arrangement, the laser systems and the data acquisition, selective determination of Pu, Np and Tc radioisotopes was carried out routinely. A variety of sample materials, *e.g.*, from the former above ground nuclear weapons test sites, from regular sampling of local soil and sludge, as well as from suspected or known releases from nuclear facilities were analyzed [15-17]. A sketch of the arrangement is given in fig. 1.

Today, a well-adapted but in principle very common analytical device of a TOF-RIMS is at hand, set up as combination of a tungsten filament sample atomization at a reflectron time-of-flight (TOF) mass spectrometer with a dedicated high performance solid state laser system operating at high repetition rate of 10 kHz for resonance ionization [18]. The latter became available in 2004, replacing former unreliable systems, and is steadily optimized and adapted to the analytical applications since then. The ionization by stepwise absorption of laser photons is carried out in a simple well controlled perpendicular
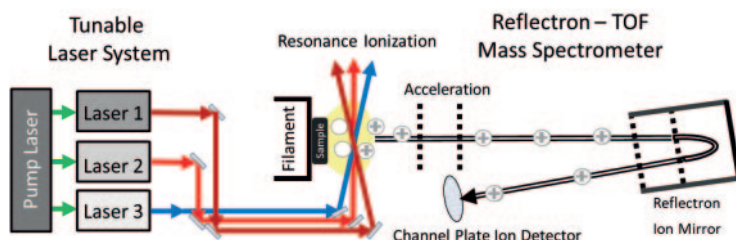

Fig. 1. – Sketch of the TOF-RIMS system for bulk analysis as used for Pu, Np and Tc determination

geometry directly in front of the filament. The laser beams transmit the atomic vapour cloud effusing from the heated filament with the interaction spot being located inside the first of two consecutive acceleration stages of the TOF-MS. This sturdy arrangement provides most favourable and reliable operation conditions, which include

- simple and fast sample exchange,

- complete removal of interfering surface ions and vagabonding electrons through repeller electrodes,

- fast recording of mass spectra and isotope ratios synchronous to each individual laser pulse,

- uncomplex and almost maintenance free operation of the lasers, and finally,

- prevention of memory effects or cross contaminations.

An overall efficiency in the range of 10^{-6} to 10^{-5} in the ratio of counted ions to initial sample content is reported mostly independent of element or isotope. This value is determend on artificially added, well calibrated amount of a tracer isotope, *e.g.*, ^{236}Pu, ^{244}Pu or ^{97}Tc, which are inserted for quantification and verification of process efficiency. The strong suppression of any kind of background from the initial sample/filament region even compensates for considerable losses in overall ionization efficiency, which are caused by the spatially limited overlap region of expanding atomic vapour and laser beams. While a combination of a hot cavity laser ion source with a high transmission magnetic sector field mass spectrometer or alternatively a radiofrequency quadrupole mass spectrometer is known to be superior in case of very pure sample materials, for which ionization efficiencies in the order of 10% are reported [19], the application on real world samples for this sophisticated and extensive approach suffers from severe limitations regarding the LOD due to unavoidable high background rates. Thus it is used only for very exceptional and highly specialized applications, similar as those dedicated versions of high resolution RIMS, which were developed and applied for selective ultra-trace determination of the rare isotopes ^{41}Ca and ^{89,90}Sr in the presence of the neighbouring stable isotopes of the same element [20, 21]. These applications will not be discussed here.

For TOF-RIMS a suitable atomization of the sample during evaporation from the filament implies an efficient reduction of the chemical, usually oxidic form of the initial sample, which is obtained in specific filament preparation as a sandwich with a reduction agent. By this step and due to the high cross sections for resonant optical excitation processes on atoms and the laser induced ionization together with the high transmission of the TOF MS, LODs in the region of 10^5 to 10^6 atoms are achieved, mostly independent of the sample matrix, confirming the high figures of merit of the technique [22].

Spatial resolved particle analysis. – Based on the expertise gained as well as motivated by frequent requests from authorities, a dedicated system offering spatial resolution for sensitive and selective radioisotope analysis on particles and surfaces has been explored at Mainz University since 2008 [23]. It is shown in fig. 2 and has lately been brought to maturity in a collaboration with the Institute of Radioecology and Radiation Protection (IRS) at Hannover University [24]. The developed technique addresses the highly relevant aspect of a direct, largely non-destructive characterization of hot particles and contaminated surfaces including the spatial mapping of activities. The approach is based upon a well-adapted commercial secondary ion mass spectrometer (SIMS) and combines
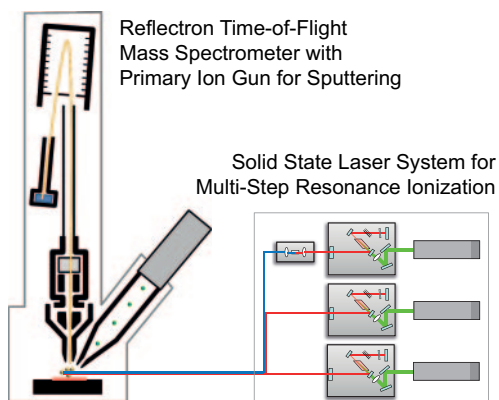
Fig. 2. – Schematical sketch of the rL-SNMS apparatus including the laser system for multi-step resonance ionization.

the primary ion beam sputtering with resonant laser ionization of the emitted secondary neutral particles for subsequent mass spectrometry. The technique thus is abbreviated as rL-SNMS, it is performed in a widely identical reflectron-TOF-MS system as the one for bulk analysis (converted into a vertical arrangement), which is equipped with different additional initial ion guns for sputtering and preparation of the sample surface. The analytical device utilizes the identical high-power, high-repetition rate laser system for atom-light interaction in a similar ionization geometry as the filament-type bulk machine. A rapid switching of electric potentials at the acceleration stage, synchronized to the laser pulses, removes primary ions from the sputtering process entirely and assures background free laser ionization of remaining neutral atoms. A photo of the rL-SNMS apparatus is shown in fig. 3 with the remotely installed laser system added in the inlay. Specific aspects of this methical development are described in [25] including a detailed comparison to conventional SIMS analytics. A corresponding plot of a mass spectrum,
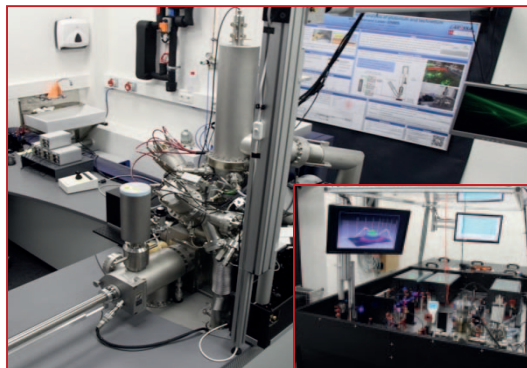

Fig. 3. – Photo of the rL-SNMS apparatus at the IRS of Hannover University with the remotely installed laser system included in the inlay.
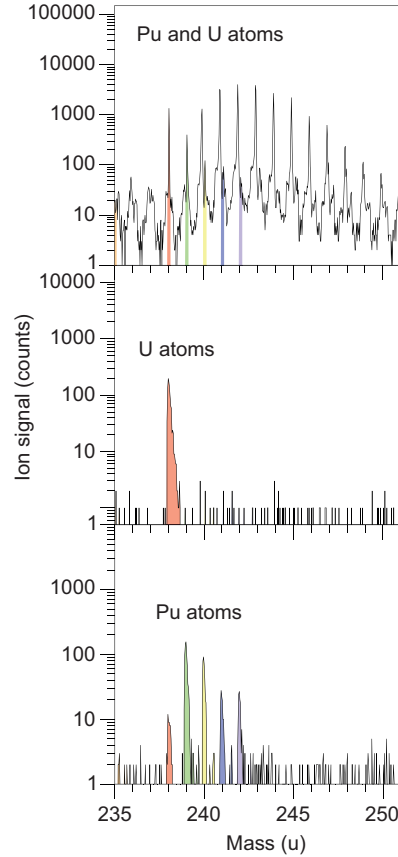
Fig. 4. – Plot of a mass spectrum, obtained by conventional SIMS on a mixed oxide fuel pellet in the mass interval 235 to 250 amu (top panel) in comparison with two rL-SNMS spectra obtained with lasers tuned to either U (middle panel) or Pu (bottom panel).

obtained by conventional SIMS on a mixed oxide fuel pellet in the mass range of the major actinides of 235 to 250 amu is compared to two rL-SNMS spectra with lasers tuned to either U or Pu, respectively, in fig. 4. The high gain in selectivity and the almost full suppression of any background or the surplus of U are clearly visible. A similar comparison in the range of Tc isotopes is discussed in [25]. Already these early data on samples prepared from nuclear fuel confirmed the expected universality and detection strength of this direct technique superseding any kind of chromatographic or radiochemical sample pre-treatment.

Applications of rL-SNMS range from radioecology, radiation protection and, nuclear forensics to safety assessment of a possible nuclear waste repository. As an outstanding demonstration, the analyses of elemental and isotopic composition of hot particles with diameters in the 10 μm range, collected with in the Chernobyl exclusion zone, are discussed in [26, 27]. Both, conventional SIMS as well as selective rL-SNMS data were taken, the latter consuming only few fg of the overall particle and leaving it widely intact for further studies. They deliver most useful information on the radioisotope content of the particle, including, *e.g.*, isotopic compositions of ^{234,235,236,238}U, $^{238-244}$Pu and the
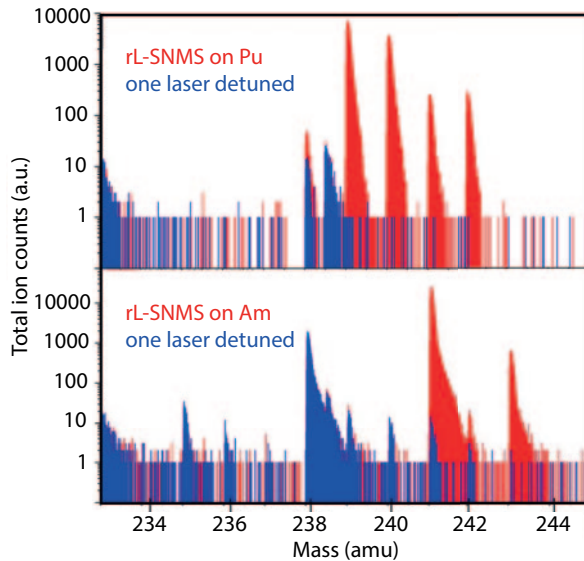
Fig. 5. – Selective hot particle analysis: rL-SNMS spectrum (red traces) on Pu (upper) and Am (lower) in comparison to background (blue traces).

minor actinide isotopes ^{241,242m,243}Am as well as ^{244}Cm, as discussed in detail in [26]. For visualization of the strength of rL-SNMS, two spectra obtained on a hot particle from the Chernobyl exclusion zone with lasers in resonance on Pu and Am, respectively, are shown in fig. 5 (red traces), together with background spectra (blue traces), obtained by detuning the laser for the first excitation step. The strong suppression of isobaric interferences from U in the case of Pu-determination and from Pu in the case of Am-determination is clearly visible, with the non-resonant signal on the mass of 238.5 amu (*i.e.*, the SIMS signal) serving for quantification of the data.

Furthermore, rL-SNMS is also used for the analysis of the migration of radionuclides, *e.g.*, in low diffusive materials such as clay minerals, which is monitored on the sub-micron scale in a widely similar rL-SNMS set-up installed at Mainz University [28]. In all these studies, ultra-trace amounts of less than 10^7 atoms, corresponding to fg levels well below radiometric detection limits, are identified and quantified. Isotope-selective imaging of surfaces or depth profiles is performed with a spatial resolution down to 100 nm.

3. – Conclusion

Resonance ionization mass spectrometry is presented as a well suited technique for sensitive and selective ultra-trace determination of specific radiocontaminations in the environment and in technical samples. For long lived α- and β-emitters, *i.e.*, the majority of the major and minor actinides from the nuclear fuel cycle as well as many fission products, the method frequently outperforms radiometric techniques in respect to measuring speed, sensitivity, selectivity and significance of the data achieved, most useful for the comprehensive analysis of μm sized objects. Studies include analysis of hot particles from the Chernobyl exclusion zone, isotopic compositions of U, Pu and the minor actinides ^{241,242m,243}Am and the isotope ^{244}Cm were measured. Together with the high

resolution mapping of radioisotope composition on a particle, a surface or in a depth profile, valuable information on origin of the contamination including age, burnup and enrichment grade of the nuclear fuel, are obtained.

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