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# Oxide ion formation of long-lived radionuclides in double-focusing sector field inductively coupled plasma mass spectrometry and their analytical applications

J. Sabine Becker\*, Hans-Joachim Dietze

*Zentralabteilung für Chemische Analysen, Forschungszentrum Jülich GmbH, D-52425 Jülich, Germany*

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## Abstract

The oxide ion formation of the long-lived radionuclides  $^{226}\text{Ra}$ ,  $^{230}\text{Th}$ ,  $^{237}\text{Np}$ ,  $^{238}\text{U}$ ,  $^{239}\text{Pu}$ , and  $^{241}\text{Am}$  was investigated in a mixed aqueous solution by double-focusing sector field inductively coupled plasma mass spectrometry (DF-ICP-MS) with a shielded torch under hot plasma conditions. The measurements of the relative oxide ion intensities by DF-ICP-MS were performed using different nebulizers [Meinhard nebulizer, microconcentric MicroMist nebulizer and a direct injection high-efficiency nebulizer (DIHEN)] for the solution introduction of aqueous standard solutions into the ICP. The highest oxide ion formation rate was observed for thorium in DF-ICP-MS under hot plasma conditions with a shielded torch ( $\text{ThO}^+/\text{Th}^+ = 0.13, 0.26, \text{ and } 0.41$  for Meinhard nebulizer, MicroMist nebulizer and DIHEN, respectively). The application of the shielded torch in DF-ICP-MS yielded an increase in oxide ion formation for the Meinhard nebulizer by a factor of 2.7–7, for MicroMist nebulizer 1.6–13 and for DIHEN 1.7–2.8, compared to the original configuration without plasma shielding. The direct injection of sample solution by DIHEN-DF-ICP-MS results in a relatively high oxide ion formation rate (e.g.  $\text{PuO}^+/\text{Pu}^+$  of about 0.16 and 0.35 without and with a shielded torch, respectively). For the relative oxide ion intensities using the Meinhard and the microconcentric MicroMist nebulizers in DF-ICP-MS with shielded torch a decrease in the following sequence is observed:  $\text{ThO}^+/\text{Th}^+ > \text{UO}^+/\text{U}^+ > \text{NpO}^+/\text{Np}^+ > \text{PuO}^+/\text{Pu}^+ > \text{AmO}^+/\text{Am}^+ \gg \text{RaO}^+/\text{Ra}^+$ . The observed correlation of measured relative oxide ion intensities ( $\text{ThO}^+/\text{Th}^+$ ,  $\text{PuO}^+/\text{Pu}^+$ , and  $\text{UO}^+/\text{U}^+$ ) and bond energies of these oxides allows for the estimation of unknown bond energies for AmO and NpO (730 and 670 kJ/mol, respectively). High oxide ion intensity of long-lived radionuclides in DF-ICP-MS could be used in some cases for analytical purposes, e.g. the oxide ions are applied as analyte ions for interference-free isotope analysis and thus for checking the analytical results using the atomic ions of the analyte. (Int J Mass Spectrom 202 (2000) 69–79) © 2000 Elsevier Science B.V.

**Keywords:** Oxide ions; Radionuclides; Double-focusing sector field inductively coupled plasma mass spectrometry

## 1. Introduction

Plasma mass spectrometric methods [1]—such as inductively coupled plasma mass spectrometry (ICP-

MS) [2,3], laser ablation ICP-MS [4], spark source mass spectrometry (SSMS) [5], glow discharge mass spectrometry [6] or laser ionization mass spectrometry (LIMS) [7] are sensitive methods for the determination of trace elements and isotope ratios in inorganic materials. The quantification of analytical results is sometimes difficult, not only in solid state

\* Corresponding author. E-mail: s.becker@fz-juelich.de

mass spectrometry if standard reference materials are not available, but also in ICP-MS and the other inorganic mass spectrometric techniques due to incomplete knowledge of ion-formation processes. Especially the molecular ions (e.g.  $\text{MO}_n^+$ ,  $\text{MH}_n^+$ ,  $\text{MAr}^+$ ,  $\text{MCl}^+$ ,  $\text{MN}^+$  with M-matrix element;  $\text{Ar}_n\text{X}_m^+$  with X = H, O, N, Cl, and others) formed in an argon plasma and behind the sampler cone in ICP-MS complicate the analysis of trace elements through isobaric interferences with atomic ions of the analyte. The systematic investigation of molecular ion formation in plasmas as a function of experimental parameters (e.g. rf power, nebulizer gas flow rate, and sampling depth) can help to find out under which conditions molecular ion formation could be influenced in order to avoid disturbing interferences and decrease the detection limits of elements in trace and ultratrace analyses, especially if low-resolution mass spectrometry (e.g. quadrupole ICP-MS) is used.

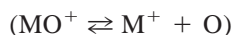
Some efforts have been made with different sample introduction systems [8] (e.g. by desolvation [9], hydride generation [10], electrothermal vaporization [11], thermospray and membrane separator [12], laser ablation [13]), by the application of so-called cool plasma techniques (at low rf power and increased nebulizer gas flow rate) [14] or the dissociation of some disturbing molecular ions in dynamic reaction cells [15] in order to reduce the interferences of molecular ions and atomic ions of analyte. Plasma shielding proposed by Gray with quadrupole-based ICP-MS (ICP-QMS) for measurements under “cool” plasma conditions [16] have been studied by different Japanese groups [17–19] with the aim of removing the molecular ions formed behind the sampling cone. A reduction of some disturbing molecular ions (e.g.  $\text{ArH}^+$ ,  $\text{Ar}_2^+$ ,  $\text{CO}_2^+$ , and  $\text{ArO}^+$ ) was observed under cool plasma conditions. On the other hand, new molecular and cluster ions, such as water cluster ions, were observed with high ion intensities [20,21].

Further, analytical results with high accuracy and precision for the determination of trace and ultratrace elements and the isotopic composition of elements in inorganic materials can be obtained—e.g. by the application of double-focusing sector field ICP-MS (DF-ICP-MS)—if these interference problems of ana-

lyte ions with molecular ions are overcome by a mass spectrometric separation of interferences at the required mass resolution. However, the commercially available double-focusing sector field ICP-MS with a maximum mass resolution ( $m/\Delta m$ ) of approximately 10 000 cannot separate all possible interferences of molecular ions and atomic ions as demonstrated in recent work [22]. For example maximum mass resolution ( $m/\Delta m \approx 4 \times 10^6$ ) is required for the separation of interference from  $^{90}\text{Zr}^{18}\text{O}^+$  and  $^{108}\text{Pd}^+$ . Possible interferences of  $\text{MO}^+$  and analyte ions in the mass range between 70 and 130 u are difficult to separate by double-focusing sector field ICP-MS.

On the other hand, as an excellent and important analytical tool mass spectrometry is often used for basic research into molecular and cluster ion formations in a plasma. By comparing relative ion intensities in mass spectrometric measurements and bond dissociation energies as a result of experimental and/or theoretical investigations a correlation was found, e.g. for oxide ions of rare earth elements (REE) in ICP-MS [13,23]. This correlation of measured relative molecular ion intensities which was also found for the oxide, carbide, and dicarbide ion intensities of rare earth elements in two solid state mass spectrometric techniques—SSMS and LIMS—with bond dissociation energies could be attributed to the electronic structure of REE [24]. A correlation of measured  $\text{MO}^+$  ion intensities and experimentally determined or theoretically calculated bond energies of oxides was described firstly in laser mass spectrometry using a LAMMA 500 (laser microprobe mass analyzer, Leybold Hereaus AG, Cologne) by Michiels and Gijbels [25].

By the analysis of aqueous solutions Kubota et al. [26] observed in ICP-MS a correlation of relative oxide ion intensities ( $\text{MO}^+/\text{M}^+$ ) for different metal ions  $\text{M}^+$  with dissociation energies of the  $\text{MO}^+$  and estimated a dissociation temperature assuming of the existence of dissociation equilibrium



The correlation of the diatomic argon molecular ion intensities in DF-ICP-MS and bond dissociation en-

ergies was discussed in recent articles by Becker et al. [13,23]. The theoretical investigation of the argon molecular ions for elements of the second and third period in the periodic table of elements by means of quantum chemical calculation (linear combination of atomic orbitals-density function theory-local spin density approximation: LCAO-DFT-LDA) indicated that small binding energies were obtained for metal argide ions at the beginning of the period and that the bond energies rose with increasing atomic number. Higher intensities of nonmetal argon molecular ions in comparison to the metal argide ions in DF-ICP-MS can be interpreted as being due to higher stability. Furthermore, the correlation of  $\text{MAr}^+$  ions found in ICP-MS with bond dissociation energies was used for the determination of unknown bond dissociation energies.

In the previous article different nebulizers for solution introduction in the inductively coupled plasma [such as Meinhard nebulizer, microconcentric MicroMist nebulizer, direct injection high efficiency nebulizer (DIHEN) and ultrasonic nebulizer (USN)] were compared by double-focusing sector field ICP-MS with and without a shielded torch for the sensitive determination of long-lived radionuclides in the ultratrace concentration range down to the subpicogram per liter concentration range [27]. For plasma shielding, a grounded platinum electrode is inserted between the quartz ICP torch and the rf load coil to prevent capacitive coupling from the load coil into the ICP and the secondary discharge between ICP and sampling cone is reduced. In DF-ICP-MS under hot plasma conditions the application of the shielded torch yielded an increase of sensitivity of long-lived radionuclides for the Meinhard, ultrasonic and MicroMist nebulizers up to a factor of 5 compared to the original configuration without a shielded torch. In order to characterize the different nebulizer types used in DF-ICP-MS with and without shielded torch the formation of molecular ions is of interest. The oxide formation rate ( $\text{MO}^+/\text{M}^+$ ) using a Meinhard nebulizer and microconcentric MicroMist nebulizer in DF-ICP-MS in the original configuration without the shielded torch for long-lived radionuclides is lower than  $\approx 0.03$ . This result is in agreement with the

measured oxide ion formation rate of thorium and uranium in ICP-QMS using a cross-flow nebulizer with Scott spray chamber and the microconcentric nebulizer MicroMist with minicyclonic spray chamber [28] and described by Garcia Alonso et al. [29] using a Meinhard nebulizer and a Scott spray chamber. The spray chamber are noncooled in all experiments, with cooled spray chamber a decreasing of oxide ion intensities was observed.

Oxide formation which can disturb the determination of long-lived radionuclides by isobaric interferences should be carefully considered in the ICP-MS of aqueous solutions for different nebulizers with the experimental parameters employed. To reduce sample consumption and minimize instrumental radioactivity contamination and doses to the operator for the characterization of radioactive waste solutions micronebulizers have been increasingly used instead of the conventional Meinhard or ultrasonic nebulizer for solution introduction in ICP-MS with a solution uptake rate of  $1 \text{ mL min}^{-1}$  or greater. With the direct injection high-efficiency nebulizer (a solution uptake rate up to some microliters per minute is possible) which was first used by Montaser and co-workers [30], for direct solution introduction into the inductively coupled plasma of an ICP-MS, a higher oxide formation rate (e.g.  $\text{ThO}^+/\text{Th}^+ = 0.075$  and  $\text{UO}^+/\text{U}^+ = 0.051$ ) is observed compared to conventional nebulizers [31,32].

However, no detailed data of molecular ion formation have been published for DF-ICP-MS with a shielded torch under hot plasma conditions. The aim of this article is the investigation of the oxide ion formation of long-lived radionuclides using different nebulizers in DF-ICP-MS with a shielded torch.

## 2. Experimental

### 2.1. Instrumental

The experimental parameters of solution introduction using different nebulizers and of mass spectrometric measurements by a double-focusing sector field ICP-MS ELEMENT from Finnigan MAT, Bre-

Table 1

Experimental parameters for the double-focusing sector field ICP-MS "ELEMENT" (Finnigan MAT, Bremen)

Nebulizer type	Meinhard nebulizer	MicroMist nebulizer	DIHEN	USN
Spray chamber	Scott type (double pass)	Mini-cyclonic, Cinnabar	...	...
rf power, W	1300	1100	1500	1150
Sample uptake rate, mL min <sup>-1</sup>	1.0	0.085	0.085	2
Nebulizer gas flow rate, L min <sup>-1</sup>	0.92	1.067	0.18	1.157
Sample size, pg (1 ng L <sup>-1</sup> solution)	5	0.4	0.4	10
<i>For all nebulizer types</i>				
Auxiliary gas flow rate, L min <sup>-1</sup>	0.8			
Coolant gas flow rate, L min <sup>-1</sup>	15			
Total acquisition time per replicate, min	1			
Number of replicates	5			
Mass range	225.5–241.5 u (peak hopping)			
Mass resolution $m/\Delta m$	300			

men, Germany are summarized in Table 1. The experimental parameters are optimized with respect to maximum ion intensity of <sup>238</sup>U<sup>+</sup> as described in a recent article [27]. The grounded platinum electrode [GuardElectrode™ (GE), Finnigan MAT] for plasma shielding is located between the quartz ICP torch and the rf load coil, the GE is automatically moved into and out of position. The mass spectrometric measurements with and without GE were performed in this work under the same (hot) plasma conditions. For the determination of the concentration and isotope ratios of long-lived radionuclides in the ultralow concentration range we mostly used a microconcentric MicroMist nebulizer with a minicyclonic spray chamber (Glass Expansion, Australia) and the direct injection high-efficiency nebulizer (DIHEN, J.E. Meinhard Associates)—both nebulizers work with solution uptake rates of 0.085 mL min<sup>-1</sup>—in comparison to the conventional Meinhard nebulizer with Scott spray chamber at a solution uptake rate of 1 mL min<sup>-1</sup> and a U-6000AT ultrasonic nebulizer without desolvator (USN, Cetac Technologies, Omaha, Nebraska, USA) with solution uptake rates of 2 mL min<sup>-1</sup>. The minicyclonic and the Scott spray chambers are not cooled and the sample depth was constant at 12 mm in all experiments. The DIHEN works at a very low nebulizer gas flow rate of 0.16 L min<sup>-1</sup> and higher rf power of 1500 W in comparison to the other nebulizers used. The sample size for 1 ng L<sup>-1</sup> solution was 0.4 pg of radionuclide using both micronebulizers, compared

to 5 pg for the Meinhard nebulizer. All mass spectrometric measurements were performed for an acquisition time of 5 min only.

## 2.2. Materials and sample preparation

In order to characterize different nebulizer types for the determination of oxide formation rates of long-lived radionuclides, a mixture of <sup>226</sup>Ra, <sup>228</sup>Th, <sup>230</sup>Th, <sup>232</sup>Th, <sup>233</sup>U, <sup>235</sup>U, <sup>237</sup>Np, <sup>238</sup>U, <sup>239</sup>Pu, and <sup>241</sup>Am in aqueous solution (1 ng L<sup>-1</sup> of each radionuclide) was investigated.

Further, soil samples and aqueous radioactive waste solutions from the vicinity of a nuclear power plant were analyzed using the oxide and atomic ions as analyte ions by ICP-MS as well. Whereas the radioactive aqueous waste solutions were measured after dilution, the soil samples were leached with concentrated subboiled nitric acid. The uranium was extracted from diluted leached solution with methyl isobutyl ketone (MIBK) and after backextraction the aqueous solution was analyzed by ICP-MS [32].

## 3. Results and discussion

### 3.1. Formation of oxide ions in ICP-MS using different nebulizers

In Table 2 the relative oxide ion intensities for different nebulizers in DF-ICP-MS under hot plasma

Table 2  
Relative intensities of oxide ions ( $\text{MO}^+/\text{M}^+$ ) of long-lived radionuclides in DF-ICP-MS

Molecular ion	Meinhard nebulizer		MicroMist nebulizer		DIHEN	
	Without GE	With GE	Without GE	With GE	Without GE	With GE
$^{226}\text{Ra}^{16}\text{O}^+$	<0.001	<0.001	<0.001	0.0018	n.d. <sup>a</sup>	n.d.
$^{232}\text{Th}^{16}\text{O}^+$	0.019	0.132	0.020	0.255	0.241	0.407
$^{237}\text{Np}^{16}\text{O}^+$	0.013	0.047	0.018	0.095	0.125	0.324
$^{238}\text{U}^{16}\text{O}^+$	0.022	0.060	0.040	0.150	0.104	0.283
$^{239}\text{Pu}^{16}\text{O}^+$	0.007	0.023	0.015	0.069	0.157	0.346
$^{241}\text{Am}^{16}\text{O}^+$	<0.001	0.003	0.008	0.013	0.024	0.067

<sup>a</sup> n.d.: not determined.

conditions with and without a shielded torch are presented. The oxide ion formation rate ( $\text{MO}^+/\text{M}^+$ ) using Meinhard and microconcentric MicroMist nebulizers without plasma shielding is observed to be lower than or equal to about 0.04. The highest oxide formation was observed using the DIHEN in DF-ICP-MS. This result is in agreement with findings in ICP-QMS [31], higher oxide ion intensities are observed for direct solution injection of the primary aerosol into the ICP (without waste water separation in a spray chamber). The relative oxide ion intensity varied in DIHEN-DF-ICP-MS without a shielded torch from 0.024 for  $\text{AmO}^+/\text{Am}^+$  to about 0.24 for  $\text{ThO}^+/\text{Th}^+$ . Using the shielded torch in DF-ICP-MS at the same rf power and nebulizer gas flow rate (under hot plasma conditions) in general an increase of the oxide formation rate was measured (for the Meinhard nebulizer by a factor of 2.7–7; for the MicroMist nebulizer 1.6–13, and for DIHEN: 1.7–2.8) compared to the original configuration without plasma shielding. An increase of the oxide formation rate with shielding in DF-ICP-MS using different nebulizers compared to the unshielded configuration could be explained as follows. In the shielded plasma compared to the unshielded plasma, electrons possess a lower kinetic energy, so that the relatively stable oxide bonds of radionuclides investigated from the original compounds were not dissociated completely.

The oxide formation rates for Th, Np, U, Pu, and Am using the DIHEN in DF-ICP-MS with and without a shielded torch and in ICP-QMS without a shielded torch are compared in Fig. 1. The experiments using the DIHEN without aerosol desolvation

which were performed at the rf power of 1500 W and with the slightly different nebulizer gas flow rate of  $0.16 \text{ L min}^{-1}$  in ICP-QMS and  $0.18 \text{ L min}^{-1}$  in DF-ICP-MS, yielded significantly higher oxide ion formation rates in DF-ICP-MS.

Figure 2 demonstrates the higher relative oxide ions of U and Th in DF-ICP-MS (Meinhard nebulizer) using the shielded torch compared to experiments without plasma shielding as a function of rf power. With increasing rf power the oxide formation rate decreases for both experimental configurations, but a greater extent for the configuration with the shielded torch. Similar behavior for the relative oxide ion intensities of long-lived radionuclides was found as a function of rf power in DF-ICP-MS with and without GE using microconcentric MicroMist nebulizers. Fig. 3 shows the curves for  $\text{ThO}^+/\text{Th}^+$ ,  $\text{UO}^+/\text{U}^+$  and  $\text{PuO}^+/\text{Pu}^+$  as a function of rf power in DF-ICP-MS with GE. The decreasing oxide formation rate with increasing rf power (that means an increase of plasma temperature, kinetic energy of electrons and electron density) could be explained because under these conditions the electrons possess more energy for dissociation processes of original oxide compounds at higher plasma temperature.

The formation of oxide ions of Th, U, and Pu in DF-ICP-MS with plasma shielding as a function of nebulizer gas flow rate for Meinhard and microconcentric MicroMist nebulizers in DF-ICP-MS with GE is compared in Fig. 4. Both nebulizers show the similar behavior. An increasing formation of oxide ions with increasing nebulizer gas flow rate in the double-focusing ICP-MS with guard electrode was

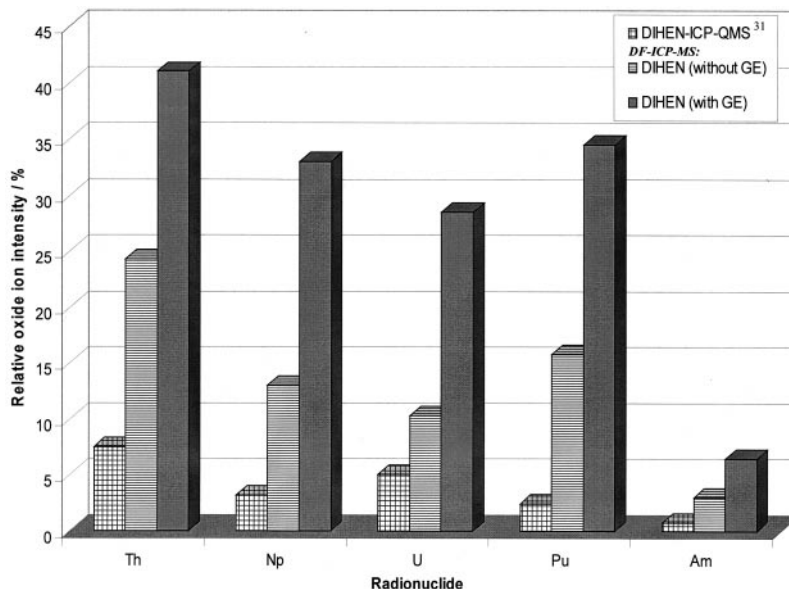


Fig. 1. Relative oxide ion intensities ( $\text{MO}^+/\text{M}^+$ , in %) for  $\text{M} = \text{Th}, \text{Np}, \text{U}, \text{Pu}$  and  $\text{Am}$  in DIHEN-DF-ICP-MS with and without shielded torch in comparison to quadrupole-based ICP-MS [31] (rf power: 1500 W, nebulizer gas flow rate: 0.18 and 0.16  $\text{L min}^{-1}$ , respectively).

observed, because at higher nebulizer gas flow rate the residence time of the nebulized aerosol in the plasma region is lower and the oxides were not dissociated completely. A similar effect of nebulizer

gas flow rate on the ion intensity ratio of  $\text{CeO}^+/\text{Ce}^+$  in ICP-QMS using an USN was described by Montasser et al. [12].

It is important to note, that the measured oxide ion

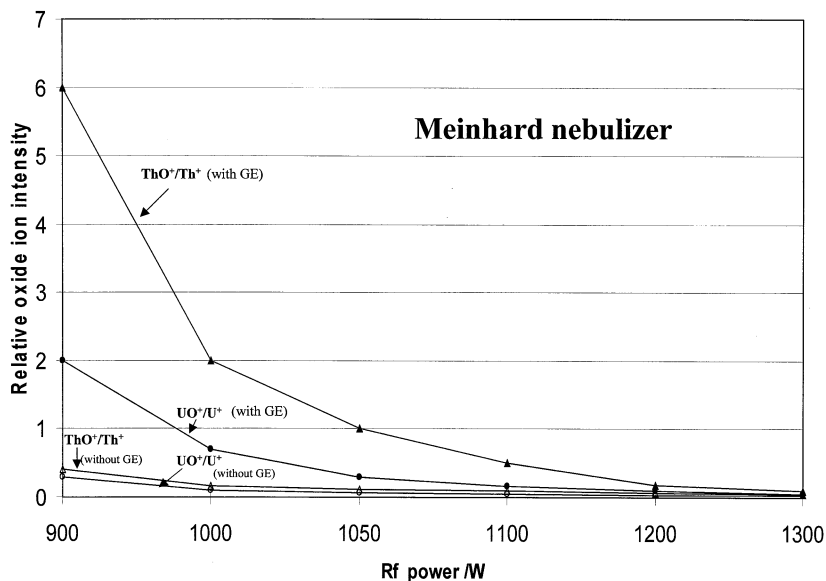


Fig. 2. Dependence of relative oxide ion intensities of  $\text{ThO}^+/\text{Th}^+$  and  $\text{UO}^+/\text{U}^+$  in double-focusing sector field ICP-MS with and without GE on rf power (Meinhard nebulizer: gas flow rate = 0.92  $\text{L min}^{-1}$ ).



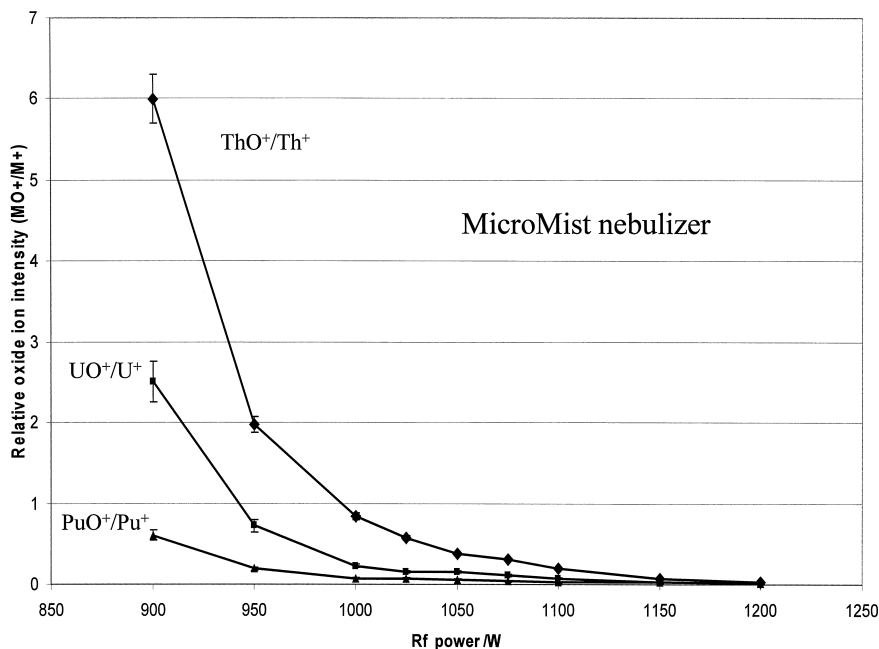
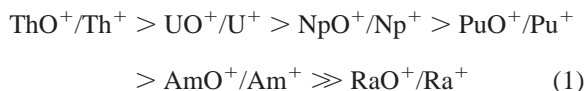


Fig. 3. Relative oxide ion intensity of ThO<sup>+</sup>/Th<sup>+</sup>, UO<sup>+</sup>/U<sup>+</sup> and PuO<sup>+</sup>/Pu<sup>+</sup> for microconcentric MicroMist nebulizers in double-focusing sector field ICP-MS with shielded torch as a function of rf power (nebulizer gas flow rate: 1.067 L min<sup>-1</sup>).

formation rate of long-lived radionuclides is reproducible only under exactly the same experimental conditions as given in Table 1 (including the same torch position, sample depth, type of nebulizers, ion lens voltages, and geometry of sampler and skimmer cones) using the highest purity aqueous solution and a background-free instrument. The molecular ion formation is sensitive with respect to any changes of these parameters and in the presence of matrix and memory effects. For example quite different behavior from that described was observed for ThO<sup>+</sup> ion formation due to memory effect on the sample cone. In the case of observed contamination nonreproducible relations of oxide ion formation as a function of rf power and nebulizer gas flow rate were observed. No statements and corrections are possible, because the oxide ion intensity changes as a function of time. Therefore a clean ICP-MS and the realization of exact experimental conditions is an important prerequisite for a reproducible measurement.

### 3.2. Correlation of oxide ion intensities of long-lived radionuclides with bond energies

Similar to the results in DIHEN-ICP-QMS [31] the relative oxide ion intensities of long-lived radionuclides using the Meinhard and microconcentric MicroMist nebulizers in DF-ICP-MS with a shielded torch decrease in the following sequence:



This sequence (1) was also observed at lower rf power and higher nebulizer gas flow rate as given in Table 1 without shielded torch using the USN (without desolvator) in DF-ICP-MS.

A relatively high molecular ion intensity in mass spectrum correlates with a relatively high bond energy. In recent work such a correlation was found for the formation of stable argon molecular ions (ArX<sup>+</sup> with X = nonmetal) in DF-ICP-MS [13,23]. From

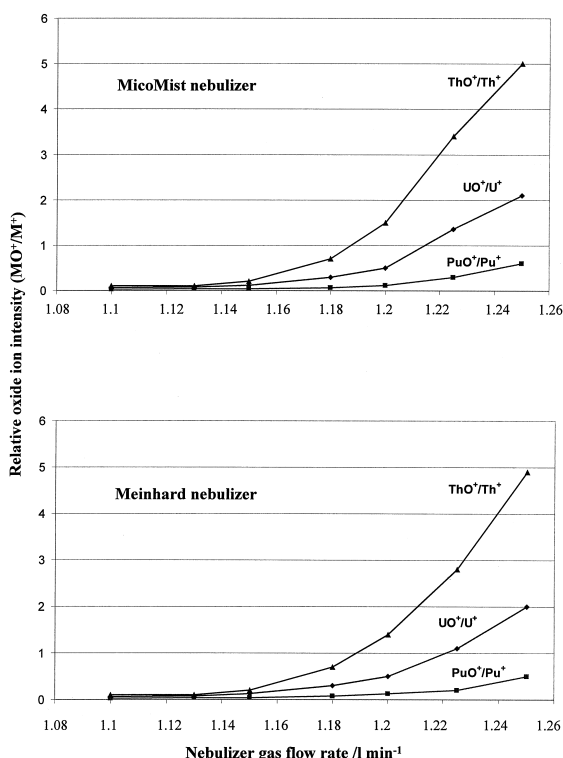


Fig. 4. Comparison of the relative ion intensity of  $\text{ThO}^+/\text{Th}^+$ ,  $\text{UO}^+/\text{U}^+$ , and  $\text{PuO}^+/\text{Pu}^+$  for microconcentric MicroMist and Meinhard nebulizers in double-focusing sector field ICP-MS with shielded torch as a function of nebulizer gas flow rate (rf power: 1100 and 1300 W, respectively).

the long-lived radionuclides investigated the most stable oxide formed thorium with a bond dissociation of  $878.6 \pm 12.1 \text{ kJ mol}^{-1}$  followed by uranium ( $759.4 \pm 13.4 \text{ kJ mol}^{-1}$ ) and plutonium ( $715.9 \pm 33.9 \text{ kJ mol}^{-1}$ ) [33].

Fig. 5 shows the correlation of the relative oxide ion intensity of long-lived radionuclides (rf power—1075 W; nebulizer gas flow rate  $1.07 \text{ L min}^{-1}$ ; sample uptake rate  $0.085 \text{ mL min}^{-1}$ ) with the bond energies of oxides. The relative oxide ion intensities were measured in DF-ICP-MS with shielded torch using the MicroMist nebulizer. For the long-lived radionuclides an excellent correlation of the measured relative oxide ion intensity with the bond energies was found for Th, Pu and U (correlation coefficient—0.9968). Using this correlation curve and the measured relative oxide ion intensities ( $\text{NpO}^+/\text{Np}^+$  and

$\text{AmO}^+/\text{Am}^+$ ) the unknown bond energies of  $\text{NpO}$  and  $\text{AmO}$  were estimated to be  $730$  and  $673 \text{ kJ mol}^{-1}$ , respectively. Recently the experimental bond dissociation energy with  $718 \pm 42 \text{ kJ/mol}$  was published for  $\text{NpO}$  [34]. The experimental bond enthalpy is in an excellent agreement with our mass spectrometric determined value of  $730 \pm 15 \text{ kJ mol}^{-1}$  for DF-ICP-MS. By laser ablation ICP-QMS we determined the bond dissociation energy for  $\text{NpO}$  of  $733 \pm 36 \text{ kJ mol}^{-1}$  [35].

The lowest oxide ion formation rate was observed for Ra (e.g.  $\text{RaO}^+/\text{Ra}^+ = 0.0018$  using MicroMist nebulizer in DF-ICP-MS with GE). Therefore the bond energy of  $\text{RaO}$  which is unknown should be the lowest of the studied long-lived radionuclide oxides. The sequence (1) of intensities of long-lived radionuclides and bond dissociation energies was not observed in DF-ICRMS under different experimental conditions of measurements with DIHEN (with and without shielded torch, see Fig. 1) or MicroMist nebulizer and Meinhard nebulizer (without shielded torch). The reason for a different sequence when using the e.g. DIHEN in DF-ICP-MS is unclear. Using a USN Montaser et al. [12] observed for  $\text{CeO}^+/\text{Ce}^+$  and  $\text{ThO}^+/\text{Th}^+$  in ICP-QMS (bond energy of  $\text{ThO} > \text{CeO}$ ; 9 and 8.18 eV, respectively) a change in the relation of ion intensity ratios as a function of nebulizer gas flow rate (for nebulizer gas flow rate  $0.8\text{--}0.9 \text{ L min}^{-1}$   $\text{ThO}^+/\text{Th}^+ > \text{CeO}^+/\text{Ce}^+$  as expected, but at higher nebulizer gas flow rate  $\text{CeO}^+/\text{Ce}^+ > \text{ThO}^+/\text{Th}^+$ ). The authors mentioned that, ideally, the dissociation energy of the molecular ( $\text{MO}^+$ ), not that of the neutral molecule ( $\text{MO}$ ), must be used in the comparison of the oxide levels, but such data are not readily available [12].

### 3.3. Application of oxide ions for analytical purposes

The knowledge of oxide-ion formation in ICP-MS is of special interest for at least two different reasons. On the one hand, interferences of oxide ions of the long-lived radionuclides with atomic ions of radionuclides at a mass higher by 16 u in mass spectra are possible (see Table 3). Due to the relatively high



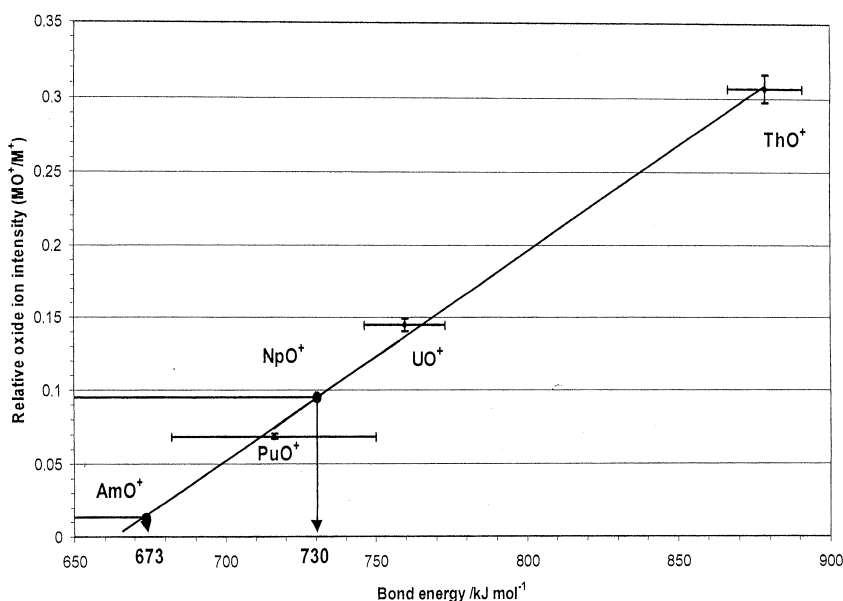


Fig. 5. Correlation of the relative ion intensity of long-lived radionuclides (DF-ICP-MS with shielded torch MicroMist nebulizer; rf power—1075 W; Nebulizer gas flow rate 1.07 L min<sup>-1</sup>; sample uptake rate 0.085 mL min<sup>-1</sup>) with bond energies [33].

oxide ion intensities in DF-ICP-MS the determination of e.g. <sup>244</sup>Pu, <sup>246</sup>Cm, and <sup>248</sup>Cm is difficult in the presence of a high content of <sup>228</sup>Th, <sup>230</sup>Th, and <sup>232</sup>Th. On the other hand, because of their relatively high intensity of oxide ions in DF-ICP-MS these ionic species can also be used as analyte ions in some cases for interference-free determination of element concentration and isotope ratios of long-lived radionuclides. The application of oxide ions for analytical purposes we demonstrated in ICP-QMS for the iso-

tope ratio measurement of Th and U in a radioactive waste solution using the DIHEN in [31] and for the determination of uranium isotope ratios in different soil samples using the microconcentric MicroMist nebulizer in ICP-QMS for solution introduction in [32].

The sensitivity of oxide ions for determining concentrations greatly depends on the experimental parameters and can exceed the sensitivity of atomic ions at low rf power and high nebulizer gas flow rate as

Table 3  
Possible interferences of oxide ions with radionuclides

Disturbed analyte ion	Half-life of actinide nuclide (yr)	Molecular ion	Mass (u)	Relative oxide ion intensity (MO <sup>+</sup> /M <sup>+</sup> ) using USN <sup>a</sup>
<sup>242</sup> Pu <sup>+</sup>	3.8 × 10 <sup>5</sup>	<sup>226</sup> Ra <sup>16</sup> O <sup>+</sup>	242	0.002
<sup>244</sup> Pu <sup>+</sup>	8.2 × 10 <sup>7</sup>	<sup>228</sup> Th <sup>16</sup> O <sup>+</sup>	244	0.149
<sup>246</sup> Cm <sup>+</sup>	9.3 × 10 <sup>3</sup>	<sup>230</sup> Th <sup>16</sup> O <sup>+</sup>	246	0.149
<sup>248</sup> Cm <sup>+</sup>	4.7 × 10 <sup>5</sup>	<sup>232</sup> Th <sup>16</sup> O <sup>+</sup>	248	0.149
<sup>249</sup> Cf <sup>+</sup>	360	<sup>233</sup> U <sup>16</sup> O <sup>+</sup>	249	0.056
<sup>251</sup> Cf <sup>+</sup>	892	<sup>235</sup> U <sup>16</sup> O <sup>+</sup>	251	0.056
<sup>252</sup> Cf <sup>+</sup>	2.65	<sup>236</sup> U <sup>16</sup> O <sup>+</sup>	252	0.056
<sup>253</sup> Es <sup>+</sup>	20.47 d	<sup>237</sup> Np <sup>16</sup> O <sup>+</sup>	253	0.028
<sup>254</sup> Es <sup>+</sup>	276 d	<sup>238</sup> U <sup>16</sup> O <sup>+</sup>	254	0.056
<sup>257</sup> Fm <sup>+</sup>	80 d	<sup>241</sup> Am <sup>16</sup> O <sup>+</sup>	257	0.012

<sup>a</sup> USN without desolvator, DF-ICP-MS without shielded torch.

Table 4

Determination of  $^{235}\text{U}/^{238}\text{U}$  isotope ratio in soil sample using the atomic ions and oxide ions as analyte ions in DF-ICP-MS with GE and microconcentric MicroMist nebulizer

Sample	$^{235}\text{U}/^{238}\text{U}$	RSD	$^{235}\text{U}^{16}\text{O}/^{238}\text{U}^{16}\text{O}$	RSD
1	0.009 05	0.08%	0.008 93	0.13%
2	0.013 35	0.11%	0.013 13	0.24%
3	0.008 21	0.06%	0.008 11	0.18%
4	0.022 06	0.07%	0.022 14	0.09%

demonstrated in Figs. 3 and 4. In principle, double-focusing sector field ICP-MS with shielded torch permits the determination of ultratrace concentrations and isotope ratios of long-lived radionuclides using oxide ions with detection limits from nanogram per liter to picogram per liter range.

The results of uranium isotope ratio measurements in four soil samples by DF-ICP-MS with GE (microconcentric MicroMist nebulizer) using atomic and oxide ion species of uranium are summarized in Table 4. The uranium concentration in the original sample was  $<1 \mu\text{g/g}$ . The isotope ratio measurements were performed subsequently without any disturbing interferences after careful uranium separation by liquid-liquid extraction with methyl isobutyl ketone (MIBK) from (with concentrated nitric acid) leachate of the soil sample [32]. In general, the precision of isotope ratio measurements using the atomic ions of 0.06%–0.11% is better than the precision using the oxide ions (RSD varied from 0.09% to 0.24%) due to higher atomic ion intensities in these experiments. Good agreement of the  $^{235}\text{U}/^{238}\text{U}$  isotope ratio measurements using the atomic ions and oxide ions of uranium was found as well. The application of oxide ions for the determination of isotope ratios is therefore interesting in ICP-MS because these measurements in comparison to the atomic ions of analyte are useful for validation of experimental results and help to avoid systematic errors. For all investigated soil samples an enrichment of the  $^{235}\text{U}/^{238}\text{U}$  isotope ratio (up to a factor of 3) was found in comparison to the value in nature ( $^{235}\text{U}/^{238}\text{U}$ —0.007 25). The natural  $^{235}\text{U}/^{238}\text{U}$  isotope ratio was determined in an additional experiment with good accuracy and precision on a certified

Table 5

Determination of thorium and uranium isotope ratio in radioactive waste solutions using the atomic ions and oxide ions as analyte ions in DF-ICP-MS with GE and microconcentric MicroMist nebulizer

	Sample 1	Sample 2
$^{228}\text{Th}/^{232}\text{Th}$	$(1.38 \pm 0.33) \times 10^{-6}$	$(3.47 \pm 0.83) \times 10^{-6}$
$^{228}\text{ThO}/^{232}\text{ThO}$	$(1.31 \pm 0.41) \times 10^{-6}$	$(3.37 \pm 0.80) \times 10^{-6}$
$^{230}\text{Th}/^{232}\text{Th}$	$(2.21 \pm 0.11) \times 10^{-3}$	$(2.20 \pm 0.07) \times 10^{-2}$
$^{230}\text{ThO}/^{232}\text{ThO}$	$(2.33 \pm 0.22) \times 10^{-3}$	$(2.35 \pm 0.13) \times 10^{-2}$
$^{235}\text{U}/^{238}\text{U}$	$(1.12 \pm 0.03) \times 10^{-2}$	$(8.94 \pm 0.50) \times 10^{-3}$
$^{235}\text{UO}/^{238}\text{UO}$	$(1.05 \pm 0.09) \times 10^{-2}$	$(8.97 \pm 0.80) \times 10^{-3}$
$^{236}\text{U}/^{238}\text{U}$	$(1.40 \pm 0.07) \times 10^{-4}$	$(1.06 \pm 0.05) \times 10^{-3}$
$^{236}\text{UO}/^{238}\text{UO}$	$(1.29 \pm 0.06) \times 10^{-4}$	$(1.30 \pm 0.20) \times 10^{-3}$

reference material (soil sample, TILL 2, Canada) for defining the element concentration.

A summary of the isotope ratio measurements of U and Th in two radioactive waste solutions using atomic ions and oxide ions as analyte ions in DF-ICP-MS with a shielded torch and the MicroMist nebulizer are presented in Table 5. The precision of measured isotope ratios varied from 2.5% (isotope ratio  $\approx 10^{-2}$ ) to 25% (isotope ratio  $\approx 10^{-6}$ ) at the subnanogram per liter concentration level for U and Th in the radioactive waste solution. The agreement of measured isotope ratios is sufficient considering the low radioelement concentration. The non-natural radionuclides  $^{228}\text{Th}$ ,  $^{230}\text{Th}$ , and  $^{236}\text{U}$  with low abundance were detected in the radioactive waste solution.

#### 4. Conclusions

Knowledge of the formation, abundance distribution, and electronic stability of molecular ions is of great analytical significance if mass spectrometric systems with low mass resolution (e.g. ICP-QMS) are applied for trace, ultratrace, and isotopic analysis. The correlation of relative oxide ion intensities of long-lived radionuclides found in DF-ICP-MS (with a shielded torch using Meinhard and microconcentric MicroMist nebulizers) with bond energies of diatomics can be used for the determination of unknown bond energies of radionuclide oxides of Am and Np. The application of microconcentric nebulizers, which

are of special interest for the ultrasensitive determination of long-lived radionuclides in the subpicogram per liter concentration range in order to reduce the contamination of the instrument and the dose to the operator, causes relatively high oxide ion formation in DF-ICP-MS with a shielded torch. Relatively high oxide formation rates of long-lived radionuclides in DF-ICP-MS can be used for determination of element concentrations and isotope ratio measurements in order to verify the results of analysis using the atomic ions. The good sensitivity of oxide ions of long-lived radionuclides (e.g., for th and n) in double-focusing sector field ICP-MS with shielded torch permits their application as analyte ions in ultratrace and isotope analysis down to the picogram per liter and nanogram per liter concentration range, respectively.

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