International Journal of Mass Spectrometry 208 (2001) 193–204

Ultratrace and isotopic analysis of long-lived radionuclides by double-focusing sector field inductively coupled plasma mass spectrometry using direct liquid sample introduction

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Received 29 December 2000; accepted 27 March 2001

Abstract

This report is concerned with the investigation of double-focusing sector field inductively coupled plasma mass spectrometry (DF-ICPMS) for ultratrace and isotopic ratio analysis of long-lived radionuclides (^{226}Ra, ^{230}Th, ^{232}Th, ^{233}U, ^{237}Np, ^{238}U, and ^{241}Am) using the direct injection high efficiency nebulizer (DIHEN). A new shielded torch arrangement, known as the guard electrode, improves relative sensitivity by a factor of six when the DIHEN is used. Absolute sensitivity with the DIHEN is on the order of 1300 (^{226}Ra) to 1700 (^{238}U) counts/fg at a solution consumption rate of 5 μL/min. This is a factor of from three to 20 better than the results obtained by a conventional nebulizer-spray chamber arrangement (e.g., ultrasonic and pneumatic nebulizers). The DIHEN-DF-ICPMS is successfully tested for isotope ratio measurements of ^{235}U/^{238}U standards and environmental radioactive waste solutions. (Int J Mass Spectrom 208 (2001) 193–204) © 2001 Elsevier Science B.V.

Keywords: Double-focusing sector field inductively coupled plasma mass spectrometry; direct injection high efficiency nebulizer; actinides; isotope ratio analysis, radioactive waste

1. Introduction

Accurate and precise ultratrace and isotopic analysis of long-lived radionuclides is required in areas ranging from radiobioassay and nuclear waste management to nonproliferation oversight and monitoring of clandestine activities. To determine the enrichment of radioactive isotopes in the environment caused by nuclear weapons testing and fallout from nuclear power plants or nuclear accidents, it is essential to measure the concentration of long-lived radionuclides and their isotopic ratios. These measurements are also important in geochronology (e.g., U-Th-Pb method) [1].

Inductively coupled plasma mass spectrometry (ICPMS), is one of the strongest techniques for trace and ultratrace determination of a wide range of elements [2,3]. Most ICPMS instruments are quadrupole based; however, double-focusing sector field ICPMS (DF-ICPMS) arrangements have become increasingly pop-

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PII S1387-3806(01)00432-8

ular owing to low instrumental background, high sensitivity (in low-mass-resolution operation, $m/\Delta m \approx 300$), and the ability to separate many isobaric interferences of molecular ions from atomic ions of analytes in higher-mass-resolution mode [4–7].

The typical conventional nebulizer-spray chamber arrangement suffers from high sample consumption (1–2 mL/min), low analyte transport to the plasma (1%–20%), memory effects, and spray-chamber-induced matrix and acid effects [8–13]. To minimize radioactive contamination, investigative derived waste, and exposure to the operator, a reduction in the sample consumption and an increase in the sample utilization are necessary. Recent attention has focused on micronebulizers, which operate at low sample-consumption rates (<100 μL/min) and provide high analyte-transport efficiency (up to 100%) [14,15]. One such device is the direct injection high efficiency nebulizer (DIHEN), which operates at solution flow rates of 1–100 μL/min [14–25]. The DIHEN replaces the injector tube of the ICPMS torch and injects 100% of the sample into the plasma in the absence of a spray chamber. No solution waste is generated because the entire sample is consumed. The high sensitivity and low sample size requirements of the DIHEN-DF-ICPMS allow analysis of long-lived radionuclides in facilities not licensed for the analysis of radioactive materials. For example, in the United States, the free limit is considered to be $<0.05\%$ w/w of the source material [26], but nuclear regulations vary worldwide.

In direct liquid-sample introduction, the solvent load in the plasma is four to five times larger (80–100 mg/min vs. ~20 mg/min) than conventional nebulization [16,27–29]. This high solvent load enhances capacitive coupling between the load coil and plasma, increasing the strength of secondary discharge between the plasma and the grounded MS interface. The secondary discharge increases ion kinetic energy and broadens ion energy distributions, which in turn impairs ion transmission through the mass analyzer [30–33]. A grounded conductive shield is often positioned between the load coil and the ICP torch to attenuate the plasma potential [31–33] and molecular-based interferences [34–36] and to improve spatial ion distribution in the first vacuum stage of the ICPMS interface [37]. Plasma shielding, however, is not as effective as a Colpitts-based oscillator used with a balanced load coil or the interlaced–load coils approach in reducing or eliminating the plasma potential [31,32].

A plasma-shielded torch can provide up to a factor of 10 improvement in sensitivity with nebulizer-spray chamber arrangements [6,38]. However, initial studies with direct liquid sample introduction provided relative sensitivities in DF-ICPMS that were approximately five times lower than micronebulizers used with spray chambers [6]. In contrast, quadrupole-based ICPMS provides similar sensitivity when an electronically balanced load coil is used [16,17]. The impaired analytical figures of merit are attributed to the particular shielded torch used. In this work, a new configuration of the plasma-shielded torch is explored for DIHEN-DF-ICPMS to improve sensitivity and precision in the analysis of long-lived radionuclides. Figures of merit are presented in terms of relative and absolute sensitivity, detection limits, and precision obtained with the new shield for comparison with the previous arrangement. Analytical performance indices are compared to ultrasonic nebulization and a micronebulizer-spray chamber arrangement. The accuracy and precision of the DIHEN-DF-ICPMS approach for the determination of isotopic ratios is examined in the analysis of $^{235}U/^{238}U$ standards and small-volume radioactive waste solutions.

2. Experimental

2.1. ICPMS instrumentation

The DF-ICPMS instrument (ELEMENT, Finnigan MAT, Bremen, Germany) was used under the conditions listed in Table 1. The configuration of the new and old guard electrode (GuardElectrode™ [CD-1], Finnigan MAT) for reducing plasma potential are shown in Fig. 1. The new shield is commercially supplied in platinum form. To reduce cost, it was fabricated in-house by using either Pt or Pt/Ta foil of 0.1 mm thickness and 20 mm in length.

Table 1
Operating parameters for the double-focusing sector-field ICPMS and three sample introduction systems

Instrumental parameters	Sample introduction system		
Nebulizer	b-DIHEN	q-DIHEN	MicroMist
Spray chamber	None	None	Minicyclonic
RF power, W	1100	1100	925
RF generator frequency, MHz	27.1	27.1	27.1
Outer gas flow rate, L/min	14	14	14
Intermediate gas flow rate, L/min	1.6	1.4	1.3
Nebulizer gas flow rate, L/min	0.25	0.18	1.25
Solution flow rate, μL/min	1–40	1–60	40–200
For all nebulizers			
Runs		5	
Passes		100	
Replicates		5	
Sampling cone		Nickel with a 1.2-mm orifice	
Skimmer cone		Nickel with a 0.9-mm orifice	
Mass resolution, (m/Δm)		300	

2.2. The sample introduction systems

Two DIHENs were used in this study. The first one (Model DIHEN-170-AA, JE Meinhard Associates, Inc., Santa Ana, CA) was constructed of borosilicate glass and is designated here as b-DIHEN [16]. A second DIHEN was constructed of quartz (Model Quartz-DIHEN-170-AA, JE Meinhard Associates, Inc.) and is referred to as q-DIHEN. The DIHEN replaced the injector tube of the ICP torch and was held 2 mm below the intermediate torch tube by a PEEK adapter. The dead volume was reduced to <15 μL by inserting 0.008 inner diameter (i.d.) tubing (SB Fittings Assembly Kit 1-Micro, J.E. Meinhard Associates) into the solution passageway to the point where the capillary tapers. For solution flow rates <40 μL/min, a syringe pump (Model CMA/100, CMA Microdialysis AB, Solna, Sweden) was used. To permit fast switching of samples, in some cases a pulseless peristaltic pump (Model Perimax 16, Spetec GmbH, Erding, Germany), was used with narrow-bore peristaltic tubing (0.0075″ i.d., Spetec GmbH). Nebulizer gas was supplied via a precise (± 10 μL/min) external mass flow controller (Model PR 4000, MKS Instruments, Andover, MA). For comparison, a MicroMist microconcentric nebulizer (Model MicroMist AR40-1-FM01, Glass Expansion, Camberwell, Victoria, Australia) was used with a 20-mL minicyclonic spray chamber (Cinnabar, Glass Expansion).

2.3. Measurement procedures

The DIHEN-DF-ICPMS system was optimized daily for maximal ion intensity of $^{238}U^{+}$, using a 100 ng/L standard solution. For the determination of short-term precision and sensitivity, the concentration of each radionuclide was 100 ng/L. Detector dead time and mass discrimination were corrected by the procedures described elsewhere for the determination of isotopic ratios [39,40]. Mass discrimination was evaluated by measuring a 1 ng/mL solution of an isotopic laboratory standard of uranium (CCLU-500, $^{235}U/^{238}U$ of 0.99991), described below.

2.4. Reagents and materials

A mixture of long-lived radionuclides (^{226}Ra, ^{230}Th, ^{232}Th, ^{233}U, ^{237}Np, ^{238}U, and ^{241}Am) was prepared in high-purity water (18 MΩ cm) for characterization and comparison of the sample introduction systems. Solutions for ^{232}Th and ^{238}U were prepared from single-element standard reference materials (SRMs; SRM 3159 and 3164, National Institute of Standards and Technology [NIST], Gaithersburg, MD). α-spectrometry was used to confirm the concentration of stock ^{226}Ra, ^{233}U, ^{237}Np, and ^{241}Am standards (prepared at Research Center Jülich, Jülich, Germany). For isotope ratio ($^{235}U/^{238}U$) measure-

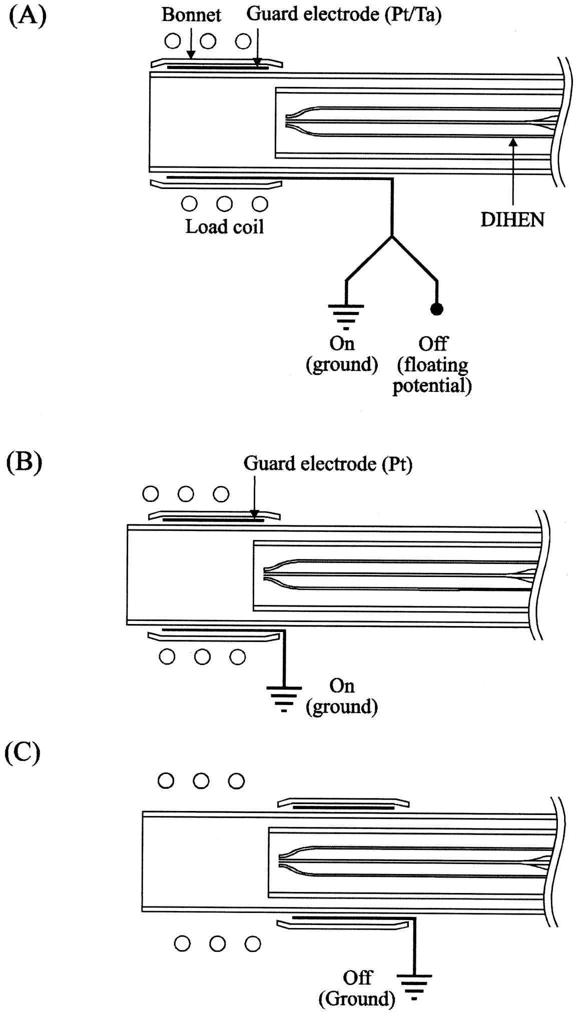

Fig. 1. Schematic diagrams showing the configuration of the guard electrode used in this work (A) and the previous guard electrode when it is on (B) and when it is off (C). The present configuration remains positioned between the load coil and torch at all times and is switched on (earth ground) and off (floating potential) electronically. The previous configuration [6] pneumatically positions the electrode between the load coil and the torch when in use (B) and is retracted when not in use (C).

ments, three different isotopic standards were used for ratios of 0.00725, 0.02081, and 0.99991: a natural U composition standard (SRM 3164, NIST), a certified isotopic reference material (CRM-U020, New Brunswick Laboratory, Argonne, IL [formerly National Bureau of Standards SRM U-020]), and a laboratory isotopic standard (CCLU-500, Nuclear Research Center, Prague, Czech Republic) [41,42], respectively. Furthermore, three aqueous radioactive waste samples from the vicinity of a nuclear power plant in Eastern Europe were analyzed.

3. Results and Discussion

3.1. Effects of guard electrode in double-focusing ICPMS

The new guard electrode (Fig. 1A) is always positioned between the load coil and torch and is switched on (ground potential) or off (floating potential) electronically. Previously, the guard electrode was either pneumatically positioned between the load coil and the torch (on; Fig. 1B) during ICPMS measurements, or it was withdrawn (off; Fig. 1C) during plasma ignition. As described below, this difference in mode of operation and geometry plays a significant role in optimizing the DIHEN for ICPMS measurements.

With the previous guard electrode (Fig. 1B), optimum DF-ICPMS measurements were conducted at 1500 and 1100 W for the DIHEN and the MicroMist-minicylonic spray chamber, respectively. With the new GE (Fig. 1A), both the optimal RF power (1100 W) and solution flow rate (40–60 μL/min) for DIHEN-DF-ICPMS are reduced compared with conditions used in quadrupole-based ICPMS (1500 W, 80–100 μL/min) [16,17]. Similarly, the MicroMist-minicyclonic spray chamber combination offers optimum sensitivity at RF powers of 925 W versus 1250 W for DF-ICPMS and ICP-QMS, respectively. Fig. 2 shows plots of sensitivity for ^{226}Ra, ^{230}Th, ^{232}Th, ^{233}U, ^{237}Np, ^{238}U, and ^{241}Am as a function of nebulizer gas flow rate, RF power, and solution flow rate for the DIHEN when the new GE was maintained at ground potential. In general, lower optimum RF power was required compared to the prior work for a pneumatically positioned shield [6]. Optimal sensitivity for the q-DIHEN (b-DIHEN) is obtained at low nebulizer gas flow rates of 0.18–0.19 L/min (0.25 L/min), an RF power of 1100 W (1100 W), and a solution uptake rate of 60 μL/min (40 μL/min). This

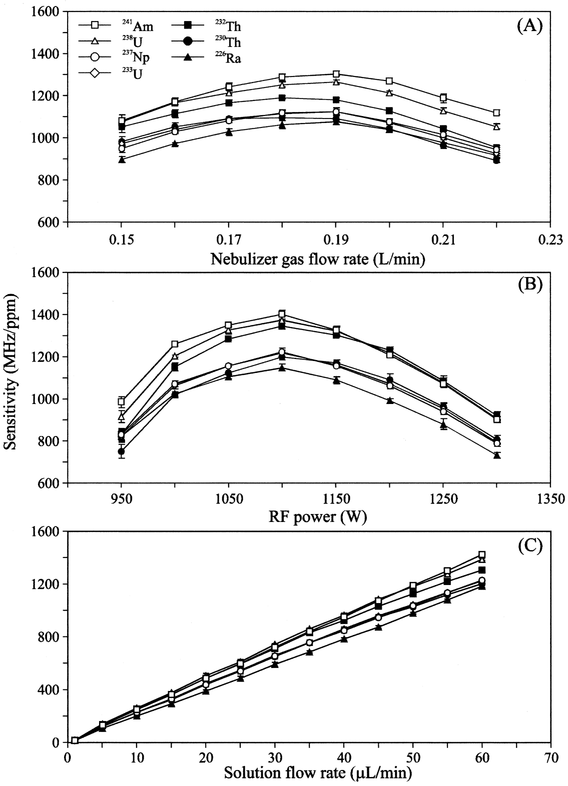

Fig. 2. Plots of the sensitivity of long-lived radionuclides measured with the q-DIHEN-DF-ICPMS. (A) Effect of nebulizer gas flow rate. The RF power and solution flow rate was 1100 W and 60 μL/min, respectively. (B) Effect of RF power. The nebulizer gas flow rate and solution flow rate was 0.18 L/min and 60 μL/min, respectively. (C) Effect of solution flow rate. The RF power and nebulizer gas flow rate was 1100 W and 0.18 L/min, respectively. Error bars represent 1σ, and in most cases, these reside within the data point marker.

general reduction in optimum RF power must be related to the effectiveness of the new GE in reducing the plasma potential and, thus, maintaining narrow ion kinetic energy distribution for measurements. The effectiveness of the guard electrode in shielding the plasma and, thus, improving the ion transmission efficiency, is reduced above 1100 W. We recommend high RF power (1500 W) for maintaining a robust plasma for direct sample introduction with the DIHEN [16–22,25].

Sensitivity increases linearly (Fig. 2C) with solution flow rate in DF-ICPMS with a correlation coefficient (r^2) of >0.997 in all cases. However, above 40 and 60 μL/min for the b-DIHEN and q-DIHEN, respectively, plasma stability is compromised and often the ICP is extinguished. This observation is attributed to increased solvent load and consequently enhanced secondary discharge. Unfortunately, no observation port at the MS interface is available to investigate this hypothesis. One may also speculate that the impedance-matching network used in this instrument for the crystal-controlled generator cannot quickly correct for changes in the plasma conditions at higher solution flow rates.

Relative sensitivities obtained using the old and new guard electrodes are presented in Table 2, along with optimum conditions. With the new GE on (at ground potential), sensitivity is improved for both direct injection and the pneumatic nebulizer-spray chamber arrangement. Sensitivity for the b-DIHEN ranges from 1590 MHz/ppm (^{230}Th) to 2510 MHz/ppm (^{241}Am); for the q-DIHEN, it ranges from 1180 MHz/ppm (^{226}Ra) to 1420 (^{241}Am) at solution flow rates of 40 and 60 μL/min, respectively. This represents a five- to eightfold improvement in sensitivity for ^{238}U to ^{241}Am over the previous GE even after nearly a twofold reduction in solution flow rate compared to operation with no GE. Sensitivity was increased four- to sixfold with the old GE for the MicroMist nebulizer-minicylonic spray chamber arrangement. In contrast, sensitivity obtained with the DIHEN was decreased (by a factor of 1.2–1.4) when the old GE was inserted. In sum, the previous GE was not effective for the direct introduction of solution in DF-ICPMS. Unfortunately, the new GE does not provide optimal performance at 1500 W, a power level suitable for operating a robust plasma for direct injection of solution.

3.2. Sensitivity and short-term precision at reduced solution flow rates

Table 3 presents sensitivity and precision for solution flow rates ranging from 1 to 60 μL/min. A linear relationship for sensitivity is noted. At a solution flow rate of ~5 μL/min, the sensitivity obtained on the DF-ICPMS nearly approximates that achieved with quadrupole-based instrumentation using the b-DIHEN

Table 2
Sensitivity (MHz/ppm) for long-lived radionuclides by DF-ICPMS using two guard electrodes and three sample introduction systems.

	Old Guard Electrode (Fig. 1B)[a]				New Guard Electrode (Fig. 1A)			
Nebulizer	b-DIHEN		MicroMist[b]		b-DIHEN	q-DIHEN	MicroMist[b]	
Guard electrode	On	Off	On	Off	On	On	On	On
Solution flow rate, μL/min	85	85	85	85	40	60	40	200
Nebulizer gas flow rate, L/min	0.18	0.18	1.07	1.07	0.25	0.18	1.25	1.25
RF power, W	1500	1500	1100	1100	1100	1100	925	925
Radionuclide								
^{226}Ra	—	—	1370	290	1930	1180	420	2220
^{230}Th	—	—	—	—	1590	1200	490	1890
^{232}Th	315	430	2080	390	2430	1310	600	2140
^{233}U	—	—	1840	430	1690	1230	460	2350
^{237}Np	390	460	1975	420	—	1230	—	—
^{238}U	370	500	2110	440	2040	1390	530	2730
^{241}Am	310	430	2435	400	2510	1420	550	3250

[a] From reference [6].

[b] Used with a minicylonic spray chamber.

at 100 μL/min [17]. Such excellent performance for a nebulizer is important in speciation studies, particularly when coupling low solution flow rate (μL/min to nL/min) techniques such as capillary electrophoresis and microbore high-performance liquid chromatography, with the DF-ICPMS instrumentation [43–45]. However, as expected from counting statistics, there is a concomitant reduction in precision from generally <1% RSD to 3%–7% RSD at solution flow rates of 60 μL/min and 1 μL/min, respectively.

Table 3
Sensitivity (MHz/ppm) and precision (%RSD)[a] for several long-lived radionuclides as a function of solution flow rate (μL/min) with the DIHEN-DF-ICPMS[b]

	Solution flow rate (μL/min)							
	1	5	10	20	30	40	50	60
Sensitivity								
Radionuclide								
^{226}Ra	15	108	202	391	591	784	980	1180
^{230}Th	16	121	229	441	651	849	1030	1200
^{232}Th	18	135	255	486	712	925	1130	1310
^{233}U	16	123	229	446	660	860	1050	1230
^{237}Np	16	122	228	438	654	849	1037	1230
^{238}U	18	140	261	506	744	965	1180	1390
^{241}Am	16	130	249	486	720	951	1190	1420
Precision								
Radionuclide								
^{226}Ra	4.7	1.8	2.0	1.8	2.5	1.3	0.7	0.8
^{230}Th	7.6	0.5	2.5	3.0	2.8	1.9	0.7	0.8
^{232}Th	4.3	4.3	2.3	2.6	2.2	1.8	0.8	1.1
^{233}U	1.8	4.0	2.1	1.9	2.0	1.6	1.0	0.7
^{237}Np	3.4	2.1	4.1	3.3	1.5	2.2	0.4	0.5
^{238}U	6.1	2.8	3.6	3.4	0.7	1.4	1.2	0.6
^{241}Am	4.1	2.5	3.5	2.7	1.3	1.5	0.7	1.2

[a] Measured over 7 min, for a 100 ng/L solution ($N = 5$).

[b] The q-DIHEN was operated at an RF power of 1100 W and a nebulizer gas flow rate of 0.18 L/min.

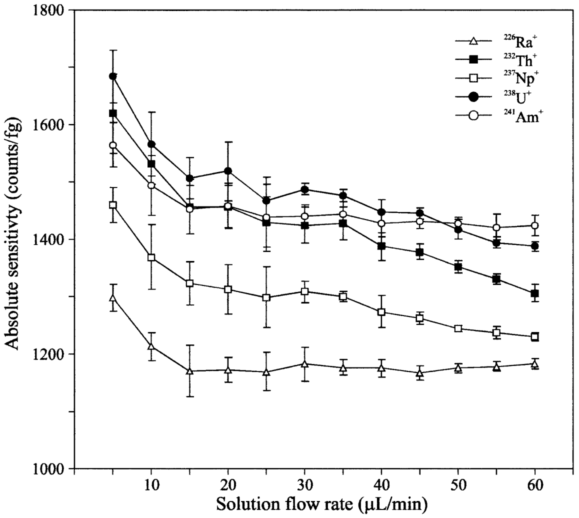

Fig. 3. Plot of the absolute sensitivity (counts/fg) for several long-lived radionuclides as a function of solution flow rate using the q-DIHEN. The q-DIHEN was operated with a nebulizer gas flow rate and an RF power of 0.18 L/min and 1100 W, respectively.

It is prudent to compare the analytical performance indices of the DIHEN (Tables 2 and 3) with data (Table 2) for the MicroMist nebulizer-spray chamber operated at both its optimum solution flow rate of 200 μL/min and at a solution flow rate of 40 μL/min using the new GE at ground potential. Under optimal conditions, sensitivity for the MicroMist ranges from 1890 MHz/ppm (^{230}Th) to 3250 MHz/ppm (^{241}Am), which is similar to or slightly improved over the results obtained for the b-DIHEN and is approximately a factor of two improved over the q-DIHEN. As the solution flow rate is reduced fivefold (to 40 μL/min), the sensitivity for the MicroMist decreases by a factor of 3.6 (^{232}Th) to 5.9 (^{241}Am). Consequently, when the sample volume is limited, higher relative sensitivity can be obtained by the DIHEN at low solution flow rates. If sample is not limited, the nebulizer-spray chamber combination can provide an improvement in the relative sensitivity operated at higher solution flow rates. Relative detection limits (3 σ) obtained with the q-DIHEN are typically in the low pg/L range (3 [^{226}Ra], 3 [^{230}Th], 16 [^{232}Th], 2 [^{233}U], 2 [^{237}Np], 1 [^{238}U], and 2 [^{241}Am] pg/L, respectively).

3.3. *Absolute sensitivity*

Absolute sensitivity (ion intensity per gram of analyte) is an important figure of merit compared to relative sensitivity in the analysis of samples that are limited, expensive, or hazardous. Fig. 3 shows a plot of the absolute sensitivity as a function of the solution flow rate for the q-DIHEN. As the solution flow rate is reduced to 5 μL/min, a slight increase in absolute sensitivity is observed to 1300 counts/fg and 1700

Table 4
Absolute sensitivity (counts/fg) obtained in the determination of long-lived radionuclides with the DF-ICPMS instrument using four nebulization systems[a]

	Absolute Sensitivity			
Nebulizer	Ultrasonic[b]	MicroMist	Meinhard[b]	q-DIHEN
Guard electrode	On	On	On	On
Solution flow rate, μL/min	2000	200	1000	5
Nebulizer gas flow rate, L/min	1.16	1.25	0.92	0.18
RF power, W	1150	925	1300	1100
Radionuclide				
^{226}Ra	390	670	56	1300
^{230}Th	—	570	—	1450
^{232}Th	440	640	85	1620
^{233}U	460	705	88	1480
^{237}Np	660	—	95	1460
^{238}U	630	820	97	1680
^{241}Am	640	980	99	1570

[a] The ultrasonic nebulizer, the MicroMist, and the Meinhard nebulizers are used with their own spray chambers.

[b] From reference [6].

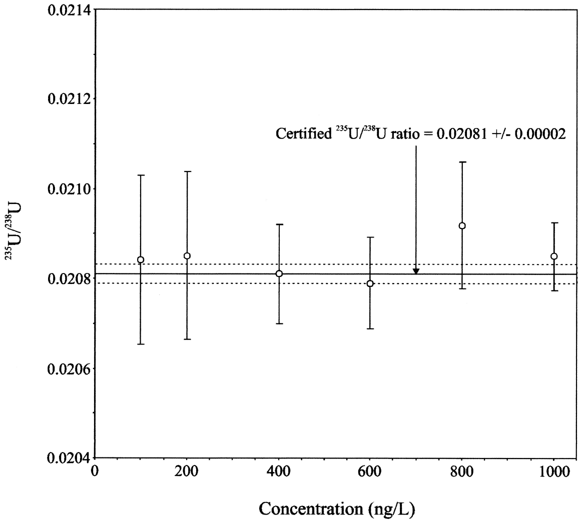

Fig. 4. Plot of the measured $^{235}U/^{238}U$ ratio as a function of concentration using the q-DIHEN-DF-ICPMS. Error bars represent 1σ. Total sample consumption for each data point was 210 μL. The q-DIHEN-DF-ICPMS was operated using an RF power, nebulizer gas flow rate, and solution flow rate of 1100 W, 0.18 L/min, and 60 μL/min, respectively.

counts/fg for ^{226}Ra and ^{238}U, respectively. Thus, the sample size requirement can be minimized to a great extent without a concomitant loss in sensitivity when the DIHEN is used.

Table 4 shows a comparison of the absolute sensitivity obtained for four nebulization systems: an ultrasonic device, the MicroMist, a conventional Meinhard® nebulizer, and the q-DIHEN. These data illustrate the benefits of micronebulization when samples are limited. In terms of absolute sensitivity, the ultrasonic nebulizer only provides ~390 (^{226}Ra) to 660 (^{237}Np) counts/fg of material based on a solution flow rate of 2 mL/min. In contrast, the q-DIHEN consumes 400 times less sample (5 μL/min) and provides absolute sensitivity that is better than the ultrasonic and the conventional Meinhard nebulizer by factors of three and 20, respectively.

3.4. Applications of DIHEN-DF-ICPMS

The performance of DIHEN-DF-ICPMS was evaluated in the analysis of a ^{235}U-enriched isotopic standard and in the analysis of radioactive waste solutions. The enriched isotopic standard consisted of $^{235}U/^{238}U$ (U-020 certified ratio of $^{235}U/^{238}U = 0.02081 \pm 0.00002$). The ratios of $^{235}U/^{238}U$, determined at uranium concentrations ranging from 100 to 1000 ng/L, are illustrated in Fig. 4. In all cases, the determined and certified ratios agree well within 1σ of the measurement precision. The isotopic ratio precision ranged from 0.36% RSD at 1000 ng/L to 0.90% RSD at 100 ng/L. This isotopic ratio precision, obtained at a solution flow rate of 60 μL/min, is slightly inferior to that achieved using an ultrasonic nebulizer at a solution flow rate of 2 mL/min, where a precision of 0.23% RSD was measured for the isotopic standard U-020 at a concentration of 100 ng/L [40].

The DIHEN-DF-ICPMS system was also tested for isotopic ratio analysis of radioactive waste solutions acquired in the vicinity of a nuclear power plant in Eastern Europe (Table 5). Three radioactive waste solutions were analyzed as having $^{234}U/^{238}U$, $^{235}U/^{238}U$, and $^{236}U/^{238}U$ ratios on the order of 10^{-3} to 10^{-5}. All three samples contained ^{236}U, a uranium isotope not found in nature. The $^{236}U/^{238}U$ isotope ratios in Table 5 were corrected, taking into account

Table 5
Determination of U isotope ratios in radioactive waste solutions from the vicinity of a nuclear power plant

	Solution 1		Solution 2	Solution 3
Isotope ratio	b-DIHEN DF-ICPMS	MicroMist-minicyclonic Quadrupole-ICPMS[a]	b-DIHEN DF-ICPMS	b-DIHEN DF-ICPMS
$^{234}U/^{238}U$	0.0000631 ± 0.0000055	0.0000650 ± 0.0000053	0.0000212 ± 0.0000006	0.0000611 ± 0.0000103
$^{235}U/^{238}U$	0.00876 ± 0.00047	0.00871 ± 0.00060	0.00367 ± 0.00008	0.00747 ± 0.00014
$^{236}U/^{238}U$	0.0001050 ± 0.0000085	0.0000952 ± 0.0000059	0.0000720 ± 0.0000018	0.0000204 ± 0.0000059

[a] Elan 6000 ICPMS.

formation of hydride ions $^{235}UH^+$ (from the measured $^{238}UH^+/^{238}U^+$ ratio in a natural uranium solution). For comparison, a blind analysis of Solution 1 (Table 5) was also performed by quadrupole-based ICPMS using a MicroMist nebulizer-minicylonic spray chamber. In all cases, the determined isotope ratios agree within 1σ error. On the basis of the linear dynamic range of most ICPMS instrumentation, it should be feasible to measure isotope ratios down to 10^{-8} with the DIHEN, a subject currently under investigation in our laboratories.

3.5. Molecular ion formation in DF-ICPMS using the DIHEN

Solvent loading gives rise to high levels of molecular species with direct injection devices [16,17,46]. A variety of approaches may be utilized to reduce mass spectral interferences [47]. For example, mathematical corrections may be used to account for the portion of the molecular interferences; however, such corrections are difficult to implement in some cases [47–49]. Alternatively, molecular ions can be used as the analyte ions for quantitation or confirmation of the analytical results [17,25,50]. In general, one approach to reduce mass spectral interferences (e.g., $^{207}Pb^{16}O^{12}C^+$ or $^{203}Tl^{16}O_2^+$ on $^{235}U^+$) is high resolution, but this is achieved by sacrificing sensitivity and precision.

Fig. 5 shows the intensity of oxide ions relative to metal ions (MO^+/M^+) for long-lived radionuclides as a function of nebulizer gas flow rate, RF power, and solution flow rate. Nearly identical dependence on the experimental conditions is found for isotopes of thorium and uranium (^{230}Th, ^{232}Th, ^{233}U, and ^{238}U), indicating that these isotopes are interference free. The MO^+/M^+ ratios decrease in the sequence of $ThO^+/Th^+ > UO^+/U^+ > NpO^+/Np^+ > AmO^+/Am^+$, similar to behavior observed previously [17,25]. In general, the measured relative oxide ion intensities correlate well with the bond dissociation energies of oxides. The bond dissociation energies of oxide ions are mostly unknown. The dissociation energy of the neutral metal-oxide species are D^o_{298}, ThO (878.6 kJ/mol) [51], UO (759.4 kJ/mol) [51], NpO (~730 kJ/mol) [50], and AmO (~673 kJ/mol) [50]. Previous work on nebulizer spray-chamber arrangements has yielded excellent correlation between the neutral metal-oxide bond dissociation energies and the oxide formation rate [50].

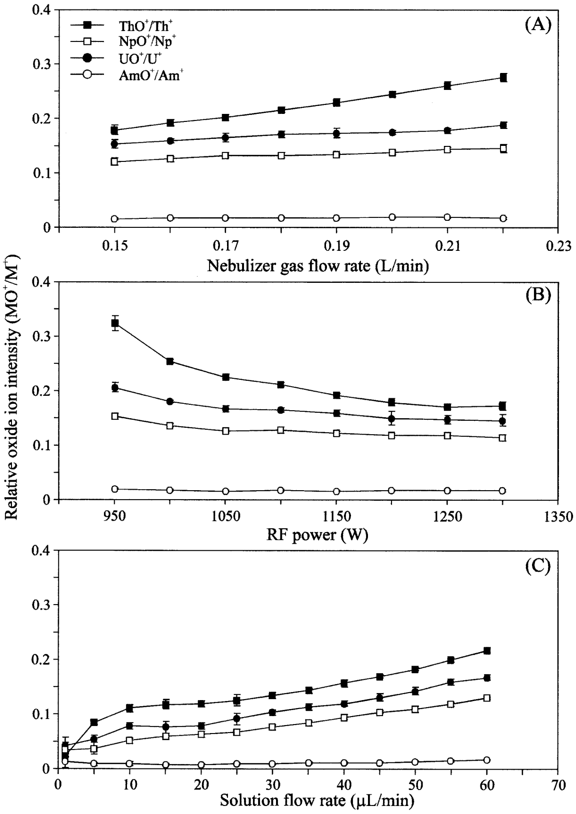

Fig. 5. Plots of the relative oxide ion intensities of long-lived radionuclides using q-DIHEN-DF-ICPMS. (A) Effect of nebulizer gas flow rate. The RF power and solution flow rate was 1100 W and 60 μL/min, respectively. (B) Effect of RF Power. The nebulizer gas flow rate and solution flow rate was 0.18 L/min and 60 μL/min, respectively. (C) Effect of solution flow rate. The RF power and nebulizer gas flow rate was 1100 W and 0.18 L/min, respectively. Error bars represent 1σ; however, in most cases these reside within the data point marker.

In general, relative oxide ion intensities are enhanced at higher nebulizer gas flow rates and solution flow rates and decrease with RF power. Table 6 presents the relative intensities of oxide and hydride molecular ions obtained with several nebulizers under optimal conditions for the analyte metal ion. This is in contrast with what is typically observed using qua-

Table 6
Relative molecular ion intensities of long-lived radionuclides with DF-ICPMS and quadrupole-ICPMS using several nebulization systems[a]

	Double-Focusing ICPMS			Quadrupole-ICPMS[b]	
Nebulizer	b-DIHEN	q-DIHEN	MicroMist[c]	b-DIHEN	MicroMist[c]
Guard electrode	On	On	On	—	—
Solution flow rate, μL/min	60	40	200	100	85
Nebulizer gas flow rate, L/min	0.25	0.18	1.25	0.16	0.98
RF power, W	1100	1100	925	1450	1250
Molecular ion	Relative ion intensity (MX^+/M^+, $X = $ O, H)[d]				
ThH^+	4.0×10^{-4}	6.5×10^{-4}	2.4×10^{-4}	2.4×10^{-5}	1.6×10^{-5}
UH^+	2.7×10^{-3}	2.9×10^{-3}	2.7×10^{-3}	2.5×10^{-5}	1.9×10^{-5}
ThO^+	3.2×10^{-1}	2.2×10^{-1}	3.3×10^{-1}	7.5×10^{-2}	2.8×10^{-2}
UO^+	1.7×10^{-1}	1.8×10^{-1}	1.0×10^{-1}	5.1×10^{-2}	3.1×10^{-2}
UO_2^+	1.8×10^{-1}	6.8×10^{-2}	2.0×10^{-1}	Not measured	Not measured

[a] Values for Th and U were obtained for the ^{230}Th and ^{233}U isotopes and ^{232}Th and ^{238}U isotopes for DF-ICPMS and quadrupole-ICPMS, respectively.

[b] From reference [17] obtained on an Elan 6000 ICPMS.

[c] Used with a minicylonic spray chamber.

[d] For DF-ICPMS and Quadropole-ICPMS values represent the average of five and three measurements, respectively.

drupole ICPMS [17]. These oxide formation rates are reasonable considering that previous work with a micronebulizer-spray chamber arrangement has provided an intensity ratio for UO^+/U^+ of 94% when using the new configuration of the GE at ground on a similar DF-ICPMS instrument [52]. Interestingly, with the GE held at floating potential (off), the UO^+/U^+ ratio decreased to ~1% [52]. In general, the hydride ion intensities are nearly 100-fold smaller than the oxide ion intensities. Furthermore, except for UO_2^+, the MO^+ levels for these nebulization systems are comparable. Relative oxide ion intensities are approximately 22%, 18%, 13%, and 2% for ThO^+/Th^+, UO^+/U^+, NpO^+/Np^+, and AmO^+/Am^+, respectively, for the q-DIHEN. Considering the level of oxides on direct injection, the analyst is advised to consider using them in acquiring analytical results or at least for comparison purposes [17,25,50].

4. Conclusions

The direct injection high efficiency nebulizer is well suited for sample introduction in DF-ICPMS, in particular when the sample is limited, expensive, or hazardous, as in the determination of long-lived radionuclides. A new guard electrode improved relative sensitivity by a factor of six over the previous design. At a solution flow rate of ~5 μL/min, the relative sensitivity obtained on the DF-ICPMS is nearly the same as that obtained on quadrupole-based ICPMS, which consumes 20 times more sample (100 μL/min). Absolute sensitivity obtained using the DIHEN at 5 μL/min is three to 20 times higher than that for different conventional or micronebulizers used with spray chambers. The performance of the DIHEN-DF-ICPMS was demonstrated in the analysis of a certified isotope ratio standard and radioactive waste samples.

With the new guard electrode providing optimum DIHEN-DF-ICPMS sensitivity at 1100 W, its shielding capability is apparently reduced at 1500 W, a power level suitable for formation of a robust plasma for direct injection of solution. We also suspect that even at 1100 W the new GE does not entirely eliminate the secondary discharge. This is because oxide ion formation rates are similar for the DIHEN and conventional nebulizer-spray chamber arrangements if the new guard electrode is used. In sum, a residual discharge is perhaps reducing the higher oxide levels that are produced on direct injection. The hypothesis requires both optical and Langmuir probe measurements at the ICPMS interface.

Acknowledgements

Research by A.M./J.A.M. was sponsored by grants from the U.S. Department of Energy (DE-FG02-93ER14320), the National Science Foundation (CHE-9505726 and CHE-9512441), and JE Meinhard Associates, Inc. J.A.M. gratefully acknowledges support provided by the Central Department of Analytical Chemistry, Research Center Jülich, Jülich, Germany. S.F.B. acknowledges support provided by a research fellowship from the Alexander von Humboldt Foundation, Bonn, Germany.

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