Application of glow discharge Fourier-transform ion cyclotron resonance mass spectrometry to isotope ratio measurements

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Abstract

The combination of a glow discharge ionization source with a Fourier transform ion cyclotron resonance (FTICR) mass spectrometer provides several advantages for elemental analysis; among these is an isotope ratio measured at the highest possible mass resolving power. In this report, lead ratios ($^{206}Pb/^{208}Pb$, $^{207}Pb/^{208}Pb$, and $^{207}Pb/^{206}Pb$) in a sample composed of 10% lead oxide, 10% mercuric oxide, and 80% silver powder (w/w) were observed to be precise to better than $\pm 3\%$ relative standard deviation (RSD at 1 σ) in a commercial FTICR instrument that used a conventional elongated cell. Upon incorporation of a cell whose excitation voltages approximated those in an ideal cell of infinite length, the precision improved to better than $\pm 0.4\%$ RSD. The isotopic bias between measured and known values was also evaluated. Using a cathode composed of 5% National Institute of Standards and Technology (NIST) SRM 987 $SrCO_3$ in silver powder, biases that averaged less than 2.5% were detected using the cell of improved design. These results compared favorably with those obtained using a commercial magnetic sector glow discharge mass spectrometer, although it is still unclear how glow discharge mass spectrometry biases vary in general. (Int J Mass Spectrom 178 (1998) 73–79) © 1998 Elsevier Science B.V.

1. Introduction

The ability to measure isotope ratios accurately and with good precision is important in such diverse areas as geology and medicine, yet is often quite difficult to achieve. The quality of results required from such measurements is as varied as the number of isotopic pairs of interest. In some instances, the precision of a measurement needs to be no better than 1% relative standard deviation (RSD), while in others it must be better than 1 part in 10 000 [1,2].

A number of factors are important in making a precise mass spectrometric isotope ratio measurement, including the ionization source, mass analyzer, and data collection scheme. Because of the stable beam and narrow energy spread of ions produced, thermal ionization is often used to obtain precise measurements. Combining this ionization source with a multicollector magnetic sector mass spectrometer has provided precision on the order of 5–10 ppm [3]. Less precise, but equally important, are results ob-

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tained by using a quadrupole mass analyzer (most often with inductively coupled plasma ionization) where precision is 2–4 orders of magnitude poorer [4], but the lower precision is offset by the flexibility of hopping from peak to peak (isotope to isotope and element to element) more easily than with a magnetic sector instrument.

Fourier transform ion cyclotron resonance (FTICR) mass spectrometry offers the advantage of very high mass resolving power (in excess of 200 million by using electron ionization [5]), but there have been relatively few studies of the precision of isotopic ratio measurements by this technique. Recently, Spell et al. made isotope ratio measurements by using electron ionization and laser ablation as ionization sources for FTICR [6]. Precision of better than ±0.4% was obtained for research purity krypton gas with electron ionization, but significantly poorer precision (±1–6% for abundant and ±9–12% for trace elements) was obtained by using laser ionization.

Glow discharge is another ionization source that has been used for isotope ratio measurements, but little has been done to evaluate its performance. Isotopic precision was evaluated for a limited number of elements by using a VG9000 (VG Elemental, Winsford, Cheshire, UK) magnetic sector glow discharge mass spectrometer (GDMS). The most precise measurement to date, 0.03% RSD, was first reported by Donohue and Petek [7] for Pd and later confirmed by Riciputi et al. [8] in a study of the isotope ratios of B, Cu, Sr, Ag, Sb, Re, and Pb. There have been no GDMS results with better precision than this reported to date. For certain applications, such as monitoring soils for elevated levels of enriched uranium [9] and screening of $^{10}B/^{11}B$ levels in rock prior to costly chemical separation and thermal ionization mass analysis [10], this precision is sufficient. However, for some geological applications, such as age dating, an even more precise measurement is necessary.

Another technique requiring accurate isotope ratio measurements is isotope dilution (ID). The (IDMS) technique provides the most accurate measure of elemental concentration [11], and quantification accurate to better than 2% has been obtained by using

isotope dilution mass spectrometry in combination with glow discharge solution residue sampling [12].

Routine GD isotope ratios are also important to assure good quantitative accuracy. Deviation of an isotope ratio from the accepted value is often evidence of an interference that must be identified prior to further quantification. Isotope ratio precision on the order of 5% or better can immediately bring this problem to light.

A recent development in elemental mass spectrometry is the use of a glow discharge source with Fourier transform ion cyclotron resonance mass analysis (GD-FTICR). Quantitative results accurate to better than 10% [13–16] with mass resolving powers in excess of 650 000 [17] have been achieved. However, the precision of GD-FTICR isotope ratio measurements has yet to be investigated.

In this study, we have determined the precision of GD-FTICR isotopic analysis of lead in a lead oxide powder and the biases of the GD-FTICR analysis of strontium in a NIST reference material. Also investigated was a comparison of the conventional elongated ion cyclotron resonance (ICR) cell to one of improved design [18] whose excitation voltages approximate an ideal cell of infinite length.

2. Experiment

The glow discharge-Fourier transform ion cyclotron resonance mass spectrometer used for these studies is described in detail elsewhere [15]. Briefly, the glow discharge cathode is of a coaxial geometry, brought into the source housing on the end of a direct insertion probe. The GD source is attached in place of the electron ionization source of a Bruker APEX 47*e* mass spectrometer (Bruker Analytical Systems, Inc., Billerica, MA), external to the 4.7 tesla superconducting magnet. To facilitate pumping (at least 8 orders of magnitude pressure decrease from source to cell), three cryogenic pumps (Edwards High Vacuum International, Wilmington, MA) are used to pump the source region (640 Ls^{-1} for argon), the ion optics and transfer region (275 Ls^{-1} for argon), and the analyzer

region (275 L s^{-1} for argon) in studies with the conventional analyzer cell.

The glow discharge cathodes were prepared by homogenizing an appropriate amount of the analyte of interest with sufficient silver powder (99.99+%, Aldrich Chemical, Co., Milwaukee, WI) to bring the total mass to 1.0 gram. Electrodes were pressed in polyethylene slugs at 24 000 psi for 5 min to form pin cathodes 1.5 mm in diameter by 20.0 mm in length. The pins were trimmed to allow 8 mm to be exposed to the discharge.

The discharge support gas for this study was argon (99.99+%), maintained at 53.3–106.6 Pa (0.4–0.8 Torr) in the source region. The cathode was held at a constant voltage during the course of a single experiment, adjusted over the range -1000 to -1500 V depending on the sample being analyzed. At these pressures and voltages, the current was between 1 and 3 mA. The pressure outside the cell was reduced dramatically across a 0.5-mm-diameter orifice to be in the range 6.7×10^{-2}–1.1×10^{-1} Pa (5.0×10^{-4}–8.3×10^{-4} Torr). Two additional stages of differential pumping permitted the analyzer pressure to be maintained at 1.3×10^{-7}–5.3×10^{-7} Pa (9.8×10^{-10}–4.0×10^{-9} Torr) (uncorrected cold cathode gauge reading). The beam was extracted with a -3 kV accelerating potential and focused using the instrument's standard ion optics.

Ions were accumulated by pulsing a set of ion deflection plates (used for *x* and *y* deflection) to allow ions to enter the analyzer cell for 20–100 ms. The event sequence used was similar to that described previously [19] for pulsed-gas glow discharge experiments, except that no "valve open" or "pump down delay" events were necessary. Thirty-two individual accumulation events comprised one data set, and fifty data sets were accumulated for each isotope ratio measurement, requiring approximately 30 min for data collection.

Two different ICR analyzer cells were used during the several year time span of this study: (1) a conventional elongated cylindrical cell and (2) a novel cylindrical cell whose geometry simulates the rf characteristics of an infinitely long cell (the Infinity Cell, Bruker Analytical Instruments, Inc., Billerica,

MA). It has been reported that this type of cell provides reproducible and reliable relative ion abundances because of increased control of the ion excitation process [18]. Dipolar detection, with its associated nonlinearities, is still performed conventionally with this cell. A capacitively shimmed cubic trap [20] achieves linearity in both excitation and detection, and would probably provide further improvements in the reproducibility with which ion abundances are measured.

The first measurements were made by using the conventional analyzer cell. Data were composed of 128 k data points and were subjected to one order of zero-filling and Gaussian multiplication apodization [21]. Peak heights were obtained after Fourier transformation by using a parabolic fitting function. The most recent data were obtained by using the Infinity Cell. Broadband mode data were composed of 32 k data points, and the heterodyne mode data were composed of 2 k data points. A recent study has shown that optimal data analysis of elemental FTICR mass spectra involves use of a Hanning apodization function, followed by one order of zero filling to increase the number of points defining the peak, and then fast Fourier transformation [22]. To interpolate the true peak maximum, the three data points nearest the maximum were fit with the function $y = (ax^2 + bx + c)^{5.5}$ [23], where *x* is the mass-to-charge ratio value of a particular data point and *y* is its magnitude.

3. Results and discussion

3.1. Precision

3.1.1. Low mass resolving power ($m/\Delta m_{1/2} < 4000$)

To evaluate the measurement precision of GD-FTICR mass spectrometry, the lead isotopes in a cathode composed of 10% PbO, 10% HgO, and 80% silver powder were measured with both a commercial magnetic sector instrument (VG9000) and a commercial Fourier transform ion cyclotron resonance instrument (Bruker Apex 47*e* with both conventional and Infinity Cell analyzers). Table 1 lists the results obtained. Nominal mass resolving power (*R*) for the

Table 1
Lead isotope ratio precision measured by magnetic sector mass analysis and by glow discharge—Fourier transform ion cyclotron resonance mass spectrometry at low mass resolving power ($m/\Delta m_{1/2} < 4000$) (the sample was composed of 10% PbO, 10% HgO, and 80% silver powder; the lead in the sample was assumed to have the accepted natural isotope ratios)

| Isotope ratios | Measured ratios | | | | Percent relative standard deviation | | |
	Natural ratios	Magnetic sector	GD-FTICR conventional cell	GD-FTICR infinity cell	Magnetic sector	GD-FTICR conventional cell	GD-FTICR infinity cell
$^{206}Pb^+/^{208}Pb^+$	0.4612	0.51847 ± 0.00055	0.541 ± 0.017	0.4977 ± 0.0014	± 0.11	± 3.2	± 0.29
$^{207}Pb^+/^{208}Pb^+$	0.4218	0.39972 ± 0.00051	0.437 ± 0.014	0.4049 ± 0.0012	± 0.13	± 3.2	± 0.30
$^{207}Pb^+/^{206}Pb^+$	0.9146	0.7710 ± 0.0011	0.809 ± 0.013	0.8136 ± 0.0031	± 0.15	± 1.6	± 0.38

VG9000 was $m/\Delta m_{1/2} \sim 400$ (full width at half height) to provide the best peak shape for analysis (trapezoidal). The trapped ions in the FTICR analyzer cell were excited with a broadband frequency excitation, and R was nominally less than 4000. Column 2 lists the accepted natural ratios for lead. However, because lead is a radiogenic element, it is not unusual to find ratios deviating from the values in column 2. Since the lead oxide used to prepare the cathode was not certified, the analysis concentrated on the measurement precision rather than accuracy. The results obtained by using the conventional ICR analyzer cell are adequate if the objective is to obtain quantification accuracy of a few percent relative standard deviation, but better precision is needed prior to drawing any conclusions about isotopic composition.

Prior work in this laboratory and others has shown that the Infinity Cell provides greatly improved ion excitation conditions. Improvements in dynamic range and sensitivity accompany the use of this cell, as well as more reproducible and reliable ion abundance determinations [18]. Column 8 of Table 1 lists the precision obtained by using this analyzer cell with GD ionization, an average of $\pm 0.35\%$ relative standard deviation at the 1σ level. These values are only slightly higher than those obtained on the VG9000 and have the added advantage of being obtained at mass resolving powers tenfold higher than that of the VG-9000. This capability can be very useful in performing an analysis when interferences are present. For example, polyatomic ions resulting from the discharge gas and traces of nitrogen and oxygen, ArN^+ and ArO^+ (m/z = 53.965 457 and 55.957 297 6, respectively),

can be serious interferences in measurements of $^{54}Fe^+$ (m/z = 53.939612)/$^{56}Fe^+$ (m/z = 55.934939) ratios. When the necessary baseline resolving power is less than about 10 000, a fairly precise measurement can be made by using either instrument. However, when the required R exceeds this value the magnetic sector falls short, while the ICR can resolve interferences requiring R of up to 10^6, allowing uninterfered measurements to be made.

3.1.2. Moderate to high mass resolving power ($m/\Delta m_{1/2} > 20\,000$)

We have previously reported [17] mass resolving power in excess of 600 000 (full line width at half-maximum magnitude-mode peak height, $m/\Delta m_{1/2}$) for GD-FTICR mass spectrometry. In this same paper, we noted that an analysis of $^{235}U/^{238}U$ in the presence of ^{238}Pu demands an isotope ratio measurement made at a mass resolving power in excess of 200 000 and with precision to better than 1%. To obtain these types of results, long transients must be recorded. Typically, this is accomplished with heterodyne detection [24] to separate peaks differing by less than 1 u. In the normal heterodyne experiment, a single frequency high power excitation in the center of the mass window of interest is employed. This frequency is then mixed with the signal and the output is digitized. In this excitation mode, it is difficult to reliably quantify species differing in mass-to-charge ratio by more than 1 u; we chose to measure the $^{207}Pb/^{208}Pb$ ratio by this procedure. To insure equal excitation of two peaks of interest, the single-frequency excitation should be centered exactly between the two (reduced)

Table 2

Lead isotope ratio precision measured by glow discharge Fourier transform ion cyclotron resonance mass spectrometry at moderate ($m/\Delta m_{1/2} \sim$ 20 000–50 000) and high mass resolving power ($m/\Delta m_{1/2} >$ 100 000) (the sample was composed of 10% PbO, 10% HgO, and 80% silver powder)

Isotope ratios	Natural ratios	Measured ratios		Percent relative standard deviation	
		GD-FTICR Infinity Cell (moderate resolving power)	GD-FTICR Infinity Cell (high resolving power)	GD-FTICR Infinity Cell (moderate resolving power)	GD-FTICR Infinity Cell (high resolving power)
$^{207}Pb^+/^{208}Pb^+$	0.4218	0.3856 ± 0.0011	0.4655 ± 0.0080	±0.28	±1.7
$^{206}Pb^+/^{208}Pb^+$	0.4612	0.4575 ± 0.0016		±0.36	
$^{207}Pb^+/^{206}Pb^+$	0.9146	0.8429 ± 0.0015		±0.18	

ICR frequencies of interest [25]. Because excitation was centered between the masses of the two ions in this work, a small (reproducible) discrimination in the excitation of the two ions whose isotope ratio was being calculated might have been produced.

Results of ratio measurements obtained with the Infinity Cell at moderate (m/Δm$_{1/2}$ $\sim$ 20 000–50 000) and high (m/Δm$_{1/2}$ > 100 000) resolving powers are presented in Table 2. The RSD's at moderate R are comparable to those obtained with the Infinity Cell at low R. However, with increased resolving power, the precision was poorer (increase in RSD from 0.28% to 1.7%). This problem might be alleviated by the use of a broadband excitation that incorporates multiple excitation pulses, tailored pulses [26], or tailored waveform excitation [27] in place of the narrowband excitation. For any excitation a detailed correction for the nonuniform excitation profiles associated with the scheme should be applied for optimal results. Such correction was beyond the scope of the current experiments. Alternatively, the absolute magnitudes of each ion could be measured in separate experiments, similar to the procedure for a magnetic sector instrument.

3.2. Isotopic bias

Glow discharge isotopic bias is defined as the difference between the accepted isotope ratio and that actually measured by mass spectrometric analysis using a GD source. Although fractionation might contribute to the bias, GD isotopic bias is different from fractionation as defined in thermal ionization [7]. Isotope bias is also instrument dependent. Day-to-day variations in the isotope ratios measured by GDMS for a particular element have been shown [4] to be as large as the isotopic bias between different elements. To evaluate the bias of GD-FTICRMS, a cathode was prepared containing 5% of NIST SRM #987 SrCO$_3$ in silver powder.

Results of the strontium analyses are shown in Table 3. The $^{87}Sr/^{86}Sr$ and $^{88}Sr/^{86}Sr$ ratios showed an average isotopic precision of $\pm1.7\%$ RSD, which is greater than that shown in Table 1 for lead isotope ratios. The higher RSD is due primarily to the greater degree of uncertainty in measuring the 86 and 87 isotopes, present at <0.5% natural abundance. The magnetic sector bias was on the order of 0.6%, and the

Table 3

Strontium isotope ratio biases measured by glow discharge—Fourier transform ion cyclotron resonance mass spectrometry (the sample was composed of 5% NIST 987 and 80% silver powder)

Isotope ratios	Absolute abundance ratios	Measured ratios		Percent relative standard deviation		Percent bias	
		Magnetic sector	GD-FTICR Infinity Cell	Magnetic sector	GD-FTICR Infinity Cell	Magnetic sector	GD-FTICR Infinity Cell
$^{87}Sr^+/^{86}Sr^+$	0.71034 ± 0.00026	0.71478 ± 0.00010	0.722 ± 0.013	±0.13	±1.8	$+0.61$	$+1.6$
$^{88}Sr^+/^{86}Sr^+$	8.3786 ± 0.00325	8.4266 ± 0.0080	8.64 ± 0.13	±0.095	±1.5	$+0.57$	$+3.1$

FTICR bias was on the order of 2.4%. Date [4] reported magnetic sector biases for other elements on the order of 0.1–2% [4], and the results obtained by GDFTICR compare well with these values. It is unclear if the somewhat higher biases obtained by using the FTICR are significant because the manner in which GDMS biases vary in general is still unknown. It has been suggested [4] that daily variations in the isotopic biases mean that daily calibration of the instrument will be required for precise work where accuracy is important. While we agree with this assessment, work continues on trying to find a systematic cause for isotopic biases in order to reduce the magnitude of this error in GDMS measurements.

4. Conclusions

The precision of isotope ratio measurements in glow discharge-Fourier transform ion cyclotron resonance mass spectrometry was shown to improve when an analyzer cell whose excitation voltages approximated an ideal cell of infinite length was used. Relative standard deviation at 1σ was on the order of $\pm 0.35\%$ in the best case. As can be seen from Table 1 the poorest results were obtained by using a conventional analyzer cell and when the ratios for isotopes of lower abundance (^{206}Pb and ^{207}Pb) were determined. The measurement precision was also slightly poorer at high resolving power (1.7% for the ^{207}Pb/^{208}Pb ratio) where the excitation frequency is believed to be unequal for the two isotopes. The poorer precision could also be due to differing numbers of data points defining the peaks in the high resolution versus the lower resolution experiments. This type of measurement may still be valuable given the unequivocal certainty with which the isotopes can be measured (i.e., no interferences present). The isotopic bias was shown to be in good agreement with, although slightly larger than, results obtained by using the GD in combination with a magnetic sector. The variations in isotopic bias observed in this study, as well as those reported in the literature, strongly suggest that calibration will be necessary prior to each sample analysis for the most precise measurement.

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