

Improving the analytical capabilities of femtosecond laser ablation multicollector ICP-MS for high precision Pb isotopic analysis: the role of hydrogen and nitrogen†

Mohamed Shaheen^{*ab} and Brian J. Fryer^a

Received 4th March 2010, Accepted 22nd April 2010

First published as an Advance Article on the web 17th May 2010

DOI: 10.1039/c003879b

The effect of nitrogen and hydrogen addition to the central gas flow in femtosecond LA-ICP-MS has been investigated. Enhanced sensitivity of most elements was observed as a result of nitrogen and hydrogen addition to the Ar carrier gas before the ablation cell. Both gases resulted in decreased oxide ratios and increased abundances of doubly charged ions. The effect of nitrogen on sensitivity and mass bias of Pb isotopes in fs-LA-MC-ICP-MS was then investigated. The intensity of Pb and Tl was enhanced by a factor of 3–4 when nitrogen was mixed with Ar carrier gas. At the same time there was a systematic decrease in the mass bias (13%) of Pb and Tl with nitrogen addition. The mass bias of Tl is not identical to that of Pb but accurate and precise Pb isotope ratios were obtained when correcting for the mass bias difference. The results of this work indicate the usefulness of mixed gas plasma to improve signal intensities in ICP-MS in general and MC-ICP-MS in particular where large ion beams and robust and controlled mass bias corrections are necessary for precise and accurate isotopic analysis using Faraday detectors.

Introduction

Over the last few decades much work has been done to improve the analytical capabilities of ICP-MS since its first commercial introduction in 1983. Mixed-gas Inductively Coupled Plasma (ICP) has been extensively investigated to overcome analytical limitations of the Ar plasma.^{1–11} Different gases such as helium,¹ oxygen,¹² nitrogen,^{1,2,4,13,14} hydrogen,^{1,6} methane^{5,7} and other gases^{10,15,16} that have been mixed with Ar showed different effects on enhancement and suppression of analyte sensitivity as well as oxide formation and matrix effects. Sesi *et al.*¹ studied the effect of adding helium, nitrogen, and hydrogen to the central and intermediate gas flow channels of an Ar-ICP. The effect of these gases on calcium ion emission and the fundamental plasma parameters (*i.e.* electron number density, electron temperature and gas kinetic temperature) has been shown to depend on the type and the amount of gas added to the plasma and whether the gas is introduced into the central or intermediate gas flow channel. Xiao and Beauchemin¹³ investigated the effect of nitrogen addition (2–10%) to the outer gas flow of Ar ICP-MS on sensitivities, detection limits, mass discrimination and matrix effects for multi-element standard solutions containing different concentrations of Na. Improvement in sensitivities and detection limits were observed for some elements when nitrogen was added

to the outer gas flow compared to pure Ar. Also mass discrimination and matrix effects were reduced with nitrogen addition. Beauchemin and Craig¹⁷ investigated addition of nitrogen (up to 10%) to Ar ICP-MS operating at constant flow and uptake rates and different power (from 1 to 1.4 kW). Although their results showed reduced sensitivities by a factor of up to 5, the plasma stability and detection limits of Se and Fe were improved by a factor of 4. Other studies^{18–23} have indicated reduction of molecular interferences ArCl and ArAr, ArO, ArOH, ClO and oxides by introducing a small amount of nitrogen into the central gas flow or the coolant gas flow.

The addition of other gases to the Ar plasma in Laser ablation (LA)-ICP-MS has been studied by different authors.^{24–29} Durrant²⁴ reported increased sensitivities of Ce and Th and reduced oxide to metal ratios (CeO/Ce and ThO/Th) upon the addition of 1% v/v or 12% v/v of nitrogen to the coolant gas and cell flow, respectively. Crowe *et al.*²⁵ showed that adding 2% v/v of nitrogen gas to the nebulizer gas flow before the sample cell resulted in a significant increase of sensitivity (by a factor of up to 2–3 times) and reduced mass bias in determination of Pb isotope ratios by quadrupole LA-ICP-MS. Iizuka and Hirata²⁶ reported that using a new design of sample cell and nitrogen mixing (at a rate of 4 ml min^{−1}) with the carrier gas has improved sensitivities of Hf, Lu and Yb by a factor of 2–3 as well as precision and accuracy of Hf isotope microanalysis in zircon by LA-Multicollector (MC)-ICP-MS. Recently Guillong and Heinrich²⁸ studied the effect of mixing gases such as nitrogen, methane and hydrogen with He prior to the ablation cell using a 193 nm excimer LA-ICP-MS system. They reported an increase in sensitivity for the 47 investigated elements by a factor of 2–4 upon addition of 4–9 ml min^{−1} of hydrogen to the He carrier gas flow. In the same study, a weak sensitivity enhancement was reported for a few heavy elements like gold and uranium while

^aGreat Lakes Institute for Environmental Research (GLIER), University of Windsor, Windsor, Ontario, Canada N9B-3P4. E-mail: shahee2@uwindsor.ca; mshaheen73@yahoo.com; Fax: +1 519 971 3616; Tel: +1 519 253 3000 ext. 3752

^bDepartment of Physics, Faculty of Sciences, Tanta University, Tanta, Egypt

† This article is part of a themed issue highlighting some of the most recent and significant developments in the area of Sector Field ICP-Mass Spectrometry.

other elements were not affected by nitrogen addition. In another study, Hu *et al.*²⁹ reported an increase in the sensitivities for most of the 65 investigated elements upon the addition of 5–10 ml min⁻¹ of nitrogen to the central channel gas (Ar + He) for a 193 nm excimer LA-ICP-MS system. They also reported a significant reduction in the oxide ratio ThO/Th and hydride ratio ArH/Ar with the nitrogen–Ar mixed plasma.

The introduction of multiple collectors to ICP-MS has produced a technique competitive to thermal ionization mass spectrometry (TIMS) which has been considered as the reference technique for high precision isotope ratio measurements.^{30,31} Simultaneous detection of ions by Faraday detectors minimizes the effects of ion beam instabilities and allows accurate and high precision isotope ratio measurements. Useful information at high spatial resolution can be obtained by the application of laser ablation to MC-ICP-MS, however, precise and accurate isotope ratio measurements by LA-MC-ICP-MS are affected by fractionation and mass bias effects. Many processes involved in LA-ICP-MS (particle formation, particle transport, atomization and ionization in the ICP) can contribute to elemental and isotopic fractionation. The proper choice of laser parameters (wavelength, pulse width, fluence) and ICP-MS operating conditions (RF power, gas flow, sampling depth) helps to minimize the extent of fractionation and mass bias. Recently, the use of femtosecond laser pulses has been reported to improve the analytical capabilities of LA-ICP-MS through reduction of fractionation and matrix effects.^{32–35} Mass bias is an important factor affecting precision and accuracy of isotope ratio determinations by LA-MC-ICP-MS and must be minimized and robustly corrected for to obtain the most precise and accurate isotope ratio analyses.^{30,31,36} It is a significant feature of plasma source mass spectrometry and is related to preferential extraction and transmission of the heavier ions within the ICP-MS. Mass bias decreases with increasing atomic mass and its magnitude in ICP-MS is approximately an order of magnitude higher than that observed in TIMS.^{30,36,37} Mass bias is generated within the plasma, in the interface region between the skimmer and the sampler cones, and in the ion extraction optics. The dominant source of mass bias is related to space charge effects which cause more repulsion and deflection of lighter ions compared to heavier ones.^{30,31,36,38} As a result, the measured isotope ratio of lighter to heavier isotopes is smaller than the true value. A number of different approaches have been used to correct for mass bias.^{31,36–39} (i) Internal normalization: this method can be applied only to elements which have two or more stable (non-radiogenic) isotopes such as Sr, Nd, and Hf where the (assumed) constant isotopic ratios of the two stable isotopes can be used to calculate the mass bias from the measured value. (ii) External normalization: by using external standards to correct for mass bias assuming the mass bias for the external standard is identical to that of the sample, *e.g.* standard–sample–standard bracketing. (iii) Use of a surrogate: by using another element of a similar mass to the element of interest assuming a similar mass bias behavior (*e.g.* Tl for Pb, Ni for Cu and Zn for Cu and *vice versa*).

Few studies have been done to understand the effects of instrument operating conditions on mass bias.^{38,40,41} Andr n *et al.*⁴⁰ concluded from isotope ratios determined for analytes deposited on the sampler and skimmer cones and on extraction lenses that ion extraction from the plasma and processes in the

interface region alter isotopic composition and contribute to mass bias. They also reported that any factor affecting the ion distribution (*i.e.* instrumental parameters and operating conditions) in the plasma will affect the mass bias. Fontaine *et al.*⁴¹ reported the presence of systematic variation in mass bias in MC-ICP-MS with changes of the operating conditions (carrier gas flow rate, sampling depth, and extraction lens voltage), sample introduction and matrix effects.

The aim of this work is to investigate whether the effect of hydrogen and nitrogen additions on sensitivities of a number of elements across the entire mass range is the same for femtosecond laser ablation as it is with nanosecond lasers and to investigate the effect of nitrogen addition on sensitivity enhancement and mass bias corrections for fs-LA-MC-ICP-MS using Pb isotope ratio measurements as an example.

Experimental set up

LA-ICP-MS

Experiments were carried out using a Quantronix Integra C® femtosecond laser ablation system located at Great Lakes Institute for Environmental Research (GLIER), University of Windsor, Canada. It is a regenerative and multi-pass Ti:sapphire laser ablation system based on the Chirped Pulse Amplification (CPA) technique. The maximum energy that can be obtained from this laser system is 2 mJ (at 1 kHz) in the near infrared (NIR, $\lambda = 795$ nm). Ar was used as a carrier gas and mixed with nitrogen or hydrogen before the ablation cell using a T-shaped connector. The ablated material was detected using Thermo-Electron X7-II® ICP-MS. The instrument was optimized using pure Ar and NIST 610 for maximum sensitivity and low oxide formation (ThO/Th <0.5%). After each gas addition, the instrument was re-optimized for maximum sensitivity. All data were acquired on NIST 610 and NIST 612 SRMs in line scan ablation mode at a speed of 5 μ m per second with sample surface at the focus of the laser beam. The measurements were carried out using time resolved analysis in fast peak jumping mode. Each line scan analysis consists of 60 seconds gas background collection followed by another 60 seconds ablation for signal collection. Each analyte signal was corrected for background by subtracting the background signal from the corresponding gross signal (signal obtained after firing the laser). The ablation cell was flushed for 2 minutes (no ablation) between analyses to reduce memory effects and allow the instrument to stabilize after each gas addition. A summary of the laser system and ICP-MS specifications and operating conditions is shown in Table 1.

LA-MC-ICP-MS

Lead isotope measurements of NIST 610 were carried out by fs-LA-MC-ICP-MS using the previously described femtosecond laser ablation system coupled with a Finnigan™ Neptune MC-ICP-MS. The Finnigan™ Neptune is a double-focusing high resolution MC-ICP-MS with a movable multicollector array consisting of nine faraday detectors and five ion counters. A thallium solution of 100 ppb concentration in 3% HNO₃ was introduced before the ablation cell (to correct for mass bias) at a flow rate of 100 μ l min⁻¹ using the Apex® system (see Fig. 1). The Apex® is an inlet system that can be connected directly to

Table 1 LA-ICP-MS, MC-ICP-MS specifications and operating conditions

Laser ablation system	Quantronix
Manufacture	Integra C®
Model	Ti:sapphire based on the Chirped
Type	Pulse Amplification (CPA) technique
Wavelength	Fundamental: 785 nm
Repetition rate	Up to 1 kHz, experiment: 20 Hz for quadruple ICP-MS and 100 Hz for MC-ICP-MS
Pulse energy	Maximum: 2 mJ per pulse, experiment: 0.2, 0.3, 0.8 mJ
Pulse width	<130 fs
Fluence	12.3 J cm ⁻² for quadruple ICP-MS and 7.4 J cm ⁻² for MC-ICP-MS
Crater size:	47 µm for quadruple ICP-MS and 67 µm for MC-ICP-MS
Objective lens	10×
ICP-MS	
Manufacture	ThermoElectron®
Model	X7-II®
Detector type	ETP® dual mode (pulse and analogue counting)
Dynamic range	~1.3 × 10 ⁹ ICPS
Sensitivity (sol.)	~350 × 10 ⁶ ICPS per ppm
Cone type	High Performance Interface (HPI)
Resolution	Standard (125), High (160)
RF power	1400 W
Plasma gas	13 l min ⁻¹
Auxiliary gas	0.98 l min ⁻¹
Nebulizer gas	0.88–1.02 l min ⁻¹
MC-ICP-MS	
Manufacture	ThermoElectron®
Model	Finnigan™ Neptune
Coolant gas	15 l min ⁻¹
Sample gas	0.91 l min ⁻¹
Auxiliary gas	0.7 l min ⁻¹
RF power	1200 W
Integration time	1.049 s
Apex setting	
Tl flow rate	100 µl min ⁻¹
N ₂ flow rate	0–20 ml min ⁻¹

the torch injector and allows for sample desolvation and self-aspiration at rates from 20 µl min⁻¹ to 1000 µl min⁻¹. The Apex® also allows the addition of other gases such as nitrogen (in this

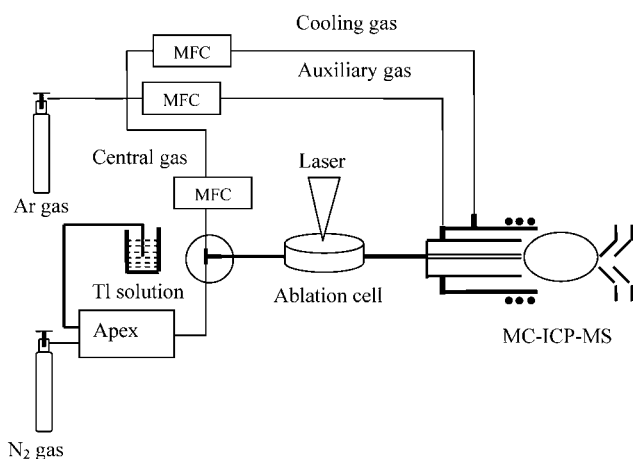


Fig. 1 A schematic set-up of fs-LA-MC-ICP-MS for the addition of small amounts of N₂ and the Tl solution through the Apex® introduction system. MFC: mass flow controller.

study, nitrogen was added to Ar gas before the ablation cell). The laser energy used to ablate NIST 610 was 0.3 mJ but was increased to 0.8 mJ for NIST 612 (Pb concentration in NIST 612 is about 10 times lower than its concentration in NIST 610) to increase the amount of ablated material and consequently the signal intensity. The repetition rate of fs laser pulses was kept at 100 Hz and data were acquired in line scan ablation mode with the laser focus at the sample surface. Data were acquired for 300 cycles (1.049 seconds for a cycle): the first 100 cycles for background collection (no laser ablation) and the remaining 200 cycles for signal collection. After each ablation, the cell was flushed for five minutes to minimize memory effects. Isotopes ²⁰²Hg, ²⁰³Tl, ²⁰⁴Hg, ²⁰⁴Pb, ²⁰⁵Tl, ²⁰⁶Pb, ²⁰⁷Pb and ²⁰⁸Pb were measured using the Faraday detector configuration shown in Table 2.

Data reduction

The raw mass spectrometric intensity data were processed offline using a spreadsheet application by subtracting the average background (average of background integrations obtained during the first 100 cycles while the laser was off) from the signal integrations of each isotope. The first few cycles (in the background and signal obtained after laser ablation commenced) were rejected for more stable signals. The interference of ²⁰⁴Hg on ²⁰⁴Pb was corrected by subtracting the ²⁰⁴Hg intensity (calculated from the measured background-corrected ²⁰²Hg intensity, by assuming ²⁰⁴Hg/²⁰²Hg = 0.2299⁴²) from the background-corrected ²⁰⁴Pb intensity. The ratio of ²⁰⁴Hg to ²⁰⁴Pb was calculated to be 0.009 on average in NIST 610 under the experimental operating conditions. Isotope ratios (²⁰⁵Tl/²⁰³Tl, ²⁰⁶Pb/²⁰⁴Pb, ²⁰⁷Pb/²⁰⁴Pb, ²⁰⁸Pb/²⁰⁴Pb, ²⁰⁸Pb/²⁰⁶Pb and ²⁰⁷Pb/²⁰⁶Pb) were calculated from background- and interference-corrected isotopic data.

Pb isotopic determinations are not straightforward due to the fact that Pb has only one stable (non-radiogenic) isotope, ²⁰⁴Pb, which prevents the application of an internal normalization approach to correct for mass bias. However, as suggested by Longerich *et al.*,⁴³ Tl can be used as a surrogate to correct for mass bias provided that Tl mass bias can be related to that of Pb. No significant differences between mass bias were observed when applying the three commonly used mass fractionation laws (linear, exponential and power) therefore we used the power law: $R_{\text{true}} = R_{\text{meas.}}(1 + \alpha)^{\Delta m}$ and the mass bias per atomic mass unit α :

$$\alpha = \left[\frac{R_{\text{Tl,true}}}{R_{\text{Tl,meas.}}} \right]^{1/\Delta M} - 1$$

where R_{true} and $R_{\text{meas.}}$ are the true and measured Pb isotope ratios, respectively; $\Delta m = (M_i - M_j)$ is the mass difference between masses M_i and M_j of Pb. $R_{\text{Tl,true}}$ and $R_{\text{Tl,meas.}}$ are the true and measured Tl isotope ratios, respectively; and $\Delta M = 2$ is the mass difference of Tl isotopes (*i.e.* ²⁰⁵Tl – ²⁰³Tl).

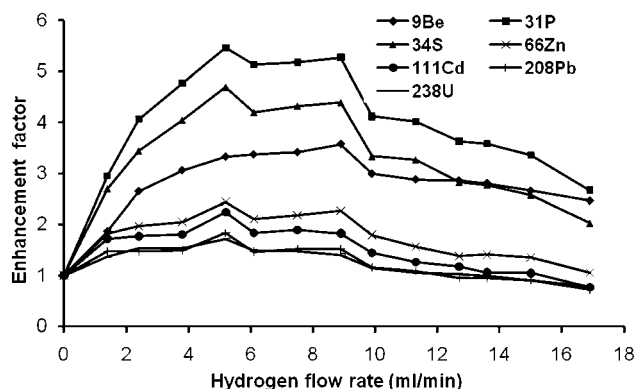
Results and discussion

Hydrogen addition (fs-LA-ICP-MS)

The addition of hydrogen to the Ar carrier gas before the ablation cell increased the intensity of most investigated elements by

Table 2 Faraday cup configurations used for Pb isotope ratio measurements

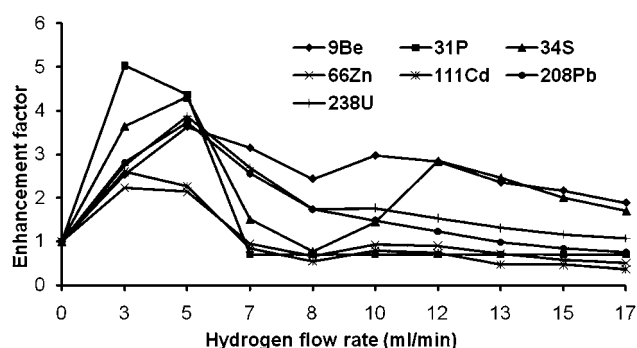
Collector	L3	L2	L1	Center	H1	H2	H3
Mass isotope	^{202}Hg	^{203}Tl	^{204}Pb , Hg	^{205}Tl	^{206}Pb	^{207}Pb	^{208}Pb

**Fig. 2** The effect of hydrogen flow rates on signal enhancement factor (signal intensity with the introduction of hydrogen relative to the intensity with Ar only) in fs-LA-ICP-MS of NIST 612.

a factor of 1.5–2.5. The degree of intensity enhancement is higher for elements with high first ionization potentials such as Be, P, S, As, Se and Au (factor of 3–5). Fig. 2 shows the background-corrected intensity normalized to pure Ar for selected elements as a function of hydrogen flow rates. The oxide ratios marginally decreased with hydrogen addition from 0.1% and 0.35% (pure Ar) to 0.09% and 0.25% ($6 \text{ ml min}^{-1} \text{ H}_2$) for UO/U and ThO/Th, respectively. The slight decrease in the oxide ratios may be an indication of increased plasma gas temperature. Hydrogen has higher thermal conductivity than argon and the plasma gas temperature has been reported to increase by 2000 K when hydrogen was added to the central gas flow.¹ The introduction of hydrogen into the central gas flow increased hydride ratios from 0.001% and 0.002% (pure Ar) to 0.002% and 0.005% ($6 \text{ ml min}^{-1} \text{ H}_2$) for UH/U and ThH/Th, respectively. Higher backgrounds are observed for masses with polyatomic species of hydrogen. The addition of hydrogen also leads to an increase of doubly charged ions from 0.44 to 0.79% and from 0.93 to 1.36% for $^{238}\text{U}/^{238}\text{U}$ and $^{140}\text{Ce}/^{140}\text{Ce}$, respectively. The magnitude of this increase cannot be accurately determined because of interferences from matrix elements in the NIST glasses (^{119}Sn on ^{238}U and ^{70}Ge and ^{70}Zn on ^{140}Ce).

Nitrogen addition

Fig. 3 shows the effect of nitrogen flow rates on signal intensity normalized to pure Ar of selected elements across the entire mass spectrum. The addition of nitrogen before the ablation cell enhanced the sensitivities of most investigated elements by a factor of 2–3. The enhanced sensitivity could be related to the increased thermal conductivity since nitrogen has a thermal conductivity higher than that of Ar by a factor of 32 at 7000 K.²⁴ Backgrounds were found to increase with nitrogen addition only for some lighter isotopes such as ^{29}Si , ^{31}P , ^{39}K , ^{55}Mn and ^{66}Zn .

**Fig. 3** The effect of nitrogen flow rate on the signal enhancement factor (signal intensity with the introduction of nitrogen relative to the intensity with Ar only) in fs-LA-ICP-MS of NIST 612.

The oxide ratios decreased with nitrogen addition from 0.28% and 0.46% (pure Ar) to 0.19% and 0.26% ($5 \text{ ml min}^{-1} \text{ N}_2$) for UO/U and ThO/Th, respectively. An increase of doubly charged ions from 0.01 to 0.02% and from 0.01 to 0.04% for $^{238}\text{U}/^{238}\text{U}$ and $^{140}\text{Ce}/^{140}\text{Ce}$, respectively, is also observed with nitrogen addition.

Sensitivity enhancement can be beneficial for some applications that require analysis of limited amount of materials or analysis of materials with low elemental concentrations. More importantly the addition of nitrogen or hydrogen can benefit isotope ratio determinations using LA-MC-ICP-MS where high spatial resolution sampling and large ion beams are required for high precision isotopic analysis. The next section investigates the role of nitrogen addition as an effective means for improving sensitivity and reducing mass bias in Pb isotope measurements using fs-LA-MC-ICP-MS.

Pb isotope measurements

Effect of nitrogen on Pb and Tl sensitivities in LA-MC-ICP-MS. The addition of nitrogen to Ar before the ablation cell enhanced the signal intensity of Tl by a factor of 4 and Pb by a factor of 3 (at nitrogen flow rate of 5 ml min^{-1}) in fs-LA-MC-ICP-MS of NIST 610, Fig. 4a and b, which is similar to the results with the quadrupole mass spectrometer. This intensity enhancement is important for isotopic analysis using Faraday detectors where large ion beams are necessary for high precision analysis. During the Pb isotopic analyses the Tl solution was continuously aspirated and desolvated into the laser ablation cell where it mixed with the laser ablated material. The behavior of Tl from the desolvated liquid might be different from that of Tl in the dry ablated material as a result of different transport efficiencies or changed plasma conditions. This is clear from Fig. 5 where the intensity variation of the Tl isotopes and the $^{205}\text{Tl}/^{203}\text{Tl}$ ratio at constant nitrogen flow rate (8 ml min^{-1}) during data acquisition of 300 cycles on NIST 612 are shown. The intensity drop for the Tl isotopes when the laser was fired may be related to changes in the plasma conditions as a result of ablated material being introduced into the ICP. A reduction in the plasma temperature as a result of plasma loading may be the reason for the observed drop in intensity. However, the $^{205}\text{Tl}/^{203}\text{Tl}$ ratio was not affected by the signal intensity changes or the source of Tl (simple desolvated liquid or a mixture with ablated

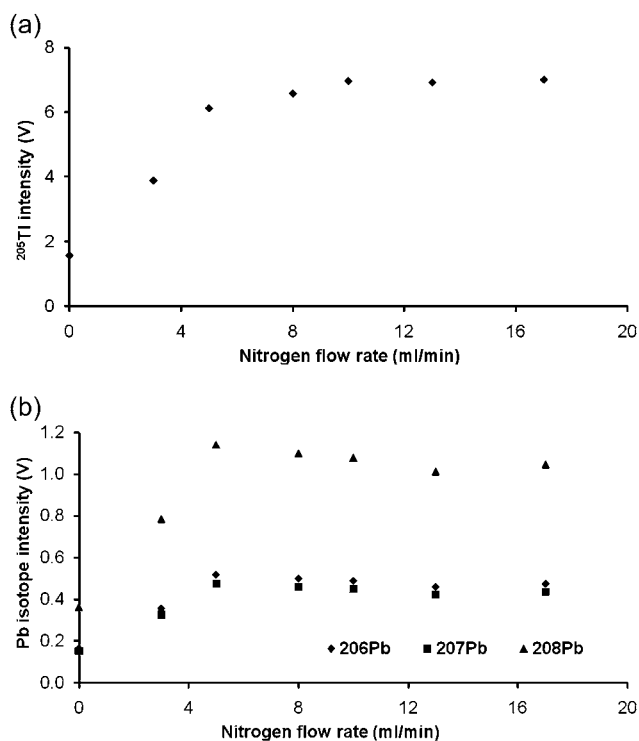


Fig. 4 (a) Effect of nitrogen flow rate on signal intensity of ^{205}Tl in fs-LA-MC-ICP-MS. (b) Effect of nitrogen flow rate on signal intensity of Pb isotopes in fs-LA-MC-ICP-MS.

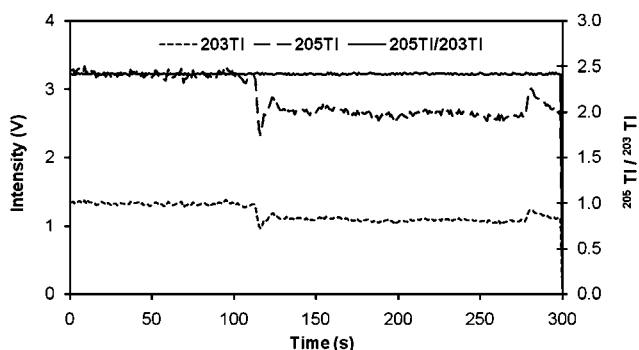


Fig. 5 Intensity variation of Tl isotopes and the measured $^{205}\text{Tl}/^{203}\text{Tl}$ ratio during 300 cycles of data acquisition on NIST 612. The first 100 cycles are measurements of the Tl solution only (no laser ablation) while the last 200 cycles are measurements of both the Tl solution and laser ablated NIST 612. Nitrogen flow rate constant at 8 ml min^{-1} .

NIST glass) and was stable during the whole data acquisition time.

Effect of nitrogen on mass bias. Fig. 6 shows the calculated mass bias of $^{205}\text{Tl}/^{203}\text{Tl}$ and $^{208}\text{Pb}/^{206}\text{Pb}$ as a function of nitrogen flow rate during fs-LA-MC-ICP-MS analysis of NIST 610. The addition of nitrogen decreased the mass bias coefficient (α) from -0.76% and -0.75% for $^{208}\text{Pb}/^{206}\text{Pb}$ and $^{205}\text{Tl}/^{203}\text{Tl}$ to -0.67% and -0.65 , respectively (reduction of about 13% at 5 ml min^{-1} nitrogen). The negative sign indicates that the measured isotope ratios are higher than the true values due to the loss of light isotopes. The power law was used to calculate mass bias

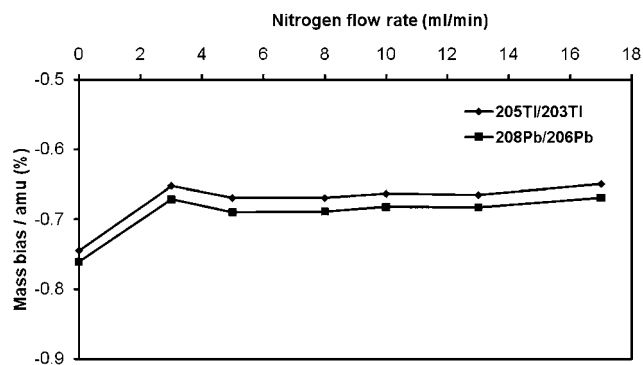


Fig. 6 Mass bias of $^{205}\text{Tl}/^{203}\text{Tl}$ and $^{208}\text{Pb}/^{206}\text{Pb}$ as a function of nitrogen flow rate in fs-LA-MC-ICP-MS of NIST 610. The nitrogen and thallium were added before the ablation cell.

coefficients using the values of $^{208}\text{Pb}/^{206}\text{Pb} = 2.168$ and $^{205}\text{Tl}/^{203}\text{Tl} = 2.3889$ as obtained from ref. 44 and 45 respectively. It is clear from Fig. 6 that the mass bias coefficient α_{Pb} of $^{208}\text{Pb}/^{206}\text{Pb}$ is not identical to α_{Tl} of $^{205}\text{Tl}/^{203}\text{Tl}$ and in contrast to the common mass bias–mass relationship where heavier elements have lower mass bias than lighter elements, inspection of Fig. 6 shows the reverse (Tl, a lighter element has lower mass bias than Pb, a heavier element) but there is consistency in the mass bias behavior of both isotopes as a function of nitrogen flow rate. We do not know the reason for this discrepancy but it could be related to incorrect isotope ratios of $^{205}\text{Tl}/^{203}\text{Tl}$ and $^{208}\text{Pb}/^{206}\text{Pb}$ that have been used for normalization or some other effects. In LA-ICP-MS analyses, nitrogen from air will always be entrained in variable amounts into the system through tubing and connections, from the ablation cell and in the ICP. Under these “standard” conditions, the mass bias is not stable as can be seen from Fig. 6 at “zero” nitrogen flow rate. The addition of more nitrogen helps to improve and stabilize mass bias for both Tl and Pb (Fig. 6, plateau region). Fig. 7 shows the relationship between $^{205}\text{Tl}/^{203}\text{Tl}$ and $^{208}\text{Pb}/^{206}\text{Pb}$ mass bias factors calculated from the power law at constant nitrogen flow rates (8 ml min^{-1}), for 6 replicate measurements of NIST 610, where a strong linear

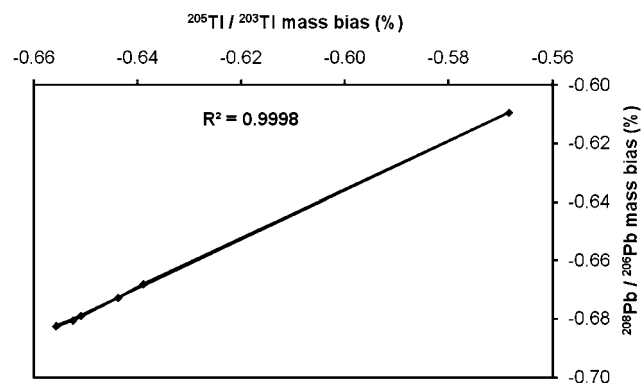


Fig. 7 Relationship between $^{205}\text{Tl}/^{203}\text{Tl}$ and $^{208}\text{Pb}/^{206}\text{Pb}$ mass bias factors as calculated using the power law at constant nitrogen flow rates (8 ml min^{-1}). For 6 replicate measurements of NIST 610, a strong linear correlation ($R^2 = 0.9998$) exists between both factors. Values of $^{205}\text{Tl}/^{203}\text{Tl} = 2.3889$ and $^{208}\text{Pb}/^{206}\text{Pb} = 2.168$ were obtained from ref. 45 and 44 respectively.

correlation ($R^2 = 0.9998$) between both factors is clear. The ratio of mass bias factors $\alpha_{\text{Pb}}/\alpha_{\text{Tl}}$ was found to be equal to 1.0214 for $^{208}\text{Pb}/^{206}\text{Pb}$ in this study. This ratio is higher than that of White *et al.*⁴⁶ who reported a mass bias ratios $\alpha_{\text{Pb}}/\alpha_{\text{Tl}}$ of 0.9746 for NBS981 in solution using the exponential law. The difference in mass bias coefficients between Pb and Tl was interpreted as the reason why Tl was unable to provide accurate normalization of most SRM981 solutions and about 30% of silicate samples measured by Isoprope MC-ICP-MS.⁴⁵ In this study, as well, the use of Tl as a surrogate for Pb mass bias would not give accurate determinations of Pb isotope ratios if mass bias differences between Pb and Tl were not taken into account. In our calculations of isotope ratios we corrected for this difference by determining the ratio of mass bias factor of $^{208}\text{Pb}/^{204}\text{Pb}$, $^{207}\text{Pb}/^{204}\text{Pb}$, $^{206}\text{Pb}/^{204}\text{Pb}$, $^{207}\text{Pb}/^{206}\text{Pb}$ and $^{208}\text{Pb}/^{206}\text{Pb}$ to that of $^{205}\text{Tl}/^{203}\text{Tl}$ (*i.e.* $\alpha_{\text{Pb}} = 1.0214\alpha_{\text{Tl}}$ for $^{208}\text{Pb}/^{206}\text{Pb}$) for each measurement and then applied the power law to get the corrected isotope ratios instead of renormalizing to a different Tl isotopic composition (*i.e.* adjustment of $^{205}\text{Tl}/^{203}\text{Tl}$ to provide the closest values of Pb isotope ratio to the reference values) as done in other studies.^{47–49}

In this way we obtained accurate isotope ratios as listed in Table 3. Fig. 8 shows the effect of mass bias correction using different values of $^{205}\text{Tl}/^{203}\text{Tl}$ on $^{208}\text{Pb}/^{206}\text{Pb}$ ratio of NIST 610 as measured by fs-LA-ICP-MS. It is clear that the value of $^{205}\text{Tl}/^{203}\text{Tl}$ used to correct for mass bias has an effect on the degree of mass bias correction. However, Tl normalization has greatly corrected the measured isotope ratio compared to the raw ratios.

We also applied the standard–sample–standard bracketing technique as another method to correct for mass bias. NIST 612 was used as a bracketing standard for Pb isotope ratio determinations in NIST 610. Alternate measurements of NIST 612 and NIST 610 were carried out using high laser energy on NIST 612 (0.8 mJ) and low laser energy on NIST 610 (0.3 mJ) to get more similar ion intensities for both matrices when switching between NIST 610 and NIST 612. The isotope ratio was calculated according to the following equation:³¹

$$R_{\text{true}} = R_{\text{meas.}} \frac{R_{\text{std}}}{\sqrt{r_{\text{std}}^1 \times r_{\text{std}}^2}}$$

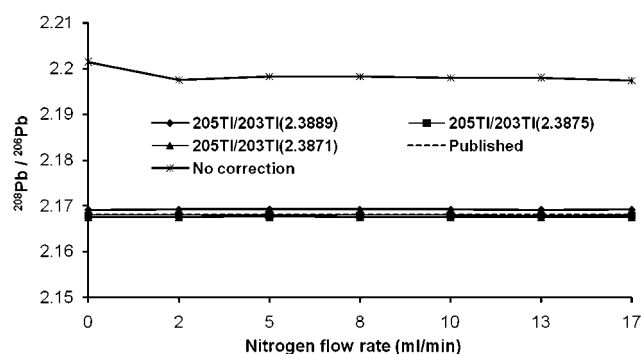


Fig. 8 The effect of mass bias correction using different values of $^{205}\text{Tl}/^{203}\text{Tl}$ on corrected $^{208}\text{Pb}/^{206}\text{Pb}$ ratio of NIST 610 as measured by fs-LA-ICP-MS. It is clear that the value of $^{205}\text{Tl}/^{203}\text{Tl}$ used to correct for mass bias has an effect on the degree of mass bias correction. The values of $^{205}\text{Tl}/^{203}\text{Tl}$: 2.3875, 2.3889, and 2.3871 were obtained from ref. 48, 56 and 57 respectively. The $^{208}\text{Pb}/^{206}\text{Pb}$ published value was obtained from ref. 44.

where R_{true} and $R_{\text{meas.}}$ represent the true and measured isotope ratios of the sample, respectively; R_{std} is the true isotope ratio of the bracketing standard; and r_{std}^1 and r_{std}^2 are the isotope ratios of the bracketing standard measured before and after the sample.

Table 3 lists the measured Pb isotope ratios after being corrected for mass bias using both Tl normalization and standard–sample–standard bracketing together with published values. For Tl normalization, the gross means of 6 measurements with 1 standard deviation are: $^{206}\text{Pb}/^{204}\text{Pb} = 17.0472 \pm 0.0045$, $^{207}\text{Pb}/^{204}\text{Pb} = 15.5087 \pm 0.0048$, $^{208}\text{Pb}/^{204}\text{Pb} = 36.9715 \pm 0.0137$, $^{208}\text{Pb}/^{206}\text{Pb} = 2.1685 \pm 0.0003$ and $^{207}\text{Pb}/^{206}\text{Pb} = 0.9097 \pm 0.0001$. These values are in good agreement with published data. For standard–sample–standard bracketing, twelve raw isotope ratios (after being corrected for background and ^{204}Hg interferences on ^{204}Pb) of alternate NIST 610 and NIST 612 were used to get five values of each isotope ratio in NIST 610 with means: $^{206}\text{Pb}/^{204}\text{Pb} = 17.0608 \pm 0.0132$, $^{207}\text{Pb}/^{204}\text{Pb} = 15.5219 \pm 0.0124$, $^{208}\text{Pb}/^{204}\text{Pb} = 37.0076 \pm 0.0300$, $^{208}\text{Pb}/^{206}\text{Pb} = 2.1692 \pm 0.0002$ and $^{207}\text{Pb}/^{206}\text{Pb} = 0.9098 \pm 0.0001$.

Table 3 Measured Pb isotope ratios of NIST 610 using Tl normalization and standard–sample–standard bracketing

	$^{206}\text{Pb}/^{204}\text{Pb}$	$^{207}\text{Pb}/^{204}\text{Pb}$	$^{208}\text{Pb}/^{204}\text{Pb}$	$^{208}\text{Pb}/^{206}\text{Pb}$	$^{207}\text{Pb}/^{206}\text{Pb}$
Tl normalization (this study), average \pm SD	17.0472 ± 0.0045	15.5087 ± 0.0048	36.9715 ± 0.0137	2.1685 ± 0.0003	0.9097 ± 0.0001
Standard–sample bracketing (this study), average \pm SD	17.0608 ± 0.0132	15.5219 ± 0.0124	37.0076 ± 0.0300	2.1692 ± 0.0002	0.9098 ± 0.0001
Reference values ⁴⁴ (used in this study)	17.045 ± 0.008	15.504 ± 0.009	36.964 ± 0.022	2.168 ± 0.001	0.9096 ± 0.0003
Walder <i>et al.</i> ⁵⁰	17.0510 ± 0.0160	15.5090 ± 0.0180	36.9480 ± 0.0380	2.1670 ± 0.0018	0.9096 ± 0.0008
Woodhead and Hergt ⁵¹	17.0470 ± 0.0018	15.5090 ± 0.0001	36.9750 ± 0.0026	2.1699 ± 0.0003	0.9101 ± 0.0001
Baker <i>et al.</i> ⁵²	17.0520 ± 0.0020	15.5150 ± 0.0020	36.9910 ± 0.0050	2.1694 ± 0.0001	0.9099 ± 0.0005
Platzner <i>et al.</i> ⁵³	17.0510 ± 0.0090	15.5070 ± 0.0080	36.9650 ± 0.0160	2.1677 ± 0.0006	0.9095 ± 0.0002
Belshaw <i>et al.</i> ⁵⁴	17.0490 ± 0.0120	15.5060	36.9790	2.1690 ± 0.0010	0.9095 ± 0.0006
Machado and Gauthier ⁵⁵	17.0640 ± 0.0070	15.5250	37.0460	2.1710 ± 0.0010	0.9098 ± 0.0002

^a For Tl normalization, data are reported for 6 measurements as the mean \pm 1 standard deviation (SD). These data represent the mean of 200 integrations (1.049 seconds each integration) after background correction. For standard–sample–standard bracketing, NIST 612 was used as a bracketing standard for NIST 612. All isotope ratio measurements were carried out by adding 8 ml min^{−1} N₂ to Ar before the ablation cell.

Discussion

The idea of using a mixed gas plasma is not new. It was originally used with ICP-MS and ICP-AES to improve their sensitivities, stabilities and analytical capabilities. However, there are contradictions in published data regarding enhancement or depression of sensitivities under different gas mixture conditions. For example, in some studies^{11,24–26,29} whether based on solution- or LA-ICP-MS, addition of nitrogen to Ar gas was found to enhance sensitivity whereas in some other studies^{17,20,28} a depression or little enhancement in sensitivity was reported. This wide variation in published data can be attributed to differences in instrumentation, experimental conditions and different ways of optimization among different laboratories. In this study, the addition of hydrogen and nitrogen to Ar carrier gas has improved elemental sensitivities, likely due to the higher thermal conductivities of these gases which results in higher plasma temperature and increased excitation and ionization efficiency of many elements. Nitrogen and hydrogen were added before the ablation cell. Therefore the observed sensitivity enhancement could also be related to processes occurring not only in the ion source (ICP) but also in the ablation cell and transport system. For example the ablation process could be affected by the added gases and consequently lead to changes in the amount of ablated material and particle size distribution. This would affect the transport efficiency and the degree of ionization inside the ICP with a subsequent enhancement or suppression of signal intensity. It should also be mentioned that consistent optimization of the large number of potential focusing parameters in ICP-MS after each gas addition is difficult. Thus accounting for the effect of all parameters to study the effect of gas addition is not possible.

Accurate and precise isotopic measurements are hindered by many obstacles in LA-ICP-MS such as elemental and isotopic fractionation, mass bias, abundance sensitivity, matrix effects and interferences. Careful optimization of experimental conditions can reduce these problems. The use of femtosecond laser pulses for ablation has been reported to minimize fractionation and matrix effects. Introduction of multicollectors with double focusing high resolution sector field analyzers has minimized ion beam instabilities, improved abundance sensitivity and eliminated some interferences when used at high resolution. Use of mixed gas plasmas is another way to reduce these effects. Addition of nitrogen to the Ar carrier gas, as indicated in this study, has reduced mass bias by about 13%, robustly stabilized the mass bias ratios of Tl/Pb and increased sensitivity of Tl and Pb by a factor of 3–4. There do not appear to be any negative effects for Pb isotope analyses by introducing nitrogen to the plasma.

For other isotope systems the increase in sensitivity achieved with addition of hydrogen or nitrogen will generally enhance precision of the measured isotope ratios. However, the production of hydride ions in the ICP will introduce new interferences that may degrade precision and accuracy. For example in LA-MC-ICP-MS analyses of Sr isotopes, the presence of significant quantities of KrH^+ , RbH^+ and SrH^+ in the analyzed ion beam will require significant inter-element and inter-isotope corrections that will be difficult to quantify with potential serious degradation in the ability to measure both Sr mass bias

(from $^{86}\text{Sr}/^{88}\text{Sr}$) and the isotope ratio ($^{87}\text{Sr}/^{86}\text{Sr}$) which varies naturally by radioactive decay of ^{87}Rb . The increase of doubly charged ions with the hotter plasmas produced with hydrogen or nitrogen addition, e.g. of rare earth elements (REEs), can be a problem in the determination of the isotopic composition of elements of interest such as Sr (interferences from $^{172}\text{Yb}^{2+}$ on $^{86}\text{Sr}^{1+}$, $^{176}\text{Yb}^{2+}$, $^{176}\text{Lu}^{2+}$ and $^{176}\text{Hf}^{2+}$ on $^{88}\text{Sr}^{1+}$) and Rb (interferences from $^{170}\text{Er}^{2+}$ and $^{170}\text{Yb}^{2+}$ on $^{85}\text{Rb}^{1+}$, $^{174}\text{Yb}^{2+}$ and $^{174}\text{Hf}^{2+}$ on $^{87}\text{Rb}^{1+}$). Therefore it may become important to make a compromise between the benefits of enhanced sensitivity and the drawbacks of increased doubly charged ions and other interferences induced by addition of different gases to the plasma.

Conclusions

It has been shown in this study that addition of nitrogen and hydrogen to Ar carrier gas has improved signal intensity of most investigated elements in fs-LA-ICP-MS. At the same time there was an increase of polyatomic species of nitrogen and hydrogen. The observed decrease in the oxide ratios and increase of doubly charged ions can be related to the increase of the plasma temperature as a result of high thermal conductivities of these gases. Careful optimization of instrumental parameters after gas addition is important since adding a gas will alter the plasma conditions, therefore it is important to make sure that the changes in sensitivities are caused only by gas addition and not by changes in optimum conditions.

We have also shown that adding nitrogen to Ar carrier gas before the ablation cell in fs-LA-MC-ICP-MS has improved the intensity of Tl and Pb by a factor of 3–4. This enhancement of sensitivity is important for isotopic analysis using Faraday detectors where large ion beams are necessary for precise and accurate isotopic analysis. Femtosecond laser systems with controllable energy and repetition rates (up to few kHz) can also be a tool for achieving the high count rates. The mass bias for Pb and Tl isotopes was reduced by about 13% when nitrogen was added to Ar carrier gas. This reduction can be related to improvement of ion transmission as a result of more robust plasma in the presence of nitrogen. It has been also shown that Tl and Pb do not have identical mass bias and the mass bias difference should be taken into account for accurate and precise isotope ratios determination based on Tl normalization.

Acknowledgements

The authors would like to thank Dr Zhaoping Yang for her help during this work. Support for this research was provided by a National Sciences and Engineering Research Council Discovery Grant to B. Fryer. Infrastructure support was provided by CFI/OIT grants to B. Fryer and by the University of Windsor. M. Shaheen was supported, in part, by Cultural Affairs and Missions Sector, Ministry of Higher Education, Egypt. Two journal reviewers are thanked for improving the manuscript.

References

- 1 N. N. Sesi, A. M. Mackenzie, K. E. Shanks, P. Y. Yang and G. M. Hieftje, *Spectrochim. Acta, Part B*, 1994, **49**, 1259–1282.
- 2 R. S. Houk, A. Montaser and V. A. Fassel, *Appl. Spectrosc.*, 1983, **37**, 425–428.

- 3 D. Hausler, *Spectrochim. Acta, Part B*, 1987, **42**, 63–73.
- 4 E. H. Choot and G. Horlick, *Spectrochim. Acta, Part B*, 1986, **41**, 889–906.
- 5 K. S. Park, S. T. Kim, Y. M. Kim, Y. J. Kim and W. Lee, *Bull. Korean Chem. Soc.*, 2003, **24**, 285–290.
- 6 M. Murillo and J. M. Mermet, *Spectrochim. Acta, Part B*, 1989, **44**, 359–366.
- 7 I. Rodushkin, P. Nordlund, E. Engstrom and D. C. Baxter, *J. Anal. At. Spectrom.*, 2005, **20**, 1250–1255.
- 8 A. Montaser and R. L. Vanhoven, *CRC Crit. Rev. Anal. Chem.*, 1987, **18**, 45–103.
- 9 A. Montaser, S. K. Chan and D. W. Koppenaal, *Anal. Chem.*, 1987, **59**, 1240–1242.
- 10 L. Ebdon, M. J. Ford, R. C. Hutton and S. J. Hill, *Appl. Spectrosc.*, 1994, **48**, 507–516.
- 11 Z. Hu, S. Gao, Y. Liu, S. Hu, H. Chen and H. Yuan, *J. Anal. At. Spectrom.*, 2008, **23**, 1093–1101.
- 12 R. C. Hutton, *J. Anal. At. Spectrom.*, 1986, **1**, 259–263.
- 13 G. Xiao and D. Beauchemin, *J. Anal. At. Spectrom.*, 1994, **9**, 509–518.
- 14 A. E. Holliday and D. Beauchemin, *J. Anal. At. Spectrom.*, 2003, **18**, 1109–1112.
- 15 Z. Hu, S. Hub, S. Gao, Y. Liua and S. Lin, *Spectrochim. Acta, Part B*, 2004, **59**, 1463–1470.
- 16 Z. Hu, S. Gao, S. Hu, H. Yuan, X. Liua and Y. Liu, *J. Anal. At. Spectrom.*, 2005, **20**, 1263–1269.
- 17 D. Beauchemin and J. M. Craig, *Spectrochim. Acta, Part B*, 1991, **46**, 603–614.
- 18 E. H. Evans and L. Ebdon, *J. Anal. At. Spectrom.*, 1989, **4**, 299–300.
- 19 E. H. Evans and L. Ebdon, *J. Anal. At. Spectrom.*, 1990, **5**, 425–430.
- 20 J. M. Craig and D. Beauchemin, *J. Anal. At. Spectrom.*, 1992, **7**, 937–942.
- 21 J. W. Lam and G. Horlick, *Spectrochim. Acta, Part B*, 1990, **45**, 1313–1325.
- 22 S. J. Hill, M. J. Ford and L. Ebdon, *J. Anal. At. Spectrom.*, 1992, **7**, 719–725.
- 23 H. Louie and S. Y. P. Soo, *J. Anal. At. Spectrom.*, 1992, **7**, 557–564.
- 24 S. F. Durrant, *Fresenius' J. Anal. Chem.*, 1994, **349**, 768–771.
- 25 S. A. Crowe, B. J. Fryer, I. M. Samson and J. E. Gagnon, *J. Anal. At. Spectrom.*, 2003, **18**, 1331–1338.
- 26 T. Iizuka and T. Hirata, *Chem. Geol.*, 2005, **220**, 121–137.
- 27 Q. Ni, Z. C. Hu, Z. Y. Bao and Y. F. Zhang, *Chin. Chem. Lett.*, 2009, **20**, 92–95.
- 28 M. Guillon and C. A. Heinrich, *J. Anal. At. Spectrom.*, 2007, **22**, 1488–1494.
- 29 Z. Hu, S. Gao, Y. Liu, S. Hu, H. Chen and H. Yuan, *J. Anal. At. Spectrom.*, 2008, **23**, 1093–1101.
- 30 I. T. Platzner, Modern Isotope Ratio Mass Spectrometry, in *Chemical Analysis: A Series of Monographs on Analytical Chemistry and its Applications*, John Wiley, England, 1997, vol. 145.
- 31 F. Albarede and B. Beard, Analytical methods for non traditional isotopes, *Rev. Mineral. Geochem.*, 2004, **55**, 113–152.
- 32 R. E. Russo, X. Mao, J. J. Gonzalez and S. S. Mao, *J. Anal. At. Spectrom.*, 2002, **17**, 1072–1075.
- 33 M. Shaheen, J. E. Gagnon, Z. Yanga and B. J. Fryer, *J. Anal. At. Spectrom.*, 2008, **23**, 1610–1621.
- 34 I. Horn and F. von Blanckenburg, *Spectrochim. Acta, Part B*, 2007, **62**, 410–422.
- 35 J. Chmeleff, I. Horn, G. Steinhofel and F. von Blanckenburg, *Chem. Geol.*, 2008, **249**, 155–166.
- 36 M. Rehkamper, F. Wombacher and J. K. Aggarwal, Stable Isotope Analysis by Multiple Collector ICP-MS, in *Handbook of Stable Isotope Analytical Techniques*, ed. P. A. de Groot, Elsevier, 2004, vol. 1.
- 37 J. S. Becker, *Inorganic Mass Spectrometry: Principles and Applications*, John Wiley & Sons Ltd, 2007.
- 38 N. J. Pearson, W. L. Griffen and S. Y. O'Reilly, Mass Fractionation Correction in Laser Ablation Multiple-Collector ICP-MS: Implication for Overlap Correction and Precise and Accurate *in situ* Isotope Ratio Measurement, in *Laser Ablation in Earth Sciences: Current Practices and Outstanding Issues, Short Course Series*, Paul Sylvester, Vancouver, BC, 2008, vol. 40.
- 39 H. Zou, Mass Fractionation in Ionization Processes, in *Quantitative Geochemistry*, Imperial college press, London, 2007.
- 40 H. André, I. Rodushkin, A. Stenberg, D. Malinovsky and D. C. Baxter, *J. Anal. At. Spectrom.*, 2004, **19**, 1217–1224.
- 41 G. H. Fontaine, B. Hattendorf, B. Bourdon and D. Günther, *J. Anal. At. Spectrom.*, 2009, **24**, 637–648.
- 42 M. G. Zadnik, S. Specht and F. Begemann, *Int. J. Mass Spectrom. Ion Processes*, 1989, **89**, 103.
- 43 H. P. Longerich, B. J. Fryer and D. F. Strong, *Spectrochim. Acta, Part B*, 1987, **42**(1–2), 39–48.
- 44 http://georem.mpcch-mainz.gwdg.de/sample_query_pref.asp.
- 45 M. F. Thirlwall, *Chem. Geol.*, 2002, **184**, 255–279.
- 46 W. M. White, F. Albarede and P. Telouk, *Chem. Geol.*, 2000, **167**, 257–270.
- 47 M. Rehkämper and A. N. Halliday, *Int. J. Mass Spectrom. Ion Processes*, 1998, **181**, 123–133.
- 48 N. S. Belshaw, P. A. Freedman, R. K. O'Nions, M. Frank and Y. Guo, *Int. J. Mass Spectrom. Ion Processes*, 1998, **181**, 51–58.
- 49 C. Gallon, J. Aggarwal and A. R. Flegal, *Anal. Chem.*, 2008, **80**, 8355–8363.
- 50 A. J. Walder, I. D. Abell and I. Platzner, *Spectrochim. Acta, Part B*, 1993, **48**(3), 397–402.
- 51 J. D. Woodhead and J. M. Hergt, *Geostand. Newsl.*, 2001, **25**, 261–266.
- 52 J. Baker, D. Peate, T. Waight and C. Meyzen, *Chem. Geol.*, 2004, **211**, 275–303.
- 53 I. Platzner, S. Ehrlich and L. Halicz, *Fresenius' J. Anal. Chem.*, 2001, **370**, 624–628.
- 54 N. S. Belshaw, R. K. O'Nions, D. J. Martel and K. W. Burton, *Chem. Geol.*, 1994, **112**, 57–70.
- 55 N. Machado and G. Gauthier, *Geochim. Cosmochim. Acta*, 1996, **60**, 5063–5073.
- 56 R. Kent, *Geostand. Geoanal. Res.*, 2008, **32**, 129–147.
- 57 P. J. De Bievre, M. Gallet, N. E. Holden and I. L. Barnes, *J. Phys. Chem. Ref. Data*, 1984, **13**, 809.