

# Performance characteristics of a tandem spray chamber arrangement in double focusing sector field ICP-MS

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A tandem cyclone-Scott type spray chamber configuration combined with infrared heating and a low-flow Micromist nebulizer was evaluated for the use in a ICP-SFMS sample introduction system. The system provides about a 3-fold sensitivity gain and lower oxide formation compared to the standard introduction system, although matrix-induced signal suppression is more pronounced, especially for elements with high ionization potential. The technique was evaluated by accurate analysis of riverine water reference material SLRS-3 with generally good agreement with certified and literature values. Long-term precision at a  $20 \mu\text{g l}^{-1}$  concentration level was 0.7% RSD in low resolution and 1.6% RSD in medium resolution. Precision in the range 0.03–0.09% RSD for lead isotope ratios at  $1 \mu\text{g l}^{-1}$  was obtained.

## Introduction

Inductively coupled plasma mass spectrometry (ICP-MS) has become a widely accepted technique for both elemental and isotope ratio determinations in a variety of matrices.<sup>1</sup> Sector field ICP-MS (ICP-SFMS), whose commercial introduction dates back to 1989, offers the ability to resolve many spectral interferences and provides improved instrumental detection limits and isotope ratio precision compared with conventional ICP-MS instruments equipped with quadrupole mass filters (ICP-QMS).<sup>2</sup> Over the last few years the unique detection capabilities of ICP-SFMS have been used for such demanding analytical tasks as determination of ultra-trace impurities in production chemicals,<sup>3</sup> alpine ice and snow,<sup>4,5</sup> sea-waters<sup>6,7</sup> and biological matrices<sup>8,9</sup> as well as for precise isotope analysis at low analyte concentrations.<sup>4,10–13</sup> Requirement for accurate determinations at sub  $\text{ng ml}^{-1}$  concentrations often associated with limited sample amounts facilitates rapid development of new components for ICP-MS sample introduction systems. Research efforts have been aimed at high-efficiency nebulizers,<sup>14–16</sup> spray chambers,<sup>17</sup> shielded torches<sup>18</sup> etc. Parameters such as sensitivity, short- and long-term signal stability, severity of matrix effects and formation of spectral interferences should be considered when comparing performance characteristics of commercially available sample introduction systems. Robustness of assembly and operation and cost are also of importance. It often appears that gain in one of the parameters is accompanied by compromising others. For example, a 10-fold increase in sensitivity by using ultrasonic nebulization (USN), a microconcentric nebulizer (MCN) with desolvation unit, or a capacitive decoupling (CD) system is achieved at the expense of an increase in matrix influences (all above mentioned systems), a higher sample uptake and worse signal stability (USN),<sup>13,19</sup> and significantly high oxide formation (CD).<sup>20</sup>

Hamester and co-workers<sup>21</sup> recently demonstrated a significant improvement in precision of isotope ratio measurements with ICP-SFMS, partly attributed to the use of a specially designed sample introduction system, consisting of a tandem spray chamber arrangement with a low-flow Micromist MCN. During an attempt to reproduce this arrangement, it was found that, while short-term signal stability was significantly improved compared to a standard Scott-type spray

chamber using the same nebulizer, long-term stability suffered from liquid build-up in the conjunction between the spray chambers, which resulted in a modification of the aerosol transport. In order to maintain signal intensity and stability, re-adjustment of sample gas flow was necessary every hour of operation. It was possible to overcome this drawback by heating the first spray chamber while cooling the second. As an additional advantage a significant sensitivity gain should be mentioned. The aim of this note is to assess applicability of the upgraded tandem spray chamber arrangement for trace and ultra-trace analysis of natural waters and for isotope ratio measurements on a routine basis.

## Experimental

### Instrumentation

An ELEMENT (Finnigan MAT, Bremen, Germany) ICP-SFMS instrument was used. Instrument configuration and operating conditions are reported elsewhere.<sup>6,8,12</sup> The standard sample introduction system consists of a water-cooled Scott-type double pass spray chamber. In the tandem arrangement, a cyclone spray chamber (Glass Expansion Ltd., Hawthorn, Australia) was coupled to the Scott-type spray chamber using an end-cup intended for connection of a V-groove nebulizer. The first spray chamber is heated by means of an infrared lamp (IR100R, Philips, Netherlands) placed just above the conjunction. In order to maintain a stable temperature of this system, both the lamp and the cyclone spray chamber are operated inside a box made of aluminum foil. In this system, the second spray chamber further reduces droplet size distribution and serves as a cooling stage to remove excess of the solvent leaving the heating stage. Both spray chambers are drained using a peristaltic pump operated at  $2 \text{ rev min}^{-1}$ . The time needed for the system to equilibrate after light-up and prior to gas flow optimization is about 30 min. Optimum nebulizer gas flow was found to be significantly lower compared to the standard configuration. Though the ELEMENT is equipped with a CD system, this option has not been activated during experiments. The same low-flow nebulizer (Micromist, Glass Expansion Ltd., Hawthorn, Australia) operated in the self-aspiration mode at a sample uptake below  $200 \mu\text{l min}^{-1}$  was used for both arrangements.

## Reagents and materials

SLRS-3 riverine water reference material for trace metals was obtained from the National Council of Canada, Ottawa, Canada. Lead isotope standards SRM 981–983 (National Institute of Standards and Technology, Gaithersburg, USA) were used for isotope ratio measurements. For the preparation of standards, blank solutions and for dilution of lead isotope standards,  $0.14 \text{ mol l}^{-1} \text{ HNO}_3$  [obtained by dilution of  $14 \text{ mol l}^{-1}$  analytical-grade  $\text{HNO}_3$  (Merck, Darmstadt, Germany), purified by sub-boiling distillation in a quartz still, with de-ionized, distilled water prepared from laboratory de-ionized water (Millipore Milli-Q, Bedford, MA, USA) using Teflon still distillation] was used. A set of calibration solutions was prepared by diluting  $10 \text{ mg l}^{-1}$  multi-element standard solutions (PE Pure Plus Atomic Spectroscopy Standards, Norwalk, USA). NaCl (Merck) was added to these standards to 0.02% and 0.2% concentration for assessment of matrix effects. To minimize contamination, all preparations were carried out in a laminar flow hood located in a clean room. All plastic material utilized for preparation and storage of the solutions was thoroughly acid-cleaned before use.

## Result and discussion

### Sensitivity

With the standard configuration introduction system, the response of  $^{115}\text{In}$  in low resolution mode is about 180–200 MHz per  $\text{mg l}^{-1}$ , which is consistent with previously published values.<sup>22</sup> The tandem spray chamber arrangement provides intensity enhancement by a factor of 2.5–4, with the highest gain for low mass elements (Fig. 1).  $^{115}\text{In}$  response increases to about 500–550 MHz per  $\text{mg l}^{-1}$ , which is higher compared to the sensitivity reported for ICP-QMS equipped with USN.<sup>23</sup> This enhancement is an expected result of improvement in analyte transport, particularly due to aerosol desolvation in the cyclone spray chamber. Although the effectiveness of this system is lower than in a membrane desolvation unit, it is not affected by losses of volatile analytes<sup>3</sup> or clogging of the membrane by matrix salts.<sup>24</sup>

### Matrix effects

Since increased analyte load into the ICP is accompanied by a proportional increase in matrix element load, the severity of matrix effects is expected to be higher with high-efficiency introduction systems.<sup>25</sup> The effect of varying the NaCl concentration on the intensities of Li, Be, In and Cd is presented in Fig. 2. For both introduction systems, an increase in matrix concentration results in gradual intensity losses. For elements with high ionization potential (*i.e.*, Be, Cd), the signal recovery in 0.2% NaCl is about 10% lower with the tandem arrangement, and no differences in recovery are found between the introduction systems for elements with low ionization potential. Except for P, Zn, Cd, I and Bi, signal suppression caused by the matrix is less than 40%. Significantly more severe matrix effects (up to 80% signal suppression) are found for a similar matrix concentration by using a membrane desolvation unit and CD option.<sup>7</sup>

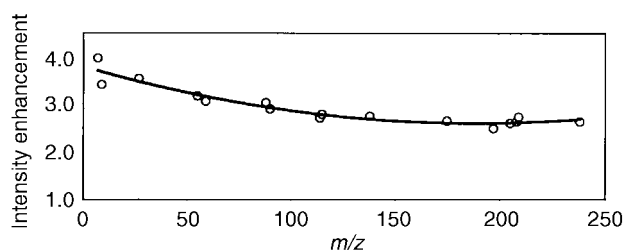


Fig. 1 Intensity enhancement with tandem spray chamber arrangement as function of mass.

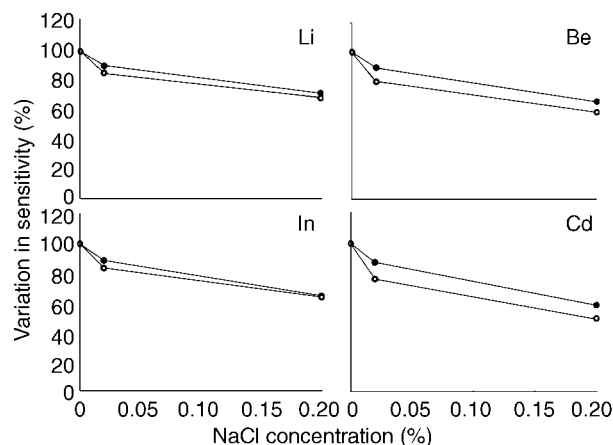


Fig. 2 Signal suppression caused by NaCl matrix with standard configuration (solid circles) and with tandem arrangement (open circles).

### Oxide formation

As a significant part of the spectral interferences originated from oxide, and hydroxide species cannot be resolved even using high resolution, it is important to keep oxide formation in the ICP at the lowest possible level. It was shown that about a 10-fold increase in oxide formation when using the CD system is one of the major obstacles for a wider use of the system for routine applications.<sup>20</sup> In contrast to membrane desolvation, for which about a 100-fold decrease in oxide species abundance has been reported,<sup>24</sup> the tandem arrangement provides only moderate (2-fold) decrease in oxide formation (monitored as  $\text{UO}^+/\text{U}^+$  ratio) compared to the standard configuration. It should be noted that the use of the Micromist MCN instead of a conventional Meinhard-type nebulizer alone results in about a 4-fold decrease in uranium oxide formation.

### Precision and accuracy

The precision and accuracy of the elemental analysis of natural waters using the tandem arrangement were determined on SLRS-3 water reference material. Three distinct consecutive measurements were performed within 50 min (10 min washout was included between each measurement). Medium resolution mode was used for isotopes potentially affected by spectral interferences in the mass range from 31 to 76 u and mathematical correction was used for higher mass elements. Isotope  $^{115}\text{In}$  was used for internal standard correction. Analytical results for the reference material together with certified and published values are presented in Table 1. From 62 elements included in the experiment, only 5 were not detected in the sample because of a high blank level (Hg), insufficient detection power (Ir, Pd) or severe unresolved interferences (Rh, Ru). For the majority of the elements, precision [expressed as the relative standard deviation (RSD)] is better than 5% even at low  $\text{ng l}^{-1}$  concentrations. The results obtained agree well with available, certified and published values, except for Pd, Sn and Ti. These differences may be caused by variations in concentrations of uncertified elements between SLRS-3 bottles or by introduced contamination. Total acquisition time was about 2 h, including time needed for analysis of blanks and standards. The long-term stability, determined as RSD for internal standard intensity (In added to all solutions at  $20 \mu\text{g l}^{-1}$ ) was 0.7% in low resolution and 1.6% in medium resolution ( $n=12$ ).

Precision of the isotope ratio measurements was assessed using the  $^{206}\text{Pb}/^{207}\text{Pb}$  ratio measured in SRM 981–983 isotope standards diluted to  $1 \mu\text{g l}^{-1}$  Pb concentration (Table 2). The data represent average values and standard deviations for 7 consecutive measurements comprising 2000 sweeps each. These

**Table 1** Analytical results for the CRM SLRS-3 ( $\text{ng l}^{-1}$ ) and comparison with certified and published data

Element	Found <sup>a</sup>	Certified	Element	Found <sup>a</sup>	Certified
Ag	1.20 (0.99)	1.8 (0.4) <sup>b</sup>	Nb	2.66 (0.07)	—
Al	31500 (900)	31000 (3000)	Nd	209 (3)	200 (2) <sup>b</sup> , 239 <sup>b</sup>
As	722 (22)	720 (50)	Ni	831 (5)	830 (80)
Au	2.01 (0.14)	1.8 (0.2) <sup>b</sup>	P	4180 (110)	—
B	4480 (50)	4240 (10)	Pb	67.8 (0.6)	68 (7)
Ba	13860 (40)	13400 (600)	Pd	<0.02	3.26 (0.06) <sup>b</sup>
Be	5.61 (0.47)	5.0 (1.0)	Pr	54.1 (0.5)	53.0 (0.5) <sup>b</sup> , 61 <sup>b</sup>
Bi	2.02 (0.08)	1.8 (0.1) <sup>b</sup>	Pt	2.11 (0.09)	2.37 (0.04) <sup>b</sup>
Cd	13.1 (0.4)	13 (2)	Rb	1620 (6)	1620 (17) <sup>b</sup>
Ce	260 (2)	250 (1) <sup>b</sup> , 293 <sup>b</sup>	Re	3.78 (0.12)	—
Co	29.0 (1.0)	27 (3)	Rh <sup>c</sup>	<0.55	—
Cr	294 (2)	300 (40)	Ru <sup>c</sup>	<0.24	—
Cs	6.67 (0.19)	—	Sb	130 (2)	120 (10)
Cu	1390 (20)	1350 (70) <sup>b</sup>	Sc	7.08 (0.42)	—
Dy	19.4 (0.4)	19.8 (0.6) <sup>b</sup> , 22 <sup>b</sup>	Sm	39.8 (0.1)	39 (1.5) <sup>b</sup> , 43 <sup>b</sup>
Er	11.1 (0.2)	11.0 (0.3) <sup>b</sup> , 14 <sup>b</sup>	Sn	5.30 (0.30)	282 (7)
Eu	6.35 (0.15)	6.5 (0.6) <sup>b</sup> , 6.6 <sup>b</sup>	Sr	30900 (100)	28100
Fe	98700 (1200)	100000 (2000)	Ta	0.073 (0.009)	—
Ga	3.74 (0.20)	—	Tb	3.41 (0.01)	3.6 (0.1) <sup>b</sup> , 4.5 <sup>b</sup>
Gd	28.3 (0.4)	238 (1.6) <sup>b</sup> , 39 <sup>b</sup>	Te	3.23 (0.29)	—
Ge	5.54 (0.54)	—	Th	17.2 (0.3)	—
Hf	4.79 (0.12)	—	Ti	695 (41)	280 (60) <sup>b</sup>
Hg	<2.0	—	Tl	7.26 (0.19)	—
Ho	3.81 (0.03)	3.8 (0.1) <sup>b</sup> , 4.9 <sup>b</sup>	Tm	1.54 (0.02)	1.5 (0.1) <sup>b</sup> , 1.6 <sup>b</sup>
I	1510 (80)	—	U	44.8 (0.9)	45
Ir	<0.002	—	W	2.81 (0.05)	—
La	220 (1)	210 (1) <sup>b</sup> , 250 <sup>b</sup>	V	329 (6)	300 (20)
Li	524 (10)	620 (20) <sup>b</sup>	Y	114 (1)	—
Lu	1.47 (0.07)	1.4 (0.1) <sup>b</sup> , 1.6 <sup>b</sup>	Yb	9.60 (0.21)	9.4 (0.2) <sup>b</sup> , 12 <sup>b</sup>
Mn	3980 (30)	3900 (300)	Zn	1030 (30)	1040 (90)
Mo	192 (2)	190 (10)	Zr	75.0 (0.8)	—

<sup>a</sup>Uncertainties expressed as standard deviation ( $n=3$ ). <sup>b</sup>From references 5, 23, 26. <sup>c</sup>Reported as less than uncorrected value because of high degree of mathematical correction.

**Table 2** Analytical results for the CRMs NIST 981, NIST 982, NIST 983

	Found <sup>207</sup> Pb/ <sup>206</sup> Pb ( <i>s</i> )	Reference values <sup>207</sup> Pb/ <sup>206</sup> Pb ( <i>s</i> )
NIST 981	0.91579 (0.00024)	0.91464 (0.00033)
NIST 982	0.46758 (0.00016)	0.46707 (0.00020)
NIST 983	0.07124 (0.00006)	0.07120 (0.00004)

results were corrected for detector dead-time by instrument software, but not for mass discrimination. The precision thus obtained is 10-fold better than that reported by Poitrasson and Dundas<sup>13</sup> for the same isotope standards at the same concentration. This difference is probably caused by reduced signal stability with the USN used by these authors in order to increase sensitivity.

## Conclusions

The use of a tandem spray chamber configuration combined with IR heating and a low-flow nebulizer provides a straightforward, robust and cost-effective approach for enhancement of ICP-SFMS figures of merit. The configuration can be routinely used for both ultra-trace and isotopic determination when sensitivity and signal stability is of great importance.

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