

# Determination of $^{90}\text{Sr}$ at ultratrace levels in urine by ICP-MS

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$^{90}\text{Sr}$  appears as a radionuclide in the decay series of nuclear fission and can therefore be found in nuclear waste or released by nuclear accidents. Current methods for the detection of this radionuclide are time consuming and may be prone to a large variety of interferences. In this work, inductively coupled plasma mass spectrometry is explored for the determination of  $^{90}\text{Sr}$  in the presence of stable zirconium in urine. Specific techniques are investigated to remove this as well as other contributions to the background at  $m/z = 90$ . A quadrupole ICP-MS equipped with a hexapole collision cell is first explored (final LOD =  $2 \text{ ng L}^{-1}$  for water samples), however, the desired limit of detection for  $^{90}\text{Sr}$  in urine is quite low ( $0.02 \text{ pg L}^{-1}$ ). The performance of a double-focusing sector field ICP mass spectrometer (ICP-SFMS) is further investigated, which allows measurement of  $^{90}\text{Sr}$  at the ultratrace level. Other potential interferences were investigated and instrumental detection limits are calculated as  $3 \text{ pg L}^{-1}$  for water samples. Final parameters include the use of a cool plasma and medium mass resolution in ICP-SFMS. The method is applied to the analysis of  $^{90}\text{Sr}$  extracted from urine using a crown ether extraction resin and concentrated (enrichment factor: 200); high levels of natural strontium in the separated fraction (of about  $1 \text{ } \mu\text{g mL}^{-1}$ ) equate to higher detection limits ( $80 \text{ pg L}^{-1}$ ) due to  $^{88}\text{Sr}^+$  at  $m/z = 90$  and the relatively low abundance sensitivity of ICP-SFMS at medium mass resolution of  $6 \times 10^{-7}$ . This detection limit in the separated fraction corresponds to the detection limit of  $0.4 \text{ pg L}^{-1}$  in the original urine sample. The recovery of  $^{90}\text{Sr}$ , determined with the developed analytical method in spiked urine samples, was in the range of 82–86%.

## Introduction

$^{90}\text{Sr}$  is a by-product of the nuclear fission of uranium and plutonium in nuclear reactors and in nuclear weapons. It is a major radionuclide in spent nuclear fuel and radioactive waste and it is considered one of the more hazardous constituents of nuclear wastes. Large amounts of  $^{90}\text{Sr}$  were produced during atmospheric nuclear weapons tests of the 1950s and 1960s and dispersed worldwide. Additionally, the accident at the Chernobyl nuclear power plant introduced a great amount of  $^{90}\text{Sr}$  into the environment and a large part of the  $^{90}\text{Sr}$  was deposited in the Soviet Republics. The rest was dispersed as fallout over Northern Europe and worldwide. As this radionuclide decays, it releases radiation and forms  $^{90}\text{Y}$ , which in turn decays to stable zirconium ( $^{90}\text{Zr}$ ).  $^{90}\text{Sr}$  ( $T_{1/2} = 29.1$  years) emits moderate energy beta particles, and  $^{90}\text{Y}$  ( $T_{1/2} = 64$  h) emits very strong (energetic) beta particles.

Radioactive strontium is of interest because of its impact in both environmental and health areas. Deposition mainly occurs with rain or other precipitation and strontium is very accessible to plants *via* soil uptake mechanisms.<sup>1</sup>  $^{90}\text{Sr}$  is also very significant with regard to health concerns as it is efficiently transferred to humans through the food chain. It is taken up *via* the gastrointestinal tract and behaves chemically much like calcium, and therefore tends to concentrate in the bones and teeth. When people ingest  $^{90}\text{Sr}$ , about 70–80% of it passes through the body and urine therefore presents an attractive medium by which to measure exposure. Virtually all of the remaining 20–30% that is absorbed is deposited in the bone. About 1% is distributed among the blood volume, extracellular fluid, soft tissue and surface of the bone, where it may stay and decay or be excreted.<sup>2</sup> The radiation affects the production of

new blood cells, which eventually leads to death. Furthermore, internal exposure to  $^{90}\text{Sr}$  is linked to bone cancer, cancer of the soft tissue near the bone, and leukemia.<sup>2</sup>

Radiochemical analysis techniques are typically used for the determination of  $^{90}\text{Sr}$  and may yield method detection limits as low as  $0.02 \text{ pg L}^{-1}$  after sample concentration.<sup>3</sup> These methods require the isolation of  $^{90}\text{Sr}$  so as to eliminate interference from other radioactive species. Isolation of  $^{90}\text{Sr}$  from the radioactive isotopes of lead, polonium, plutonium, neptunium and potassium has proved difficult with current extraction techniques.<sup>4</sup> Furthermore, the liquid scintillation techniques that may be used for detection present a challenge in the analysis of  $^{90}\text{Sr}$  in the presence of  $^{90}\text{Y}$ . Spectra of both radionuclides overlap in a certain zone and this may be resolved by mathematical calculations of  $^{90}\text{Y}$  ingrowth or by simply waiting for radiochemical equilibrium to be reached (2–3 weeks). Monitoring the effluent of nuclear power plants is a continuous process and readily available, faster analysis times may prove favorable.<sup>5</sup>

In the event of an atomic accident, an even more rapid, efficient and reproducible method is needed. Some have investigated the inductively coupled plasma-mass spectrometer (ICP-MS) because of its selectivity, sensitivity and accuracy in the detection of different radioactive isotopes.<sup>6–8</sup> The newly developed ICP-MS methods have been found to possess higher sensitivity and greater efficiency and may replace many of the radiometric techniques.<sup>9</sup> Furthermore, they are not encumbered with the uncertainty of removing all other beta-emitting nuclides from the sample. ICP-MS is therefore investigated for detection of radioactive strontium and potential interferences in this type of analysis are addressed. Sensitivity and selectivity issues of the newly developed method are also discussed.

## Experimental

### Instrumentation

A double-focusing sector field ICP-MS instrument (ELEMENT, ThermoFinnigan, Bremen, Germany) was used in this study. A grounded platinum electrode GuardElectrode<sup>®</sup> (GE) from Finnigan-MAT, was inserted between the quartz ICP torch and rf load coil. Solution introduction into the ICP was performed by a Micromist nebulizer (Glass Expansion, Romainmotier, Switzerland) with a Scott double-pass quartz spray chamber cooled to 4 °C.

The second instrument employed was a quadrupole-based ICP-MS with a hexapole collision cell (Platform, Micromass Ltd., Manchester, UK). Oxygen was introduced into the collision cell of the ICP-CC-MS as a collision and reaction gas. For solution introduction into the instrument, a Meinhard nebulizer (J.E. Meinhard Associates, Inc, Santa Ana, CA, USA) with a Scott double-pass quartz spray chamber cooled to 4 °C was used. Aqueous solutions were introduced in the continuous flow mode *via* a peristaltic pump (Perimax 12, Spetec GmbH, Erding, Germany). Specific instrument operating conditions for both instruments are shown in Table 1.

### Nebulization

All experiments were performed solely with the Meinhard nebulizer with the ICP-CC-MS and the Micromist nebulizer with the ICP-SFMS. Others have noted an order of magnitude improvement with the use of an ultrasonic nebulizer (USN)<sup>10–12</sup> as only the dry aerosol is introduced into the plasma. However, its typical uptake rate is 1 mL min<sup>-1</sup> and the dose to the operator as well as contamination of the instrument were considered critical issues in the analysis of this radionuclide.<sup>13</sup>

### Reagents and standards

All water was deionized (18 MΩ cm) and was obtained from a Millipore Milli-Q-Plus water purifier. Commercial chemicals

were analytical reagent grade and were used without further purification. Solutions were acidified with sub-boiled nitric acid. Specific reagents used in the sample preparation procedure are discussed in the section below.

### Sample preparation

Extraction chromatography is a particular form of liquid–liquid column chromatography in which the stationary phase is constituted by an organic extractant held on a supporting surface and the mobile phase is an inorganic solution, usually an acid. For example, Gjerci<sup>14</sup> and Alvarez<sup>3,15</sup> both utilized specific crown ether stationary phases that selectively enacted the retention of Sr. The resin consists of an octanol solution of 4,4'(5')-bis(*t*-butylcyclohexano)-18-crown-6 sorbed on an inert polymeric support and is commercially available under the trade name Sr.Spec. The extraction chromatography resin used in this work was obtained as pre-packaged 2 mL columns from Eichrom Industries (Darien, Illinois, USA). Note, the uptake of Sr by this resin increases with increasing nitric acid concentration. At 8 M nitric acid, *k'* is approximately 90 and it falls to less than 1 at concentrations of nitric acid less than 0.5 M.

After acidification with 60 mL of concentrated HNO<sub>3</sub>, urine samples were heated at 70–80° and stirred constantly with a magnetic stir plate. A volume of 1 mL of concentrated H<sub>3</sub>PO<sub>4</sub> and a volume of 2 mL of a 40 mg L<sup>-1</sup> Ca(NO<sub>3</sub>)<sub>2</sub> (as calcium) were added and the sample was heated at this constant temperature for ½ hour. Concentrated ammonia was added until the calcium phosphate appeared (which would be carrying the strontium). The sample was then heated for one hour and the resulting solution was centrifuged. The supernatant was decanted and the residue was dissolved in 10 mL of 8 M HNO<sub>3</sub>. This 10 mL volume then was passed through the Sr column. Prior to this, columns were washed with 25 ml of 0.05 M HNO<sub>3</sub> to elute residual Sr from the resin. A vacuum manifold was used to facilitate the passage of the sample through the resin. The strontium remained on the resin of the column and was then eluted with a 5 mL volume of 0.05 M HNO<sub>3</sub>.

Table 1 Experimental conditions

ICP-CC-MS parameters	
Forward power	750 W
Coolant gas flow rate	13.5 L min <sup>-1</sup>
Auxiliary gas flow rate	1.0 L min <sup>-1</sup>
Nebulizer gas flow rate	0.8 L min <sup>-1</sup>
Solution uptake rate	0.9 mL min <sup>-1</sup>
Sampling and skimmer cones	Nickel
Dwell time	0.2 s per isotope
Extraction lens (cone) potential	-600 V
Transfer lens (hexapole exit) potential	-400 V
Hexapole bias potential	-0.8 V
Quadrupole bias (ion energy) potential	-2.0 V
Nebulizer	Meinhard
Spray chamber	Scott double-pass
Cell gas	O <sub>2</sub>
Flow rate of cell gas	1.9 mL min <sup>-1</sup>
ICP-SFMS parameters	
Forward power	750 W (with guard electrode)
Coolant gas flow rate	14 L min <sup>-1</sup>
Auxiliary gas flow rate	0.8 L min <sup>-1</sup>
Nebulizer gas flow rate	1.04 L min <sup>-1</sup>
Solution uptake rate	0.3 mL min <sup>-1</sup>
Sampling and skimmer cones	Nickel
Dwell time	0.2 s per isotope
Extraction lens potential	-2000 V
Focus lens potential	-1000 V
Nebulizer	Micromist
Spray chamber	Cinnabar low volume cyclonic
Mass resolution	4450

## Results and discussion

### Isobaric interferences of atomic ions

The use of sector field ICP-MS or ICP-MS with a collision cell eliminates many of the interferences encountered with radiochemical detection and both have been found to be selective and sensitive means by which to measure various elements. However, difficulties may arise with isobaric interferences of atomic ions or molecular ions that result from the matrix of the sample or the plasma itself. The most critical issue is the appearance of radioactive and stable nuclides at the same mass with a different atomic number. All interferences must be considered and eliminated to obtain accurate and sensitive analysis of radioactive strontium at *m/z* = 90.

<sup>90</sup>Y is the first decay product of <sup>90</sup>Sr decay. Although yttrium may be removed by the use of strontium-specific resins, once the procedure is completed <sup>90</sup>Y will be produced by the decay of <sup>90</sup>Sr. This is of concern when using radiochemical detection techniques<sup>16</sup> as they are very sensitive. Therefore, when using these types of detection, the samples are not analyzed until an equilibrium is reached (2–3 weeks). Alternatively, mathematical correction formulae may be employed. As described later in this paper, detection limits of <sup>90</sup>Sr are quite low. Therefore, because the <sup>90</sup>Y/<sup>90</sup>Sr concentration ratio will be 0.025% in the activity equilibrium, ICP-MS will not be sensitive enough to detect the yttrium ingrowth that would be expected from typical levels of <sup>90</sup>Sr.

<sup>90</sup>Zr<sup>+</sup> represents a second isobaric interference and its removal may be accomplished by several means. Again, it may

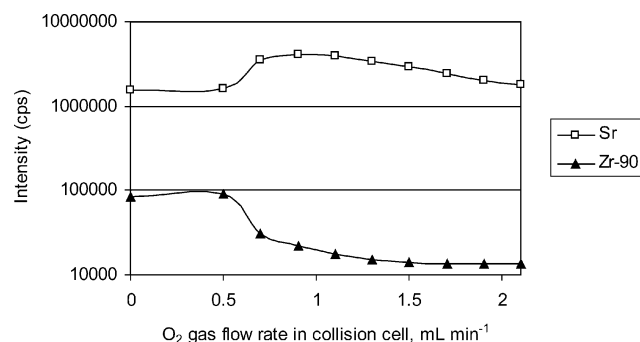
be possible for the separation to be specifically conducted prior to analysis.<sup>17</sup> However, the current techniques utilized for strontium isolation prior to measurement, such as precipitation, ion exchange or solvent extraction,<sup>18,19</sup> are not considered selective or safe and, additionally, may require large amounts of resins/acids and solvents as well as time. A new advance in the isolation of radioactive strontium has been the use of extraction chromatography. Although this preparation technique may serve to eliminate some of the zirconium, others have noted that similar resins may not completely remove all interferents of interest.<sup>20</sup>

Instrumental techniques used for interference elimination may include the utilization of a sector field ICP mass spectrometer at its maximum mass resolution ( $m/\Delta m$ ) of 12 000, the application of a collision cell or a cool plasma in ICP-MS.<sup>21</sup> A sector field ICP-MS can be used to accomplish mass measurements at required mass resolution and subsequently, it may be possible to separate interferences from the isotopes of interest.<sup>22</sup> However, it is generally not possible to separate isobaric singly charged atomic ions, such as  $^{90}\text{Sr}^+$  from  $^{90}\text{Zr}^+$ , due to the low mass difference (mass of  $^{90}\text{Sr} = 89.9077$  u and  $^{90}\text{Zr} = 89.9047$  u) using commercial ICP mass spectrometers, because a mass resolution of approximately 30 000 would be necessary for their separation.

A possible way to solve the interference problem is the application of ICP-MS with a collision cell as unwanted ions produced in the plasma can be selectively removed or shifted in  $m/z$  ratio prior to mass spectral analysis by the addition of specific reagent gases.<sup>23</sup> In studies of ion/molecule reactions performed by Eiden *et al.*, it was shown that Y and Zr react with  $\text{O}_2$  over two orders of magnitude faster than Sr.<sup>24</sup> Further research showed that  $\text{Sr}^+$  was not reactive with the chosen reaction gas,  $\text{O}_2$ , and a stronger oxidant, nitrous oxide, was needed to form strontium oxide with the purpose of separating it from same mass Rb.<sup>25</sup>

Initial experiments in this laboratory using a collision cell pressurized with  $\text{O}_2$  were successful. Strontium was monitored at  $m/z$  88 and zirconium at  $m/z$  90. A flow rate of  $1.9 \text{ mL min}^{-1}$   $\text{O}_2$  was sufficient to promote the oxide ion formation of zirconium, as can be seen in Fig. 1. With increasing  $\text{O}_2$  gas flow rate, the  $^{90}\text{Zr}^+$  intensity decreases. The zirconium isotope at  $m/z$  90 is oxidized and therefore will be observed as  $^{90}\text{ZrO}^+$  at  $m/z$  106. Additionally, scattering losses were offset by initial collisional focusing, hence the strontium signal was unaffected overall. The calculated limit of detection for strontium was  $2 \text{ ng L}^{-1}$  with ICP-CC-MS, primarily due to the relatively high background count rate of the Daly-type detector in the ICP-CC-MS system.<sup>26</sup> Detection limits are defined as the equivalent concentration of three times the standard deviation of the blank response. The standard deviation was calculated from six consecutive measurements of the blank solution at  $m/z = 90$ .

Unfortunately, this instrumental configuration did not meet the desired limit of detection, which is  $0.1 \text{ Bq L}^{-1}$ . This unit of



**Fig. 1** Response of  $^{88}\text{Sr}^+$  and  $^{90}\text{Zr}^+$  with increasing flow rate of  $\text{O}_2$  in the collision cell. Both elements are at a concentration of  $50 \mu\text{g L}^{-1}$ .

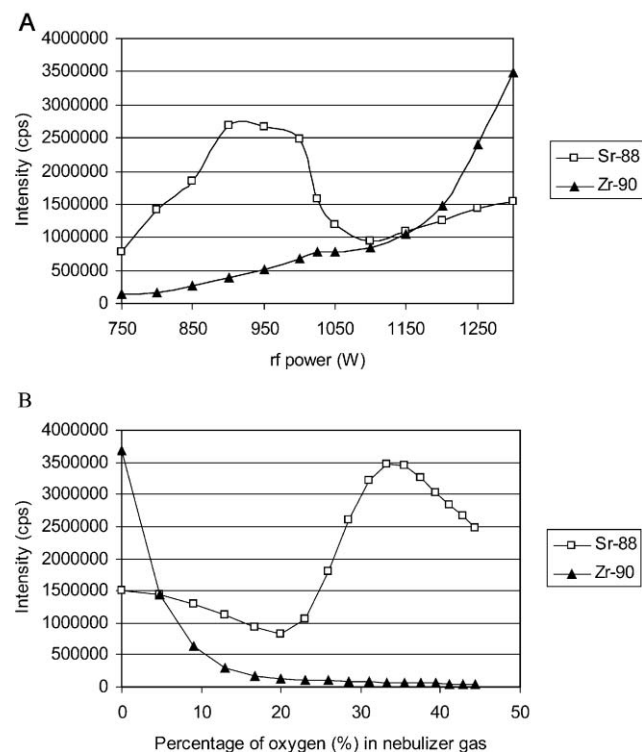
activity is directly proportional to the half-life when converting it to a unit of concentration:

$$N = (A/\ln 2) \times T_{1/2}$$

Therefore, if  $N$  represents the number of atoms, an activity,  $A$ , of  $0.1 \text{ Bq L}^{-1}$  translates to  $0.02 \text{ pg L}^{-1}$ . Current sample preparation procedures for radioactive strontium (extraction chromatography, discussed earlier) possess an effective concentration factor of 200 (yielding a desired limit of detection for the method of  $4 \text{ pg L}^{-1}$ ).

Another alternative to the collision cell in the removal of interferences is the use of a cool plasma: this is a plasma which works at lower forward powers in an effort to suppress ionization of elements of higher ionization potential. The ionization potentials of strontium and zirconium are 5.7 eV and 6.8 eV, respectively, therefore  $\text{Zr}^+$  could theoretically be suppressed under cool plasma conditions. Forward power was varied and plotted against ion intensity of the elements of interest; other instrument parameters were held constant. In a second experiment, oxygen was added to the plasma at varying percentages of the flow rate of the argon nebulizer gas. Others have noted that when argon and oxygen are used for the nebulizer gas, cool plasma conditions are achieved.<sup>27</sup> Results of both experiments on the quadrupole instrument can be seen in Fig. 2. It is unclear whether the similar results in the second graph are due to the application of this cool argon–oxygen plasma or whether this is due to some oxide formation, as seen by others,<sup>28</sup> and it may be a combination of both phenomena. However, this speculation could not be verified due to the high background at  $m/z = 106$ . Becker and Dietze noted a general increase in the oxide formation rate of other radionuclides with the use of a shielded torch under hot plasma conditions<sup>10</sup> and others have noted that the strong bonds of oxides usually withstand plasma conditions.<sup>21</sup> The calculated detection limits ( $3\sigma$ ; blank Milli-Q water) can be found in Table 2 and again these were not found to be adequate for the analysis of  $^{90}\text{Sr}$  in urine.

Sector field mass spectrometers utilizing an ICP ionization source are used widely in the area of elemental and isotopic

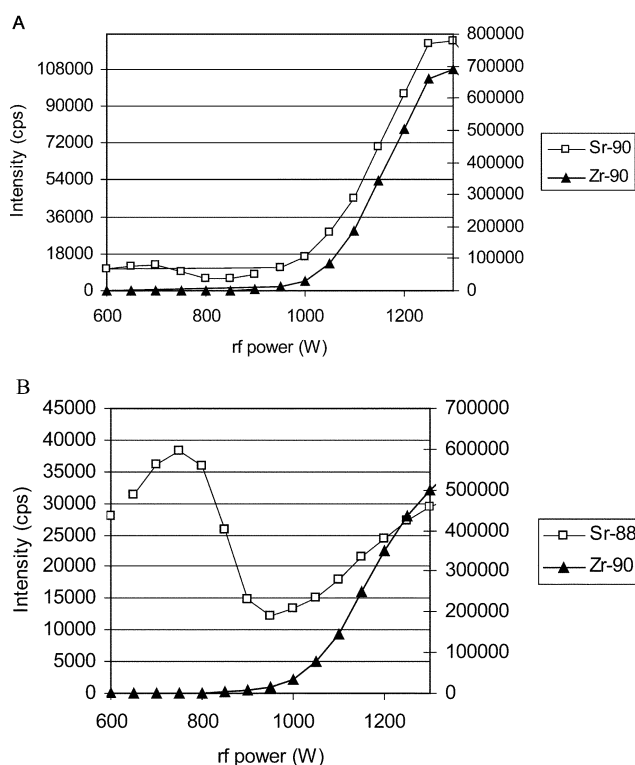


**Fig. 2** Effect of rf power (A) and percentage of  $\text{O}_2$  in nebulizer gas (B) on the response of  $^{88}\text{Sr}^+$  and  $^{90}\text{Zr}^+$  with the ICP-CC-MS. Strontium concentration is  $50 \mu\text{g L}^{-1}$  and zirconium is  $1000 \mu\text{g L}^{-1}$ .

**Table 2** Limits of detection for ICP-CC-MS in water samples

Collision cell	rf power/W	Percentage of O <sub>2</sub> in nebulizer gas/%	Limit of detection/ng L <sup>-1</sup>
1.9 ml min <sup>-1</sup> O <sub>2</sub>	1350		3
	900		2
	750		5
0.9 ml min <sup>-1</sup> O <sub>2</sub>	900		3
	1350	40	2

analysis, and especially in the determination of long-lived radionuclides,<sup>29</sup> because of two distinct advantages with regard to resolution and sensitivity.<sup>30,31</sup> Fig. 3 shows the results obtained using a cool plasma and the ICP-SFMS with the shield torch. The concentration of Sr was 100 ppt and of Zr was 5 ppb; the concentration of natural zirconium in urine may be approximately 25 ppt and this translates to as much as 5 ppb in the final extract (assuming a 200-fold enrichment factor resulting from the sample preparation process). The first graph of Fig. 3 shows the results of varying the rf power after tuning the instrument at 1350 W. In the second graph of the figure, the nebulizer gas flow rate and the ion focus lens were adjusted to maximize the <sup>88</sup>Sr<sup>+</sup> intensity while minimizing that of <sup>90</sup>Zr<sup>+</sup> at a forward power of 750 W.<sup>32</sup> This equated to a nebulizer gas flow rate of 1.04 L min<sup>-1</sup> (versus 0.88 L min<sup>-1</sup>



**Fig. 3** Effect of rf power on the response of <sup>88</sup>Sr<sup>+</sup> and <sup>90</sup>Zr<sup>+</sup> with the ICP-SFMS. A = Nebulizer gas flow rate of 0.88 L min<sup>-1</sup> and ion focus lens voltage of -855 V. B = Nebulizer gas flow rate of 1.04 L min<sup>-1</sup> and ion focus lens voltage of -1000 V.

**Table 3** Limits of detection for ICP-SFMS in water samples

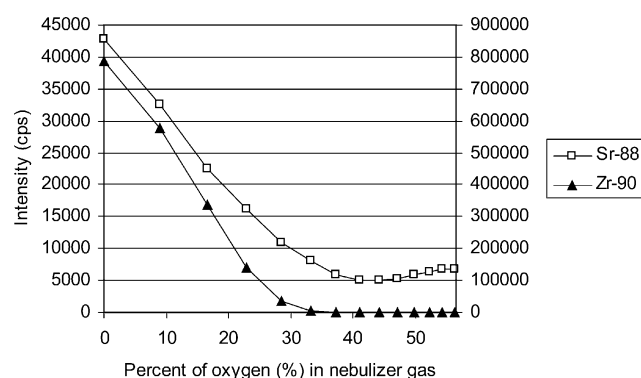
rf power	Resolution	O <sub>2</sub> in nebulizer gas/%	Limit of detection/ng L <sup>-1</sup>
750 (lens and nebulizer gas tuned at 1350 W)	Low		0.017
750 (lens and nebulizer gas tuned for cold plasma)	Low		0.004
750 (lens and nebulizer gas tuned at 1350 W)	Medium		0.005
750 (lens and nebulizer gas tuned for cold plasma)	Medium		0.003
1350 W (50% O <sub>2</sub> in nebulizer gas)	Low	50	0.013

under hot plasma conditions) and ion focus lens voltage of -1000 V (versus -855 V under hot plasma conditions). Both graphs show a lower effect for Sr<sup>+</sup> compared with the collision cell instrument. This may be due to the additional focusing that occurs with the hexapole of the quadrupole instrument as the cell is still pressurized with gases from the plasma even when not purposely in use. Also, the interaction time of the ions with oxygen will be significantly longer in ICP-CC-MS without collision gases due to the lower kinetic energy of the ions and relatively long ion trajectories in the hexapole, compared with other instruments. Calculated detection limits are given in Table 3.

Oxygen was also added to the nebulizer gas of the sector field instrument to effect the formation of a cool plasma as described above. Intensity of <sup>88</sup>Sr<sup>+</sup> and <sup>90</sup>Zr<sup>+</sup> as a function of the percentage of oxygen in the nebulizer gas is shown in Fig. 4. The voltage of the focus lens was optimized with the addition of 50% oxygen in the nebulizer gas and the calculated detection limit for strontium was 13 pg L<sup>-1</sup>. Further experiments were conducted solely with an rf power of 750 W as this setting demonstrated acceptable limits of detection in addition to the fact that a cool plasma generated from lowering the rf power only requires slight modification of existing instrumentation without any additional high-purity gases.

### Polyatomic interferences

There exists the potential for ion formation of argon-carbon based interferences such as <sup>38</sup>Ar<sup>40</sup>Ar<sup>12</sup>C<sup>+</sup>. Generally, cool plasma conditions inhibit the formation of argon-based polyatomic ions.<sup>33</sup> In work published by Vanhaecke *et al.*, an rf power of 750 W was applied and this was sufficient to reduce the formation of the <sup>40</sup>Ar<sup>12</sup>C<sup>+</sup> diatomic ion that interfered with the determination of the major chromium isotope at *m/z* = 52.<sup>34</sup> The formation of <sup>38</sup>Ar<sup>40</sup>Ar<sup>12</sup>C<sup>+</sup> was investigated through the introduction of a solution of 0.01% trichloroacetic acid under the optimized conditions and with a cool plasma. An increase in background at *m/z* = 90 was not observed in this experiment. Other potentially less prevalent argon-based diatomic ions, such as <sup>38</sup>Ar<sup>52</sup>Cr<sup>+</sup>, <sup>36</sup>Ar<sup>54</sup>Fe<sup>+</sup>, <sup>40</sup>Ar<sup>50</sup>Ti<sup>+</sup> and <sup>40</sup>Ar<sup>50</sup>Cr<sup>+</sup>, were also investigated by analysis of solutions containing the respective elements; again, no increase in the background at *m/z* = 90 was observed under established conditions.



**Fig. 4** Effect of percentage of O<sub>2</sub> in nebulizer gas on the response of <sup>88</sup>Sr<sup>+</sup> and <sup>90</sup>Zr<sup>+</sup> with the ICP-SFMS.

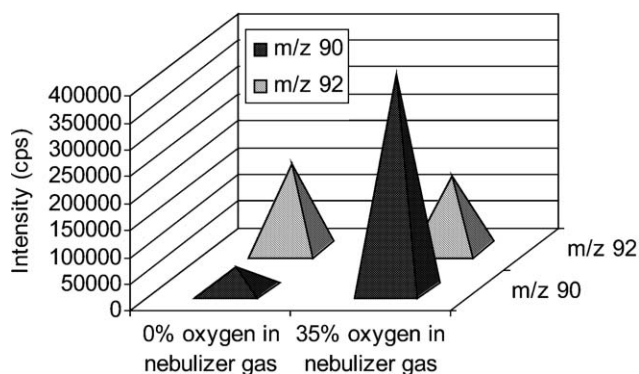


Fig. 5 Effect of oxygen in the nebulizer gas on the background at  $m/z = 90$  with the ICP-CC-MS instrument.

A second potential contribution to the background at  $m/z = 90$  is the formation of nickel-based interferences, such as  $^{58}\text{Ni}^{16}\text{O}_2^+$  or  $^{60}\text{Ni}^{16}\text{O}^{14}\text{N}^+$ , due to the use of nickel extraction cones. This was more prevalent when  $\text{O}_2$  was added in sequential percentages to the nebulizer gas of the ICP-CC-MS instrument, as can be seen in Fig. 5. With the addition of oxygen, the interferent at  $m/z = 90$  increases by approximately one order of magnitude. Interestingly, there is no change in the abundance of the interferent at  $m/z = 92$ , as would be expected due to  $^{60}\text{Ni}^{16}\text{O}_2^+$ , and this may be due to the elimination of the carbon-based interference under the cooler plasma generated with the addition of oxygen. With the sector field instrument, a medium resolution setting ( $m/\Delta m = 4450$ ) was adequate to separate these nickel-based polyatomics and therefore eliminate all background at  $m/z = 90$ . The limit of detection obtained with this resolution setting is given in Table 3 and is comparable to the reported detection limit found by other workers of 7 ppq for  $^{88}\text{Sr}$  with a USN coupled to an ICP-SFMS with hot plasma and no shield torch.<sup>11</sup>

A third possible contribution to the background at  $m/z = 90$  is the hydride ion formation of stable  $^{89}\text{Y}$ , although if extraction chromatography is used for sample preparation, yttrium removal is expected. A solution containing only yttrium at a concentration of 200 ppb was prepared and analyzed in conjunction with a nitric acid blank. The background at  $m/z = 90$  was examined for hydride formation and no such phenomenon was observed.

#### Abundance sensitivity

In all magnetic sector mass spectrometers, there is a small contribution to peak intensity from adjacent peaks.<sup>35</sup> This abundance sensitivity of sector field instruments is less than that of quadrupole instruments.<sup>36</sup> The average concentration of stable strontium in urine was experimentally determined to be approximately  $5 \mu\text{g L}^{-1}$ ; abundance sensitivity was studied at medium mass resolution ( $m/\Delta m = 4450$ ) using a standard solution with concentration of  $1 \mu\text{g mL}^{-1}$  of strontium. In order to correct for possible interferences, intensity was measured at the masses  $m \pm 0.5 \text{ u}$ ,  $m \pm 1.5 \text{ u}$ ,  $m \pm 2.5 \text{ u}$ , etc. Abundance sensitivity was calculated as the intensity at  $m/z = 90$ /intensity at  $m/z = 88$ <sup>26</sup> and in medium mass

resolution mode was found to be  $6 \times 10^{-7}$  ( $2 \times 10^{-5}$  in low mass resolution mode). Additionally, peak-tailing can be reduced further by applying a higher mass resolution and abundance sensitivity was measured at  $4 \times 10^{-7}$  at  $m/\Delta m = 12000$ , but this was accompanied by a decrease in the intensity of the analyte ions.

#### $^{90}\text{Sr}$ determination in real urine samples

In this work, urine samples were prepared as outlined in the Experimental section. As stated previously, the sample preparation procedure represented an effective sample concentration factor of 200. Additionally, as described earlier, natural levels of strontium in urine were experimentally determined to be in the range of 5 ppb. Taking into account these two facts results in a final extract with a concentration of approximately 1 ppm of natural strontium. Medium mass resolution would therefore not be capable of removing all counts at  $m/z = 90$  due to the peak tail of  $^{88}\text{Sr}^+$  and this was shown experimentally. The background at  $m/z = 90$  was increased by approximately two orders of magnitude. Correction was performed; however, this served to decrease the precision of the measurements and therefore detection limits would be expected to increase.

The method detection limit was calculated as three times the standard deviation of the intensity signal on  $m/z = 90$ , measured on six independently prepared procedural blanks. The increase as compared with the instrumental detection limit amounted to 20-fold, as can be seen in Table 4. The resulting method detection limit for concentrated urine solution was  $80 \text{ pg L}^{-1}$ , which corresponds to the  $0.4 \text{ pg L}^{-1}$  in the original urine sample. For all investigated urine samples, the concentration of  $^{90}\text{Sr}$  was below the method detection limit of  $0.4 \text{ pg L}^{-1}$ .

A final point worthy of note concerns the inherently high levels of natural strontium contained within the extractions resins. Although this would not be problematic with the use of radiochemical analysis schemes, with ICP-MS these high levels serve to increase the background at  $m/z = 90$  and hence the limit of detection. Three washes of the extraction resin with 0.05 M  $\text{HNO}_3$  was found to be sufficient to remove all natural Sr from extraction resin, as shown in Fig. 6.

In a final evaluation of the sample preparation procedure,

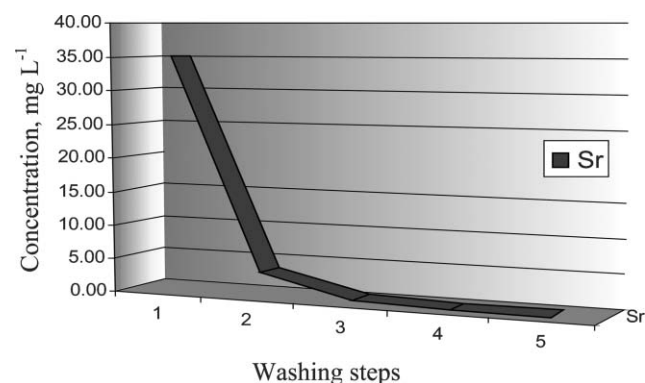


Fig. 6 Washing of Sr from Sr-resin prior to use in separation procedure.

Table 4 Figures of merit in calculation of limit of detection of  $^{90}\text{Sr}$  in urine

Natural Sr concentration in analyte solution after enrichment	Prepared urine sample (concentration factor of 200)
Ion intensity of $^{88}\text{Sr}^+$	$\sim 1 \text{ mg L}^{-1}$
Abundance sensitivity (medium resolution)	$3.8 \times 10^7 \text{ cps}$
Average background counts at $m/z = 90$	$6.0 \times 10^{-7}$
Average corrected background counts at $m/z = 90$	29
Limit of detection (concentration)	5.2 (average sd = 1.1)
Limit of detection (activity)	$80 \text{ pg L}^{-1}$ ( $0.4 \text{ pg L}^{-1}$ in original urine samples)
	$400 \text{ Bq L}^{-1}$ ( $2 \text{ Bq L}^{-1}$ in original urine samples)

the capacity of the extraction resin with respect to the high concentration of  $^{88}\text{Sr}$  in urine was assessed. Additional analyses of urine samples spiked with  $1\text{ ng L}^{-1}$  and  $5\text{ ng L}^{-1}$  of  $^{90}\text{Sr}$  were conducted. The recovery of  $^{90}\text{Sr}$ , determined with the developed analytical method, was in the range of 82–86%.

## Conclusion

Although a collision cell pressurized with oxygen was able to remove ions that would interfere in the measurement of  $^{90}\text{Sr}$ , issues specific to the analysis of radionuclides, such as the low limit of detection in  $\text{Bq L}^{-1}$  as well as natural strontium concentrations in pertinent samples, were not considered in work done by others.<sup>24,25</sup> The need for an instrument of high sensitivity was shown and a sector field inductively coupled plasma mass spectrometer was applied to the analysis of radioactive strontium in urine. The isobaric interference of zirconium was removed by a cool plasma operated at 750 W. Argon-based polyatomic ions did not interfere at  $m/z = 90$  as their formation was prohibited in the low power plasma. A medium mass resolution setting proved adequate in the separation of nickel-based interferences, such as  $^{58}\text{Ni}^{16}\text{O}_2^+$ , resulting from use of nickel sampler and skimmer cones. Additionally, the formation of  $\text{YH}^+$  did not occur under ultimate operating conditions and a final instrument detection limit of  $3\text{ pg L}^{-1}$  was reported for water samples. However, the abundance sensitivity of the ICP-SFMS in medium mass resolution ( $6.0 \times 10^{-7}$ ) was not adequate with regard to the natural levels of strontium in urine. The limit of detection after sample concentration of this matrix was increased about 20-fold. Future work should extend to the application of a mass spectrometer with better abundance sensitivity. Although thermal ionization mass spectrometry has shown an abundance sensitivity of  $1.2 \times 10^{-10}$  in the measurement of  $^{236}\text{U}$ ,<sup>37</sup> and others have shown equally good abundance sensitivity with resonance ionization mass spectrometry for the measurement of  $^{90}\text{Sr}$ ,<sup>38</sup> ICP-MS has been shown to be more suitable for routine measurement with regard to sample preparation and quantification procedures.<sup>39</sup> Furthermore, reported figures of merit for both abundance sensitivity (better than  $10^{-8}$  for  $^{90}\text{Sr}$ ) as well as sensitivity with a multicollector ICP-MS<sup>40</sup> should allow the detection of  $^{90}\text{Sr}$  at low  $\text{fg L}^{-1}$  levels (in original sample) in samples high in natural strontium.

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