

Determination of $^{129}\text{I}/^{127}\text{I}$ isotope ratios in liquid solutions and environmental soil samples by ICP-MS with hexapole collision cell

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The determination of ^{129}I in environmental samples at ultratrace levels is very difficult by ICP-MS due to a high noise caused by Xe impurities in argon plasma gas (interference of $^{129}\text{Xe}^+$), possible $^{127}\text{IH}_2^+$ interference and an insufficient abundance ratio sensitivity of the ICP mass spectrometer for $^{129}\text{I}/^{127}\text{I}$ isotope ratio measurement. A sensitive, powerful and fast analytical technique for iodine isotope ratio measurements in aqueous solutions and contaminated soil samples directly without sample preparation using ICP-MS with a hexapole collision cell (ICP-CC-QMS) was developed. Oxygen is used as reaction and carrier gas for iodine thermal desorption *via* the gas phase from solid environmental material in the sample introduction device coupled on-line to ICP-CC-QMS. A mixture of oxygen and helium as reaction gases in the hexapole collision cell was applied for reducing disturbing background intensity of $^{129}\text{Xe}^+$. After optimization of measurement procedures the detection limit for $^{129}\text{I}^+$ in aqueous solution was $8 \times 10^{-13} \text{ g ml}^{-1}$, which is better by about two orders of magnitude in comparison to the detection limit for $^{129}\text{I}^+$ in sector field ICP-MS. The detection limit for direct $^{129}\text{I}^+$ determination in contaminated environmental (soil) samples *via* gas-phase desorption without any additional sample preparation was $3 \times 10^{-11} \text{ g g}^{-1}$ (30 ppt). Furthermore, the results of the determination of $^{129}\text{I}/^{127}\text{I}$ isotope ratios at the 10^{-5} – 10^{-6} level in synthetic laboratory standards and environmental soil samples from contaminated areas are given.

1. Introduction

Iodine is an essential trace element in the organic cycle and particularly in the human diet. Being an integral part of the thyroid hormones iodine plays an important role in controlling the rate of basic metabolism and in reproduction.¹ Thus, humans need a daily uptake of about 180–200 μg of iodine, otherwise a disease due to iodine deficiency can occur. Besides one stable iodine isotope ^{127}I artificial radionuclides of iodine ^{129}I ($T_{1/2} = 1.57 \times 10^7$ years) and ^{131}I ($T_{1/2} = 8.02$ days) are present in the environment mainly as a result of human activities. Both radionuclides of iodine have been released continuously into the environment as a result of nuclear weapon tests, nuclear accidents and by emission from nuclear fuel reprocessing plants.² Iodine and its compounds are volatile and highly mobile in the environment. Therefore, radioactive iodine is ubiquitous and bioavailable for living organisms. The radioisotopes of iodine can enter the human organism *via* food and drinking water or *via* inhalation and then undergo intense biological accumulation in the thyroid, creating an irradiation risk. Thus, irradiation with short-lived iodine isotopes, has probably been responsible for the increase in children's thyroid cancer observed in areas around Chernobyl since the accident in 1986.^{3,4}

Long-lived radioactive isotope ^{129}I is produced also in nature by spontaneous fission of uranium and by cosmic-ray induced spallation of xenon in the atmosphere.⁵ The natural ^{129}I inventory in the atmosphere, hydrosphere and biosphere is estimated to be about 263 kg.⁶ The artificial source of ^{129}I is neutron-induced fission of uranium and plutonium in a fission yield of 0.72% to 1.4% (accumulated). The main form of released iodine from reprocessing plants to the atmosphere is as alkyl iodides.^{7–9} In addition, volatile organoiodine compounds, *e.g.* methyl iodide, are also biogenetically produced in the marine environment.^{10–12} In general, one can expect considerable secondary contamination with ^{129}I in coastal regions

taking into account its relatively high abundance in seawater. Thus, according to Aumann and Guner¹³ the ^{129}I concentration is several times higher in the coastal areas of Northern Germany compared to areas of Southern Germany. However, the release of ^{129}I from reprocessing plants and the behavior of ^{129}I in the environment has not been explored in detail due to analytical difficulties.

The determination of ^{129}I especially in environmental materials such as waters, geological and biological samples, nuclear materials and radioactive waste is of increasing importance.

Neutron activation analysis with radiochemical separation (RNAA) and accelerator mass spectrometry (AMS)^{14,15} have been well established for ^{129}I determination. Thus, abundance sensitivity (and following minimal detectable isotopic ratio for $^{129}\text{I}/^{127}\text{I}$) of about 10^{-10} can be achieved in RNAA.¹⁵ High abundance ratio sensitivity for $^{129}\text{I}/^{127}\text{I}$ ratio down to 10^{-12} is feasible by AMS,¹⁵ but both these methods involve complicated instrumentation and the analysis is expensive. An advanced review on different analytical techniques for ^{129}I determination was published by Schmidt *et al.*¹⁶ Inductively coupled plasma mass spectrometry (ICP-MS) as an extremely sensitive analytical method for the determination of element concentrations and isotope ratios in the trace and ultratrace range has been established in the last few years for the determination of long-lived radionuclides. ICP-MS provides high sensitivity, good accuracy of isotopic measurements and relatively simple sample preparation procedure and, therefore, is well suited for routine iodine isotopic ratio determination in environmental samples.^{17–19} ICP-MS is often applied for sensitive element determination in biological, medical and environmental samples at trace and ultratrace levels. Quadrupole mass analysers are employed as standard tools in ICP-MS because of their good sensitivity, wide dynamic range, robustness and relatively low cost. Nevertheless, quadrupole-based ICP-MS possesses some well known limitations, in

particular when determination of trace elements or isotope ratios is required in the presence of elements or isotopes with much higher concentrations which represent potential sources of interference.

The determination of ^{129}I is very difficult, because low ^{129}I quantities are present with high ^{127}I concentrations in addition to the possible occurrence of $^{127}\text{IH}_2^+$. However, the precise and accurate determination of $^{129}\text{I}/^{127}\text{I}$ by ICP-MS is restricted by xenon impurities in the argon plasma gas^{19,21} and sometimes also in samples²² due to isobaric interference of $^{129}\text{Xe}^+$ on the analyte. When the cell is pressurized with O_2 for suppression of $^{129}\text{Xe}^+$, the formation of $^{127}\text{IH}_2^+$ by reaction with gas impurities limits the detection of ^{129}I .²⁰ Furthermore, there is the influence of the peak tail of ^{127}I on mass 129 u which results in too high ion intensity. Thus selective removal of Xe^+ in mass spectra is mainly required for ultratrace detection of ^{129}I .

A principal possibility for improving $^{129}\text{I}/^{127}\text{I}$ determination including an improvement of abundance sensitivity is application of a pressurized ion-guide before the quadrupole mass analyzer in ICP-MS. According to a preliminary study²³ the ion kinetic energy can be reduced down to about 1 eV by collision with helium atoms resulting in improved filtering of non-stable ions and better abundance sensitivity in ICP-QMS with collision cell. However, increasing the QMS resolution had a significantly lower influence on abundance sensitivity than reducing the ion energy by collision with helium atoms. For the measurement of abundance sensitivity it is very important to reduce the background as much possible. Thus, when introducing helium into the collision cell a reduction of peak tail of a high-abundant isotope by up to three orders of magnitude depending on the mass analyzed was observed. In addition, gas-phase ion-molecule chemistry in pressurized rf-multipoles has found wide application in mass spectrometry for selective removal of interfering isotopes, first of all Ar^+ and molecular ions of argon.^{24–26} Oxygen was applied as a collision gas for selective reduction of xenon ions in ICP-MS, whereby reaction of $^{129}\text{Xe}^+$ with O_2 was studied in ref. 27. It was observed that $^{129}\text{Xe}^+$ reacts at least 10^4 times faster with O_2 than does $^{129}\text{I}^+$. The main channel for reaction of $^{129}\text{Xe}^+$ with O_2 is charge exchange. Removing the isobaric interference of $^{129}\text{I}^+$ by $^{129}\text{Xe}^+$ by high resolution mass spectrometry requires a mass resolution of at least 600 000.²⁷

The aim of the present work was the development of a rapid and highly-sensitive analytical method based on inductively coupled plasma mass spectrometry with collision cell for determination of low $^{129}\text{I}/^{127}\text{I}$ isotope ratios in synthetic and environmental samples. Special attention was paid to reducing the interference of $^{129}\text{Xe}^+$ ion on $^{129}\text{I}^+$ in ICP-MS and to the development of an effective and sensitive direct sample introduction of iodine *via* gas-phase from soil samples.

So when determining long-lived ^{129}I , the collision cell can be useful both for improving abundance sensitivity (as the high-abundance isotope ^{127}I is usually present) and for

reducing interference from $^{129}\text{Xe}^+$ using gas-phase reactions (for instance using oxygen as the collision gas).

2. Experimental

2.1. Instrumentation of ICP-MS

A quadrupole-based inductively coupled plasma mass spectrometer (Platform ICP, Micromass Ltd., Manchester, UK) consisting of an inductively coupled plasma (ICP) source and quadrupole mass analyser with an ion transfer system based on a hexapole collision cell (ICP-CC-QMS) was used for $^{129}\text{I}/^{127}\text{I}$ isotope ratio measurements. Oxygen and helium were introduced into the hexapole cell as collision gases. Gas input into the hexapole was controlled by built-in mass flow controllers.

A Meinhard nebulizer (J. E. Meinhard Associates, Inc., USA) with a Scott double-pass quartz spray chamber cooled to 4 °C was applied for solution introduction in ICP-CC-QMS. In addition a sample introduction device for iodine thermal desorption from solid material and on-line introduction of iodine into the ICP-MS *via* the gas phase was attached to the ICP-CC-QMS (Fig. 1) and its performance was studied for improving the detection limit for ^{129}I in solid soil samples. The sample was placed into an oven and heated to 1000 °C in air, after achieving the required temperature and stabilizing it for 10 min the valve and the gas flow controller were opened and high purity oxygen (Linde Gas AG) was introduced into the oven at a flow rate of 80 ml min⁻¹. The measurement was started immediately before opening the gas flow controller.

2.2. Standards and samples

A standard solution of ^{129}I obtained from Amersham International (Amersham, Buckinghamshire, UK) was used for calibration and preparing lab standards. An aqueous standard solution of iodine (^{127}I) was prepared by diluting NaI available from Merck (Darmstadt, Germany). Synthetic laboratory liquid and solid standards were used to check the accuracy of the developed analytical method for $^{129}\text{I}/^{127}\text{I}$ isotope ratio measurements.

Synthetic laboratory standards (aqueous solutions and soil samples) with different ^{129}I concentrations and 6 contaminated soil samples were analysed by ICP-CC-QMS with respect to the $^{129}\text{I}/^{127}\text{I}$ isotope ratio.

2.3. Sample preparation

All solutions were diluted with deionised Milli-Q water (18 MΩ) obtained from a Millipore Milli-Q-Plus water purifier. The solutions were acidified with subboiled HNO_3 immediately before the introduction into a Meinhard nebulizer because this acidification of NaI solution before determination resulted in improved sensitivity by about three-fold and in better reproducibility of the results. Solutions with known $^{129}\text{I}/^{127}\text{I}$

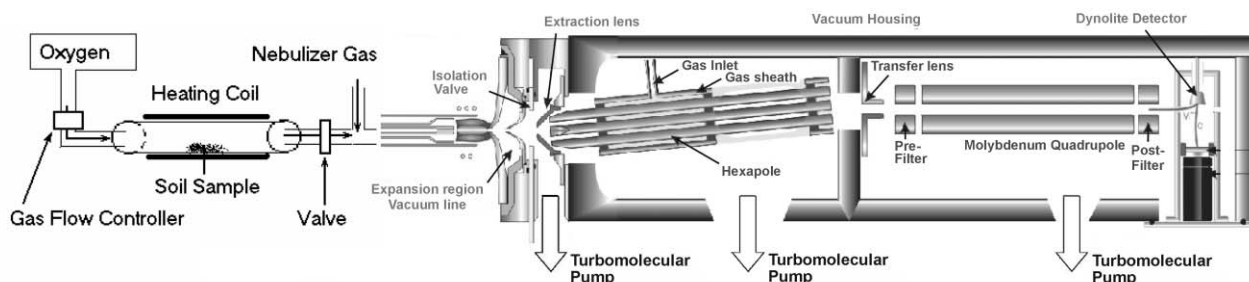


Fig. 1 Schematic diagram of the ICP-CC-QMS with attached device for iodine introduction *via* the gas phase.

isotope ratios were prepared by mixing solution with a known concentration of NaI and ^{129}I . No sample preparation was required for environmental soil samples.

2.4. Optimization of isotopic ratio measurements of iodine

The experimental parameters (coolant, auxiliary and nebulizer gas flow rates) were first optimized with respect to maximum ion intensity of $^{127}\text{I}^+$ whereby an 80 $\mu\text{g l}^{-1}$ iodine standard solution (1% HNO_3) was introduced by a Meinhard nebulizer with a cooled spray chamber into the ICP-CC-QMS.

Secondly, the optimization was performed if only helium and later oxygen were introduced into the hexapole collision cell of ICP-CC-QMS. The ICP-CC-QMS does not allow direct control of the operating gas pressure in the hexapole; therefore flow rates of collision gases were controlled in this study. Flow rates of helium and oxygen for optimization of $^{129}\text{I}/^{127}\text{I}$ isotope ratio measurement were varied between 0 and 10 ml min^{-1} and between 0 and 2 ml min^{-1} , respectively. The ICP-CC-QMS performance (sensitivity, background and precision) was checked every day before the series of measurements. Optimised experimental parameters of the ICP-CC-QMS with different sample introduction systems are summarised in Table 1.

Table 1 Experimental parameters of the ICP-CC-QMS (Platform, Micromass)

Sample introduction system	Meinhard nebulizer with Scott double-pass spray chamber	Device for gas-phase sample introduction
RF power	1400 W	1400 W
Coolant gas flow rate	13.5 l min^{-1}	13.5 l min^{-1}
Auxiliary gas flow rate	1.0 l min^{-1}	1.0 l min^{-1}
Nebulizer gas flow rate	0.85 l min^{-1}	0.85 l min^{-1}
Solution uptake rate	0.9 ml min^{-1}	—
Sample weight	—	2–10 g
O_2 sample gas flow	—	80 ml min^{-1}
Oven heating temperature	—	1000 $^\circ\text{C}$
Cone lens	300 V	300 V
Hexapole exit lens	400 V	400 V
Hexapole bias potential	1.0 V	1 V
Ion energy lens	2.0 V	2.0 V
Multiplier voltage	470 V	470 V
O_2 collision gas flow	0.9 ml min^{-1}	0.9 ml min^{-1}
He collision gas flow	6 ml min^{-1}	6 ml min^{-1}
Dwell time/s	0.2	0.2
Settle time/s	0.02	0.02
Mass resolution/ $m \Delta m^{-1}$	300	300

2.5. Sample introduction of iodine from soils *via* gas phase in ICP-MS

In this work a special sample introduction device for iodine thermal desorption from solid material and on-line introduction of iodine into the ICP-MS *via* the gas phase was proposed. The experimental arrangement is shown in Fig. 1. The solid soil sample (1–5 g) was placed into an oven and heated to $T = 1000^\circ\text{C}$ over approximately 20 min. After that oxygen was introduced into the oven as an oxidant and carrier gas at a flow rate of 80 ml min^{-1} . The evaporated iodine was transferred into the ICP-CC-QMS for on-line measurement of transient signals of $^{129}\text{I}^+$ and $^{127}\text{I}^+$ and $^{129}\text{I}/^{127}\text{I}$ isotope ratios.

3. Results and discussion

3.1. Figures of merit of ICP-CC-QMS for ^{129}I determination

Helium and oxygen as gas mixture were introduced into the collision cell at different flow rates in order to optimize the $^{127}\text{I}^+$ ion intensities and improve the detection limit for ^{129}I determination. For optimization of experimental conditions the intensity of $^{127}\text{I}^+$ was measured in comparison with the integral noise intensity at mass 129 u (caused by isobaric interference with atomic ions of $^{129}\text{Xe}^+$ and molecular ions $^{127}\text{IH}_2^+$ and by detector noise) as a function of nebulizer gas flow and rf power at constant helium and oxygen flow rates.

Fig. 2 shows dependence of $^{127}\text{I}^+$ intensity and signal-to-noise ratio on nebulizer gas flow rate at He flow rate of 6 ml min^{-1} and O_2 flow rate of 0.9 ml min^{-1} . When increasing nebulizer gas flow from 0.6 l min^{-1} to the optimum value at 0.85 l min^{-1} an increase of analyte ion intensity for $^{127}\text{I}^+$ and of signal-to-noise-ratio by about ten-fold was observed, whereby the noise intensity at mass 129 u remained almost constant.

Fig. 3 presents dependence of $^{127}\text{I}^+$ intensity and signal-to-noise ratio on rf power at the same He and O_2 flow rates. The optimum rf power was determined at 1400 W. An improvement in signal-to-noise ratio for $^{129}\text{I}^+$ of about ten-fold in comparison to 1000 W was found.

The dependence of $^{127}\text{I}^+$ intensity relative to noise intensity at mass 129 u and signal-to-noise-ratio on helium and oxygen flow rate is shown in Figs. 4 and 5. Ion transmission of $^{127}\text{I}^+$ was improved when introducing helium and oxygen into the collision cell due to decrease in ion kinetic energy and better focusing of the ion beam by the hexapole ion-guide.^{23,26} In these experiments with increasing He flow rate (at O_2 flow rate of 0 ml min^{-1}) a lower increase of 129 noise intensity was observed due to reaction of $^{129}\text{Xe}^+$ ions with helium due to collision induced neutralization of xenon ions in the collision cell. This effect results in an improvement of signal-to-noise-ratio by 2 to 3 times.

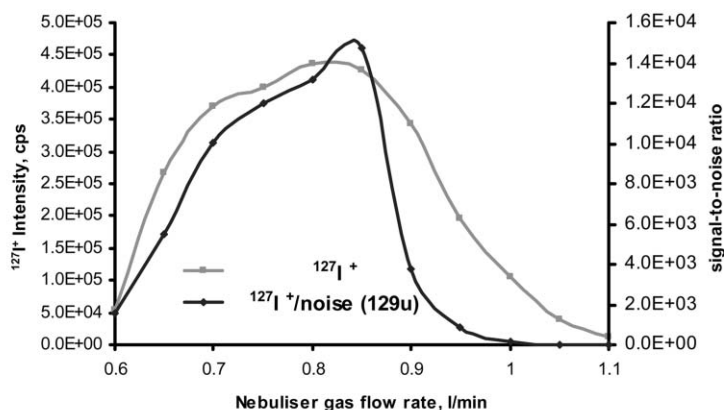


Fig. 2 Dependence of $^{127}\text{I}^+$ intensity and $^{127}\text{I}^+/\text{noise (129 u)}$ on nebulizer gas flow rate (He flow rate—6 ml min^{-1} , O_2 flow rate—0.9 ml min^{-1} , rf power—1400 W, hexapole bias—0).

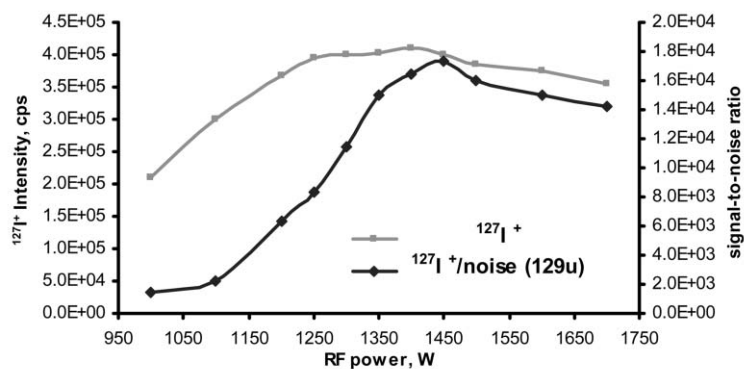


Fig. 3 Dependence of $^{127}\text{I}^+$ intensity and $^{127}\text{I}^+/\text{noise}$ (129 u) on rf power (He flow rate—6 ml min⁻¹, O₂ flow rate—0.9 ml min⁻¹, hexapole bias—0, nebulizer gas flow rate—0.85 l min⁻¹).

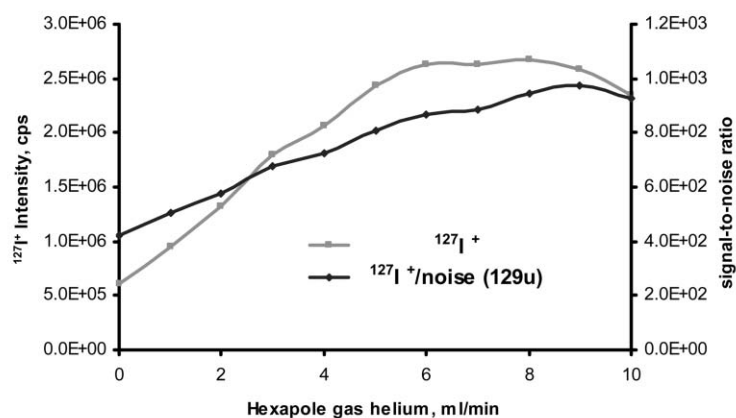


Fig. 4 Dependence of $^{127}\text{I}^+$ intensity and $^{127}\text{I}^+/\text{noise}$ (129 u) on helium flow rate (O₂ flow rate—0 ml min⁻¹, rf power—1400 W, nebulizer gas flow rate—0.85 l min⁻¹).

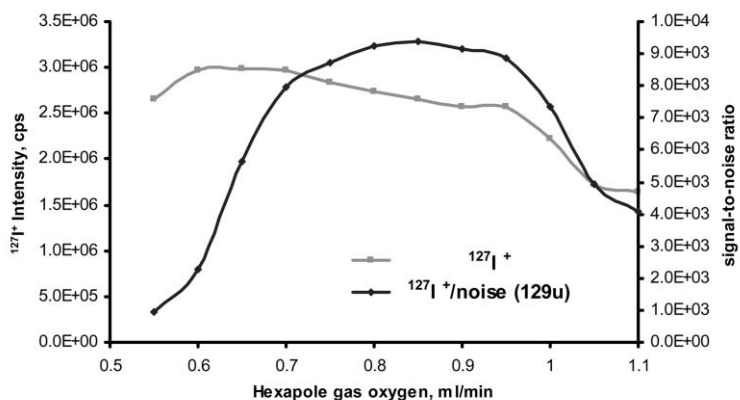


Fig. 5 Dependence of $^{127}\text{I}^+$ intensity and $^{127}\text{I}^+/\text{noise}$ (129 u) on oxygen flow rate (He flow rate—6 ml min⁻¹, rf power—1400 W, nebulizer gas flow rate—0.85 l min⁻¹).

Significantly higher improvement of signal-to-noise ratio for $^{129}\text{I}^+$ was found when introducing O₂ at a flow rate of 0.9 ml min⁻¹. In this experiment the noise measured at mass 129 u was about 25 ± 3 cps which corresponded to the noise intensity of Daly type detector used in ICP-CC-QMS in analog mode. The influence of extraction lens (cone) potential and hexapole bias potential on $^{129}\text{I}^+$ intensity and signal-to-noise ratio analyzed is presented in Fig. 6.

The maximum value of the signal-to-noise ratio for ^{129}I determination was observed at a cone potential of 300 V. Higher extraction voltages increased the intensity of iodine ions but also resulted in a worse signal-to-noise-ratio because the kinetic

energy of $^{129}\text{Xe}^+$ accelerated in the extraction lens region could not be reduced efficiently in the collision cell and overcame the reaction region with higher probability. On the contrary, application of hexapole bias potential of about 1 V resulted in improvement of signal-to-noise-ratio mainly due to suppression of IH_2^+ ion formation. Although in this experiment by applying the hexapole bias a suppression of analyte ion intensities is also observed, IH_2^+ molecular ions formed in the collision cell have lower kinetic energy and they are moderated more effectively because of larger collision cross section in comparison to analyte ions, and therefore the molecular ions are subjected to the hexapole bias to a greater extent.

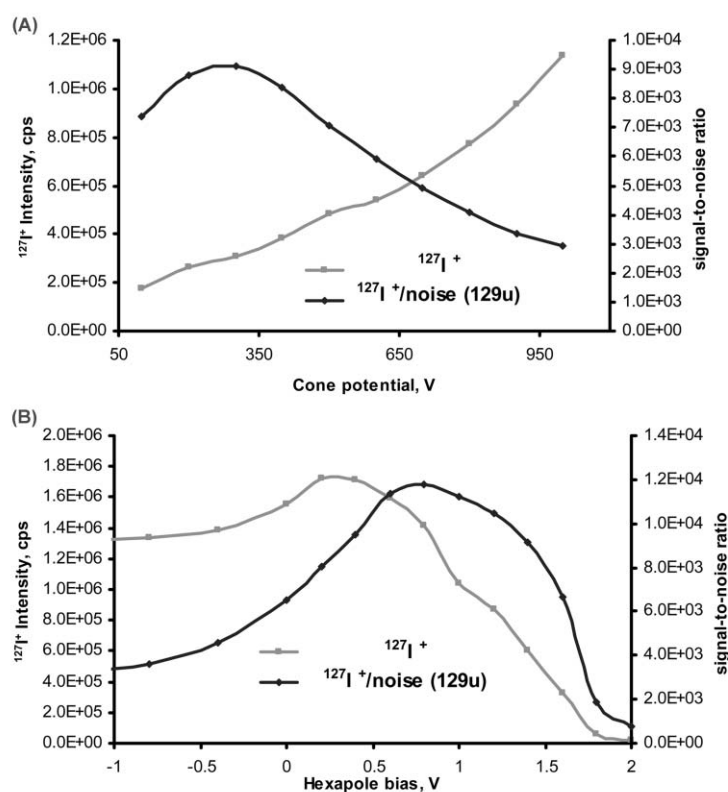


Fig. 6 (A) Dependence of $^{127}\text{I}^+$ intensity and $^{127}\text{I}^+/\text{noise}$ (129 u) on cone potential (He flow rate—6 ml min⁻¹, O₂ flow rate—0.9 ml min⁻¹, rf power—1400 W, nebulizer gas flow rate—0.85 l min⁻¹); (B) dependence of $^{127}\text{I}^+$ intensity and $^{127}\text{I}^+/\text{noise}$ (129 u) on hexapole bias (He flow rate—6 ml min⁻¹, O₂ flow rate—0.9 ml min⁻¹, rf power—1400 W, nebulizer gas flow rate—0.85 l min⁻¹).

Thus, application of O₂ as collision gas allowed the most effective reduction of the noise intensity (mainly caused by $^{129}\text{Xe}^+$ ion intensity) to the level of detector noise. The measured detection limit for ^{129}I determination in aqueous solutions was determined to be 8×10^{-13} g ml⁻¹ (0.8 ppt). Recently, the detection limit for ^{129}I determination was reported in ICP-CC-QMS with hydrogen and helium collision gases to be 3 ppt.²¹ In contrast, the detection limit for ^{129}I in aqueous solution of 100 ppt using sector field ICP-MS was about two orders of magnitude higher due to high $^{129}\text{Xe}^+$ noise which cannot be reduced more.¹⁹

The method developed was applied to the measurement of $^{129}\text{I}^+/\text{I}^+$ isotope ratios down to 10^{-6} in synthetic aqueous solutions prepared from known concentrations of NaI and doped with long-lived ^{129}I radionuclide. The results of isotope ratio measurements in aqueous solutions are summarized in Table 2. The measured isotope ratios are in good agreement (within 5%) with the expected values. The smallest $^{129}\text{I}^+/\text{I}^+$ isotope ratio which can be determined by ICP-CC-QMS in aqueous solution was 10^{-6} .

3.2. Sample introduction of iodine from soils *via* gas phase in ICP-MS

In this work a special sample introduction device (see Fig. 1) for iodine thermal desorption from solid material and on-line

introduction of iodine into the ICP-MS *via* the gas phase was proposed. The advantage of this arrangement is the possibility of separating volatile analyte from the soil matrix which allows a direct $^{129}\text{I}^+/\text{I}^+$ isotope ratio measurement *via* a desorption of iodine from the solid sample and introduction of the analyte into the ICP-MS directly. The optimised analytical procedure reduces matrix effects, improves the detection limit for ^{129}I in solid samples and for $^{129}\text{I}^+/\text{I}^+$ isotope ratio measurements. By reducing the water matrix in ICP-MS and the subsequent $^{127}\text{IH}_2^+$ ion formation, the procedure reduces analyte losses and analysis time.

Fig. 7 presents an example of a chromatogram of transient signals of $^{127}\text{I}^+$ and $^{129}\text{I}^+$ obtained when introducing iodine vapour extracted by oxidation with O₂ from a contaminated solid soil sample heated in an oven at $T = 1000$ °C. The maximum sensitivity observed during the measurements of transient I^+ signals was 10⁷ cps per ppm. The detection limit for ^{129}I in soil samples was 30 pg g⁻¹ (30 ppt). To check the accuracy of $^{129}\text{I}^+/\text{I}^+$ isotope ratio measurements synthetic soil samples doped with NaI and ^{129}I were prepared. The ^{129}I concentration was at the 50–200 ppt level. The results of $^{129}\text{I}^+/\text{I}^+$ isotope ratio measurements in three synthetic soil samples are summarized in Table 3. The relative standard deviation for measured $^{129}\text{I}^+/\text{I}^+$ isotope ratios (from 1.2×10^{-5} to 4.7×10^{-6}) was in the low % range, the accuracy varied between 1.9% and 3.0%.

Table 2 Isotope ratios of $^{129}\text{I}^+/\text{I}^+$ in aqueous synthetic laboratory solutions (LS)

Sample	Expected	Measured	Accuracy (%)	RSD (%)	Concentration of ^{129}I (g g ⁻¹)
LS1	1.18×10^{-6}	1.18×10^{-6}	-0.23	4.1	1×10^{-11}
LS2	2.45×10^{-6}	2.53×10^{-6}	-3.19	3.4	2×10^{-11}
LS3	4.65×10^{-6}	4.75×10^{-6}	-2.03	3.07	5×10^{-11}
LS4	1.18×10^{-5}	1.19×10^{-5}	-1.31	2.17	10×10^{-11}
LS5	2.35×10^{-5}	2.38×10^{-5}	-1.29	1.83	20×10^{-11}
LS6	4.71×10^{-5}	4.51×10^{-5}	4.17	1.75	50×10^{-11}

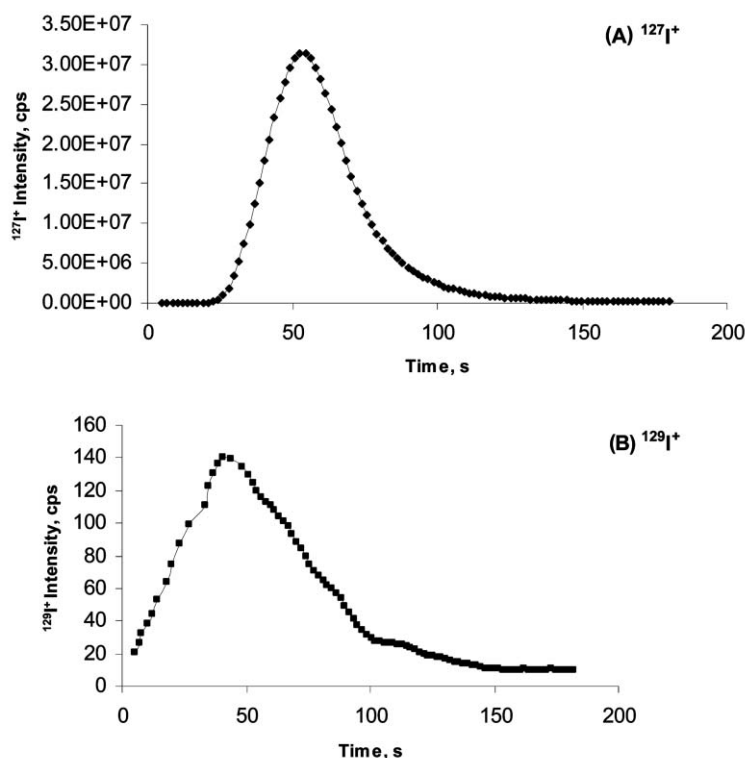


Fig. 7 Transient signals of $^{127}\text{I}^+$ (A) and $^{129}\text{I}^+$ (B) measured by ICP-CC-QMS using iodine extraction from a solid sample (temperature of oven $T = 1000\text{ }^\circ\text{C}$, flow rate of oxygen: 80 ml min^{-1}).

Table 3 Isotope ratios of $^{129}\text{I}/^{127}\text{I}$ in synthetic soil samples (S)

Sample	Expected	Measured	Accuracy (%)	RSD (%)	Concentration of ^{129}I (g g^{-1})
S1	2.3×10^{-6}	2.1×10^{-6}	1.9	11.5	5×10^{-11}
S2	1.2×10^{-5}	1.1×10^{-5}	2.6	7.8	10×10^{-11}
S3	4.7×10^{-5}	4.5×10^{-5}	3.0	3.0	20×10^{-11}

For a further optimization of the analytical procedure and a reduction of sample size the amount of contaminated soil sample (sample 3) was varied between 5 and 1 g (Table 4). The $^{129}\text{I}^+ / ^{127}\text{I}^+$ isotope ratios of 5×10^{-6} were determined with a standard deviation of about 10%, whereby a reduction of sample amount did not result in a significant increase of RSD (Table 4).

The results of $^{129}\text{I}^+ / ^{127}\text{I}^+$ isotope ratio measurements in four environmental soil samples (5 g of each soil were analyzed) are summarized in Table 5. The ^{129}I concentration in the soil

Table 4 Isotope ratios of $^{129}\text{I}/^{127}\text{I}$ in solid soil sample 3 from contaminated area with different amount of the sample

Sample	Amount of sample (g)	$^{129}\text{I}/^{127}\text{I}$	SD	RSD (%)
3	5	5.0×10^{-6}	4.7×10^{-7}	9.4
3	2.5	5.2×10^{-6}	5.4×10^{-7}	10.4
3	1	5.1×10^{-6}	5.4×10^{-7}	10.6

Table 5 Isotope ratios of $^{129}\text{I}/^{127}\text{I}$ in solid soil samples from contaminated area

Sample	$^{129}\text{I}/^{127}\text{I}$	SD	RSD (%)
1	4.1×10^{-5}	2.3×10^{-6}	5.8
2	3.9×10^{-6}	8.4×10^{-8}	2.2
3	5.0×10^{-6}	4.7×10^{-7}	9.4
4	2.0×10^{-6}	8.7×10^{-8}	4.4

samples was in the ppt range. The isotope ratios $^{129}\text{I}^+ / ^{127}\text{I}^+$ in the contaminated soil samples varied between about 4×10^{-5} and 2×10^{-6} . The precision of these small isotope ratio measurements at ultratrace levels using the developed analytical technique was mostly better than 5%. Using the described analytical procedure the smallest $^{129}\text{I}^+ / ^{127}\text{I}^+$ isotope ratio which can be determined directly by ICP-CC-QMS in soil samples was to 10^{-6} .

Further work will focus on improvement of the direct analyte introduction system in order to improve the detection limits for ^{129}I .

The present study was limited due to a relatively high background of the Daly-type ion detector and the dynamic range of ICP-CC-QMS of 10^8 . An ion detector possessing lower background and a wider dynamic range would be desirable for further studies of $^{129}\text{I}^+ / ^{127}\text{I}^+$ isotope ratio measurements in environmental and radioactive waste samples.

4. Conclusion

ICP-MS with collision cell has been shown to be an attractive means by which to measure the extremely small isotope ratios of iodine in comparison to existing techniques such as AMS and RNAA, which are both expensive and complicated.

The application of a hexapole collision cell with oxygen as collision gas is an effective tool for reducing $^{129}\text{Xe}^+$ ions and hence improving the detection limit, accuracy and precision in the determination of ^{129}I . Background ion intensities caused by $^{129}\text{Xe}^+$ ions were reduced to the level of detector specific noise

(Daly type detector used in analog mode) by introducing the mixture of oxygen and helium and application of hexapole bias. The measurement of the isotope ratio of $^{129}\text{I}/^{127}\text{I}$ down to 10^{-6} yielded good accuracy and precision of ICP-CC-QMS and detection limits were improved by approximately two orders of magnitude. The application of a gas-filled collision cell in ICP-MS allows improved abundance sensitivity, which is useful in analyzing the long-lived radionuclide $^{129}\text{I}^+$ in the presence of the highly abundant stable isotope $^{127}\text{I}^+$. Additionally, a simplified sample introduction technique was developed which delivers iodine *via* the gas phase and demonstrates detection limits of 30 pg g^{-1} for ^{129}I .

Future work will involve exploration of a cooling finger between the oven and the ICP-MS for improvement in measurement of isotope ratios.

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