Improvement of the detection limit for determination of ^{129}I in sediments by quadrupole inductively coupled plasma mass spectrometer with collision cell†

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The previously developed sample introduction device for the hot extraction of iodine from environmental samples (soils or sediments) and on-line introduction of analyte *via* the gas phase in quadrupole inductively coupled plasma mass spectrometry with hexapole collision cell (ICP-CC-QMS) was equipped with a cooling finger, which allowed intermediate iodine enrichment and improved the detection limits for ^{129}I down to 0.4 pg g^{-1} without any additional sample preparation. A mixture of oxygen and helium as reaction gases in the hexapole collision cell was used for reducing the disturbing background intensity of ^{129}Xe$^+$. Oxygen was also used as the carrier gas for iodine thermal desorption and transport into the ICP-CC-MS. The developed analytical method was applied for ^{129}I determination at the ultra-trace level and for isotope ratio measurements of ^{129}I/^{127}I down to 10^{-7} in contaminated sediments and in SRM 4357 (Ocean Sediment Environment Radioactivity Standard). The measured ^{129}I/^{127}I ratio of 5.3 $\times$ 10^{-7} corresponded to the expected value of 4.45 $\times$ 10^{-7} reported for this sediment in the certificate.

1. Introduction

The long-lived radionuclide ^{129}I ($T_{1/2}$ = 15.7 Ma) is mainly released into the environment from anthropogenic sources (nuclear weapons tests, nuclear accidents and by emissions from nuclear fuel reprocessing plants). The behavior of this radionuclide in the environment has not been explored in detail due to analytical difficulties. Neutron activation analysis with radiochemical separation (RNAA) and accelerator mass spectrometry (AMS) are capable of ^{129}I determination in environmental materials at the pg kg^{-1} concentration range with minimal detectable isotopic ratio for ^{129}I/^{127}I about 10^{-10} and down to 10^{-12}, respectively.[1] However, these mass spectrometric methods involve complicated and expensive experimental equipment and the analysis, including sample preparation, is time-consuming. In contrast, inductively coupled plasma mass spectrometry (ICP-MS) is a powerful technique for fast and accurate isotopic analysis at the ultra-trace concentration level.[2-4] ^{129}I determination in environmental samples by ICP-MS is very difficult due to a high background caused by Xe impurities in argon plasma gas (interference of ^{129}Xe$^+$),[4-7] possible ^{127}IH$_2^+$ interference and an insufficient abundance ratio sensitivity of quadrupole mass spectrometer for ^{129}I/^{127}I isotope ratio measurement.

In previous work,[8] an analytical method based on inductively coupled plasma mass spectrometry with a collision cell was developed for the determination of low ^{129}I/^{127}I isotope ratios in synthetic and environmental samples using effective and sensitive direct sample introduction of iodine *via* the gas phase from soil samples. The detection limit for direct ^{129}I$^+$ determination in contaminated environmental (soil) samples *via* gas-phase desorption without any additional sample preparation was 3 $\times$ 10^{-11} g g^{-1}. The aim of the present work was further improvement of the detection limit for ^{129}I in sediments and obtaining a lowest detectable ^{129}I/^{127}I isotope ratio for

direct measurements on environmental samples, without any additional sample preparation, by applying a cooling finger in the sample introduction device (between oven and ICP-MS).

2. Experimental

2.1. Instrumentation

A quadrupole-based inductively coupled plasma mass spectrometer (Platform ICP, Micromass Ltd., Manchester, UK) with a hexapole collision cell (ICP-CC-QMS) was used for the determination of ^{129}I and ^{129}I/^{127}I isotope ratios at the ultratrace level in sediments. In the ICP-CC-QMS a photomultiplier Daly-type detector was used for ion detection.

A mixture of oxygen and helium as collision gases was introduced into the hexapole cell. Collision gas flow rates were controlled by built-in mass flow controllers. By the collision of ions formed in the inductively coupled plasma with the collision gas mixture (*e.g.*, O$_2$–He) in the gas target, the interfering ^{129}Xe$^+$ ions (Xe as impurity of plasma gas Ar) are neutralized and the analyte ions are moderated from several eV to less than 1 eV. This improves the transmission of the ions of interest, the sensitivity of the elements and the precision in the determination of isotope ratios.[5,9] Background ion intensities caused by ^{129}Xe$^+$ ions were reduced to the level of detector-specific noise (Daly-type detector used in analog mode). In addition, 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}I in the presence of the highly abundant stable isotope ^{127}I.

The sample introduction device developed previously[8] was equipped with a cooling finger, between oven and ICP-MS, which allowed intermediate iodine enrichment and improved the overall sensitivity for iodine detection by ICP-CC-QMS, whereby iodine was hot-extracted from solid material, enriched in the cooling finger and introduced on-line using oxygen as the carrier gas *via* the gas phase into the inductively coupled plasma of an ICP-CC-QMS. The experimental arrangement of

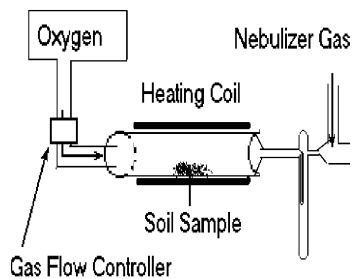*This journal is © The Royal Society of Chemistry 2004*

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

the iodine introduction device with cooling finger is shown in Fig. 1.

2.2. Standards and samples

Standard reference material SRM 4357 (Ocean Sediment Environmental Radioactivity Standard) obtained from NIST and two contaminated soil samples of unknown origin were analyzed by ICP-CC-QMS with respect to their $^{129}I/^{127}I$ isotope ratio. A standard solution of ^{129}I (Amersham, Buckinghamshire, UK) and ^{127}I (prepared by diluting NaI available from Merck, Darmstadt, Germany) were used to prepare laboratory standards. Using the special sample introduction device no sample preparation is required for environmental soil samples.

2.3. Sample introduction for direct ^{129}I determination with cooling finger in ICP-CC-QMS

The contaminated sample was placed into an oven heated to 1000 °C in air. After that the valve and the gas flow controller were opened and high-purity oxygen (Linde Gas AG) was introduced into the oven as an oxidant and carrier gas at a flow rate of 5 ml min^{-1}. The evaporated iodine was enriched in the cooling finger, which was placed between the oven for iodine hot extraction and ICP-CC-MS (see Fig. 1) and refrigerated by liquid nitrogen. During the warming sequence the cooling finger iodine was evaporated again and transferred to the ICP-CC-QMS for on-line measurement of transient signals of $^{129}I^+$ and $^{127}I^+$ and the determination of $^{129}I/^{127}I$ isotope ratios.

2.4. Measurement procedure for isotopic ratio measurement of iodine at the ultra-trace level

The experimental parameters were first optimized to maximum $^{127}I^+$ ion intensity with respect to rf-power, coolant, auxiliary and nebulizer gas flow rates. The optimization was performed with only helium and later oxygen was introduced into the hexapole collision cell of ICP-CC-QMS according to procedure described elsewhere.[8] Flow rates of helium and oxygen for the optimization of $^{129}I/^{127}I$ isotope ratio determination were varied between 0 mL min^{-1} and 10 mL min^{-1} and between 0 mL min^{-1} and 2 mL min^{-1}, respectively. ICP-CC-QMS performance (sensitivity, background and precision) was checked every day before the series of measurements. Optimized experimental parameters of the ICP-CC-QMS are summarized in Table 1.

3. Results and discussion

The figures of merit of the experimental arrangement with the cooling finger placed between oven and ICP-MS and its performance were studied to improve the detection limit for ^{129}I in solid soil samples in comparison with recent work without a cooling finger.[8] Fig. 2 presents an example of transient signals of $^{127}I^+$ and $^{129}I^+$ obtained when introducing iodine vapor extracted by oxidation with O$_2$ from a contaminated solid soil sample heated in an oven at $T = 1000$ °C. When

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

Sample introduction system	Device for gas-phase sample introduction with cooling finger
Rf power	1400 W
Coolant gas flow rate	13.5 L min^{-1}
Auxiliary gas flow rate	1.0 L min^{-1}
Nebulizer gas flow rate	0.9 L min^{-1}
Sample weight	1–5 g
O$_2$ sample gas flow	5 mL min^{-1}
Oven heating temperature	1000 °C
Cone lens	300 V
Hexapole exit lens	400 V
Hexapole bias potential	1 V
Ion energy lens	2.0 V
Multiplier voltage	470 V
O$_2$ collision gas flow	0.9 mL min^{-1}
He collision gas flow	6 mL min^{-1}
Dwell time	0.2 s
Settle time	0.02 s
Mass resolution ($m/\Delta m$)	300

applying arrangement with a cooling finger, the shape of transient signal shows significantly shorter peaks, and thus the signal to noise ratio is improved. This is especially important in the case of the weak ^{129}I signal, which could not be distinguished from the noise when using the previous arrangement. Thus, the improved sample introduction technique allows separation and intermediate enriching of the volatile analyte iodine from the soil matrix before introduction into the inductively coupled plasma. Using this improved sample introduction technique we can demonstrate a detection limit as low as 0.4 pg g^{-1} for ^{129}I in comparison with 30 pg g^{-1} (which is 75 times higher) achieved previously in ICP-CC-MS without a cooling finger.[8] The limit of detection was calculated using the 3σ criterion. Sample with only known ^{127}I was measured. So we can calculate the sensitivity (for ^{127}I and ^{129}I it must be the same). Then we calculate 3 standard deviations of
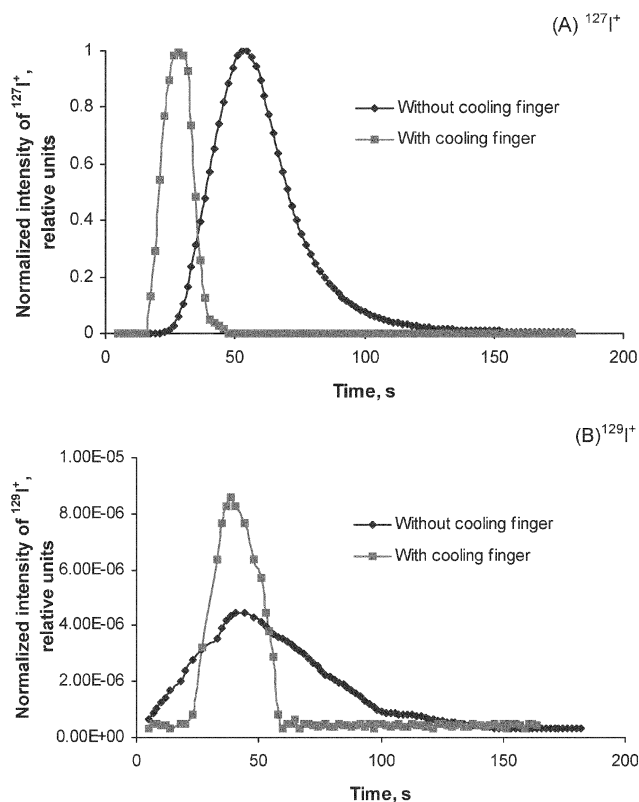

Fig. 2 Two different soil samples measured by ICP-CC-QMS using iodine extraction for soil samples with and without cooling finger.

Table 2 Limits of detection for ^{129}I in liquid and soil samples using different mass spectrometric techniques

Sample	Experimental arrangement	LOD/pg g^{-1}	Reference
Aqueous solution	ICP-SFMS[a]	100	Kerl et al., 1996[4]
Aqueous solution	ICP-CC-MS (reaction gas: O$_2$/He)	3	Becker, 2002[5]
Aqueous solution	ICP-CC-MS (reaction gas: H$_2$)	0.8	Izmer et al., 2003[8]
Sediment	ICP-CC-MS (reaction gas: O$_2$)	30	Izmer et al., 2003[8]
Sediment	ICP-CC-MS with cooling finger (reaction gas: O$_2$)	0.4	This paper
Sediment	RNAA	0.125	Szidat et al., 2000[1]
Sediment	AMS	0.000 023	Szidat et al., 2000[1]

[a] Using double-focusing sector field ICP-MS (ELEMENT, Finnigan MAT).

Table 3 Comparison of measured isotope ratio ^{129}I/^{127}I in reference material by ICP-CC-MS and ranges of lowest determinable ^{129}I/^{127}I ratios in soil achieved by RNAA and AMS[1]

Material	Instrumentation	Required sample mass/g	^{129}I/^{127}I	Reference
Ocean Sediment (SRM4357)	ICP-CC-MS with cooling finger	1–5	5.34×10^{-7}	This paper
Soil	RNAA	80	$4.1–250 \times 10^{-10}$	Szidat et al., 2000[1]
Soil	AMS	80	$0.0075–0.45 \times 10^{-10}$	Szidat et al., 2000[1]

Table 4 Isotope ratio of ^{129}I/^{127}I in soil samples from contaminated area measured by ICP-CC-QMS using device for gas-phase sample introduction with cooling finger

Sample	^{129}I/^{127}I	SD	RSD (%)
1	2.1×10^{-6}	2.0×10^{-7}	9.4
2	6.9×10^{-6}	5.3×10^{-7}	7.6

the blank for mass 129 and then using the formula LOD = $(3\sigma + \text{blank } (u = 129))/S$ we calculate LOD, where S is the sensitivity.

Detection limits for ^{129}I using different analytical methods and sample introduction systems in ICP-CC-QMS are compared in Table 2. Despite RNAA and particularly AMS providing lower detection limits for this radionuclide, the ICP-CC-MS allows ^{129}I concentration and ^{129}I/^{127}I isotope ratios to be determined at the ultra-trace level in solid samples by ICP-CC-MS directly and rapidly without any additional sample preparation step. The gas-phase sample introduction minimizes matrix effects and improves the detection limit for ^{129}I and for ^{129}I/^{127}I isotope ratio measurement in solid samples.

To check the accuracy of ^{129}I$^+$/^{127}I$^+$ isotope ratio measurements using ICP-CC-MS with a cooling finger SRM 4357 (Ocean Sediment) was used. Table 3 presents the results of the ^{129}I/^{127}I ratio analysis in this sediment in comparison to the lowest determinable ^{129}I/^{127}I isotope ratio in soil measured by AMS and RNAA. The iodine isotope ratio is not certified in SRM4357, which is why we can only expect this value from concentrations of ^{129}I and ^{127}I. The expected ^{129}I/^{127}I isotope ratio of 4.4×10^{-7} in Ocean Sediment is comparable with the measured isotope ratio of 5.3×10^{-7} using the experimental arrangement with cooling finger proposed in this work. Using the measured isotope ratio and the concentration of ^{127}I from the certificate, concentration of ^{129}I was calculated in 1.65×10^{-12} g g^{-1} range. It should be mentioned that the reported concentration of ^{129}I in this reference material varied between 0.92–1.84 pg g^{-1}.

The results of ^{129}I/^{127}I isotope ratio measurements in two contaminated environmental soil samples are summarized in Table 4. The isotope ratios ^{129}I/^{127}I in the contaminated soil samples varied between about 2×10^{-6} and 6×10^{-6}. The precision of these small isotope ratio measurements at the ultratrace level using the analytical method developed here was mostly better than 7%. Using the described analytical procedure the minimal detectable ^{129}I/^{127}I isotope ratio which can be determined directly by ICP-CC-QMS in soil samples was 10^{-7}.

This study confirms that the application of ICP-CC-MS with a hexapole collision cell using an oxygen and helium mixture as the collision gas is an effective tool for reducing interfering ^{129}Xe$^+$ ions and hence improving the detection limit, accuracy and precision in the determination of ^{129}I.

Acknowledgements

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