

Accurate determination of ^{129}I in environmental samples using triple quadrupole ICP-MS

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Goal

To demonstrate the ultratrace determination of ^{129}I in aqueous samples using triple quadrupole ICP-MS. To demonstrate that triple quadrupole technology can be used in oxygen reaction mode to attenuate potential interference problems associated with the measurement of ^{129}I .

Introduction

The most common regulatory methods for environmental analysis focus on highly toxic contaminants such as As, Cd, Hg or Pb, which are essentially present as stable isotopes only. In some cases however, the analysis of radioactive isotopes (or nuclides) is required to accurately assess potential hazards for example after incidents associated with power generation using nuclear technology. The most commonly observed product nuclides of nuclear fission of uranium are found in the mass range of about 90 amu and



140 amu. Due to their short half-lives, many direct fragments undergo further decay reactions and therefore, the isotopes causing the most concern when released to the environment are ^{90}Sr , ^{137}Cs or radioactive nuclides of iodine. Iodine is especially critical as it is incorporated into the thyroid gland of humans and can cause severe damage. For iodine, two isotopes are of most concern: ^{131}I , which has a half-life of only 8 days and decays relatively quickly and ^{129}I , which is a long lived radionuclide with a half-life of 15.7 million years. The presence of radioactive iodine in the environment is primarily due to emissions from nuclear fuel reprocessing plants alongside potential nuclear weapons testing and nuclear power plant accidents.

Concentrations of ^{129}I in the environment are normally very low and this, together with the relatively low sensitivity of iodine, can make it challenging to measure accurately by ICP-MS. Most of the radionuclides of interest can be determined by radiometric techniques, but in most cases, long exposure times are required to ensure sufficient counting statistics. The opportunity to apply ICP-MS can therefore help to decrease sample turnaround times dramatically and speed up official responses to potential sources of contamination.

ICP-MS is prone to interferences, as are all analytical techniques, which may bias the results. Whereas so-called polyatomic interferences are of most concern in the majority of applications and can be effectively eliminated using kinetic energy discrimination (KED), there are other interferences that require the use of reactive gases and subsequent chemical reactions in the cell. However, the selection of a reactive gas is not straightforward and may lead to adverse effects for other analyte ions.

Triple quadrupole instrumentation typically employs a quadrupole before the collision/reaction cell in order to allow only specific ions into the cell, while eliminating others. This pre-filtering of the ion beam prior to the cell provides improved interference removal by reducing the range of side of reactions that can occur in the cell as well as allowing selective reaction chemistries to be applied using reactive cell gases.

Challenges that need to be overcome for the measurement of ^{129}I include the potential of ^{129}Xe isobaric interference from impurities in the argon gas, potentially high levels of naturally occurring ^{127}I in the samples and possible polyatomic interferences from $^{127}\text{IH}_2^+$, Mo^+ dioxide and dioxide hydride species and Sn^+ hydroxide species.

Single quadrupole ICP-MS using oxygen in the QCell can be used to significantly reduce isobaric interference from $^{129}\text{Xe}^+$. However, potential problems with peak tailing from ^{127}I , $^{127}\text{IH}_2$ and polyatomic interferences from Mo^+ and Sn^+ based species still remain.

To overcome these issues triple quadrupole ICP-MS operating in O_2 reaction mode has been investigated to demonstrate the potential of this technique for measuring ultratrace levels of ^{129}I in aqueous environmental samples.

Instrumentation

All measurements were performed using a Thermo Scientific™ iCAP™ TQ ICP-MS. The instrument was operated using the Thermo Scientific™ Qtegra™ *Intelligent Scientific Data Solution* (ISDS) Software and was tuned daily using a mixed standard solution. The typical operation parameters are shown in Table 1.

Table 1. Typical instrumental parameters

Parameter	Value	
RF Power	1,550 W	
Nebulizer Gas Flow	1.12 Lmin ⁻¹	
Interface	High sensitivity	
QCell Settings	SQ-O₂	TQ-O₂
Gas Flow	0.6 mLmin ⁻¹	0.6 mLmin ⁻¹
CR Bias	-7.2 V	- 7.2 V
Q3 Bias	-12 V	-12 V

In order to select the appropriate instrument settings (e.g. choice of reaction gas and the mass to be transmitted to the analyser quadrupole (Q3)), the Reaction Finder Method Development Assistant was used. Reaction Finder allows analytical methods to be set up without prior detailed knowledge of potential reaction pathways caused by other components in the sample. For this work O_2 was automatically selected by Reaction Finder for the analysis of ^{129}I in TQ mode. A second measurement mode using oxygen and single quadrupole operation (SQ-O₂) was also manually added to compare differences between these two modes alongside single quadrupole no gas (SQ-STD) and single quadrupole KED (SQ-KED) modes. The scan settings for the first quadrupole were optimized using intelligent Mass Selection (iMS). As can be seen from the results, iMS was able to remove all ions potentially causing interferences whilst assuring optimized transmission of the analyte. The use of high resolution (less than 1 amu) on Q1 was found to not be required for this application.

Mechanisms of iodine interference removal using O₂ reaction gas with triple quadrupole ICP-MS

In O₂ mode, the ¹²⁹Xe interference on ¹²⁹I is extremely efficiently removed by a charge exchange reaction between Xe⁺ and O₂, while ¹²⁹I doesn't react. The presence of Mo and Sn in the samples leads to the formation of MoO₂⁺, SnO⁺ and SnOH⁺ product ions in the cell, which interfere with ¹²⁹I. In single quadrupole mode, there is no way to prevent Mo and Sn entering the cell together with Xe and I, so MoO₂⁺, SnO⁺ and SnOH⁺ interference on ¹²⁹I can't be prevented. In fact, if Mo and Sn are present in the samples, SQ-O₂ leads to worse results than can be achieved in either standard or He KED modes. In contrast, triple quadrupole operation allows Mo and Sn in the samples to be completely rejected from the ion beam before it enters the cell, preventing them from forming additional interference on ¹²⁹I. MoO₂⁺, SnO⁺ and SnOH⁺ are present in the plasma, but at very low levels (particularly SnO⁺) and furthermore, MoO₂⁺ reacts further with O₂ in the cell to form higher Mo oxides which don't interfere with ¹²⁹I. Reaction of SnO and SnOH to SnO₂ and SnO₂H also appears to occur, ensuring complete removal of these low-level interferences. The mechanism of interference removal on ¹²⁹I using a triple quadrupole ICP-MS system is shown in Figure 1.

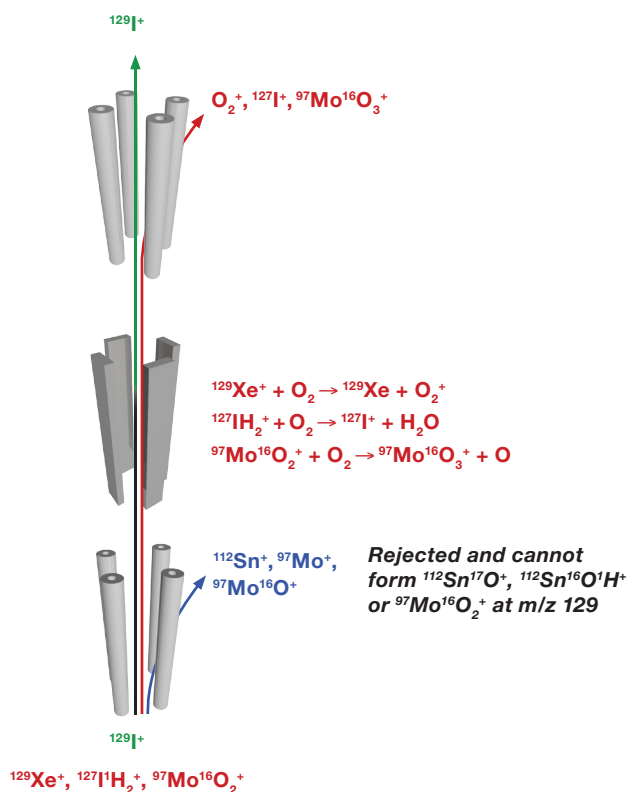


Figure 1. Interference removal mechanism for analysis of ¹²⁹I

Sample preparation

¹²⁹I calibration solution solutions were prepared in a 0.5% v/v tetra methyl ammonium hydroxide (TMAH) solution rather than dilute HNO₃, to prevent the severe memory effects caused by oxidation of iodide to iodine by nitric acid. The same matrix was used for the preparation of all blanks, calibration solutions, samples and rinse solutions for iodine analysis by ICP-MS. Interference solutions containing I, Mo and Sn were also prepared in the same matrix to demonstrate the interference removal and highlight the potential problems associated with typical environmental samples. A sample matrix intended to simulate the typical composition of soil or surface water samples was prepared containing Ca, Mg, Na (at 20 mg·L⁻¹) and Al, Fe, Mn, Cu (at 5 mg·L⁻¹), with Mo and Sn (at 1 mg·L⁻¹) also added to provide sources of interference on ¹²⁹I. Aliquots of this solution were spiked with known concentrations of ¹²⁹I to assess spike recovery.

Results

The iCAP TQ ICP-MS parameters were initially optimized for maximum sensitivity using the supplied tune solution. The QCell oxygen gas flow was then optimized to maximize removal of the ¹²⁹Xe⁺ interference whilst maintaining sensitivity for iodine.

As can be seen in Table 2, the oxygen gas flow rate determined by the instrument's autotune procedure still showed a low signal at m/z 129, which resulted in a slightly elevated blank equivalent concentration (BEC, the apparent concentration of ¹²⁹I caused by the background signal) for ¹²⁹I. In order to reduce the BEC further (whilst compromising signal to noise ratio as little as possible), the High gas flow setting was used with an offset value of 0.3 mL·min⁻¹ in addition to the default flow rate determined by the autotune routine, giving a total gas flow rate of approximately 0.6 mL·min⁻¹. This flow rate provided optimum ¹²⁷I signal intensity versus the ¹²⁹I background resulting in an ultralow BEC for ¹²⁹I (Table 2).

Table 2. Signal intensities at autotuned and optimised O₂ flow

	Signal on m/z 129 [cps]	BEC ¹²⁹ I [ng·L ⁻¹]
Result Autotune (0.34 mL·min ⁻¹)	30	1.3
Optimized O ₂ Flow (0.6 mL·min ⁻¹)	2	0.13

Figure 2 shows the calibration curves for ^{129}I in triple quadrupole mode with oxygen cell gas (TQ- O_2) and single quadrupole mode with oxygen (SQ- O_2) after optimisation of the O_2 flow.

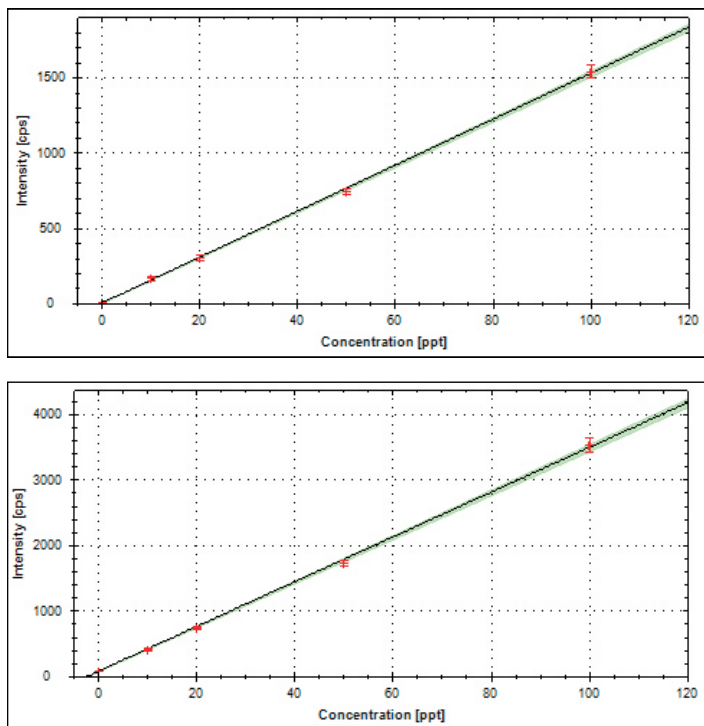


Figure 2. Calibration curves for ^{129}I (0–100 $\text{ng}\cdot\text{L}^{-1}$). On mass mode using TQ- O_2 (top) and SQ- O_2 (bottom).

Table 3 contains the calculated Instrument Detection Limits (IDL). These values are shown for both the single quadrupole in standard mode, He KED and O_2 in single quad mode and triple quadrupole mode using O_2 as the reaction gas.

Table 3. Comparison between SQ and TQ modes for the analysis of ^{129}I

Component	SQ-STD	SQ-KED	SQ- O_2	TQ- O_2
BEC ($\text{ng}\cdot\text{L}^{-1}$)	40	30	2.2	0.13
IDL ($\text{ng}\cdot\text{L}^{-1}$)	2	2	0.2	0.001

In a second step to further elucidate the potential of using triple quadrupole ICP-MS for this analysis, solutions containing elements directly interfering on m/z 129 were analysed. In many environmental samples, like soils or plant digests, it is not unusual that higher amounts of Mo and Sn can be found.

Table 4 shows the apparent concentrations at ^{129}I obtained when analyzing solutions containing $20\ \mu\text{g}\cdot\text{L}^{-1}$, $1\ \text{mg}\cdot\text{L}^{-1}$ Mo and $1\ \text{mg}\cdot\text{L}^{-1}$ Sn respectively. The comparison between SQ- O_2 and TQ- O_2 modes shows clearly that by controlling the ions that enter the QCell using Q1, the background associated from interfering species is significantly reduced. As can be seen in Figure 3 and Table 4 respectively, even moderate amounts of natural iodine (^{127}I) lead to a significant contribution to the signal observed at m/z 129 due to the formation of $^{127}\text{I}^+\text{H}_2$ in single quad mode if ^{127}I is not removed before the ion beam enters the collision/reaction cell.

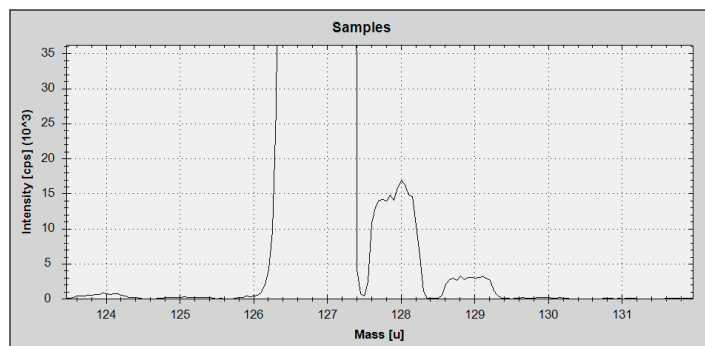


Figure 3. Full mass scan performed on a sample containing $20\ \mu\text{g}\ \text{L}^{-1}$ natural iodine (^{127}I) in SQ- O_2 mode. Xe based interferences are eliminated, but $^{127}\text{I}^+\text{H}_2^+$ causes a significant false positive signal on m/z 129.

Table 4. Interference effects in SQ- O_2 and TQ- O_2 modes for the analysis of ^{129}I

Interference test solution	SQ- O_2 apparent concentration at ^{129}I	TQ- O_2 apparent concentration at ^{129}I	Improvement factor
$20\ \mu\text{g}\cdot\text{L}^{-1}\ ^{127}\text{I}$	$45\ \text{ng}\cdot\text{L}^{-1}$	$0.09\ \text{ng}\cdot\text{L}^{-1}$	500
$1\ \text{mg}\cdot\text{L}^{-1}\ \text{Mo}$	$560\ \text{ng}\cdot\text{L}^{-1}$	$0.07\ \text{ng}\cdot\text{L}^{-1}$	8,000
$1\ \text{mg}\cdot\text{L}^{-1}\ \text{Sn}$	$30\ \text{ng}\cdot\text{L}^{-1}$	$0.07\ \text{ng}\cdot\text{L}^{-1}$	430

Utilizing triple quadrupole functionality attenuates IH^+ and IH_2^+ and eliminates problems with $^{97}\text{Mo}^{16}\text{O}_2^+$, $^{112}\text{Sn}^{17}\text{O}^+$ and $^{112}\text{Sn}^{16}\text{O}^+\text{H}^+$ ions that arise from the Mo and Sn present in typical environmental samples.

Finally, the spike recovery results for a range of ^{129}I concentrations in the simulated environmental matrix are shown in Table 5. These results show that ^{129}I can be quantitatively measured at ultratrace concentrations despite the presence of potential interferences using TQ- O_2 mode on the iCAP TQ ICP-MS.

Table 5. ^{129}I spike recoveries

Sample	Spike recovery in TQ-O ₂ [%]
10 ng·L ⁻¹	105
20 ng·L ⁻¹	98
50 ng·L ⁻¹	97
100 ng·L ⁻¹	101

Conclusion

Triple quadrupole technology can help to tackle difficult sample matrices, where significant contributions from matrix components lead to the formation of severe polyatomic interferences on the target analyte. In this work, the background signal on ^{129}I caused by the presence of ^{129}Xe and the formation of Mo^+ and Sn^+ species was significantly attenuated while maintaining high detection sensitivity, leading to ultralow detection limits for ^{129}I . Excellent spike recoveries were also obtained for ^{129}I in simulated environmental matrix samples.



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