The ultratrace determination of iodine 129 in aqueous samples using the 7700x ICP-MS with oxygen reaction mode

Application note
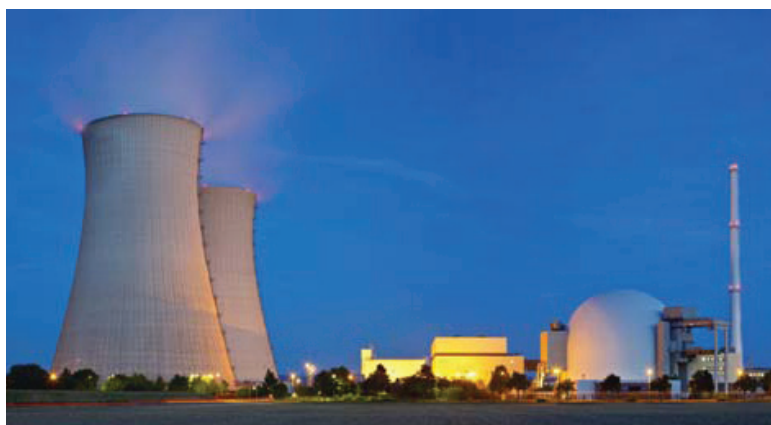
Nuclear

Authors

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Abstract

Determination of the radionuclide iodine 129 using ICP-MS has been improved by the use of an Octopole Reaction System (ORS) ICP-MS, operated in oxygen cell mode. Oxygen reaction gas removes the background signal at m/z 129, which is due to the presence of Xe as an impurity in the Ar plasma gas and to the polyatomic ion $^{127}IH_2^+$. NIST SRM standards with different $^{129}I/^{127}I$ ratios and at multiple concentrations were successfully measured, and a ^{129}I detection limit of 1.1 ppt was obtained. No sample preparation is required for aqueous samples and the method is capable of high sample throughput.

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Introduction

Iodine 129 (^{129}I) is a long-lived radionuclide (half-life of 15.7 million years), which has been released into the environment as a result of nuclear weapons testing and accidental releases from nuclear power plants and spent nuclear fuel reprocessing plants. Neutron activation analysis (NAA) and accelerator mass spectrometry are commonly used techniques for the measurement of ^{129}I at ambient (pre-nuclear age) levels, but these techniques are costly and time consuming (several weeks for NAA) involving radiochemical separation. Less sensitive but faster and more routine techniques used to monitor for ^{129}I release are liquid scintillation counting and gamma spectrometry, though measurements still take several hours and significant radiochemical sample preparation is required. Inductively Coupled Plasma Mass Spectrometry (ICP-MS) can also be used to measure ^{129}I, however detection limits are compromised by a spectral overlap from ^{129}Xe, due to the Xe impurity present in the argon plasma gas.

Since ^{129}Xe is an elemental, rather than a polyatomic interference, magnetic sector ICP-MS does not have sufficient resolution to separate the 2 isobars, so a different approach is necessary. In this study, a quadrupole ICP-MS (Agilent 7700x) with an Octopole Reaction System (ORS) was used to remove the Xe interference on ^{129}I by reaction with oxygen gas in the ORS cell.

Instrumentation

The Agilent 7700x ICP-MS features a 3rd generation ORS cell (ORS^3), which features a longer, narrower octopole, and operates at higher frequency, higher cell gas flow rates, and higher collision energy than in previous ORS versions [1]. In combination, these enhancements give better interference removal efficiency in both collision and reaction modes. The ORS^3 cell operates effectively in both collision mode, using an inert collision gas (helium) with kinetic energy discrimination (KED), and reaction mode, using a reactive gas such as hydrogen. In this study, the ORS^3 was operated in reaction mode, using oxygen as a reaction gas. Oxygen reacts with Xe, converting Xe$^+$ ions to Xe atoms by charge transfer,

and also removes the ^{127}IH$_2$ overlap on ^{129}I by chemical reaction, thereby removing both the interferences on ^{129}I. Helium was also added to the cell to thermalize the ion beam. This minimizes the high mass tail of the ^{127}I peak, which might otherwise contribute to the signal measured at m/z 129 when ^{127}I is present at high concentration. The two cell gases (oxygen and helium) can be added as a pre-mixed blend or, for greater flexibility, added separately using independent mass flow controllers. The latter approach was used in this work, utilizing an optional low-flow 3rd cell gas controller. A standard Agilent glass concentric nebulizer and double-pass quartz spray chamber cooled to 2 °C were used for sample introduction. In order to ensure the chemical stability of iodine in aqueous solutions, samples are typically prepared in a basic diluent, such as tetramethyl ammonium hydroxide (TMAH). This ensures that iodine is not converted to volatile chemical forms that would rapidly be lost from the solution. Plasma parameters were automatically optimized to give 'Robust Plasma' conditions, using the pre-set plasma autotune feature in the Agilent ICP-MS MassHunter software. Robust plasma conditions are defined by a CeO$^+$/Ce$^+$ ratio of 1% or less and provide high matrix tolerance for routine use. Ion lens voltages were also autotuned for maximum sensitivity.

Optimization of oxygen flow rate
The optional low-flow 3rd cell gas mass flow controller of the 7700 Series ICP-MS can be used for several different gases and, when used for oxygen cell gas, the flow rate range is 0 to 1.12 mL/min (expressed as 0 to 100% flow, where 100% = 1.12 mL/min). Oxygen flow rate was optimized while aspirating a ^{127}I standard prepared in 0.5% TMAH (Tama Chemicals, Kawasaki, Japan) and monitoring m/z 127 and 129 (Figure 1). Assuming equal signal response for the 2 isotopes of I (127 and 129), the optimum cell gas flow rate was identified from the rate that gave the lowest background equivalent concentration (BEC) at m/z 129, using the measured ^{127}I sensitivity to calculate the BEC for ^{129}I. The lowest ^{129}I BEC achieved was 0.6 ng/L (ppt), obtained at an oxygen gas flow rate of 90% of maximum (1.01 mL/min), demonstrating the effective removal of the Xe and IH$_2$ interferences. Figure 1 shows the cell gas optimization plot.
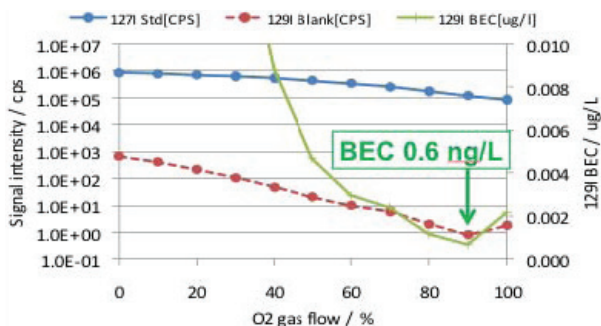
Figure 1. Profile of ^{127}I sensitivity, m/z 129 background and ^{129}I BEC versus oxygen flow rate

The Xe concentration in high purity argon varies depending on the Ar source (Xe is generally higher in bottled Ar gas than in liquid Ar tanks), but Xe peaks are always present at significant levels in ICP-MS spectra. The effectiveness of the ORS[3] in removing this Xe signal is demonstrated visually from the log scale spectra shown in Figure 2.
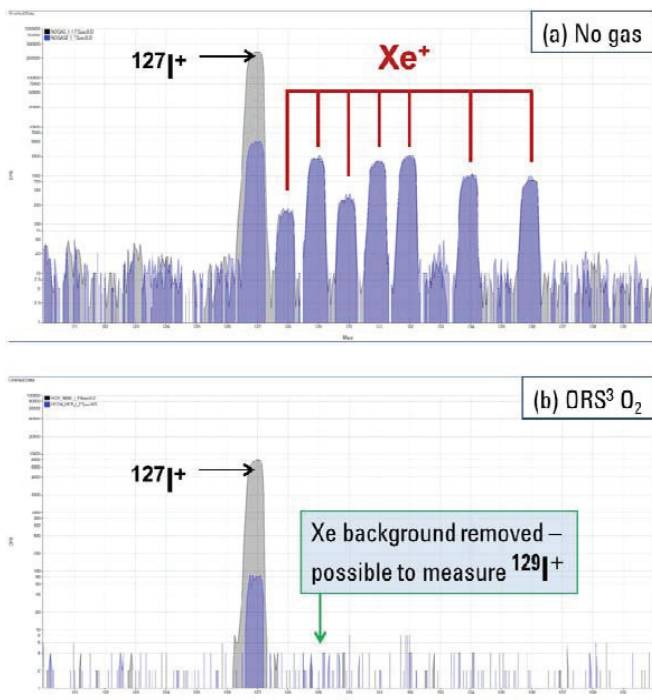
Figure 2. Mass spectra at mass range m/z 120–140 in (a) no gas mode and (b) oxygen reaction mode. In each case, the grey spectrum is 10 µg/L ^{127}I and the overlaid blue spectrum is the blank.

The upper spectrum (a) in no gas mode (no oxygen cell gas flow) clearly shows the Xe background arising from the Ar plasma gas and the background contribution from the polyatomic ion $^{127}IH_2{}^+$ that is produced in the plasma during the analysis of real samples. The grey spectrum is from a 10 µg/L ^{127}I solution, and the overlaid blue spectrum is from a blank. Switching on the cell gases (b) decreases sensitivity but the Xe^+ peaks disappear, as oxygen converts Xe^+ to Xe via a thermodynamically favorable charge transfer reaction ($Xe^+ + O_2 \rightarrow Xe + O_2{}^+$; k = 1.1x10^{-10}), freeing m/z 129 for the measurement of ^{129}I. Again, the grey spectrum is from the 10 µg/L ^{127}I solution, while the overlaid blue spectrum is from the blank, showing a small amount of memory from the iodine standard previously run. In oxygen reaction mode, m/z 131 also becomes available, allowing for the trace measurement of ^{131}I, though this is not particularly useful since its half-life is only 8 days.

Table 1 shows the ICP-MS operating parameters (at optimum oxygen flow rate). Total cell gas flow rate was 5.01 mL/min (4 mL/min He plus 1.01 mL/min oxygen).

Table 1. ICP-MS operating parameters

Parameter	Value
RF power (W)	1550
Sampling depth (mm)	8
Carrier gas (L/min)	1.05
Spray chamber temperature (°C)	2
He gas flow (mL/min)	4
Oxygen flow (mL/min)	1.01
KED (V)	10

Calibration standards
Calibration standards were prepared by diluting ^{129}I isotopic standards NIST SRM 3231 Level I and II (NIST, Gaithersburg MD, USA) with 0.5% TMAH in deionized water. The certified value for the $^{129}I/^{127}I$ ratio is 0.981x10^{-6} ± 0.012x10^{-6} in Level I, and 0.982x10^{-8} ± 0.012x10^{-8} in Level II. An intermediate standard with a $^{129}I/^{127}I$ ratio at the 10^{-7} level was prepared by spiking the Level I standard solution with ^{127}I at the appropriate concentration using a potassium iodide solution. The rinse solution was 1% TMAH.

Analytical data

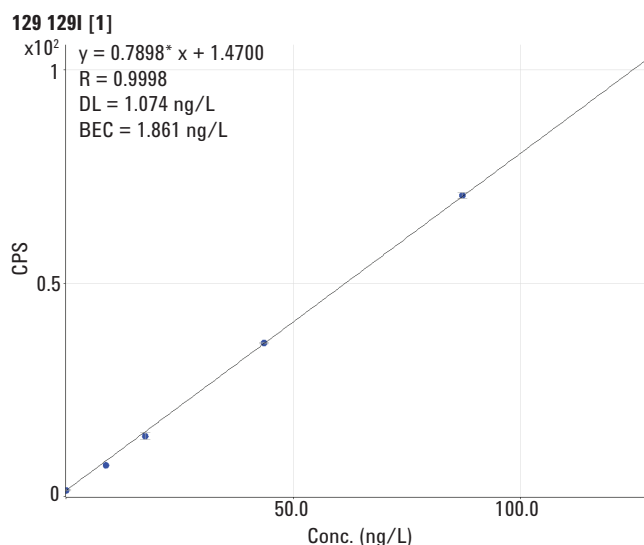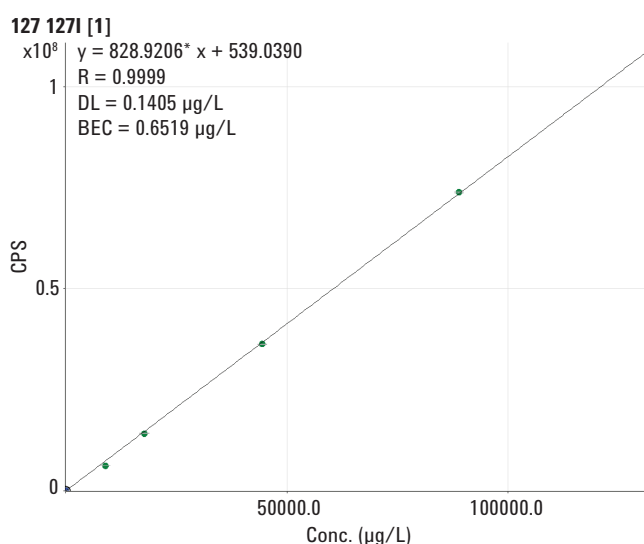### Measurement of the NIST 3231 level I standard

In order to confirm the applicability of the method to measurement of ^{129}I at varying concentration levels, the ^{129}I/^{127}I ratio was measured in 4 different solutions containing NIST 3231 at different concentrations, as shown in the data in Table 2. In the case of the highest dilution (NIST 3231 diluted x100), ^{129}I was present at the single figure ppt level. For each solution, 5 replicate measurements of the ^{129}I/^{127}I ratio were acquired, with a total data acquisition time of 10 minutes for the 5 replicates. After subtracting the reagent blank, the measured ^{129}I/^{127}I ratio corresponded well with the certified value of 0.981×10^{-6} (9.81×10^{-7}) at all concentrations. RSD values were higher than is typically achieved for a more conventional isotope ratio measurement, due to the very low count rate measured for ^{129}I, although the RSD improved to 1.5% in the x10 diluted standard as the ^{129}I count rate increased to 70 cps.

Table 2. NIST 3231 Level I — measured iodine 129/127 ratio for each dilution. (Integration time was 0.3 s for m/z=127 and 15 s for m/z=129.)

Dilution factor	^{127}I (cps)	^{129}I (cps)	^{129}I/^{127}I	^{129}I/^{127}I (average)	RSD (%)
100	6224116	6.1	9.80×10^{-7}		
	6092355	6.3	1.03×10^{-6}		
	6073353	6.4	1.05×10^{-6}	9.81×10^{-7}	8.6
	6125790	6.2	1.01×10^{-6}		
	6099791	5.1	8.37×10^{-7}		
50	14044748	12.3	8.76×10^{-7}		
	13933138	13.4	9.64×10^{-7}		
	13475103	13.6	1.01×10^{-6}	9.93×10^{-7}	7.8
	14128483	15.0	1.06×10^{-6}		
	14144548	15.0	1.06×10^{-6}		
20	36305910	33.8	9.32×10^{-7}		
	35573975	32.9	9.24×10^{-7}		
	36062147	36.4	1.01×10^{-6}	9.62×10^{-7}	3.9
	36295813	36.0	9.93×10^{-7}		
	36050890	34.3	9.51×10^{-7}		
10	75347525	72.6	9.64×10^{-7}		
	75216132	74.5	9.90×10^{-7}		
	73965391	71.2	9.62×10^{-7}	9.68×10^{-7}	1.5
	73792267	71.9	9.74×10^{-7}		
	74307176	70.7	9.52×10^{-7}		

Calibration plots for ^{127}I and ^{129}I

In order to confirm the calibration linearity for both iodine isotopes, the different dilutions of NIST 3231 Level I were processed as calibration standards, and the calibration plots generated are shown in Figure 3. Excellent linearity was achieved for both isotopes. The BECs for ^{127}I and ^{129}I were 0.65 μg/L and 1.9 ng/L, while the detection limits (3σ, n=10) for ^{127}I and ^{129}I were 0.14 μg/L and 1.1 ng/L, respectively. The BEC and DL for ^{127}I were higher due to carryover from previous measurements.

127 127I [1]

$y = 828.9206^* x + 539.0390$
$R = 0.9999$
$DL = 0.1405$ μg/L
$BEC = 0.6519$ μg/L

129 129I [1]

$y = 0.7898^* x + 1.4700$
$R = 0.9998$
$DL = 1.074$ ng/L
$BEC = 1.861$ ng/L

Figure 3. Calibration plots for ^{127}I (top) and ^{129}I (bottom) obtained from multiple dilutions of NIST 3231 Level I

Analysis of an 'intermediate' NIST 3231 standard and NIST 3231 level II

In order to validate the method, an 'intermediate' standard (nominal $^{129}I/^{127}I$ ratio 10^{-7}) was prepared by diluting NIST 3231 Level I 1:100 in a solution of potassium iodide (88.9 mg/L iodine). Measurement of the $^{129}I/^{127}I$ ratio in this intermediate standard gave good agreement with the target $^{129}I/^{127}I$ value of $1x10^{-7}$ (Table 3). NIST 3231 Level II ($^{129}I/^{127}I = 0.982 \times 10^{-8}$) was also measured and good agreement was again obtained (Table 4), though with higher RSD as the ^{129}I concentration approached the detection limit of the method.

Nevertheless, the fast, direct measurement at the 10^{-8} level for $^{129}I/^{127}I$ using standard liquid sample introduction and without sample preparation impressively demonstrates the capability of this method for rapid screening of samples for ^{129}I.

To confirm that overlap of ^{127}I on ^{129}I does not occur when ^{127}I is present at high concentration, spectra of NIST 3231 Level I, the prepared intermediate NIST 3231 standard, and a blank containing ^{127}I at the same concentration as in the standards (88.9 mg/L (ppm)) were acquired. The overlaid linear scale spectra are shown in Figure 4. Note there is no overlap of the ^{127}I high mass side peak tail on m/z 129. While some iodine hydride ($^{127}I^1H$) can be seen at m/z 128, there is no IH_2 observed at m/z 129, as had been proposed in a previous study [2].

Table 3. Measurement of the 'intermediate' NIST 3231 standard

Dilution factor	^{127}I (cps)	^{129}I (cps)	$^{129}I/^{127}I$	$^{129}I/^{127}I$ (average)	RSD (%)
I 88.9 mg/L added 1/100 diluted NIST 3231 (expected 10^{-7})	76548859	7.3	$0.95x10^{-7}$		
	76618521	8.3	$1.08x10^{-7}$		
	76523125	6.8	$0.89x10^{-7}$	$0.99x10^{-7}$	7.9
	76849756	8.1	$1.05x10^{-7}$		
	76052388	7.6	$1.00x10^{-7}$		

Table 4. Measurement NIST 3231 Level II

Dilution factor	^{127}I (cps)	^{129}I (cps)	$^{129}I/^{127}I$	$^{129}I/^{127}I$ (average)	RSD (%)
NIST 3231 Level II $^{129}I/^{127}I$ =$0.982x10^{-8}$	536908532	4.0	$0.74x10^{-8}$		
	526648579	5.9	$1.13x10^{-8}$		
	518477906	7.3	$1.41x10^{-8}$	$1.07x10^{-8}$	22.4
	508547526	5.2	$1.03x10^{-8}$		
	503530493	5.3	$1.05x10^{-8}$		

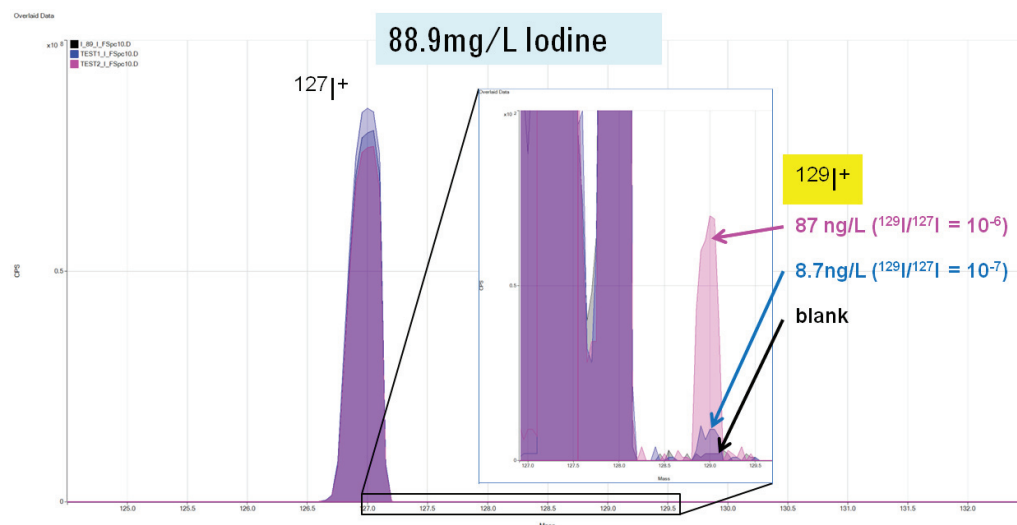**Figure 4.** Overlaid spectra of 88.9 mg/L ^{127}I blank, NIST 3231 Level I (87 ng/L ^{129}I), and the intermediate standard (8.7 ng/L ^{129}I)

Conclusions

Improvements in the performance of ICP-MS for the direct measurement of ^{129}I in solution have been made possible by the use of an Agilent 7700x ICP-MS, featuring an ORS^3 cell operated in oxygen reaction mode. The new design features of the ORS^3 cell offer improved interference removal capability such that the Xe background due to the presence of Xe in the Ar plasma gas could be completely removed. A ^{129}I detection limit of 1.1 ppt was obtained and excellent abundance sensitivity prevented spectral overlap on ^{129}I from the presence of ppm levels of ^{127}I. NIST standards with different $^{129}I/^{127}I$ ratios and at multiple concentrations including the low level NIST 3231 Level II with a $^{129}I/^{127}I$ ratio of 10^{-8} were accurately measured without any sample preparation and with a standard liquid sample introduction system. The method is applicable to routine use and is capable of high sample throughput.

References

1. Enhanced Helium Mode Cell Performance for Improved Interference Removal in ICP-MS. Agilent publication, 5990-7573EN, February 2011, available from www.agilent.com/chem/icpms

2. Bienvenue et al, CJASS, Volume 49, No. 6, 423 (2004)

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