

Determination of Iodine-129 in Aqueous Environmental Samples by ICP-MS with High Energy Oxygen Collision/Reaction Cell Technique. (PC-330)

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Introduction

Iodine-129 is a long-lived radionuclide (half life = 15.7My) which has been released continuously into the environment as a result of human nuclear activities such as nuclear weapons tests, accidents at nuclear power plants and especially by emissions from spent nuclear fuel reprocessing plants.

Radiochemical analysis, neutron activation analysis with radiochemical separation (RNAA) and accelerator mass spectrometry (AMS) are commonly used to measure iodine-129 for environmental monitoring.

Inductively coupled plasma mass spectrometry (ICP-MS) has also been used for the determination of iodine-129. However, the determination of iodine-129 in environmental samples is very difficult by ICP-MS due to its relatively low sensitivity, high background caused by ^{129}Xe impurities in the argon plasma gas and possible polyatomic interference from $^{127}\text{IH}_2^+$. In this study, in order to overcome these challenges, a newly developed high energy collision/reaction cell (CRC) technique using oxygen as the cell gas was applied to determine ultratrace levels of iodine-129 in aqueous samples without additional sample preparation. This study aimed to achieve the measurable ratio of $^{129}\text{I}/^{127}\text{I} = 10^{-7}$ or a detection limit of 0.01ug/L for ^{129}I using our new method.

Experimental

Instrumentation

Agilent's 7700x ICP-MS was used throughout this study. The 7700x incorporates Agilent's 3rd generation CRC, called the Octopole Reaction System (ORS³). The ORS³ was designed to use He mode with Kinetic Energy Discrimination (KED) as standard, although reactive gases such as H_2 or NH_3 can be also used. In this study, oxygen gas was applied to reduce Xe^+ ions via charge transfer reaction. He gas was also added to improve abundance sensitivity by thermalizing the I^+ ion energy. These reaction/collision gases are introduced to ICP-MS separately and mixed into ORS cell using independent mass flow controllers. A standard Micromist glass concentric nebulizer and Scott double-pass quartz spray chamber cooled to 2 °C were used for solution introduction to the ICP-MS.

Reference Materials and Calibration Standards

NIST (National Institute of Standards & Technology, Gaithersburg MD, USA) Standard Reference Material 3231, Iodine-129 Isotopic Standards, Level I and II, were used as calibration standards by diluting with de-ionized Milli-Q water and 0.5% TMAH alkaline solution. Level I Certified Value for $^{129}\text{I}/^{127}\text{I} = 0.981 \times 10^{-6} \pm 0.012 \times 10^{-6}$, Level II = $0.982 \times 10^{-8} \pm 0.012 \times 10^{-8}$. An intermediate standard with a $^{129}\text{I}/^{127}\text{I}$ ratio of 10^{-7} was prepared in our lab by spiking the Level 1 reference material with ^{127}I potassium iodide at the appropriate concentration.

Operating Conditions

Plasma conditions were auto-tuned prior to analysis by selecting "Robust Plasma" in the ICP-MS MassHunter software. Robust plasma conditions provide a hot plasma ($\text{CeO}^+/\text{Ce}^+ \sim 1\%$). Ion lens voltages were also auto-tuned for maximum sensitivity.

Results and Discussion

Optimization of Oxygen Cell Gas Flow

The oxygen gas flow rate was optimized by varying the O_2 flow as a percentage over the range of the mass flow controller (0–1.12mL/min for oxygen) and monitoring the ^{127}I , ^{129}I signal and blank intensity. Results are shown in Figure 1. The lowest background equivalent concentration (BEC) was obtained at an O_2 gas flow rate of 90% corresponding to the optimum signal to background of 0.6 ng/L for ^{129}I .

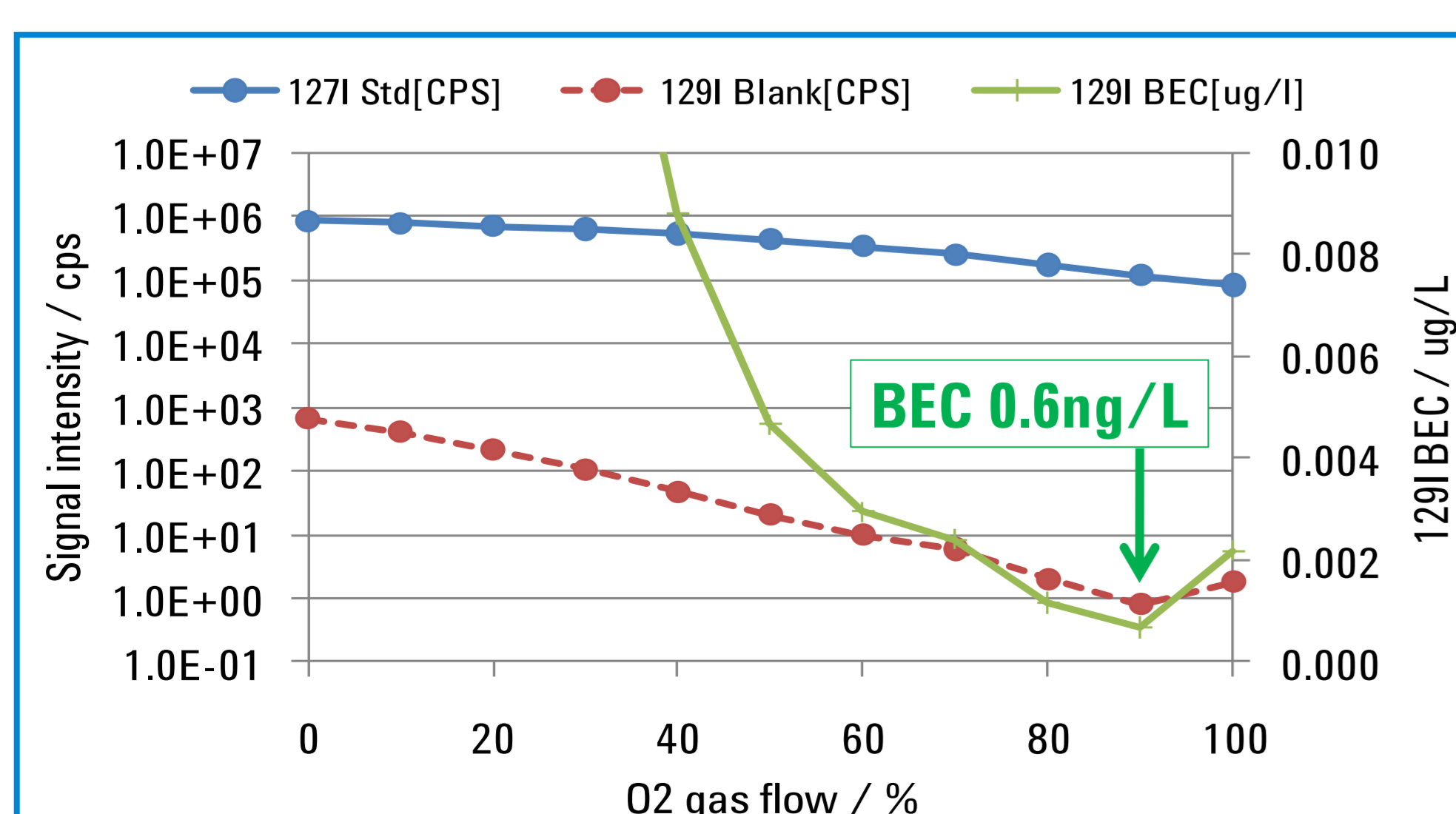


Figure 1 Profile of $^{127}\text{I}^+$, $^{129}\text{Xe}^+$ and ^{129}I BEC. The sensitivity of ^{129}I is assumed to be the same as ^{127}I . Actual O_2 flow is $(\%/100) \times 1.12$ mL/min.

Optimized instrumental parameters for high energy oxygen CRC mode are shown in Table 1. High energy mode uses a more negative cell entrance voltage in order to accelerate ions to sufficiently high kinetic energy for the necessary reactions to occur.

Table 1 Instrumental Parameters for ICP-MS.

Parameter	Value	Units
RF Power	1550	W
Sampling Depth	8	mm
Carrier Gas	1.05	L/min
Spraychamber Temp	2	Deg C
Extract 1	0	V
Extract 2	-190	V
Omega Bias	-80	V
Omega Lens	7	V
Cell Entrance	-130	V
Cell Exit	-140	V
Deflect	-55	V
Plate Bias	-140	V
He Gas Flow	4	mL/min
Oxygen Flow	90	% of max
Octopole Bias	-80	V
Quadrupole Bias	-70	V

Xe^+ Background Removal by Reaction with O_2

Figure 2 compares the plasma background spectrum in no gas mode versus high energy oxygen mode. Oxygen reacts with xenon ions via charge transfer ($\text{Xe}^+ + \text{O}_2 \rightarrow \text{Xe} + \text{O}_2^+$, $k_r = 1.1 \times 10^{-10}$). As a result, the background at m/z 129 is reduced to the level of the instrument background.

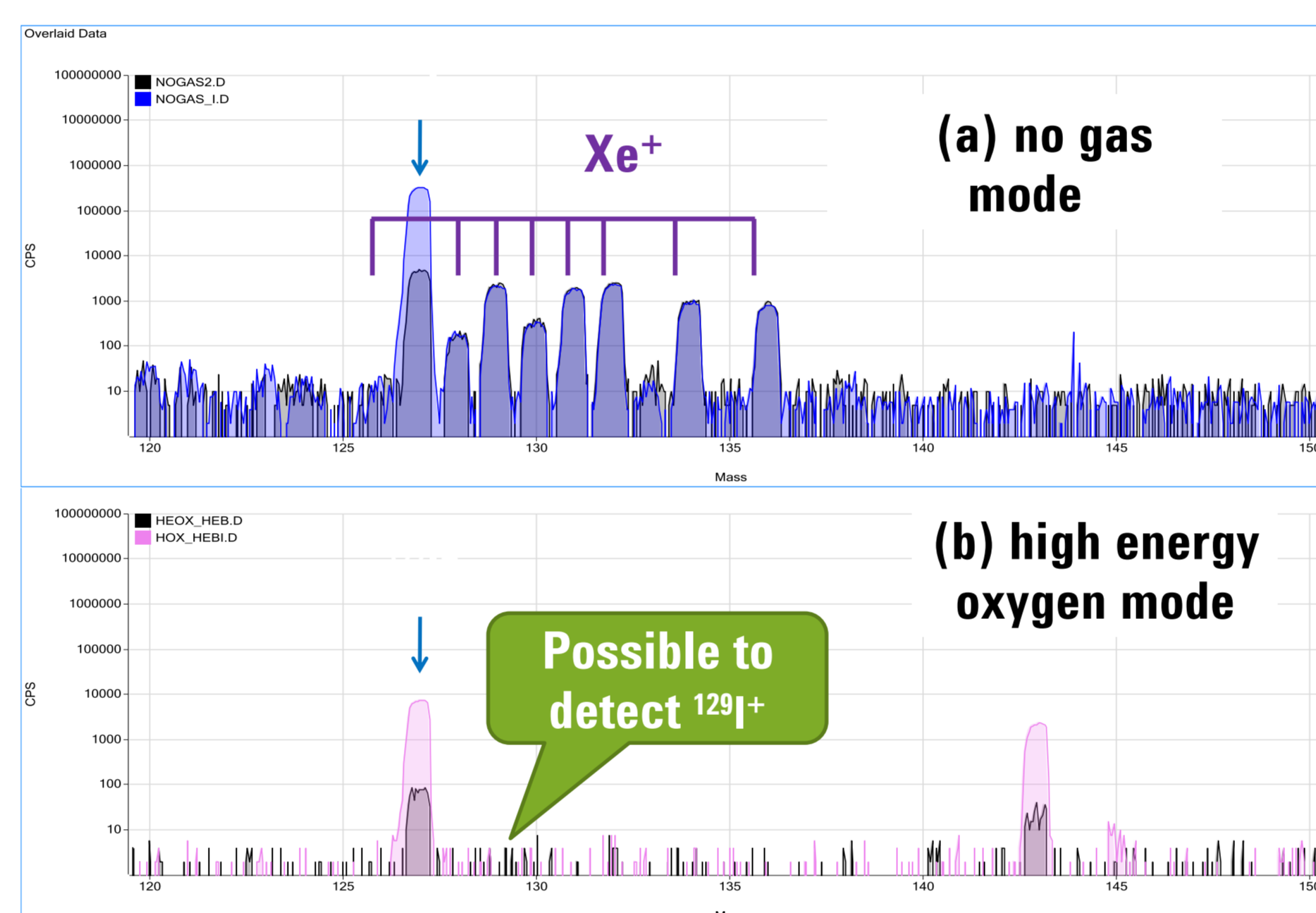


Figure 2 Mass spectra of I and Xe in 10ug/L Iodine -127 solution (a) conventional no cell gas mode (b) high energy O_2 mode.

Analysis of NIST 3231 SRM Level I ($^{129}\text{I}/^{127}\text{I} = 10^{-6}$)

The $^{129}\text{I}/^{127}\text{I}$ ratio of diluted NIST3231 SRM at 4 different concentrations was analyzed using the newly developed method. The results are summarized in Table 2. After subtracting the ^{129}I blank, the measured $^{129}\text{I}/^{127}\text{I}$ ratio of NIST 3231 SRM corresponded well with the certified value of 0.981×10^{-6} as reported in the certificate.

Table 2 Analytical result of NIST 3231 Level I.

Dilution Factor	^{127}I (cps)	^{129}I (cps)	$^{129}\text{I} / ^{127}\text{I}$	$^{129}\text{I} / ^{127}\text{I}$ (average)	RSD(%)
100	6224116	6.1	9.80E-07	9.81E-07	8.6
	6092355	6.3	1.03E-06		
	6073353	6.4	1.05E-06		
	6125790	6.2	1.01E-06		
	6089791	5.1	8.37E-07		
50	14044748	12.3	8.76E-07	9.93E-07	7.8
	13933138	13.4	9.64E-07		
	13475103	13.6	1.01E-06		
	14128483	15.0	1.06E-06		
	14144548	15.0	1.06E-06		
20	36305910	33.8	9.32E-07	9.62E-07	3.9
	35573975	32.9	9.24E-07		
	36062147	36.4	1.01E-06		
	36295813	36.0	9.93E-07		
	36050890	34.3	9.51E-07		
10	75347525	72.6	9.64E-07	9.68E-07	1.5
	75216132	74.5	9.90E-07		
	73965391	71.2	9.62E-07		
	73792267	71.9	9.74E-07		
	74307176	70.7	9.52E-07		

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

In order to check the linearity of both isotopes, diluted NIST 3231 SRM in different concentrations in 0.5% TMAH alkaline solutions were analyzed as calibration standards. Calibration curves are shown in Figure 3. From Figure 3, BEC for ^{127}I and ^{129}I were 0.65ug/L and 1.9ng/L, detection limit (3σ , $n=10$) for ^{127}I and ^{129}I were 0.14ug/L and 1.1ng/L, respectively.

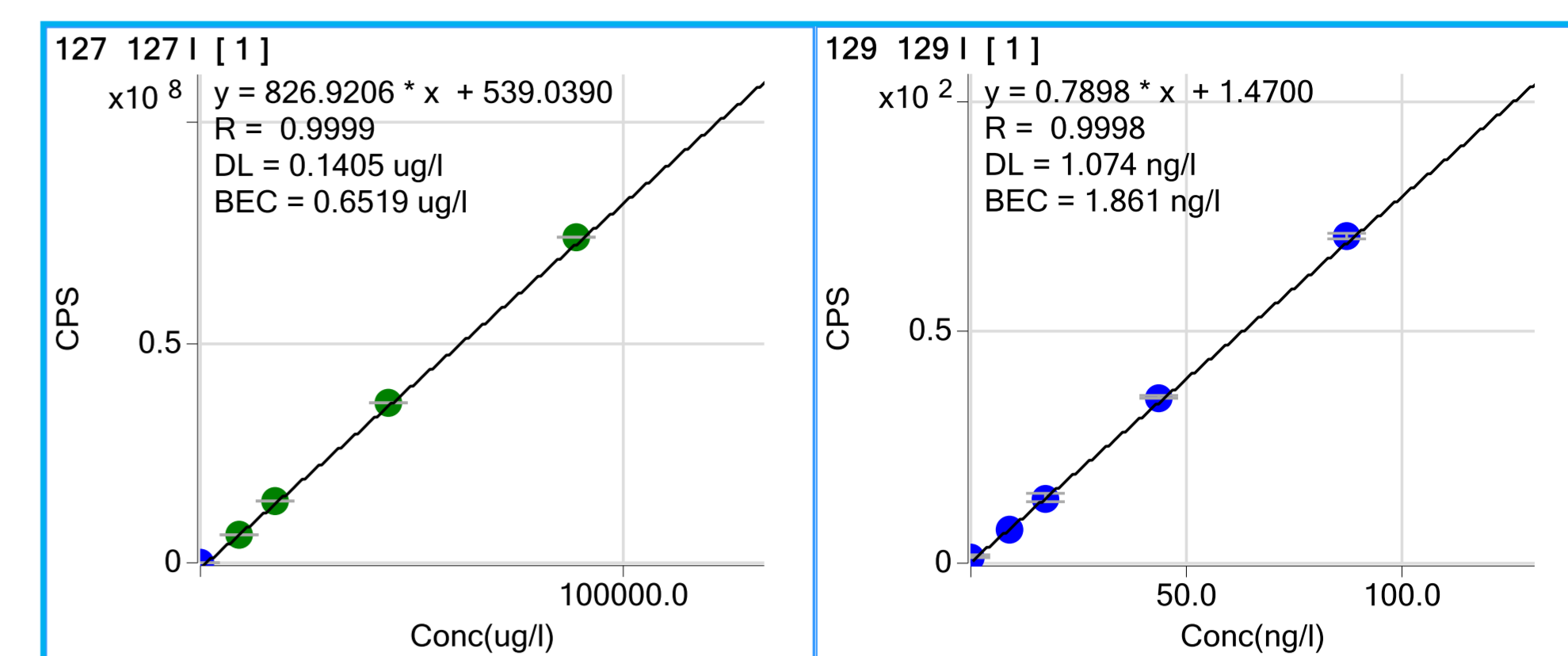


Figure 3 Calibration curves for ^{127}I and ^{129}I obtained from diluted NIST 3231 SRM (Level I).

Analysis of "modified" NIST 3231 ($^{129}\text{I}/^{127}\text{I} = 10^{-7}$) and NIST 3231 Level II ($^{129}\text{I}/^{127}\text{I} = 10^{-8}$)

In order to validate the method when the ratio of $^{129}\text{I}/^{127}\text{I} = 10^{-7}$, the intermediate NIST 3231 sample prepared in our lab was analyzed using the new method. The analytical results are shown in Table 3 and the mass spectra for each concentration are shown in Figure 4. The developed method was also applied to the analysis of NIST 3231 Level II ($^{129}\text{I}/^{127}\text{I} = 10^{-8}$).

Table 3 Analytical result of Lab "modified" NIST 3231 Level I.

sample	^{127}I (cps)	^{129}I (cps)	$^{129}\text{I} / ^{127}\text{I}$	$^{129}\text{I} / ^{127}\text{I}$ (average)	RSD(%)
I 88.9mg/L added 1/100 diluted NIST 3231 (expected 10^{-7})	76548859	7.3	9.50E-08	9.96E-08	7.9
	76618521	8.3	1.08E-07		
	76523125	6.8	8.89E-08		
	76849756	8.1	1.05E-07		
	76052388	7.6	1.00E-07		

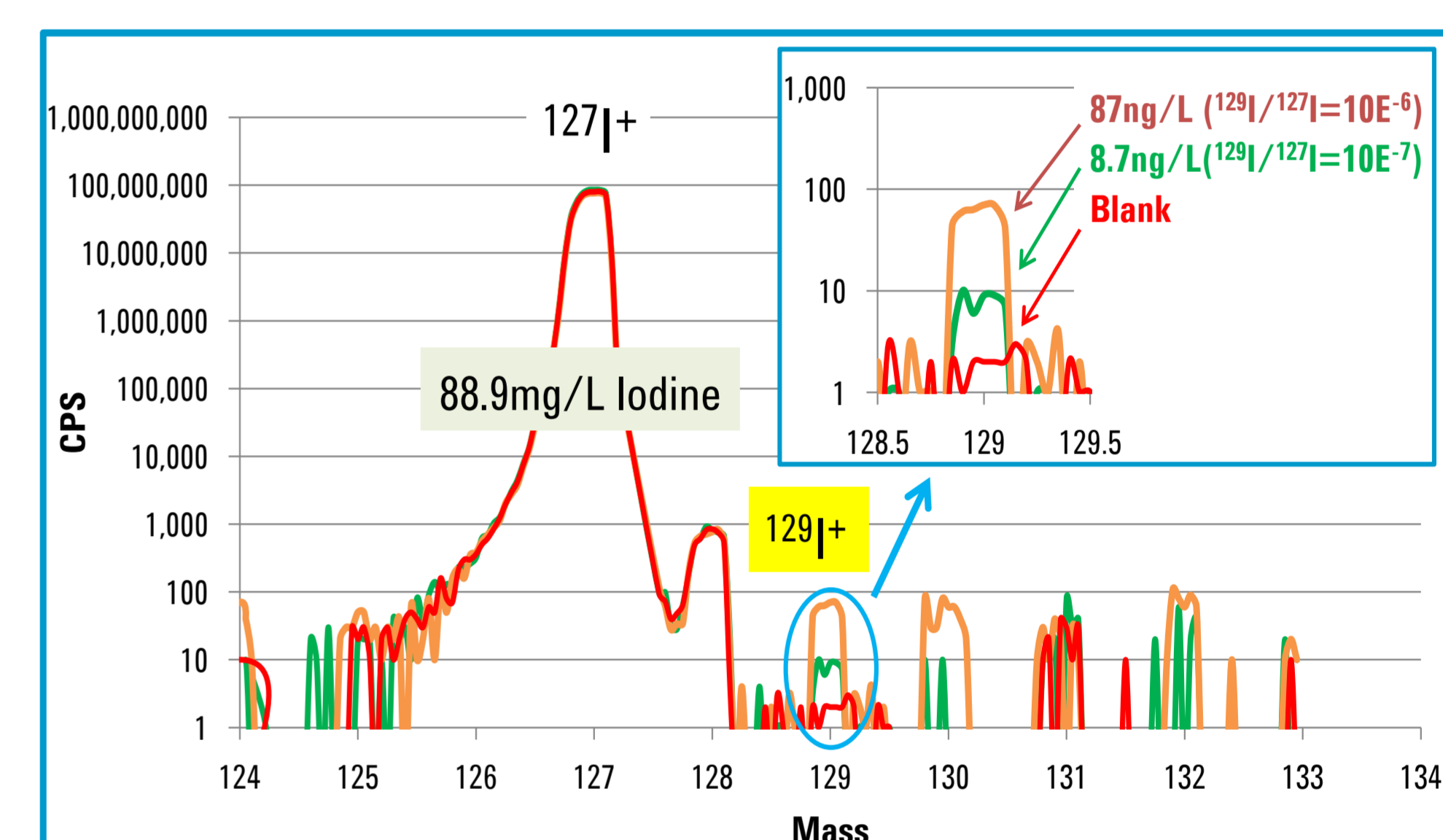


Figure 4 Overlaid mass spectra of blank, 2 levels of ^{127}I and ^{129}I made from NIST 3231 Level I. Concentrations of Iodine are 88.9mg/L for ^{127}I , 87ng/L, 8.7ng/L for ^{129}I , respectively.

Table 4 Analytical results for NIST 3231 Level II.

sample	^{127}I (cps)	^{129}I (cps)	$^{129}\text{I} / ^{127}\text{I}$	$^{129}\text{I} / ^{127}\text{I}$ (average)	RSD(%)
NIST 3231 LEVEL II $^{129}\text{I} / ^{127}\text{I}$ = 0.982×10^{-8}	536908532	4.0	7.43E-09	1.07E-08	22.4
	526648579	5.9	1.13E-08		
	518477906	7.3	1.41E-08		
	508547526	5.2	1.03E-08		
	503530493	5.3	1.05E-08		

Conclusions

Using the high energy oxygen collision/reaction cell technique for ICP-MS, we demonstrated:

- $^{129}\text{Xe}^+$ background ions were significantly reduced
- Achieved analysis of $^{129}\text{I}/^{127}\text{I}$ ratio of c.a. 1×10^{-6} ratio in NIST 3231 SRM Level I (certified value of $^{129}\text{I}/^{127}\text{I} = 0.981 \times 10^{-6}$).
- Achieved analysis of $^{129}\text{I}/^{127}\text{I}$ ratio of c.a. 1×10^{-7} ratio in modified NIST 3231 SRM Level I (expected value of $^{129}\text{I}/^{127}\text{I} = 1 \times 10^{-7}$).
- Calibration curves for ^{127}I , and ^{129}I show good linearity, respectively. This means that external calibration can be routinely applied to the analysis of ^{127}I and ^{129}I .
- Detection limits (3σ , $n = 10$) for ^{127}I and ^{129}I are 0.14ug/L and 1.1ng/L, respectively.
- May need to subtract blank for $^{127}\text{IHH}^+$ for determination of ^{129}I due to some residual signal from $^{127}\text{IHH}^+$.

Finally, we succeeded in our initial goal of measuring the ratio of $^{129}\text{I}/^{127}\text{I} = 10^{-7}$ in aqueous environmental sample solutions using the Agilent 7700x ICP-MS with high energy oxygen collision/reaction technique.

For aqueous sample solutions, the newly developed method can be applied as a simple, direct and rapid analysis technique for routine measurement of both 127 and 129 iodine.