

The ultratrace determination of iodine 129 using the Agilent 8800 Triple Quadrupole ICP-MS in MS/MS mode

Application note

Nuclear

Authors

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Introduction

Iodine 129 (^{129}I) is a long-lived radionuclide (half-life 15.7 My), 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. ICP-MS is a fast and sensitive technique, requiring minimal sample preparation for the measurement of ^{129}I and also the analytically important $^{129}\text{I}/^{127}\text{I}$ ratio in environmental samples. However, this is a challenging application for two reasons: ^{129}I suffers an isobaric spectral interference from ^{129}Xe (present as an impurity in the argon plasma gas), and ^{129}I is present at extremely low concentrations. Consequently, high sensitivity and low background are critical for the accurate measurement of the ^{129}I concentration and the $^{129}\text{I}/^{127}\text{I}$ ratio.



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In previous work [1], the ^{129}Xe interference was successfully eliminated using a single quadrupole ICP-MS (ICP-QMS) with an octopole reaction cell, operated in reaction mode. Using O_2 cell gas, Xe^+ ions are converted to Xe atoms by charge transfer, eliminating them from the spectrum. This approach enabled a detection limit (DL) of 1.1 ppt for ^{129}I and the $^{129}\text{I}/^{127}\text{I}$ ratio in NIST 3231 SRM Level I and II standards was successfully measured. Some limitations of ICP-QMS were also noted. Due to the extremely large difference in isotopic abundance ($^{129}\text{I}/^{127}\text{I}$ of 10^{-6} - 10^{-8}) that is common to many radionuclide measurements, overlap of the trace peak by the major peak becomes an issue. The ability of an MS to resolve adjacent peaks is referred to as abundance sensitivity and trace analysis of ^{129}I stretches the limits of ICP-QMS abundance sensitivity performance. In the previous work, helium gas was also added to the cell to thermalize the ion beam and improve abundance sensitivity. In this case, the trace peak was 2 amu higher than the major peak, and high mass tailing was reduced by He addition to allow accurate measurement. Low mass tailing is much more severe in ICP-QMS, and had the trace peak been 1–2 amu *lower* than the major peak, it would have not been possible to measure.

Since the previous work was completed, Agilent has developed the 8800 Triple Quadrupole ICP-MS (commonly abbreviated to ICP-QQQ). The 8800 features an additional quadrupole mass filter (Q1), situated in front of the Octopole Reaction System (ORS³) cell and quadrupole mass filter (now called Q2), in an MS/MS configuration. In ICP-MS/MS, Q1 operates as a mass filter, allowing only the target analyte mass to enter the cell, and rejecting all other masses. Because plasma and matrix ions are eliminated by Q1, the reaction efficiency is greatly enhanced and the reaction pathways and product ions remain consistent across a wide range of sample matrices. The increase in sensitivity in reaction mode with the 8800 compared to ICP-QMS, and the consistent interference removal performance regardless of sample type are both important benefits for this application. In addition, the four-stage vacuum system of the 8800 gives a lower final vacuum and therefore a lower background, which improves ^{129}I DL and $^{129}\text{I}/^{127}\text{I}$ ratio precision. Another key benefit of the 8800 for radionuclide isotope ratio measurement applications is

the tremendous improvement in abundance sensitivity over ICP-QMS. Because the abundance sensitivity of an MS/MS is the product of the abundance sensitivities of the two quadrupoles, the 8800 demonstrates the highest abundance sensitivity ever seen in ICP-MS, at $<10^{-10}$.

The purpose of this study was to apply the 8800, in MS/MS mode, to the determination of ^{129}I , improving both the ^{129}I DL and $^{129}\text{I}/^{127}\text{I}$ ratio precision over the previous work, while achieving an abundance sensitivity far better than previously achieved by ICP-QMS.

Experimental

Instrumentation

An Agilent 8800 Triple Quad ICP-MS was used for this study. The standard sample introduction system consisted of a glass concentric nebulizer, a Peltier-cooled quartz double-pass Scott-type spray chamber, and a one-piece quartz torch with 2.5 mm internal diameter (ID) injector. Table 1 shows the ICP-QQQ operating parameters.

Table 1. Agilent 8800 ICP-QQQ operating parameters

| Parameter | Value |
|---------------------------|--------------|
| RF power | 1550 W |
| Sampling depth | 8 mm |
| Carrier gas flow rate | 1.05 L/min |
| Spray chamber temperature | 2 °C |
| Cell gas | O_2 |
| Cell gas flow | 0.7 mL/min |

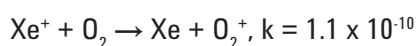
Reference materials and calibration standards

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 Level I certified value for $^{129}\text{I}/^{127}\text{I} = 0.981 \times 10^{-6} \pm 0.012 \times 10^{-6}$ and the Level II certified value = $0.982 \times 10^{-8} \pm 0.012 \times 10^{-8}$. A blank iodine matrix (no ^{129}I) was prepared from potassium iodide to give a concentration of 889 mg/L iodine (^{127}I only), that was then diluted as needed. These standards were used to check the linearity of the iodine isotope response and to measure the $^{129}\text{I}/^{127}\text{I}$ ratio.

Results and discussion

Xe⁺ interference removal by reaction with oxygen

To highlight the benefits of the MS/MS configuration compared to ICP-QMS for this application, the 8800 was first operated with Q1 set to allow all ions to pass through to the cell — that is, Q1 functions as a simple ion guide. This essentially replicates the characteristics of a traditional ICP-QMS system. Using the ¹²⁷I blank solution (diluted to 8.89 mg/L iodine), data was acquired both in no gas mode and in reaction mode using O₂ as the reaction gas. Figure 1 compares the plasma background spectrum in no gas mode versus reaction mode with O₂. O₂ reacts with Xe⁺ ions via charge transfer as follows:



Xe⁺ ions are converted to neutral Xe and therefore are removed from the spectrum. As a result, the isobaric interference from ¹²⁹Xe⁺ is reduced to the level of the instrument background, allowing ¹²⁹I to be measured. Note, however, the relatively poor abundance sensitivity of ICP-QMS — the low mass side peak of ¹²⁷I tailing into *m/z* 126 (shown in log mode). Although it does not impact the application in this case, measuring a trace peak at *m/z* 126 would be impossible.

Improved abundance sensitivity with MS/MS

The 8800 was then switched to MS/MS mode: Q1 was set to allow only ions of *m/z* 127 and 129 to pass through to the cell. Q2 was set to reject all ions except the target analyte masses (*m/z* 127 and 129). O₂ was added to the cell to remove Xe⁺ ions, as in Figure 1 (bottom). Solutions of NIST 3231 Level I and II were measured and the resulting spectra overlaid in Figure 2. Both solutions contained 88.9 mg/L ¹²⁷I.

As can be seen, the MS/MS mode spectra demonstrate abundance sensitivity far better than ICP-QMS (Figure 1), with the peak sides reaching baseline with no tailing. This vastly improved abundance sensitivity opens up new applications not previously possible with ICP-MS (either ICP-QMS or high resolution ICP-MS), for example in the trace analysis of high purity metals, clinical and petrochemical analysis, and in other radionuclide applications.

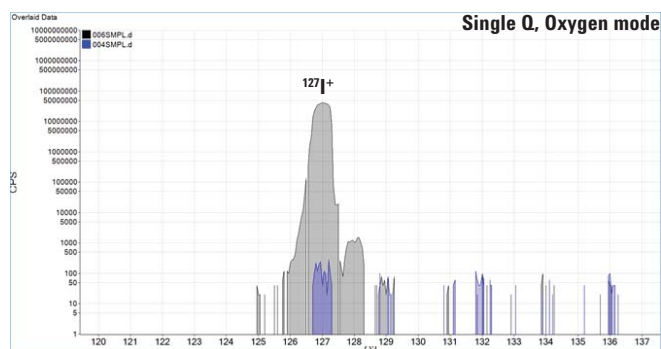
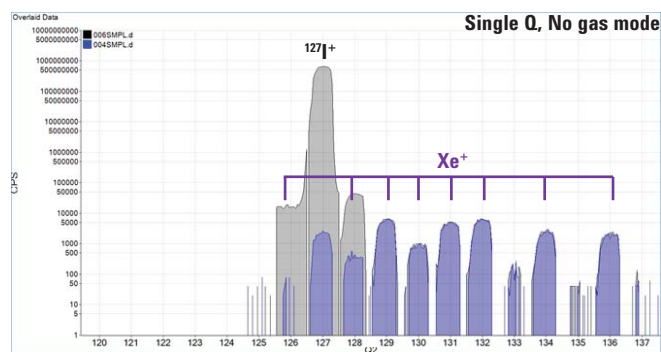


Figure 1. Mass spectra of I and Xe in an 8.89 mg/L ¹²⁷I solution. The Agilent 8800 was operated like an ICP-QMS. Top: No gas mode; Bottom: O₂ reaction mode. The overlaid blue spectrum is the blank.

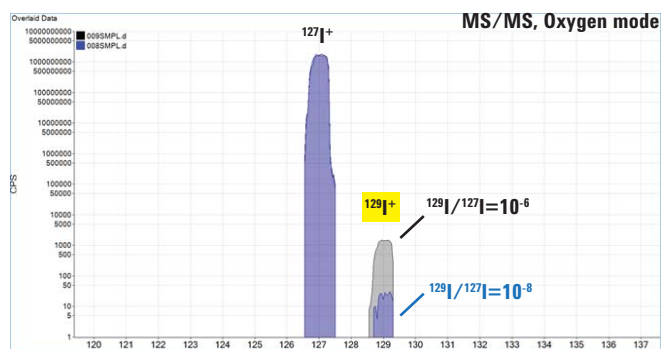


Figure 2. ¹²⁷I and ¹²⁹I measured using the Agilent 8800 in MS/MS mode with O₂ reaction gas. NIST 3231 Level I (black) and II (blue) spectra are overlaid.

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

In order to check the linearity of both iodine isotopes, different concentration solutions of NIST 3231 SRM Level I in 0.5% TMAH were prepared and analyzed as calibration standards. The calibration curves for ^{127}I and ^{129}I are shown in Figure 3. Excellent linearity was achieved in both cases. The background equivalent concentrations (BECs) for ^{127}I and ^{129}I were $2.97\ \mu\text{g/L}$ and $0.04\ \text{ng/L}$, while the detection limits (3σ , $n = 10$) for ^{127}I and ^{129}I were $0.26\ \mu\text{g/L}$ and $0.07\ \text{ng/L}$, respectively. The BEC and DL for ^{127}I were higher due to carryover from the ^{127}I solution aspirated earlier. The DL for ^{129}I was approximately 15x lower than the value obtained ($1.074\ \text{ng/L}$) in the previous work, due to the higher sensitivity and lower background level of the 8800 ICP-QQQ.

Analysis of NIST 3231 SRM Level I and II

The $^{129}\text{I}/^{127}\text{I}$ ratio of diluted NIST 3231 SRM at different concentrations was measured using the 8800 ICP-QQQ. The results are summarized in Table 2. After subtracting the ^{129}I blank, the measured $^{129}\text{I}/^{127}\text{I}$ ratio of the NIST 3231 SRM corresponded well with the certified values of 0.981×10^{-6} (Level I) and 0.982×10^{-8} (Level II). Precision was significantly improved over the previous work, especially for NIST 3231 Level II due to the superior signal/noise of the 8800.

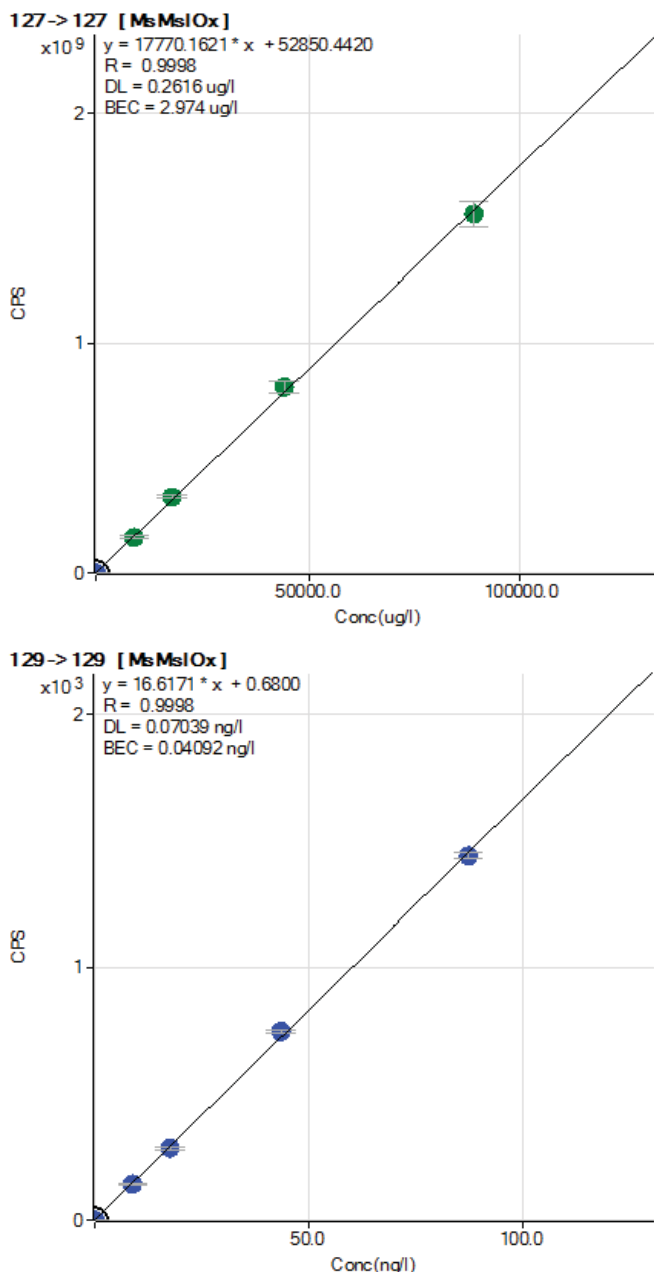


Figure 3. Calibration plot for ^{127}I (top) and ^{129}I (bottom) obtained from multiple dilutions of NIST 3231 SRM (Level I). Note the different concentration units used in these two calibration plots — $\mu\text{g/L}$ (ppb) for ^{127}I and ng/L (ppt) for ^{129}I .

Table 2. Analytical results for NIST 3231 Level I ($^{129}\text{I}/^{127}\text{I} = 0.981 \times 10^{-6}$) and Level II ($^{129}\text{I}/^{127}\text{I} = 0.982 \times 10^{-8}$)

| Sample name | Dilution factor | 127 | | | 129 | | | $^{129}\text{I}/^{127}\text{I}$ | $^{129}\text{I}/^{127}\text{I}$ (average n = 5) | RSD (%) |
|---|-----------------|-------------|-------------|---------|-------|-------------|---------|---------------------------------|--|---------|
| | | CPS | CPS average | CPS RSD | CPS | CPS average | CPS RSD | | | |
| NIST 3231 10^{-6} ($^{129}\text{I}/^{127}\text{I} = 0.981 \times 10^{-6}$) | 20 | 301,734,441 | | | 297.1 | | | 0.927×10^{-6} | | |
| | | 303,368,628 | | | 274.8 | | | 0.893×10^{-6} | | |
| | | 300,284,575 | 302,731,524 | 0.6 | 300.5 | 290.5 | 3.6 | 0.988×10^{-6} | 0.947×10^{-6} | 4.1 |
| | | 305,488,255 | | | 285.9 | | | 0.923×10^{-6} | | |
| | | 302,781,721 | | | 294.4 | | | 0.960×10^{-6} | | |
| | 10 | 594,277,896 | | | 585.6 | | | 0.971×10^{-6} | | |
| | | 592,633,576 | | | 597.4 | | | 0.994×10^{-6} | | |
| | | 590,000,723 | 592,626,739 | 0.3 | 586.5 | 589.4 | 0.8 | 0.980×10^{-6} | 0.981×10^{-6} | 0.8 |
| | | 593,387,443 | | | 588.5 | | | 0.978×10^{-6} | | |
| | | 592,834,056 | | | 588.9 | | | 0.979×10^{-6} | | |
| NIST 3231 10^{-8} ($^{129}\text{I}/^{127}\text{I} = 0.982 \times 10^{-8}$) | 10 | 608,737,949 | | | 15.1 | | | 1.12×10^{-8} | | |
| | | 608,536,242 | | | 14.8 | | | 1.07×10^{-8} | | |
| | | 602,626,536 | 605,248,499 | 0.5 | 14.2 | 14.5 | 3.3 | 0.979×10^{-8} | 1.02×10^{-8} | 7.2 |
| | | 603,091,763 | | | 13.9 | | | 0.929×10^{-8} | | |
| | | 603,250,003 | | | 14.5 | | | 1.03×10^{-8} | | |

Conclusions

The new Agilent 8800 ICP-QQQ demonstrated excellent analytical performance for this challenging application due to its superior signal/noise over ICP-QMS. Accurate determination of ultratrace levels of ^{129}I were demonstrated as well as excellent agreement with certified values for NIST 3231 iodine isotope ratios. This performance was achieved at a much better abundance sensitivity, a unique feature of MS/MS mode. While the superior abundance sensitivity of the 8800 was not essential to the determination of ^{129}I in this case, it will open up new applications in high purity metals and radionuclide measurement not currently possible by ICP-MS.

References

1. The ultratrace determination of iodine 129 in aqueous samples using the Agilent 7700x ICP-MS with oxygen reaction mode. Agilent publication 5990-8171EN, June 2011, available from www.agilent.com/chem/icpms.

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