

ICP - Mass Spectrometry

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Measurement of Iodine in Drinking Water Following GB/T-5750.5-2023 Using the NexION 1100 ICP-MS

Introduction

Iodide and iodate are two forms of iodine that can be found in water. Iodine is an essential trace element for human health, but excessive or insufficient intake can cause thyroid disorders. Iodine can also be introduced into water as a disinfectant or a disinfection by-product. Therefore, iodine analysis is important to monitor the quality and safety of drinking water.

The GB/T-5750 Standard Examination Methods for Drinking Water is a series of standards published by the Institute of Environmental and Health-related Product Safety of China and the Chinese Center for Disease Control and Prevention. This comprehensive set of standards encompasses general principles and requirements for water quality testing, along with specific methods for various parameters, including physical, chemical, organic, microbiological, and radiological aspects. The standards are based on the sanitary standard for drinking water GB 5749 and are updated periodically to reflect the latest scientific and technological developments. In the latest version GB 5749-2022¹, iodine compounds are included as target analytes and the triggered amount of elemental iodine is specified at 0.1 mg/L. The latest version of GB/T-5750-2023² was approved on March 17, 2023, and implemented on October 1, 2023.

GB/T-5750.5 Standard Examination Methods for Drinking Water - Part 5: Inorganic Anions and Inorganic Non-Metals specifies the methods for determining the concentrations of inorganic anions and inorganic non-metals in drinking water, such as fluoride, chloride, nitrite, nitrate, sulfate, phosphate, bromate, iodate, chlorite, chlorate, bromide, iodide, cyanide, sulfide, and silicate. Section 13.4 outlines the analytical procedures for the measurement of iodine in drinking water using inductively coupled plasma mass spectrometry (ICP-MS).

Compared to other analytical techniques, ICP-MS has the advantages of high sensitivity, multi-element detection, low detection limits, wide dynamic range, high speed of analysis, ease of automation, etc. In this work, we reported the analysis of iodine in a variety of drinking water samples using PerkinElmer's NexION® 1100 ICP-MS instrument. The data quality was evaluated per GB/T-5750.5.

Experimental

Reagents and Samples

Iodine is a volatile element and is easily converted to the elemental form in acidic media and can result in significant memory effects. As per Section 13.4 in GB/T-5750.5-2023, a basic solution of 0.25 % (w/w) tetra methyl ammonia hydroxide (TMAH) was used for the preparation of the calibration blank, the calibration standards, the internal standards, the High Throughput System (HTS) carrier solution, and the washout solution. It was prepared by a 100-fold dilution (v/v) of a concentrated high-purity TMAH (25 wt.%, Tama Chemicals, Moses Lake, Washington, USA) in ultrapure water (UPW, Resistivity > 18.2MΩ).

Water samples included a tap water, a coffee-maker water supply line, a local well water (underground water), two bottled pure waters, and three bottled spring waters, covering a wide range of hardness. The water samples were basified to 0.25% TMAH and measured directly without prior dilution.

Calibration Standards

The calibration standards were prepared by the dilution of a 1000 ppm sodium iodide solution (PerkinElmer TruQ MS custom standard) in the 0.25% TMAH solution with concentrations of iodine at 0.1, 1.0, 10, 50, 100, 250, and 500 µg/L. The standards with concentrations at 10 µg/L and 50 µg/L were also used as the continuing calibration verification (CCV) samples.

Internal Standards (ISTD)

The internal standard consists of 400 µg/L of Te and was prepared via the the dilution of PerkinElmer's single-element standard (see the *Consumables Used* table) in 0.25% TMAH. The internal standard solution was continuously introduced into the designated port of the High Throughput System (HTS) switching valve and mixed inline with the carrier solution/sample.

QC Samples

QC samples include two standard spiked water samples, a tap water and a well water, and CCVs.

Instrumentation

All measurements were performed using a NexION 1100 ICP-MS (PerkinElmer, Shelton, Connecticut, USA) equipped with an S20 series autosampler and a High Throughput System (HTS). Iodine-127 was measured using the helium Collision (KED) mode. The instrument components, operating conditions, and data acquisition parameters are shown in Table 1.

Table 1. NexION 1100 ICP-MS Instrument Parameters and Operating Conditions.

Instrument Component	Type/Value
ICP-MS	NexION 1100
Nebulizer	PFA-ST3 MicroFlow
Spray Chamber	Quartz Cyclonic with AMS (All Matrix System) gas port
Torch	One-Piece Quartz Torch, 2 mm Injector
Cones	Standard Ni Sampler and Skimmer AI Hyper-Skimmer
Peripump Tubing	Carrier/Internal Standard: Orange/Green (0.38 mm i.d.) Waste: Gray/Gray Santoprene (1.30 mm i.d.)
Operating Conditions	Type/Value
RF Power	1600 W
Plasma Gas Flow	15 L/min
Auxiliary Gas Flow	1.2 L/min
Nebulizer Gas Flow	Optimized for CeO ⁺ /Ce ⁺ < 2.0%.
Cell Gas	Helium
Cell Gas Flow	4.0 mL/min
Sample Uptake Rate	0.24 mL/min
Data Acquisition	Type/Value
Analyte	¹²⁷ I
Internal Standard	¹²⁸ Te
Sweeps	20
Dwell Time	50 ms
Replicates	3
Autosampler and HTS	Type/Value
Autosampler/Model	S23
Sample Loop Size	1.0 mL
Autosampler Probe	1.0 mm i.d.
Flush Delay	7 s
Read Delay	25 s
Rinse Mode	Dual
Probe Rinse	5 s
Wash 1	2 s
Wash 2	33 s
Peripump Speed	89 rpm

Results and Discussion

Linearity and Detection Limit

The calibration curves were plotted following internal standard correction and blank subtraction. A coefficient of correlation (R^2) 0.9998 was obtained in the calibrated range, as shown in Figure 1.

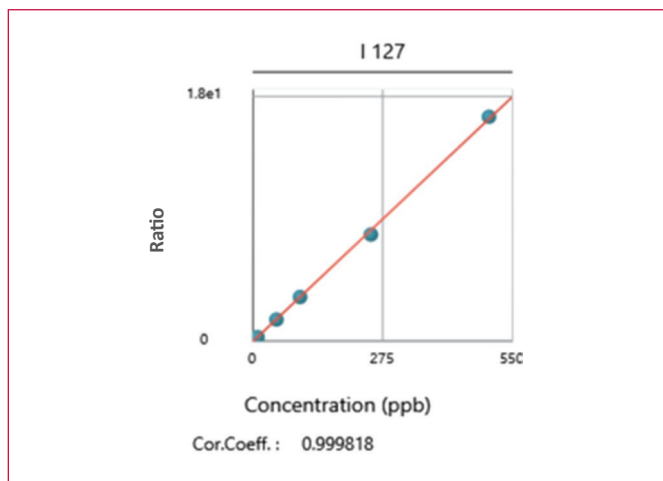


Figure 1. Calibration curve of ^{127}I in 0.25% TMAH.

The method detection limit (MDL) was determined by calculating three times the standard deviation of 10 replicated measurements of the calibration blank. In this study, the resulting MDL was determined to be 0.007 $\mu\text{g/L}$, which is well below the specifications outlined in GB/T-5750.5-2023, which stipulates a limit of detection of 0.6 $\mu\text{g/L}$.

Washout Efficiency

In this study, the utilization of alkaline conditions significantly enhanced the stability of iodine (I), thereby mitigating the memory effect. Furthermore, even greater washout efficiency was achieved by implementing the High Throughput System (HTS). The HTS incorporates a high-flow vacuum pump, a 7-port switching valve, and a sample loop. The vacuum pump expeditiously delivers the sample into the sample loop, effectively washing out the PFA-based metal-free fluid path.³ As demonstrated in Table 2, the residual iodine concentration measured after the 500 $\mu\text{g/L}$ calibration standard was only 0.12 $\mu\text{g/L}$ for the blank, corresponding to an impressive 1/4000 washout efficiency.

Table 2. Washout Efficiency Checking.

Sample	^{127}I (cps)	^{127}I ($\mu\text{g/L}$)
Calibration Blank	65	--
Calibration Standard	1,184,416	500
Calibration Blank-1st Wash	348	0.12

Accuracy

In the absence of a certified reference material (CRM) for iodine in drinking water, accuracy of the method was evaluated by checking the recoveries of iodine-spiked drinking waters. Two drinking water samples were used for this evaluation – one bottled spring water purchased from the local store, and another collected from a residential well. Each sample was spiked to three concentrations, 10, 50, and 100 $\mu\text{g/L}$, with measurements taken in triplicate. Six replicated measurements were taken for the unspiked water, and the average was used as the subtrahend for the calculation. Spike recovery was calculated as the difference between the concentrations of spiked and unspiked samples, divided by the spike concentration. As shown in Table 3, recoveries within $\pm 10\%$ were achieved for all spiked concentrations in both water sources, aligning with the stipulated range of 80% - 120%, as outlined in GB/T-5750.5-2023.

Table 3. Results of Iodine Spiked Test

Sample ID	Unspiked ($\mu\text{g/L}$)	Spike Concentration ($\mu\text{g/L}$)	Measured Concentration with Spike ($\mu\text{g/L}$)			Recovery (%)
Bottled Spring Water	4.05	10	13.53	14.35	13.77	94.8 ~ 102.9
		50	55.29	52.69	50.19	92.3 ~ 102.5
		100	105.4	103.9	110.7	99.9 ~ 106.7
Well Water	0.946	10	11.82	10.99	11.13	100.5 ~ 108.7
		50	48.20	49.96	47.57	93.2 ~ 98.0
		100	96.07	99.07	100.7	95.1 ~ 99.7

Precision

The precision was evaluated by the relative standard deviation (RSD) of replicated measurements. A variety of drinking waters were used for the precision test including a tap water, a coffee-maker water supply line, a well water, and a bottled spring

water. Each sample was measured five times and the replicates were used for the calculation of RSDs. As shown in Table 4, RSDs of 1.9% - 3.2% resulted from this method, which met the requirement of < 5% as specified by GB/T-5750.5-2023.

Table 4. Precision Test Results

Sample ID	Measured Concentration of I (µg/L)						Average Concentration (µg/L)	RSD (%)
Tap Water	2.21	2.14	2.21	2.14	2.26	2.13	2.18	2.4
Purified Tap Water	1.84	1.77	1.88	1.94	1.83	1.89	1.86	3.2
Well Water	0.964	0.913	0.962	0.948	0.943	0.947	0.95	1.9
Bottled Spring Water	4.03	3.94	4.04	4.15	3.94	4.22	4.05	2.7

Stability

To assess long-term stability, a variety of drinking water samples – including a tap water, a local well water, two bottled pure water and three spring waters – were analyzed repeatedly over an extended period of 10 hours. The recoveries of two continuous calibration verification (CCV) samples with concentrations at 10 µg/L and 50 µg/L and the internal standards were monitored throughout the analysis.

CCV Recovery: The recoveries for both concentrations were within ± 10% of the original reading, as shown in Figure 2. No apparent trending was observed through the runs, which validated the calibration over the 10-hour sample run. This is important for high-throughput laboratories in terms of overall efficiency and productivity, as it avoids the frequent reruns of the calibration standards.

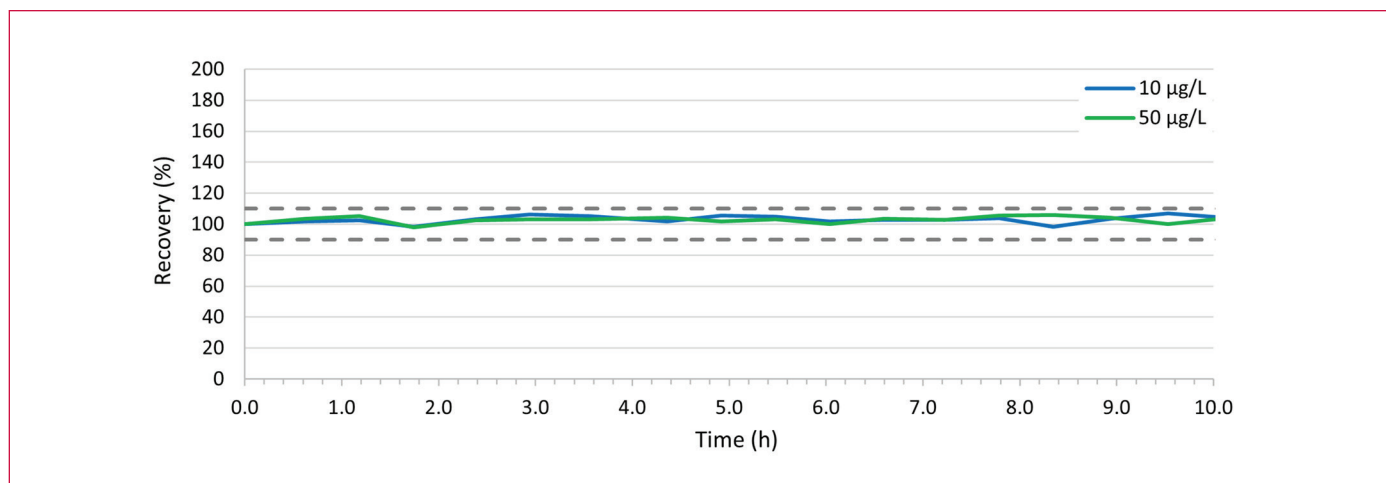


Figure 2. CCV recoveries over a 10-hour period of analysis of a variety of drinking water samples.

Internal Standard Recovery: The internal standards were normalized to the calibration blank, and the time-resolved plot is shown in Figure 3. The overall recoveries of the internal

standards were within the range of 80% - 120%, demonstrating the outstanding stability and robustness of this method and system as well as the suitability for extended sample runs.

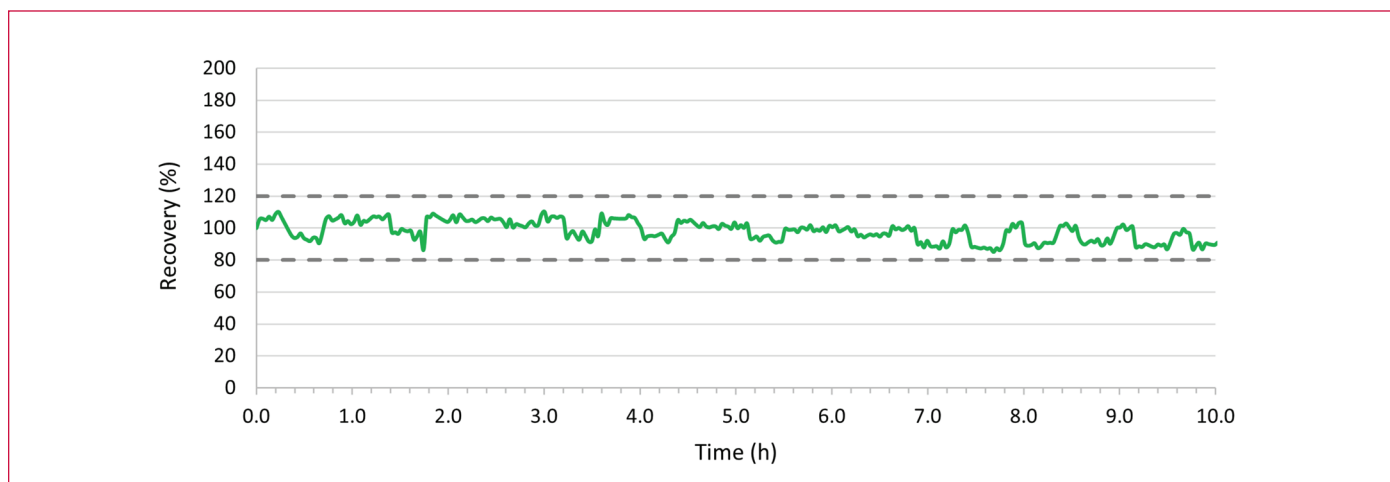


Figure 3. Internal standard recoveries (normalized to the calibration blank) during a 10-hour analysis of a variety of drinking water samples.

Conclusion

The NexION 1100 ICP-MS was used for the measurement of iodine in a variety of drinking water samples in accordance with the guidelines outlined in GB/T-5750.5-2023. The method was evaluated in terms of linearity, detection limits, washout efficiency, accuracy, precision, and stability.

A coefficient of correlation (R^2) of 0.9998 was achieved, showing the great linearity in the calibrated range up to 500 $\mu\text{g/L}$. A method detection limit (MDL) of 0.007 $\mu\text{g/L}$ was achieved, falling well below the specification of 0.6 $\mu\text{g/L}$. The accuracy was validated by a standard spike test in two water samples. Recoveries within $\pm 10\%$ were achieved for both samples, which were well within the $\pm 15\%$ specification. The precision of this work was demonstrated by the relative standard deviation (RSD) of 1.9% - 3.2% for a variety of drinking water samples, which are lower than the 5% specification. The stability was validated by the consistent recoveries of the CCVs and the internal standards over a 10-hour run of a variety of drinking water samples.

This study has demonstrated that the NexION 1100 ICP-MS has the capability to meet and/or exceed the specifications recommended by the GB/T-5750.5-2023 for the measurement of iodine in drinking waters. The method presented in this application note is reliable, consistent, and fit for its intended purpose.

References

1. GB 5749-2022: Standard for Drinking Water Quality; National Health Commission of China.
2. GB/T 5750-2023: Standard Examination Methods for Drinking Water Part 5: Inorganic Non-metallic Indicators; Standard Administration of China.
3. High Throughput System for ICP-MS/OES, Technical Note, PerkinElmer, 2020.

Consumables Used

Component	Description	Part Number
Nebulizer	PFA-ST3 MicroFlow	N8152378
Spray Chamber	Cyclonic High-Sensitivity Quartz Spray Chamber with Matrix Gas Port	N8152383
Torch	One-Piece Quartz Torch with 2.0 mm Injector	N8152472
Cones	Ni Sampler	W1033612
	Ni Skimmer	W1026356
	Al Hyper-Skimmer	W1033995
Peripump Tubing	Carrier/Internal Standard: Orange/Green (0.38 mm i.d.)	N8152403
	Waste: Gray/Gray Santoprene (1.30 mm i.d.)	N8152415
Internal Standard Probe Carrier Sample Probe	Carbon Fiber Autosampler Probe for ST Nebulizers	N0777225
Autosampler Probe used with HTS	Carbon Probe 1.0 mm i.d. 2 Blue Bands	N0811956
HTS Sample Loop	Sample Loop 1.0 mL; 1.0 mm i.d.	N8152929
Sample Tubes (50 mL)	Graduated Conical Bottom MetalFree Tubes with White Flat Caps, Qty. 500 - Racked	N0776116
Single-Element Standard	1000 µg/mL of Te in 10% HNO ₃	N9304385