Halogens by ICP-MS

Sensitive determination of halogens using triple quadrupole inductivity coupled plasma mass spectrometry (ICP-MS)

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Abstract

Purpose: To demonstrate an analytical workflow for the determination of halogens including fluorine, chlorine, bromine, and iodine at low levels using triple quadrupole ICP-MS.

Methods: A Thermo Scientific™ iCAP™ MTX ICP-MS, together with a Thermo Scientific™ iSC-65 Autosampler, was used for all analyses. Thermo Scientific™ Qtegra™ Intelligent Scientific Data Solution (ISDS) Software was used for instrument operation, data acquisition and subsequent calculations and reporting.

Results: Excellent detection limits for all four halogens (F, Cl, Br and I) were achieved using developed methodology. The method was also tested for its accuracy by spiking known concentrations of each analyte in drinking water samples. The data obtained during accuracy study indicates that the developed method can provide accurate results at lower concentrations of analytes under investigation.

Introduction

Inductively coupled plasma mass spectrometry (ICP-MS) is widely used analytical technique for trace-level quantification of elemental impurities due to its specificity, detection capability, and ability to provide isotopic information. Sensitivity in ICP-MS is influenced by the first ionization potential and element mass. Elements with ionization potentials below 6 eV (e.g., alkaline and alkaline earth elements) ionize completely in an argon plasma, while transition metals, precious metals, and rare earth elements ionize close to 100%. However, semi-metals and non-metals (e.g., silicon, sulfur, halogens) ionize poorly, and their signals often fall in the low mass range (below m/z 50), where many ions are lost.
Challenges in ICP-MS include isobaric and polyatomic interferences, which are abundant in the low mass range, and they complicate analysis. Halogen analysis is crucial in various industries such as environmental monitoring, pharmaceuticals, oil and gas, and industrial applications like Li-ion batteries and renewable fuels. While ion chromatography (IC) is commonly used for halogen analysis, argon plasma-based techniques like ICP-OES and ICP-MS have limited applications but are valuable for element-selective detection.
The iCAP™ MTX ICP-MS offers analytical workflows to mitigate these challenges, improving the accuracy and reliability of halogen detection in various sample matrices.
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Materials and methods

Sample and Standard Preparation

Analysis of chlorine and bromine
Calibration standards were prepared by gravimetric dilution of single element standards (SPEX CertiPrep™, Metuchen, NJ, USA) of chlorine and bromine using 2% (v/v) HNO3 (Optima™ grade, Fisher Chemical™). The respective concentration levels for chlorine and bromine are summarized in Table 1.
Halogens tend to bind to the surface of all components of the sample introduction system, so all sample introduction system components were cleaned, and the system was rinsed thoroughly before initializing analytical measurement.

Analysis of iodine
Calibration standards were prepared by gravimetric dilution of single element standards (SPEX CertiPrep) of iodine using 0.5% (v/v) solution of tetramethyl ammonium hydroxide (TMAH) in 0.5% (v/v) HNO_3 (Optima grade, Fisher Scientific). To determine linearity and IDL, the calibration plot was generated using four calibration standards and a blank solution. The calibration standards employed in this study were in the range of 0.1 to 10 µg·L-1.

Analysis of fluorine
For the analysis of fluorine , an alternative approach involved mixing fluorine with barium and analyzing Ba.F+ at m/z 157 was followed. Therefore, sample introduction system components and instrument parameters were optimized to maximize the formation of Ba.F and improve the signal-to-noise ratio to achieve sensitive and reliable measurement conditions. After careful investigation, a concentration of 30 mg·L-1 of Ba was found to be suitable for this measurement and provided sufficient signal at a reasonable compromise in respect to the background equivalent concentration (BEC), instrument detection limit (IDL), and linearity. Calibration standards of fluorine were prepared using 30 $mg{\cdot}L^{-1}$ Ba solution as diluent. Concentration levels of fluorine (prepared using organic salt) in calibration standards are summarized in Table 1.

Table 1. Calibration ranges for chlorine, bromine, iodine, and fluorine along with solution used as diluent and calibration blank. All concentrations are given in µg·L-1.

Analyte	Blank	Standard 1	Standard 2	Standard 3	Standard 4	Calibration Blank/diluent
Chlorine (Cl)	0	10	25	50	100	2% HNO3
Bromine (Br)	0	10	25	50	100	
Iodine (I)	0	0.1	0.5	5	10	0.5% TMAH in 0.5% HNO3
Fluorine (F)	0	100	250	1000	2000	30 mg·L-1 Ba solution

Test Method(s)

The study utilized an iCAP MTX ICP-MS in conjunction with an iSC-65 autosampler for automated sample introduction, controlled by Qtegra ISDS Software. The analysis was conducted in Sensitivity (S) mode with pure oxygen as a cell gas to enhance sensitivity and reduce interferences. Halogens like fluorine, chlorine, bromine, and iodine are challenging to quantify at low concentrations due to their high ionization potentials and spectral interferences. Chlorine, bromine, and iodine can be analyzed with reasonable detection limits if interferences are controlled using a collision/reaction cell (CRC).
Fluorine is particularly difficult to analyze because of its high ionization potential and significant interferences from ions like H_3O^+ and H_2O^+. Conventional quadrupole ICP-MS is ineffective for fluorine analysis due to these challenges. High-resolution ICP-MS can address interference issues but suffers from low ion yield, leading to poor sensitivity.
An alternative approach involved mixing fluorine with barium and analyzing Ba.F+ at m/z 157.
This mitigates ionization issues but introduces polyatomic interferences from Ba-based ions. Therefore, single quadrupole ICP-MS lacks the required accuracy and precision for this method. To overcome these challenges, the iCAP MTX ICP-MS was operated in triple quadrupole mode, with high-resolution settings for Q1 and Q3, enabling accurate and precise analysis of fluorine as $Ba.F^+$ by significantly reducing interferences.

Table 2, The halogens with their most abundant m/z, ionization potential (eV) and potential spectral interferences.

Analyte	m/z	Isotopic Abundance (%)	Ionization Potential (IP) (eV)	Interferences
Fluorine (F)	19	100	17.42	$^{16}O.^{3}H$, $^{17}O.^{32}H$, $^{18}O.^{1}H$
Chlorine (Cl)	35	75.77	12.97	$^{16}O.^{3}H.^{16}O$, $^{16}O.^{19}F$, $^{12}C.^{23}Na$
Bromine (Br)	79	50.69	11.81	$^{40}Ar.^{39}K$, $^{16}O.^{63}Cu$, $^{14}N.^{65}Cu$
Iodine (I)	127	100	10.45	$^{12}C.^{115}In$, $^{40}Ar.^{87}Rb$

Figure 1. Thermo Scientific iCAP MTX ICP-MS

Table 3. Instrument parameters for determination of fluorine, chlorine, bromine and iodine

Parameter	Fluorine	Chlorine, Bromine, Iodine
Pump speed (rpm)	40	
Spray chamber	Quartz cyclonic, cooled at 2.7˚C	
Torch	PLUS torch	
Interface	Nickel sampler and nickel skimmer cone	
Plasma power	1550 W	
Nebulizer	iCAP MX Series Nebulizer	
Nebulizer gas	0.668 L.min-1	1.0 L.min-1
Injector	1.5 mm ID	2.5 mm ID
QCell setting	TQ-O2 with pure oxygen	
Cell gas flow	0.25 ml.min-1	
Dwell time per isotope	0.5 seconds	

Analysis and method set-up

Qtegra ISDS Software was used to optimize measurement modes using comprehensive autotune routines prior to the analysis

The Reaction Finder feature in Qtegra ISDS Software for the iCAP MTX ICP-MS is designed to simplify and optimize the process of selecting the best reaction or collision gases for interference removal during analysis. Here are the key aspects of the Reaction Finder feature:
Automatic Selection: Reaction Finder automatically identifies the most suitable reaction or collision gases to use in the TQ (Triple Quadrupole) mode based on the specific analytes and potential interferences present in the sample.
Reduced Complexity: This feature reduces the complexity and time required for method development by automating the selection process, which traditionally involves extensive manual optimization.
Improved Accuracy: By selecting the optimal gases, Reaction Finder helps improve the accuracy and sensitivity of the measurements, ensuring better interference removal and more reliable results.
User-Friendly Interface: The feature is integrated into the Qtegra software, providing a user-friendly interface where users can input their analytes of interest, and the software will suggest the best gas modes to use.
Enhanced Efficiency: Reaction Finder enhances laboratory efficiency by streamlining the setup process, allowing users to achieve high-quality data more quickly and with less effort.

Overall, the Reaction Finder in Qtegra software is a powerful tool that facilitates the effective use of the iCAP TQ ICP-MS, particularly in complex matrices where interference removal is critical for accurate trace element analysis.

Figure 2. Schematic showing the use of TQ-O_2 mode and on mass measurement of $Ba.F^+$ for interference free detection of Fluorine (F).

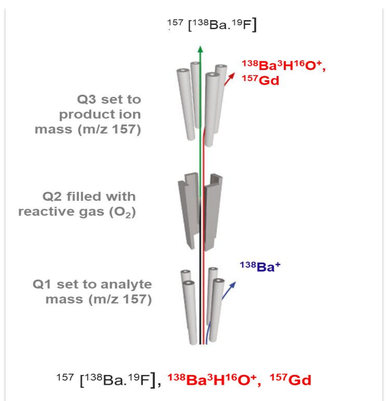


Figure 3: Overview of the Reaction Finder Method Development Assistant

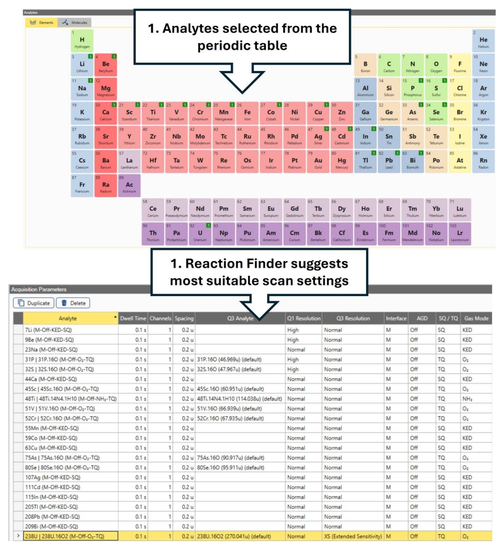
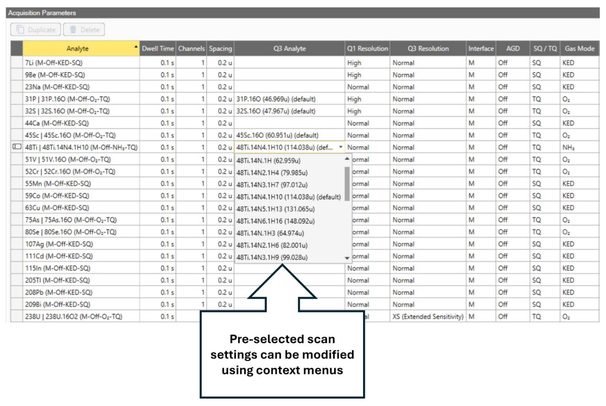


Figure 4: Modification of the Reaction Finder suggested settings



Results

To determine important figures of merit, such as instrument detection limits (IDLs), correlation coefficients (R^2), and background equivalent concentration (BEC) for each analyte, calibration plots were generated using five linearity standards including calibration blank (Table 1). The IDLs were calculated based on three times the standard deviation of three replicate measurements of the respective calibration blank of each analyte, which were the same solutions used for the preparation of the calibration standards. The achieved IDLs indicate that stable signals can be detected at specified concentration levels for each analyte under investigation.

Table 4 summarizes quadrupole settings IDL, and correlation coefficient for each analyte as observed during the study.

Table 4. Analytes, their Q1 and Q3 m/z, IDL, and correlation coefficient observed during the study

Analyte	Q1 m/z	Q3 m/z	IDL (µg·L-1)	R^2
Chlorine (Cl)	^{35}Cl	51 [$^{35}Cl.^{16}O$]	2.64	0.9946
Bromine (Br)	^{79}Br	95 [$^{79}Br.^{16}O$]	0.026	0.9997
Iodine (I)	^{127}I	^{127}I	0.0016	>0.9999
Fluorine (F)	$^{138}Ba.^{19}F$	$^{157}[^{138}Ba.^{19}F]$	27.2	0.9950

The analysis of iodine is easier compared to other halogens due to its lower ionization potential and less prominent spectral interferences and can be performed using He-KED mode. However, use of TQ-O2 mode has proven to be more beneficial as it enhances the sensitivity with more effective interference removal mechanism. The sensitivity observed for iodine in TQ-O2 mode is equivalent to that of with STD or no gas mode, which is almost five times higher than in He-KED mode. Use of TQ-O2 mode also removes isobaric xenon (Xe)-based interferences effectively, which enables sensitive determination of iodine using m/z of 129 in case it is desired for special application.

Accuracy

To further ensure the accuracy and establish the limit of quantification where reliable and precise quantification can be performed, all the elements investigated here were spiked in triplicate at lower concentration levels in drinking water, and the accuracy in spiked samples was calculated. Table 5 summarizes spiked concentrations, calculated average recovery, and relative standard deviation calculated from three replicate measurements.

Table 5. Analytes, spiked concentrations (µg·L-1) except for fluorine which are in mg·L-1, average percent recovery and % RSD (n=3)

Analyte	Spiked concentration	% Recovery
Chlorine (Cl)	10	87 ± 7.1
	25	101 ± 4.2
Bromine (Br)	0.5	97 ± 1.8
	10	102 ± 2.1
Fluorine (F)	0.3	108 ± 5.1
Iodine (I)	0.01	105 ± 2.2

The Qtegra ISDS Software provides comprehensive tools to simplify data interpretation, various calculations and data visualization. The calibration plots generated using external calibration approach for each analyte provides relevant statistical information such as correlation coefficients (R^2), Instrument Detection Limit (IDL) and Background Equivalent Concentration (BEC) for analytes under investigation.
Figure 5 and Figure 6 below are examples of typical calibration plots obtained for iodine and fluorine in this study.

Figure 5: Calibration plot obtained for iodine

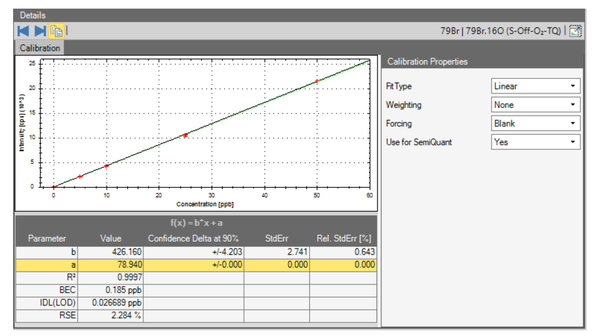
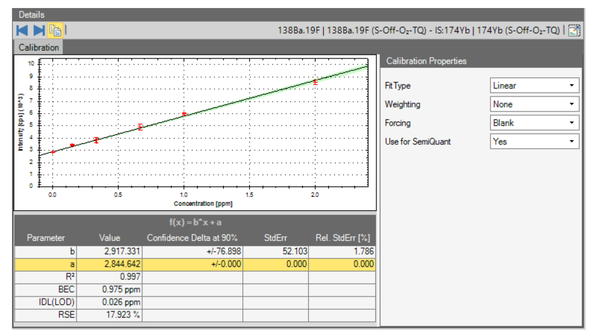


Figure 6: Calibration plot obtained for fluorine measured as Ba.F



Conclusions

This document highlights how triple quadrupole ICP-MS such as iCAP MTX ICP-MS operated in TQ-O2 mode can be used for accurate and precise quantification of challenging analytes such as chlorine, bromine and iodine can be analyzed directly using optimized instrument conditions.

It further highlights the feasibility of iCAP MTX ICP-MS for indirect but accurate and precise determination of fluorine after complex formation with barium under optimized and controlled conditions.

It further summarizes details of iodine (127I) analysis using helium as cell gas in SQ-KED mode.

The analytical data and observations made during this study strongly suggest that iCAP MTX ICP-MS equipped with dedicated mass flow controllers (MFCs) for introduction of pure oxygen and pure helium as cell gases is powerful tool to accomplish, otherwise challenging analysis of halogens.

References

1 **Jamiri et al., J. Anal. At. Spectrom., 32 (**2017), 942-950:

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