

Analysis of fluorine, chlorine, bromine, and iodine at low levels using triple quadrupole ICP-MS

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Goal

This application note will demonstrate an analytical workflow for the determination of the halogens fluorine, chlorine, bromine, and iodine at low levels using triple quadrupole ICP-MS.

Introduction

Inductively coupled plasma mass spectrometry (ICP-MS) is widely used as an analytical technique for the trace level quantification of elemental impurities in the range of different matrices due to its specificity, detection capability, and ability to provide isotopic information.

The detection sensitivity in ICP-MS is mostly determined by the first ionization potential (i.e., the energy required to remove an electron from the valence shell) and mass for a given element. In an argon plasma, complete ionization is typically only achieved for elements with ionization potentials below 6 eV, such as alkaline and alkaline earth elements. Typical transition metals, precious metals, and rare earth elements still ionize at close to 100%. However, semi-metals and in particular non-metals, like silicon, sulfur, or halogens, will only poorly ionize. At the same time, their signals are found in the low mass range (often below m/z 50), where many ions are lost in the transition through the mass spectrometer. In addition, other factors may significantly impact the analysis, for example, isobaric and polyatomic interferences leading to bias on the most abundant isotope for a given element, and hence forcing analysts to often select a less sensitive, but interference-free alternative. Especially polyatomic interferences are abundant in the low mass range and may render the analysis using ICP-MS nearly impossible.

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The analysis of halogens is of importance in a variety of sample matrices pertaining to different industries, such as environmental monitoring, pharmaceuticals, oil and gas, and industrial applications such as Li-ion battery and renewable fuels. Ion chromatography (IC) is a commonly used technique for analysis of halogens, whereas argon plasma-based techniques, like ICP-OES or ICP-MS, have limited applications for this purpose. However, its outstanding characteristics as an element selective detection system have led to the development of applications highly complementary to chromatographic techniques, for example, for the detection of PFAS.

This note describes the analytical workflows developed with the Thermo Scientific[™] iCAP[™] MTX ICP-MS to mitigate these analytical challenges associated with the analysis of halogens using ICP-MS.

Experimental

System setup

The iCAP MTX ICP-MS equipped with a Thermo Scientific[™] iSC-65 Autosampler for unattended and automated sample introduction was used during this work. Thermo Scientific[™] Qtegra[™] Intelligent Scientific Data Solution[™] (ISDS) Software was used to control the ICP-MS instrument and autosampler using dedicated software plug-ins. This analysis was performed using Sensitivity (S) mode of the iCAP MX Series ICP-MS, which is the ideal choice for analysis where highest instrument sensitivity is required. The iCAP MTX ICP-MS was operated using pure oxygen as a cell gas, which was found to be effective in removing potential interferences on each of the analytes under investigation.

The halogens fluorine, chlorine, bromine, and iodine all belong to the category of high IP elements, and thus their quantification at lower concentration levels using ICP-MS is challenging. In addition to the poor sensitivity of halogens, potential spectral interferences (polyatomic and isobaric), especially for fluorine and chlorine, also present typical limitations in achieving accurate, precise, and sensitive analysis of halogens. Table 1 contains an overview of the analytes, including ionization potentials and typical polyatomic interferences. Chlorine, bromine, and iodine at least partially ionize in an ICP and can be analyzed directly with reasonable limits of detection in case interferences are controlled by the use of a collision/reaction cell (CRC).

Fluorine is the most challenging halogen to analyze with ICP-MS, not only because it has the highest ionization potential in the group, but also because it falls into a severely interfered mass range, mainly due to the interferences generated by naturally abundant ions such as H_3O^+ and peak tailing of H_2O^+ . These two major challenges associated with fluorine analysis make it impossible to analyze in a conventional way using quadrupole ICP-MS. High-resolution ICP-MS can be used to address interference-related challenges, however, the low ion yield leads to poor sensitivity for this element.

In this study, an alternative approach for measurement of fluorine after mixing with barium (Ba) and the use of Ba.F⁺ at m/z 157 has been followed.¹ This approach helps mitigate the challenge of poor ionization of F to F⁺; however, formation Ba.F⁺ and preventing this adduct from decomposing is critical. In addition, m/z 157 also suffers significantly from polyatomic interferences due to Ba-based polyatomic interferences, such as ¹³⁸Ba.¹⁶O.³H and other combinations of these elements. Therefore, this approach is not feasible using single quadrupole ICP-MS with the required accuracy and precision. In order to tackle this challenge and perform interference-free analysis of F as Ba.F⁺, the iCAP MTX ICP-MS was operated in triple guadrupole mode and on mass measurement of Ba.F at m/z 157 was performed. To further reduce polvatomic interferences. Q1 and Q3 were set to high resolution by virtue of user definable resolution settings offered by Qtegra ISDS Software.

The settings used for the triple quadrupole ICP-MS are given in Table 2 and its functioning during the measurement of chlorine is illustrated in Figure 1.

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
lodine (I)	127	100	10.45	¹² C. ¹¹⁵ In, ⁴⁰ Ar. ⁸⁷ Rb

Table 1. The halogens with their most abundant m/z, ionization potential (eV), and potential spectral interferences

Table 2. 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	1,550 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-O ₂ with pure oxygen		
Cell gas flow	0.25 mL·min ⁻¹		
Dwell time per isotope	0.5 s		



Figure 1. Schematic of triple quadrupole ICP-MS

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 3.

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 μ g·L⁻¹.

Analysis of fluorine

For the analysis of fluorine, 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·L⁻¹ Ba solution as diluent. Concentration levels of fluorine in calibration standards are summarized in Table 3.

Table 3. Calibration ranges for chlorine, bromine, iodine, and fluorine along with solution used as diluent and calibration blank. All concentrations are given in μ g·L⁻¹.

Analyte	Blank	Standard 1	Standard 2	Standard 3	Standard 4	Calibration blank/diluent	
Chlorine (Cl)	0	10	25	50	100		
Bromine (Br)	0	10	25	50	100	2% HNO ₃	
lodine (I)	0	0.1	0.5	5	10	0.5% TMAH in 0.5% HNO ₃	
Fluorine (F)	0	100	250	1,000	2,000	30 mg·L⁻¹ Ba solution	

Results and discussion

To determine important figures of merit, such as instrument detection limits (IDLs), correlation coefficients (R²), and background equivalent concentration (BEC) for each analyte, calibration plots were generated using five linearity standards including calibration blank (Table 3). 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 <i>m/z</i>	Q3 <i>m/z</i>	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
lodine (I)	127	127	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 interferneces 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 interfence 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 interfences effectively, which enables sensitive detremination of iodine using *m/z* of 129 in case it is desired for special application.

Accuracy study

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, average percent recovery, and % RSD (n=3)

Analyte	Spiked concentration	% Recovery
Chloring (CI)	10 µg·L⁻¹	87 ± 7.1
Chiorine (CI)	25 μg·L⁻¹	101 ± 4.2
	0.5 µg·L⁻¹	97 ± 1.8
Bromine (Br)	10 µg·L⁻¹	102 ± 2.1
Fluorine (F)	prine (F) 0.3 mg·L ⁻¹	
lodine (I)	0.01 µg·L¹	105 ± 2.2

The results achieved during this test indicates that the developed analytical workflow using the iCAP MTX ICP-MS enables the accurate and precise measurement of chlorine, bromine, and iodine at the specified concentration levels. The results also indicate that fluorine can be detected and measured reliably at, and above, concentrations specified above.

Conclusion

This document highlights how triple quadrupole ICP-MS, such as the 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, which can be analyzed directly using optimized instrument conditions. It further highlights the feasibility of the 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 the iCAP MTX ICP-MS equipped with dedicated mass flow controllers (MFCs) for introduction of pure oxygen and pure helium as cell gases is a powerful tool to accomplish the otherwise challenging analysis of halogens.

Reference

 Jamiri, N.L.A. et al., Novel non-target analysis of fluorine compounds using ICPMS/MS and HPLC-ICPMS/MS, J. Anal. At. Spectrom. 2017, 32, 942-950.



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