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Sensitive and interference free analysis of halogens using triple quadrupole ICP-MS

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ABSTRACT

The analysis of halogens is important in many different industries, such as environmental monitoring, pharmaceutical, oil and gas, but also Li-ion battery and renewable fuels. Halogen analysis is commonly carried out using ion chromatography (IC), whereas argon plasma-based techniques like ICP-MS are less common, due to poor sensitivitiy, and potential spectral interferences. This study describes a complete analytical workflow using the Thermo Scientific™ iCAP™ TQe ICP-MS for the accurate and precise quantification of challenging halogen analytes like fluorine, chlorine, and bromine.

INTRODUCTION

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.
The halogens, including fluorine, chlorine, bromine and iodine, all belong to 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 limitations in achieving accurate, precise, and sensitive analysis of halogens. Table 1 contains an overview of the aforementioned analytes, including ionization potentials and typical polyatomic interferences.

Table 1. The halogens with their 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	$^{18}O.^{3}H$, $^{17}O.^{32}H$, $^{18}O.^{1}H$
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	$^{40}Ar.^{39}K$, $^{16}O.^{63}Cu$, $^{14}N.^{65}Cu$

MATERIALS AND METHODS

The iCAP TQe ICP-MS, equipped with standard configuration of the sample introduction system (unless otherwise stated), was used during this work. The instrument was operated using TQ-O_2 mode with pure oxygen as a cell gas, which was found to be effective in removing potential interferences on each of the analytes under investigation. Typical operating parameters are shown in table 2.

Table 2. Typical operating parameters.

Parameter	Fluorine	Chlorine	Bromine
Plasma power	1550 W		
Nebulizer	Borosilicate glass Micromist, 400 µL·min^{-1}		
Nebulizer gas	0.72 L·min^{-1}	1.08 L·min^{-1}	1.00 L·min^{-1}
Injector	Quartz, 1.5 mm i.d.	Quartz, 2.5 mm i.d.	
QCell setting	TQ-O_2, pure oxygen		
Cell gas flow	0.4 mL·min^{-1}	0.3 mL·min^{-1}	
Dwell time per isotope	2 s	0.5 s	0.2 s

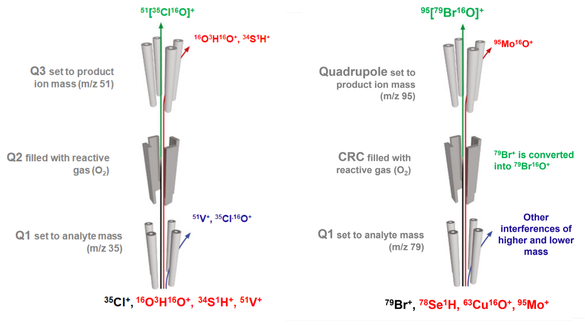

Figure 1. Illustration of the measurement of chlorine and bromine using TQ-O_2 mode

RESULTS

In order to determine important figure of merits such as instrument detection limits (IDLs), correlation coefficients (R^2) and background equivalent concentration (BEC) for each analyte, calibrations plots were generated using five linearity standards, including a calibration blank (Table 3). The IDL´s were calculated based on three times the standard deviation of 3 replicate measurements of respective calibration blank of each analyte. The achieved IDL´s indicates the fact that stable signals can be detected at specified concentration levels for each analyte under investigation.

Further to ensure the accuracy and establish a lower limit for reliable and precise quantification of these challenging analytes, all of the elements investigated here were spiked in drinking water in triplicate at concentration levels equal to about 10 times the instrumental limit of detection (IDL). For chlorine, a second spike level at approximately 4 times the IDL was also tested. This procedure allowed to calculate the accuracy and precision of the determination at lowest levels.
Table 3 and 4 summarize the results, including spiked concentrations, calculated average recovery and relative standard deviation calculated from three replicate measurements.

Table 3. 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	$^{51}[^{35}Cl.^{16}O]$	2.357	0.9965
Bromine (Br)	^{79}Br	$^{95}[^{79}Br.^{16}O]$	0.050	0.9987
Fluorine (F)	$^{138}Ba.^{19}F$	$^{138}Ba.^{19}F$	0.034	0.9995

Table 4. 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 µg·L^{-1}	87 ± 7.1
	25 µg·L^{-1}	101 ± 4.2
Bromine (Br)	0.5 µg·L^{-1}	97 ± 1.8
Fluorine (F)	0.25 mg·L^{-1}	118 ± 6.8

In this study, an alternative approach for measuring fluorine was applied, initially developed by Jamari et al.[3]. Here, fluorine is measured indirectly after mixing with barium. Therefore, all solutions prepared for the analysis of fluorine (calibration blank and individual standards at concentration levels of 0.15, 0.25, 0.5 and 1 mg·L^{-1}) contained 30 mg·L^{-1} of barium, prepared by gravimetric dilution in 2 HNO_3.

This approach helps mitigate challenge of poor ionization of F to F^+, however, formation $Ba.F^+$ and preventing adduct from decomposition and formation of Ba oxides is critical and challenging. In addition, m/z 157 also suffers significantly due to Ba based polyatomic interferences such as $^{138}Ba.^{16}O.^{3}H$ and other isotopic combinations of Ba, O and hydrogen which result into polyatomic positively charged ion with m/z 157. Therefore, analysis of flourine using single quadrupole ICP-MS remains difficult to accomplish with required accuracy and precision.
In order to tackle this challenge and perform interference-free analysis of F as $Ba.F^+$, the iCAP TQe ICP-MS was operated using TQ-O_2 mode and on mass measurement of Ba.F at m/z 157 was performed. Further to reduce polyatomic interferences, Q1 and Q3 were set to high resolution. Figure 2 gives an overview on the principle of the measurement.

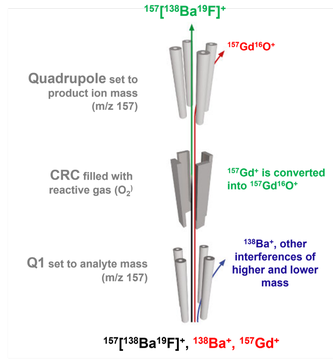

Figure 2. Illustration of the measurement of fluorine using TQ-O_2 mode

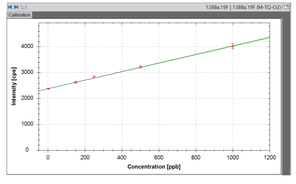

Figure 3. Calibration curve for $^{157}[^{138}Ba^{19}F]^+$

In addition to the proof data summarized in tables 3&4 and Figure 3, a survey scan was acquired in single quadrupole mode to further illustrate the successful detection of fluorine. The scanned region, measured in between m/z 125 to 175, covers the mass range where $^{134\text{-}138}Ba^+$, $^{150\text{-}154}[Ba^{16}O]^+$, as well as $^{162\text{-}170}[BaO_2]^+$.

All observed isotope clusters reveal the characteristic isotope signature of barium, and only at m/z 157, another signal corresponding to $^{157}[^{138}Ba^{19}F]^+$ is visible. The results are shown in figure 4.

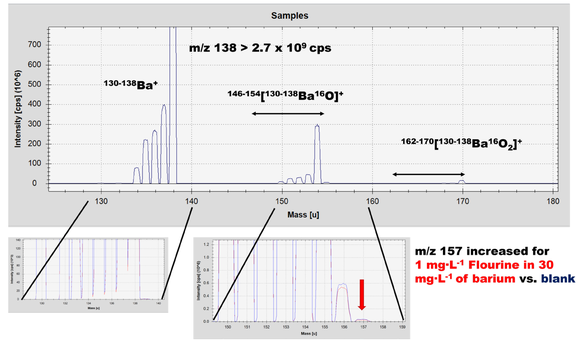

Figure 4. Survey scan between m/z 125 and 175 on a 1 mg·L^{-1} solution of flourine in 30 mg·L^{-1} of barium; Barium isotope pattern confirmed for Ba, BaO and BaO_2, BaF visible only at m/z 157.

CONCLUSIONS

This work highlights how triple quadrupole ICP-MS systems, such as the iCAP TQe ICP-MS, operated in TQ-O_2 mode can be used for accurate and precise quantification of challenging analytes such as halogens.

- It could be shown that chlorine and bromine can be analyzed directly using optimized instrument conditions.
- It further highlights the feasibility of iCAP TQe ICP-MS for indirect but accurate and precise determination of fluorine by following approach of complex formation with barium under optimized and controlled conditions
- The analytical data and observations made during this study strongly suggest that iCAP TQe 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.
- Upcoming studies will focus on the application of the fluorine measurements in hyphenated techniques, such as liquid chromatography hyphenated to ICP-MS to assess the potential for emerging contaminant screening, i.e. of PFAS.

REFERENCES

1. Jamari, N. L. A. et al, J. Anal. At. Spectrom. **32** (2017), 942-950

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