Application Note

Analysis of Chlorine, Bromine and Iodine in Water using ICP-AES

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1 Introduction

ICP-AES is a multi-element technique that allows the determination of 75 elements in the periodic table. One element that is desirable to analyze at the same time as other elements is chlorine. However, until recently, the analysis of halogens, especially chlorine, was usually not undertaken by ICP. This was because the halogens are not easy to excite in a plasma source and their emission wavelengths are challenging for conventional optics. Chlorine wavelengths, which yield good sensitivity, are low (133 nm and 134 nm) and are not possible to measure with conventional solid-state detectors or photomultiplier tubes.

This Application Note describes recent hardware improvements that allow the determination of Cl, Br and I by ICP-AES

2 Principle

2.1 Technique used

The elemental analysis of solutions was undertaken by Inductively Coupled Plasma Atomic Emission Spectrometry (ICP-AES). The sample is nebulized then transferred to an argon plasma. It is decomposed, atomized and ionized whereby the atoms and ions are excited. We measure the intensity of the light emitted when the atoms or ions return to lower levels of energy. Each element emits light at characteristic wavelengths and these lines can be used for quantitative analysis after a calibration.

2.2 Wavelength choice

The choice of the wavelength in a given matrix can be made using the "profile" function, or by using Win-IMAGE, which is rapid semi-quantitative analysis mode using multiple wavelengths. The principle is the same in either case: record the scans of analytes at low concentration, and of the matrix. By superimposing the spectra, we see possible interferences.

2.3 Limits of detection estimation

The limits of detection are calculated using the following formula:

$$LOD = k \times BEC \times RSD_0$$

With:
LOD = limits of detection,
k= 3 for the normal 3-sigma values,
BEC = Background equivalent concentration,
RSD_0 = relative standard deviation of the blank.

To calculate the LOD, a calibration curve is constructed using two points, 0 ppm and 5 ppm, or some concentration where the calibration is linear; this gives the BEC. The RSD_0 is evaluated by running the blank ten times.

3 Sample preparation

Standards were prepared by dilution of 1,000 µg/ml single-element solutions with deionized water. The standards are made from NaCl, KBr and KI and are available from Spex Certiprep.

4 Instrument specification

The work was done on a ULTIMA. The specifications of this instrument are listed in Table 1 and 2.

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Table 1: Specification of spectrometer

Parameters	Specifications
Mounting	Czerny Turner
Focal length	1 m
Thermoregulation	Yes
Nitrogen purge	Yes
Grating number of grooves	2400 gr/mm
1st order resolution	0.010 nm
2nd order resolution	0.005 nm
Order	2nd order

Table 2: Specification of RF Generator

Parameters	Specifications
Type of generator	Solid state
Observation	Radial
Frequency	40.68 MHz
Control of gas flowrate	By computer
Control of pump flow	By computer
Cooling	Air

5 Operating conditions

The operating conditions are listed in Table 3 below.

Table 3: Operating conditions

Parameter	Condition
RF Generator power	1000 W
Plasma gas flowrate	12 L/min
Auxiliary gas flowrate	0 L/min
Sheath gas flowrate	0.2 L/min
Nebulizer gas flowrate	1.2 L/min
Nebulizer flowrate	3 bars (45 psi)
Sample uptake	1 mL/min
Type of nebulizer	Concentric
Type of spray chamber	Cyclonic
Argon humidifier	Yes
Injector tube diameter	3.0 mm

6 Wavelength selection and analytical conditions

The line with the highest sensitivity was used for each of the elements, as there were no interference problems. The conditions were the same for all elements.

Table 4: Analysis conditions

Element	Slits µm	Analysis Mode	Integration Time (sec)
Cl, Br, I	20 x 15	Direct peaking	16

This instrument implemented the use of a special adaptation that allows the detection of very low wavelengths. The adaptation consists of a special PMT with a CaF_2 window, which has good efficiency below 200 nm, and special CaF_2 optics that transmit low UV light. With this adaptation, the spectral range is 120 - 800 nm.

7.1 Calibration curve

A calibration curve was made with four points, with the concentrations of the standards presented in Table 5.

Table 5: Standard concentrations

Elements	Concentration in mg/L
Cl	0, 5, 10, 50
Br	0, 5, 10, 50
I	0, 1.27, 12.7, 127

Calibration curves are presented on the following page in Figure 1.

7.2 Scans

Scans of solutions used for calibration were used to obtain profiles. They are presented on page 4 in Figure 2.

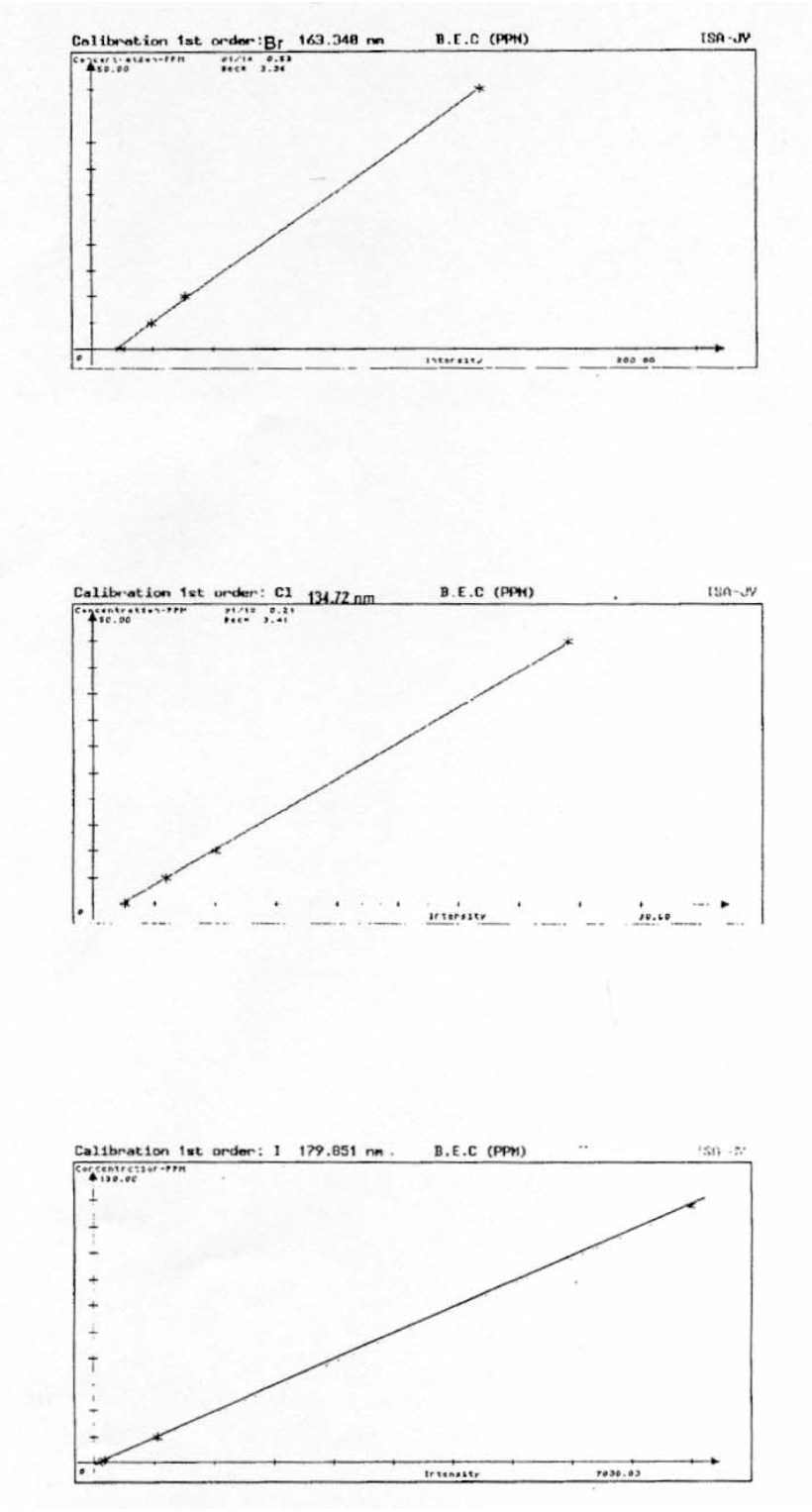

Figure 1: Calibration curves

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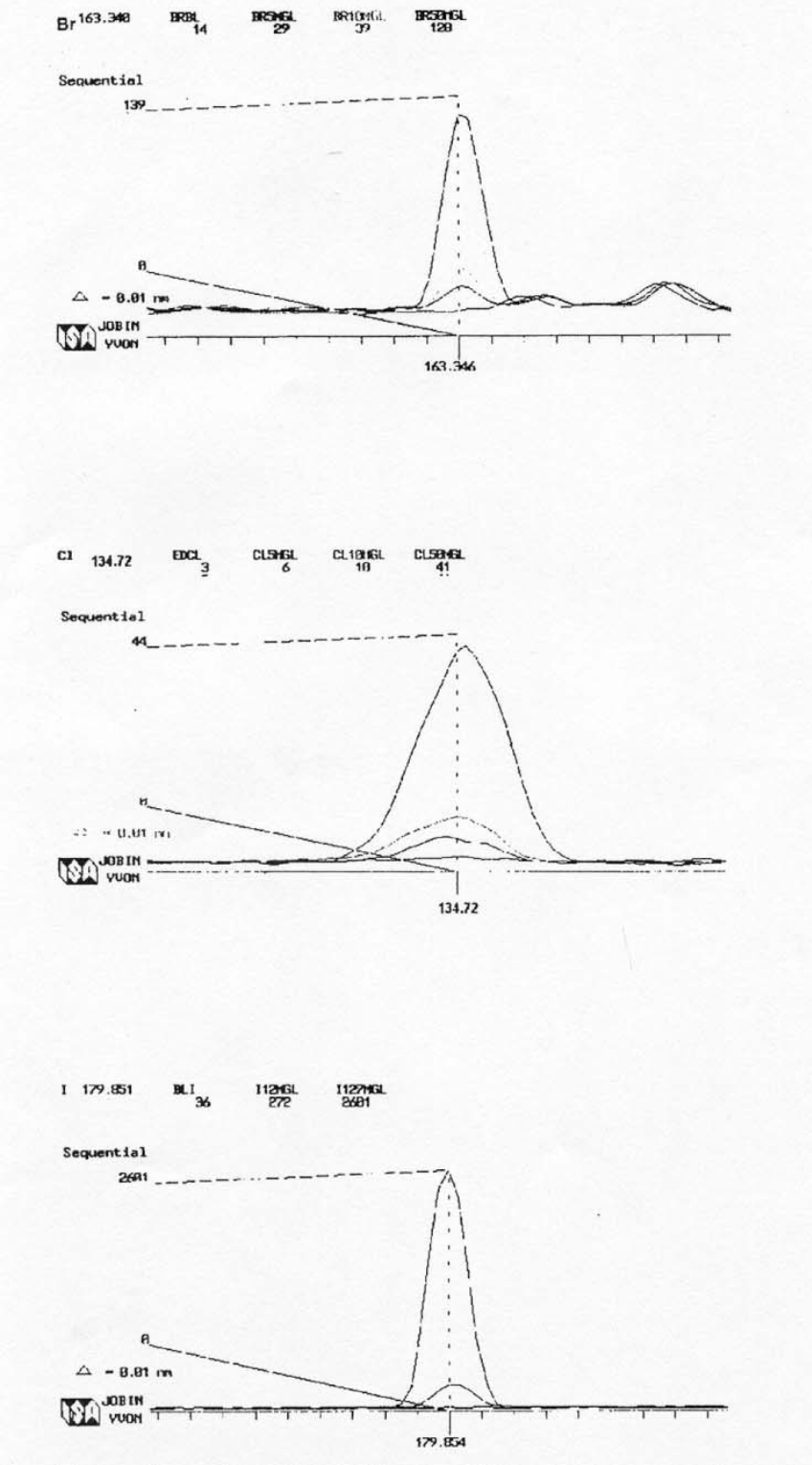

Figure 2: Profiles of Cl, Br and I

7.3 Limits of detection

The limits of detection were calculated using the formula given in Section 2.3 and are given in the table below.

Table 6: Limits of Detection

Element	Wavelength (nm)	BEC (µg/L)	LOD (µg/L)
Cl	134.72	3400	300
Br	163.34	3350	170
I	179.85	350	20
I	182.98	850	8

8 Summary

The analysis of Br, Cl and I is possible with ICP-AES at low limits of detection due to an adaptation of the instrument. This adaptation doesn't affect the determination of other elements and will generally improve analytical performance for any elemental lines below 200 nm for example, Pb at 168 nm.

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