

## ORIGINAL PAPER

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## Chromium determination in sea water by electrothermal atomic absorption spectrometry using Zeeman effect background correction and a multi-injection technique

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**Abstract** Electrothermal atomic absorption spectrometry (ETAAS) applying a Zeeman effect background correction system (ZEBC) and a transverse heated atomizer was used to directly determine chromium in sea water. Calcium chloride (at a concentration of 20 mg L<sup>-1</sup>) was applied as chemical modifier with optimum charring and atomization temperatures of 1600°C and 2000°C, respectively. The detection limit was 0.2 µg L<sup>-1</sup>, by injecting 20 µL aliquot of sea water sample. This detection limit could be reduced further to 0.05 µg L<sup>-1</sup>, using multiple injections (injection of five 20 µL aliquot of sea water). The accuracy of the methods developed were confirmed by analyses of different certified reference materials. Finally, interferences from major and minor components of sea water are studied.

### Introduction

Chromium widely found in many minerals is considered non toxic for plants, fish, birds and mammals at the concentration prevalent in natural waters, soils and foods [1]. In addition, chromium is considered to be an essential element to living organisms (e.g. as biologically active chromium, BAC, for metabolism of glucose), a deficiency of chromium in animals can produce diabetes, arteriosclerosis, growth problems, and eye cataracts [1]. Nevertheless, chromium as all trace elements can be toxic at high levels. The toxicity is dependent on the species (Cr(III)/Cr(VI)). Therefore, speciation of Cr-species is today one of the main tasks in chromium analysis. Due to the chromium release into aquatic systems, the determination of trace elements in coastal sea waters is of increasing relevance in contamination studies to guarantee the quality

of sea water. Thus, chromium is enclosed in the European Directive (79/923/CEE) [2] relative to quality of water used to keep mollusks.

Electrothermal Atomic Absorption Spectrometry (ETAAS) is successfully used for the direct determination of traces of chromium [3–9] in fresh water. Difficulties encountered in complex samples, such as sea water, owing to matrix interferences and very low concentrations of chromium have been circumvented by previous preconcentration procedures based on extractions by complexation of chromium [10–14] with different reagents and extraction of the formed complex with organic solvents, chromium coprecipitation [15–22] by using different precipitating reagents and ion-exchange resins of different materials [14, 23–31]. Some characteristics of the procedures used for the direct determination of chromium in sea water samples are summarized in Table 1.

However, these methods are time consuming and are associated with a risk of contamination. Therefore, the direct determination of chromium in sea water using multi-injection technique remains of great interest.

In the present work, using ETAAS combined with chemical modification and Zeeman effect background correction (ZEBC), a preconcentration of chromium into the graphite tube applying a multi-injection technique was developed. The optimized method was applied to the direct determination of chromium in different reference materials and sea water from the Galician Coast. The results obtained were compared with those achieved by using a conventional graphite atomizer (DABC) and deuterium arc background correction.

### Experimental

#### Apparatus

Chromium absorbance was measured using a Perkin-Elmer Zeeman 4100 ZL atomic absorption spectrometer equipped with a THGA (transverse heated graphite atomizer) furnace and an AS-71 autosampler and a Perkin-Elmer 1100B atomic absorption spectrometer equipped with a HGA-700 and an autosampler AS-70. The operating conditions are shown in Table 2.

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**Table 1** Chromium determination in sea water by ETAAS

Ref.	Preconcentration	Background corrector	Matrix modifier	LOD <sup>a</sup>
[3]	no	D <sub>2</sub>	2.5% (m/v) NaWO <sub>4</sub>	0.1 µg L <sup>-1</sup>
[5]	no	no	5 mg L <sup>-1</sup> Ca(NO <sub>3</sub> ) <sub>2</sub> and Mg(NO <sub>3</sub> ) <sub>2</sub>	4 pg
[7]	no	no	NH <sub>4</sub> VO <sub>3</sub>	0.2 µg L <sup>-1</sup>
[8]	no	D <sub>2</sub>	Mg(NO <sub>3</sub> ) <sub>2</sub>	0.1 µg L <sup>-1</sup>
[9]	no	D <sub>2</sub>	no	0.3 µg L <sup>-1</sup>
This work (single injection)		Zeeman	20 mg L <sup>-1</sup> CaCl <sub>2</sub>	0.2 µg L <sup>-1</sup>
This work (multi-injection, 100 µL)		Zeeman	20 mg L <sup>-1</sup> CaCl <sub>2</sub>	0.05 µg L <sup>-1</sup>

<sup>a</sup>LOD defined as three times the standard deviation (SD) of eleven replicates of the blank of the addition graph divided by slope of the addition graph

**Table 2** Graphite furnace temperature program and spectrometer operating conditions

Step	Temperature (°C)	Ramp (s)	Hold (s)	Argon flow (mL min <sup>-1</sup> )
Drying	130	1	5	300
	150	5	30	300
Charring	1600	10	30	300
Atomization	2000	0	3	0 (read)
Cleaning	2600	1	3	300

Cr hollow cathode lamp. Wavelength: 357.9 nm. Lamp current: 25 mA. Spectral bandwidth: 0.7 nm. Integration time: 3 s. Peak area measurements. Transverse heated pyrolytic graphite tube (THGA) with integrated platform. Injection volume: 100 µL (five 20 µL aliquot)

#### Reagents

All solutions were prepared from analytical-reagent grade chemicals using ultrapure water, resistivity 18 MΩ cm<sup>-1</sup>, which was obtained by a Milli-Q water purification system (Millipore).

Chromium nitrate stock standard solution, 1.000 g L<sup>-1</sup>; supplied by Merck (Darmstadt, Germany). Calcium chloride standard solution, 1.000 g L<sup>-1</sup>; supplied by Merck (Darmstadt, Germany) was used as chemical modifier.

Synthetic sea water samples of high salinity 72.8% (SSWI): 30 g L<sup>-1</sup> NaCl and 10 g L<sup>-1</sup> each of MgCl<sub>2</sub>, KCl, CaCl<sub>2</sub> and SrCl<sub>2</sub>, and low salinity, 34.2% (SSWII): 32 g L<sup>-1</sup> NaCl, 14 g L<sup>-1</sup> of MgSO<sub>4</sub> · 7 H<sub>2</sub>O and 0.15 g L<sup>-1</sup> of NaHCO<sub>3</sub>, prepared according to Baxter and Frech [32].

Certified water materials, saline (NASS-4, supplied by the Research Council of Canada and CRM-403, supplied by the Commission of the European Communities) and non saline (IAEA/W-4 supplied by the International Atomic Energy Agency and SLRS-2 supplied by the Research Council of Canada) were used to prove the accuracy of the method.

Argon N-50 purity (99.999%), used as sheath gas for the atomizer and to purge internally, was obtained from SEO (Madrid, Spain).

#### Procedure for sample collection

Sea water samples were collected from coastal surface waters of Galicia (north west, Spain) in 100 mL glass bottles pre-cleaned, the samples were immediately acidified with 100 µL of concentrated nitric acid (29), giving a pH < 1.6 to avoid adsorption of chromium onto the glass walls. The samples were filtrated (0.45 µm) before measurement.

#### Procedure

A portion of the sea water sample (600 µL) with calcium chloride solution (20 mg L<sup>-1</sup>) was transferred into the autosampler cup, and completed to 1 mL. A volume of 20 µL was injected into the atomizer five times inserting a drying step after each injection. Sequential dry-char-atomizer-clean program (Table 2) of the graphite furnace was run and the integrated absorbance recorded.

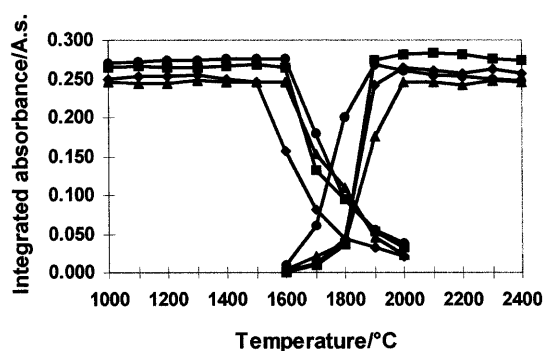
## Results and discussion

#### Optimum conditions

The drying step was optimized to reach a satisfactory drying of five 20 µL aliquots, two different drying steps had to be used (Table 2).

The influence of the charring temperature on the absorbance obtained for aqueous Cr<sup>3+</sup> standard solutions (20 µg L<sup>-1</sup>), synthetic sea water samples (SSWI and SSWII) and real sea water samples spiked with 20 µg L<sup>-1</sup> of Cr<sup>3+</sup>, are shown in Fig. 1. For these experiments, the atomization temperature was 2000°C. On the other hand, the effects of varying the atomization temperature are also shown in Fig. 1 for the same solutions, using 1600°C as charring temperature.

The chromium absorbance remained constant up to 1500°C for synthetic sea water of high salinity, and up to



**Fig. 1** Charring (left) and atomization (right) curves obtained for aqueous standard solution (◆), synthetic sea water samples of high (◆) and low (■) salinity and real sea water sample (●) spiked with Cr<sup>3+</sup> (20 µg L<sup>-1</sup>)

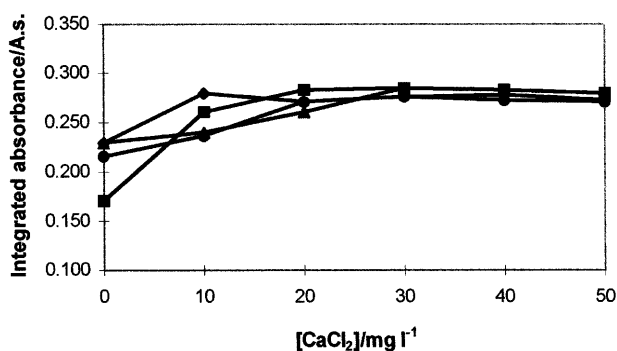
1600°C for the other solutions. The optimum atomization temperatures were 1900–2000°C. In addition, the integrated absorbance decreases for atomization temperatures higher than 2000°C, while for all kinds of solutions the peak height gradually increased up to an atomization temperature of 2200°C, and then it remained relatively constant.

For low ramp rates and short hold times of the charring step a strong scattering of the signal is found when the bulk of salts from sea water are volatilized in the atomization step. This scattering also produces a large background signal (2.0 a.u). Loss of chromium was observed during the charring step for ramp and hold times higher than 10 and 30 s, respectively. The background signal obtained was small (0.020 absorption units · seconds = As) for all combinations, except for scattering of the chromium signal.

The introduction of intermediate pyrolysis steps among each injection, at temperatures of less than 1600°C, to remove the sodium chloride matrix and possible interferences and to reduce the background signal was not found to be advantageous due to the loss of sensitivity occurring.

Although Zeeman effect background correction is used, chemical modification is necessary to achieve a satisfactory volatilization of the matrix salt from the sample, specially after preconcentration in the graphite tube by multi-injection. Among the different as chemical modifiers proposed for chromium in sea water, calcium chloride provides more consistent performances than others [33].

Thus, the effect of various amounts of CaCl<sub>2</sub> (0–50 mg L<sup>-1</sup>) on the chromium absorbance signal was studied with aqueous standard solution, synthetic sea water samples of high and low salinity and real sea water samples spiked with 20 µg L<sup>-1</sup> of Cr<sup>3+</sup>. As it can be seen in Fig. 2, the



**Fig. 2** Dependence of chromium absorbance signal on the amount of calcium chloride concentration for aqueous standard (◆), synthetic sea water of high (◆) and low (■) salinity, and real sea water sample (●) spiked with Cr<sup>3+</sup> (20 µg L<sup>-1</sup>)

chromium absorbance signal in all samples gradually increases up to 20 mg L<sup>-1</sup> CaCl<sub>2</sub>.

#### Use of a multi-injection technique

The direct ETAAS determination of chromium in sea water using CaCl<sub>2</sub> as chemical modifier was carried out and the analytical performances was studied for different injection volumes (20, 100 and 200 µL) under the optimized conditions shown in Table 2. The injection of a volume of 100 and 200 µL into the atomizer was reached by the injection of five 20 and 40 µL aliquots of sea water solution, inserting drying steps after each injection.

To reduce the drying time, a hot injection technique at 120°C was applied resulting in an efficient drying. In addition, a lower pipette speed (40%) was used to increase the drying of sample.

Equations of the standard addition obtained for Cr in synthetic sea water of high (SSWII) and low (SSWI) salinity, real sea water samples and deionized water are shown in Table 3. As it can be seen, the slopes of the graphs are more or less comparable (t-test for a confidence level of 95% (34)) when an injection volume of 20 µL is used. Thus, it can be assumed that the matrix effect was correctly compensated even at high salinity by using the Zeeman effect background corrector. Moreover, the calibration method using even deionized water is suitable for the Cr determination in sea water independently of its salinity. The detection limit (Table 4), calculated as three times the standard addition deviation of eleven replicates of a blank, divided by the slope of the calibration using synthetic sea water of low salinity, was 0.2 µg L<sup>-1</sup>. A within-batch precision of the method between 1.4 and 5.2% was obtained for 11 replicate injections of four sea water samples spiked with different amount of chromium (Table 4). The analytical recoveries were close to 100% for all kind of sea water samples. The accuracy was proved by analysis of a non saline water sample IAEA/W-4 (simulated fresh water), with a certified chromium concentration of 9.0–10.5 µg L<sup>-1</sup>. The analysis of CRM-403, NASS-4 and SLRS-2 by injecting small sample volumes (20 µL) was not possible due to the high detection limit.

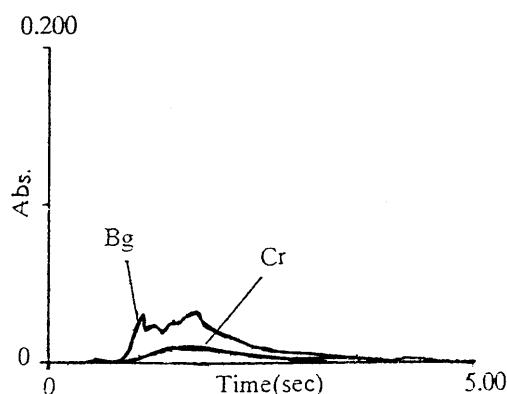
Therefore, it was attempted to use a multi-injection technique, injecting five 20 µL and 40 µL aliquots of sample into the graphite tube, to increase the chromium absorbance signal and to decrease the detection limits. The background signal obtained from real sea water samples was as small as 0.200 As when an injection volume of 100 µL was used. For an injection volume of 200 µL, the background signal was 0.350 As. These background sig-

**Table 3** Calibration and standard addition graphs corresponding to different injection volumes

Injection volume (µL)	Aqueous calibration	Calibration SSWII	Calibration SSWI	Standard addition
20	$Q_A = 0.007 + 0.013 [\text{Cr}]$	$Q_A = 0.010 + 0.012 [\text{Cr}]$	$Q_A = 0.011 + 0.010 [\text{Cr}]$	$Q_A = 0.014 + 0.012 [\text{Cr}]$
100	$Q_A = 0.012 + 0.070 [\text{Cr}]$	$Q_A = 0.016 + 0.068 [\text{Cr}]$	$Q_A = 0.031 + 0.060 [\text{Cr}]$	$Q_A = 0.026 + 0.074 [\text{Cr}]$
200	$Q_A = 0.010 + 0.111 [\text{Cr}]$	$Q_A = 0.030 + 0.137 [\text{Cr}]$	–	$Q_A = 0.040 + 0.143 [\text{Cr}]$

**Table 4** Within-batch precision, analytical recovery, LOD and LOQ corresponding to each injection volumes

Injection volume ( $\mu\text{L}$ )	[Cr] ( $\mu\text{g L}^{-1}$ )	RSD (%) <sup>a</sup>	Anal. Recovery (%)	LOD ( $\mu\text{g L}^{-1}$ )	LOQ ( $\mu\text{g L}^{-1}$ )
20	0	5.2	–	0.5	1.7
	5	3.2	99.2 $\pm$ 1.6	–	–
	10	2.1	103.4 $\pm$ 2.1	–	–
	20	1.4	102.8 $\pm$ 2.1	–	–
100	0	7.8	–	0.09	0.3
	1	2.7	106.3 $\pm$ 7.3	–	–
	2	7.2	103.8 $\pm$ 8.2	–	–
	4	4.1	104.3 $\pm$ 9.2	–	–
200	0	9.2	–	0.05	0.2
	0.5	5.6	106.3 $\pm$ 9.6	–	–
	1	7.4	105.2 $\pm$ 8.3	–	–
	2	4.6	106.3 $\pm$ 8.7	–	–

<sup>a</sup>  $n = 11$ **Fig. 3** Chromium peak profile and background signal obtained for unspiked sea water sample corresponding to an injection volume of 100  $\mu\text{L}$ 

nals can be easily corrected using Zeeman effect background correction. In Fig. 3 the peak profiles obtained for Cr and background signal are shown, for unspiked sea water using an injection volume of 100  $\mu\text{L}$ .

Differences in the slope of the calibration using sea water of high salinity were obtained compared with the slopes of low salinity and aqueous standard solutions for an injection volumes of 100  $\mu\text{L}$ . This matrix effect was due to the increase in salt concentrations. Reliable standard addition curves from synthetic sea water of high

salinity for injection volumes of 200  $\mu\text{L}$  could not be obtained due to the scattering of the chromium absorbance signal. Thus, a standard addition method is required for the determination of chromium in sea water of high salinity for an injection volume of 100  $\mu\text{L}$ , and for real and synthetic sea water samples for injection volumes up to 200  $\mu\text{L}$ . A detection limit of 0.05  $\mu\text{g L}^{-1}$  was obtained for an injection volume of 100  $\mu\text{L}$ , a detection limit of 0.03  $\mu\text{g L}^{-1}$ , in case of injection volumes of 200  $\mu\text{L}$ . The within-batch precision (Table 4) shows acceptable RSDs for both injection volumes. On the other hand, Table 4 shows analytical recoveries close to 100% for both injection volumes. The accuracy was characterized by analyzing two sea water reference materials, CRM-403 (salinity between 34.6–34.8%) and NASS-4 (salinity of 31.3%). A nonsaline reference material, SLRS-2 (riverine water) and IAEA/W-4 (simulated fresh water) was also analyzed. The concentration of chromium in the reference materials analyzed, for injection volumes of 100 and 200  $\mu\text{L}$ , are shown in Table 5. The chromium concentrations obtained are in good agreement with the certified ones for both injection volumes when non saline water reference materials are used. However, significant errors in the analysis of the CRM-403 and NASS-4 were obtained for an injection volume of 200  $\mu\text{L}$ , due to the under compensation of the signal originating from the high salt concentrations in the graphite tube when an injection volume of 200  $\mu\text{L}$  was used. Reliable results were obtained for an injection volume of 100  $\mu\text{L}$ .

#### Interference study

The effects of  $\text{Cl}^-$ ,  $\text{SO}_4^{2-}$ ,  $\text{HCO}_3^-$ ,  $\text{F}^-$ ,  $\text{BO}_3^{3-}$ ,  $\text{Na}^+$ ,  $\text{K}^+$  and  $\text{SiO}_3^{2-}$  (major components) and  $\text{NO}_3^-$ ,  $\text{HPO}_4^{2-}$ ,  $\text{IO}_3^-$ ,  $\text{MoO}_4^{2-}$ ,  $\text{Mg}^{2+}$  and  $\text{Li}^+$  (minor components) were investigated for an injection volume of 100  $\mu\text{L}$ . Different amounts of these species were added to a real sea water sample at concentrations higher than those found in sea water [35]. The constituents investigated did not cause an effect of more than  $\pm 5\%$  on the Cr absorbance signal.

Comparison of the results obtained using a conventional graphite atomizer and deuterium arc background correction (DABC)

The optimum pyrolysis and atomization temperatures achieved using DABC were 1600 and 2600°C, respec-

**Table 5** Chromium concentrations as  $\mu\text{g L}^{-1}$ , corresponding to each injection volume using different reference materials

Injection volume ( $\mu\text{L}$ )	SLRS-2 [Cr] <sup>a</sup> 0.45 $\pm$ 0.07	IAEA/W-4 [Cr] <sup>a</sup> 9.0–10.5	NASS-4 [Cr] <sup>a</sup> 0.115 $\pm$ 0.010	CRM-403 <sup>b</sup> [Cr] <sup>a</sup> 105.0 $\pm$ 7.3 <sup>d</sup>
20	– <sup>c</sup>	9.8 $\pm$ 0.6	– <sup>c</sup>	– <sup>c</sup>
100	0.47 $\pm$ 0.04	10.1 $\pm$ 0.7	0.121 $\pm$ 0.07	0.111 $\pm$ 0.03
200	0.48 $\pm$ 0.05	9.7 $\pm$ 0.7	0.154 $\pm$ 0.09	0.131 $\pm$ 0.03

<sup>a</sup> Certified Cr concentration, <sup>b</sup> Chromium concentration expressed as  $\text{ng kg}^{-1}$ , <sup>c</sup> Below LOQ, <sup>d</sup> Indicative value

**Table 6** Dissolved chromium levels in several sea water samples<sup>a</sup>

Sample	[Cr] ( $\mu\text{g L}^{-1}$ )	RSD (%)
1	0.7	4.8
2	2.7	1.1
3	1.2	1.7
4	0.6	5.3
5	1.5	1.4

<sup>a</sup>  $n = 4$  runs

tively. The difference in the atomization temperature is due to the poor efficiency of heating (in comparison with transverse heating) obtained with a conventional graphite atomizer.

For injection volumes of more than 20  $\mu\text{L}$ , matrix effects were observed, even for low salinity. In addition the accuracy obtained using the saline reference materials (NAAS-4 and CRM-403) were poor even for an injection volume of 100  $\mu\text{L}$ . This fact is due to a poor background correction achieved with the deuterium arc. For non saline waters (IAEA/W-4 and SLRS), the results obtained are in good agreement with certified values.

The detection limits obtained for 20, 100 and 200  $\mu\text{L}$  were 0.20, 0.06 and 0.03  $\mu\text{g L}^{-1}$ , respectively. As can be seen, the sensitivity using the ZEBC design was lower than for the DABC design due to the atomizer design that affects adversely the spectral absorption as expressed in Beer's law; the length of the graphite tube is 28 mm for DABC and 18 mm for ZEBC design.

## Application

The ETAAS method using Zeeman effect background correction, calcium chloride as chemical modifier, and a multi-injection technique (100  $\mu\text{L}$ ) was applied for the determination of chromium in sea water from Galician coast (north-western, Spain). A calibration method applying synthetic sea water of low salinity (SSWII) was used. The chromium concentration obtained are given in the Table 6, together with the RSDs. The values obtained, between 0.6 and 2.7  $\mu\text{g L}^{-1}$ , are in agreement with preceding studies [17, 20, 28].

## Conclusions

Due to the high charring temperature (1600°C) and low atomization temperature (2000°C) used, the background absorbance signals can be reduced widely, even for large injection volumes. Thus, chromium can be directly determined in sea water with good accuracy and precision using ETAAS combined with Zeeman effect background correction and chemical modification. The matrix interferences are completely removed, thus, a calibration curve using even aqueous standard solutions can be used for the Cr analysis. Moreover, the detection limit for Cr in sea

water can be reduced to 0.05  $\mu\text{g L}^{-1}$  using the multi-injection technique proposed (100  $\mu\text{L}$ ).

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