

Atomic Absorption Full Method

Cr in Saline Water

Key Words

- Chromium
- Seawater
- QuadLine Background Correction
- Graphite Furnace
- Atomic Absorption
- Extended Lifetime Cuvettes

Introduction

Industrial processes, such as electroplating, smelting and mining, have increased the introduction of chromium into the environment. Chromium has been linked with raised incidences of dermatitis and allergies, so monitoring of the metal in a wide variety of matrices has become increasingly important as legislation is introduced. European Community Directive 85/C 351/11 permits a maximum chromium concentration of 5 µg/L for water containing up to 50 mg/L of CaCO₃. EPA method 7191 for the Atomic Absorption Graphite Furnace analysis of chromium requires a Method Detection Limit of 1 µg/L and a Working Range of 5 to 100 µg/L.

Analytical Range

A method for the determination of chromium in water samples containing high concentrations of dissolved solids is presented. Seawater samples containing less than 10 µg/L of chromium could be analysed. The working range was up to at least 40 µg/L with no sample dilution.

Principle

Saline water samples containing 3.5 % m/v dissolved solids were determined directly with only a 5 % v/v dilution. No chemical treatment was required. Samples were analysed by direct calibration against aqueous standards using Graphite Furnace Atomic Absorption Spectrometry with Quadline background correction.

Thermo Scientific Extended Lifetime Cuvettes (ELC's) were used throughout.

Method

Reagents:

Nitric acid (Spectrosol grade).

Chromium master standard (1000 mg/L Spectrosol or equivalent).

Sample collection:

Samples should be collected in acid-washed, metal-free plastic or glass containers. Samples were acidified with 2 mL 50 % v/v hydrochloric acid for a 2 L sample (EC Directive) or to pH <2 with nitric acid for a 600 mL sample (EPA Method 7191) immediately after collection. Samples were stored at 4°C and analysed as soon as possible. The maximum holding time is 6 months.

All reagent examples available from:

Fisher Scientific
Bishop Meadow Rd
Loughborough,
LE11 5RG
UK

NRC Reference seawater samples were obtained from:

Queen's Road
Teddington
TW11 0LY
UK

Spectrometer

Measurement Mode:

Number of Resamples: ☐ High Resolution

☐ Fast B samples Background Correction:

Measurement Time (s):

Wavelength (nm):

Lamp Current (%):

Bandpass (nm):

☐ Optimize Spectrometer Parameters

Signal:

Transient Peak Measurement

Measure From (s): To:

☐ Fler Rejection

☐ Use Fler Rejection

Rejection Limit (%):

RSD Test

☐ Use Test

If RSD greater than %

AND signal greater than Abs

Then

Furnace

Cuvette:

Injection Temperature (°C): Programme Time (secs):

Furnace Programme

	Temp (°C)	Time (s)	Ramp (°C/s)	Gas Type	Gas Flow	RD	RS	TC	NL
1	90	30.0	0	2 Inert	0.2 L/min				
2	110	1.0	1	2 Inert	0.2 L/min				
3	400	20.0	20	2 Inert	0.2 L/min				
4	2500	3.0	0	2 Inert	Off				
5	2800	3.0	0	2 Inert	0.2 L/min				
6	0	0.0	0	2 Inert	Off				
7	0	0.0	0	2 Inert	Off				
8	0	0.0	0	2 Inert	Off				
9	0	0.0	0	2 Inert	Off				

☐ Clean Cuvette if sample greater than: Abs

Sampling

FS95

Sample

Sample Preparation:

Sample Volume (µL):

Injections:

Intelligent Dilution Threshold (%):

Working Volume (µL):

Standard Preparation:

Standard Additions:

☐ Wash Autosampler if sample greater than: Abs

☐ Slow Solution Uptake ☐ Automatic Spike

☐ Slow Solution Injection Spike Volume (µL):

☐ Sampling Delay Wastes:

Matrix Modification

	Name	Volume (µL)	Order	Method
1		20.0	1	None
2		20.0	2	None
3		20.0	3	None
4		20.0	4	None
5		20.0	5	None
6		20.0	6	None

Calibration

Method: ☐ Use Stored Calibration

Concentration Units:

Standards:

Standard Concentrations

	1	2	3	4	5
1	2.000	6.000	0.000		
2	3.000	7.000	0.000		
3	4.000	8.000	0.000		
4	5.000	9.000	0.000		
5	10.00	10.000	0.000		

Master Standard Conc:

Scaling Factor:

Scaled Units:

Calibration Checks

Acceptable Fit:

Excess Curvature Limits

Error (%):

To (%):

Rescale limit: %

If any calibration checks fail:

Figure 1: Analysis parameters

Method development

The instrumental parameters used are shown above in Figure 1. The optimum conditions were verified by automatically generating an ash/atomise plot for a sea water sample spiked with Cr and using the SOLAAR software, see Figure 2.

A check on the working range at 357.9 nm (figure 3) was made. A working range up to 40 µg/L was obtained. A greater working range could be obtained by dilution of the samples.

A reference sample, NASS-2 Reference Sea Water (National Research Council Canada), spiked additions to the reference sample and a Millipore water sample were analysed by standard additions. 1.9 mL of sample was diluted with 0.1 mL of a chromium standard to prepare the spiked samples

Standard solutions were automatically prepared by the FS95 autosampler from a master chromium standard containing 5.0 µg/L Cr in 0.1 % v/v nitric acid.

An injection volume of 10 µL was used for both samples and standards.

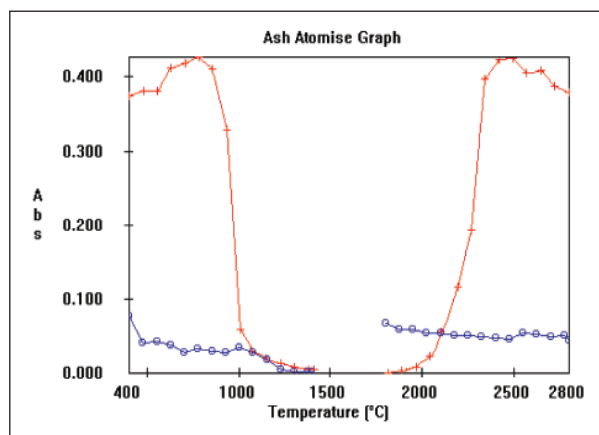


Figure 2: Cr in seawater ash/atomise plot

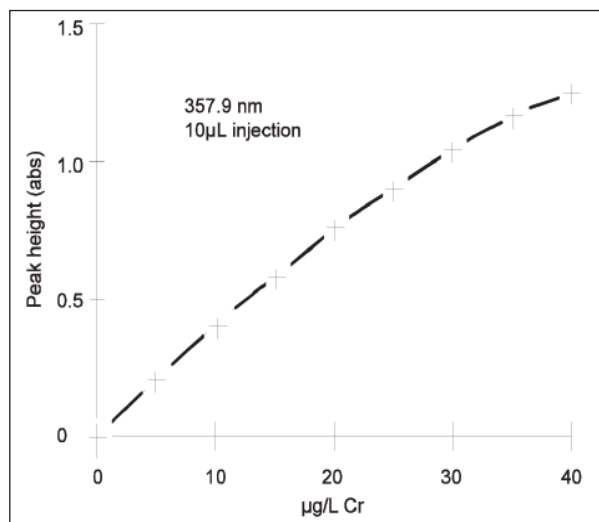


Figure 3: Cr working calibration range

Results

The results from the standard additions experiment are summarised in table 1 below.

Sample	Spike (µg/L)	Result (µg/L)	Expected (µg/L)
NASS-2	0.0	0.128	0.175
NASS-2	1.0	1.158	1.175
NASS-2	2.0	2.182	2.175

Table 1: Standard additions results

A standard addition calibration is shown in figure 4. and the relevant transient peak profiles are shown in figure 5.

Results from the analysis of 48 samples over a 24 hour period are given below in table 2, and are plotted in figure 6.

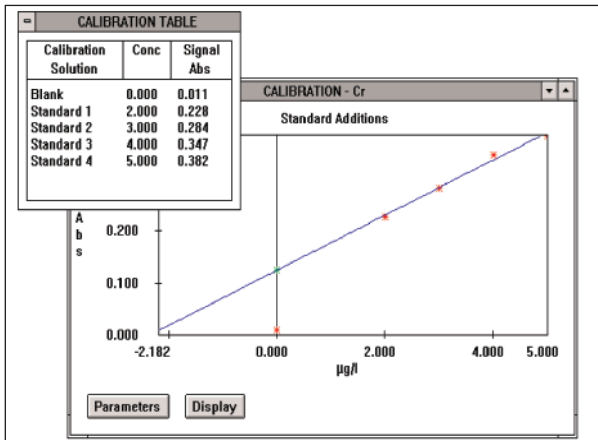


Figure 4: Chromium standard additions calibration

Sample	Spike (µg/L)	Mean result	24 hr %RSD	Number
NASS-2	2.0	0.129	5.5	12
NASS-2	4.0	0.256	4.5	12
NASS-2	6.0	0.398	3.4	12
Blank	0.0	0.016	7.7	12

Table 2: Reproducibility results

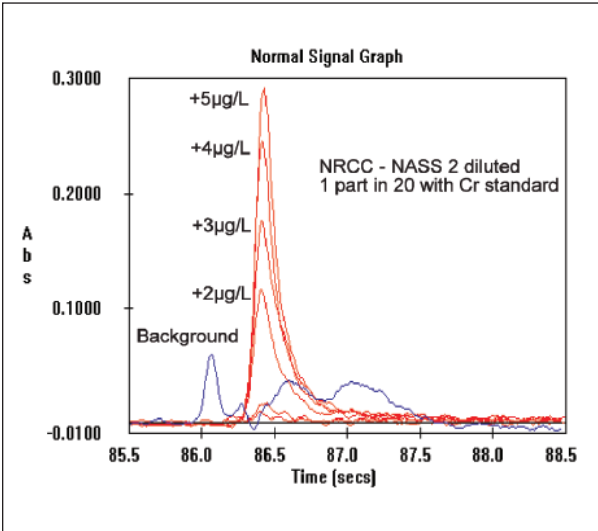


Figure 5: Chromium in seawater signals

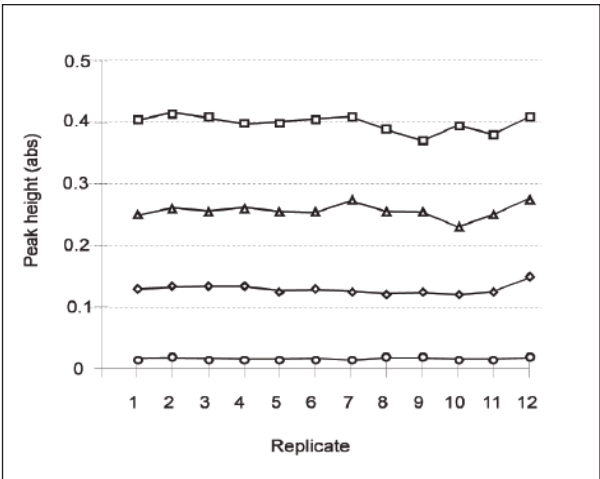


Figure 6: Reproducibility plot for 48 samples

A normal calibration procedure was used. Linear regression plots of the standard addition analyses are shown in figure 7. As the regression plots have similar gradients this indicates that normal calibration can be used for sea water samples.

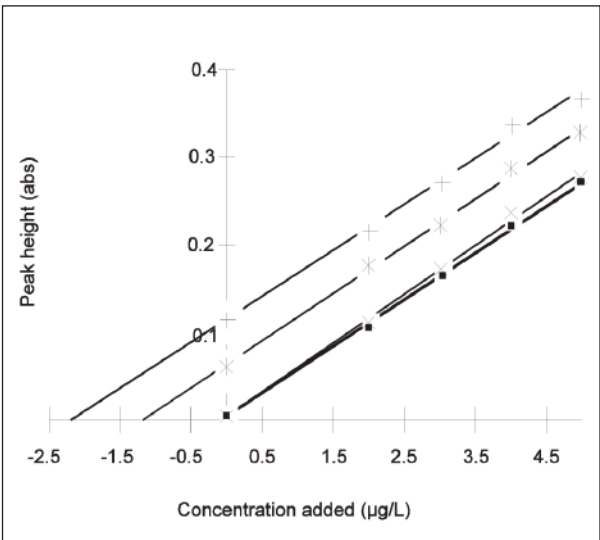


Figure 7: Linear regression plots

Conclusions

A simple method for the routine determination of chromium in seawater samples is presented. Standard additions analysis was proved not to be necessary.

Quadline background correction successfully corrected for any residual background interferences, in the samples, at the chromium wavelengths. The background and chromium signals could be accurately sampled due to the high measuring frequency of the Spectrometer. No furnace emission breakthrough was observed due to the superior echelle optics used in the spectrometer.

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