Measurement of Chromium in Environmental Waters by Zeeman Corrected Graphite Tube Atomization

Application Note

Atomic Absorption

Author

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Introduction

The measurement of trace metal levels in environmental waters is ideally performed by atomic absorption spectroscopy, and the literature on the techniques used is very extensive [1–7]. Chromium, along with other elements such as cobalt, copper, lead, manganese and nickel, requires monitoring in the environment.

The levels encountered are often too low to be measured by direct aspiration into the flame of an atomic absorption spectrometer, thus two methods are commonly employed to overcome this problem. The first is to form a metal complex using various ligands (pentan-2, 4-dione, acac; ammonium 1-pyrrolidinecarbodithioic acid, APDC) and extracting the complex into an organic solvent (4-methylpentan-2-one, MIBK; 2,5-methylheptan-4-one, DISK) [2]. By careful selection of the relative volumes, the analyte can be preconcentrated before aspiration into a flame. This method is relatively inexpensive but tedious and prone to contamination. Solvent extraction can also be used for furnace work [1–6].

The other method is by direct injection of the water sample into a graphite furnace [1,3–7]. Sample preparation and the possibility of contamination are therefore minimized [4]. The use of a background corrector is strongly recommended so that the effect of background interferences is reduced [7].

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Practical

Water samples collected under Environmental Protection Agency recommended conditions were used for method development. The method was then checked by measuring the amount of chromium in certified water samples. The first water sample was supplied by the US Environmental Protection Agency [8]. The other sample was a standard reference material obtained from the National Bureau of Standards [9].

Experimental

An Agilent SpectrAA-30 Zeeman atomic absorption spectrometer with a programmable sample dispenser and a chromium hollow cathode lamp-were used for this study. An Epson MX-80 printer was used for all printouts and signal graphics traces. A partitioned graphite tube was used in the furnace. The instrument parameters used for the final studies are reproduced in Table 1.

The chromium standard used in this study was prepared from BDH Spectrosol stock solution of 1000 mg Cr/L in 1 M nitric acid and diluted using deionized distilled water to give a final working concentration of 20 µg Cr/L.

Table 1. Instrument Parameters

PROGRAM 7 Cr EFFLUENT WATER

INSTRUMENT MODE	ABSORBANCE
CALIBRATION MODE	CONCENTRATION
MEASUREMENT MODE	PEAK HEIGHT
LAMP POSITION	1
LAMP CURRENT (mA)	7
SLIT WIDTH (nm)	0.2
SLIT HEIGHT	REDUCED
WAVELENGTH (nm)	357.9
SAMPLE INTRODUCTION	SAMPLER AUTOMIXING
TIME CONSTANT	0.05
MEASUREMENT TIME (sec)	2.0
REPLICATES	2
BACKGROUND CORRECTION	ON
MAXIMUM ABSORBANCE	2.00

FURNACE PARAMETERS

STEP NO.	TEMPERATURE (C)	TIME (sec)	GAS FLOW (L/min)	GAS TYPE	READ COMMAND
1	85	5.0	3.0	NORMAL	NO
2	95	60.0	3.0	NORMAL	ND
3	120	10.0	3.0	NORMAL	ND
4	1100	20.0	3.0	NORMAL	NO
5	1100	20.0	3.0	NORMAL	ND
6	1100	2.0	0.0	NORMAL	NO
7	2500	0.7	0.0	NORMAL	YES
8	2500	2.0	0.0	NORMAL	YES
9	2500	2.0	3.0	NORMAL	NO

SAMPLER PARAMETERS

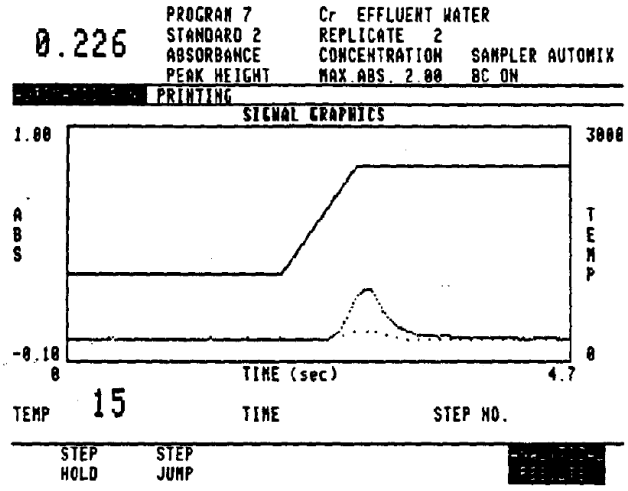
	VOLUMES (uL) SOLUTION	BLANK	MODIFIER
BLANK	--	15	
STANDARD 1	2	13	
STANDARD 2	5	10	
STANDARD 3	10	5	
SAMPLE	10	5	

RECALIBRATION RATE	0
RESLOPE RATE	0

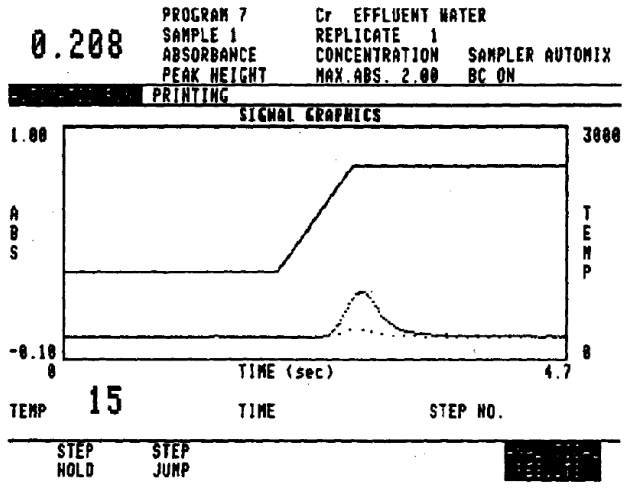
MULTIPLE INJECT NO HOT INJECT NO PRE INJECT NO

Results and Discussions

The collection of the environmental water samples and the preparation of all the standards meant that the chromium ions were present in a dilute nitric acid matrix. This particular matrix stabilizes the analyte in solution and allows the use of an ashing temperature which is high enough to remove all organic material. Signal graphics traces of a standard and a sample are reproduced together in Figure 1. Close examination reveals that there is very little difference in the respective background signals.



(i) standard



(ii) sample

Figure 1. Signal graphics traces.

A study was performed to see if there are any matrix effects. Because all organic matter is apparently destroyed, other metal ions present in the matrix could be a potential source of interferences. A standard additions calibration slope was compared to a normal concentration calibration slope. The data points and slopes are shown in Figure 2. As can be seen, the slopes are virtually identical. The concentration calibration mode was used for convenience in subsequent studies.

The validity of the method was checked by analyzing samples of known concentration. A concentration calibration curve was determined followed by analysis of samples of USEPA sample 4 and NBS SRM 1643b respectively. The autorun report is reproduced in Figure 3. The solutions being dilute aqueous solutions, their density would be the same as pure water to a very good approximation. Hence the numerical value for ng/L would be equal to the value in ng/g. The results obtained are compared in Table 2, and are seen to be in very good agreement.

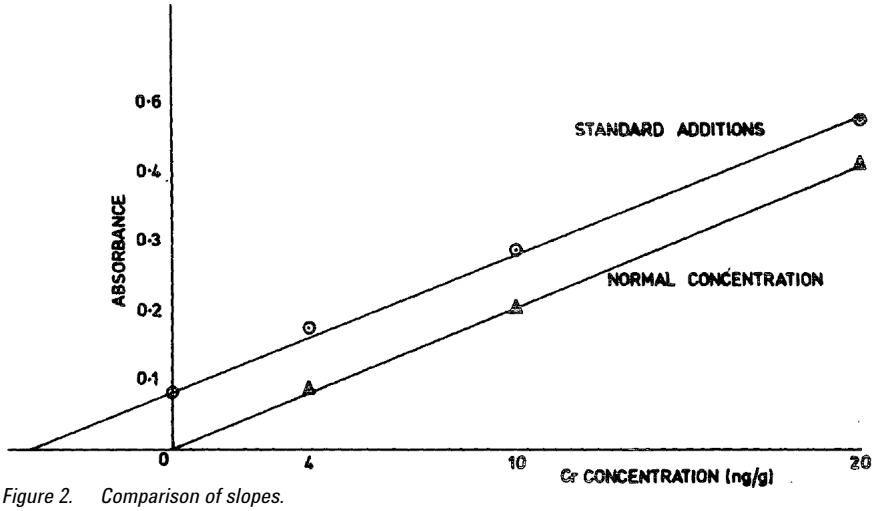


Figure 2. Comparison of slopes.

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                OPERATOR      JONATHAN  MOFFETT
                DATE          10 SEPTEMBER 1986
                BATCH         EPA#4/NBS

                PROGRAM 7     Cr  EFFLUENT WATER

SAMPLE          CONC          %RSD      MEAN                READINGS
                ug/L                    ABS

BLANK             0.00                  0.008     0.008     0.007
STANDARD 1        4.00          3.1     0.118     0.115     0.120
STANDARD 2       10.00          0.2     0.282     0.281     0.282
STANDARD 3       20.00          0.3     0.543     0.544     0.542
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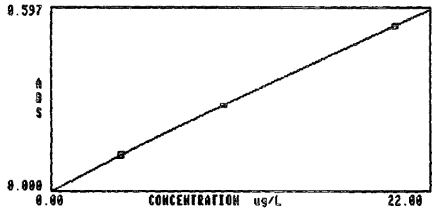


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USEPA #4          9.75          1.6     0.275     0.278     0.272
NBS SRM1643B     18.65          1.3     0.507     0.512     0.503
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Figure 3. Autorun report.

Table 2. Results Comparison

Comparison of experimentally determined results with quoted results

Standard		Quoted (ng/g)	Found (ng/g)
US EPA	Sample 4	10.2 ± 1.1	9.75 ± 0.16
NBS SRM	1643b	18.6 ± 0.4	18.65 ± 0.24

Conclusion

The determination of trace levels of chromium in waters and effluents can be done quickly and accurately and with good precision using a graphite furnace with an effective Zeeman background corrector.

References

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2. Lucinda Voth, Varian Instruments At Work No AA-17, August 1981.
3. Douglas Shrader, Lucinda Voth, Lawrence Covick, Varian Instruments At Work No AA-30, June 1983.
4. Douglas Shrader, Lucinda Voth, Lawrence Covick, Varian Instruments At Work No AA-31, June 1983.
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7. Lucinda Voth, Varian Instruments At Work No AA-35, September 1983.
8. Environmental Monitoring and Support Laboratory, US Environmental Protection Agency., Cincinnati, USA.
9. National Bureau of Standards, US Department of Commerce, Washington DC, USA.

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