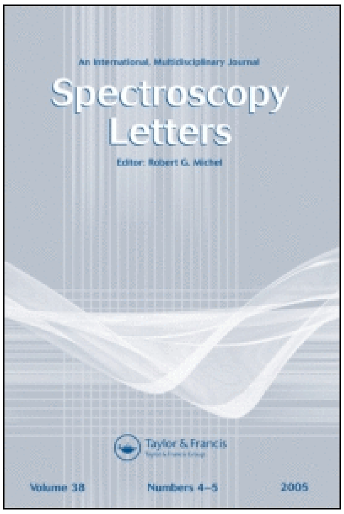

Spectroscopy Letters
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713597299

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W. L. Fong[a]; J. Gaston Wu[a]
[a] Department of Chemistry, National Taiwan Normal University, Taipei, Taiwan, R. O. C.

To cite this Article Fong, W. L. and Wu, J. Gaston(1991) 'Chromium Speciation Using Ion Chromatography-Atomic Absorption System with On-Line Preconcentration', Spectroscopy Letters, 24: 7, 931 — 941

To link to this Article: DOI: 10.1080/00387019108020672

URL: http://dx.doi.org/10.1080/00387019108020672

SPECTROSCOPY LETTERS, 24(7&8), 931-941 (1991)

CHROMIUM SPECIATION USING ION CHROMATOGRAPHY-ATOMIC ABSORPTION SYSTEM WITH ON-LINE PRECONCENTRATION

W. L. Fong, and J. C. GASTON WU*
Department of Chemistry, National Taiwan Normal University,
Taipei, Taiwan 11718, R. O. C.

ABSTRACT

A method using ion chromatography-atomic absorption system (IC-AA) with on-line preconcentration unit is developed for the speciation of chromium in aqueous samples. Both Cr(III) and Cr(VI) species are pretreated with sodium salt of ethylenediaminetetraacetic acid (EDTA) in consecutive steps. The treated samples can then be injected into an on-line preconcentration unit followed by ion chromatographic separation with UV or selective flame AA detection. Both chromium species can be separated within 10 minutes, and the method is applicable for aqueous samples with ppm levels of chromium.

INTRODUCTION

Chromium compounds are widely used in different types of industry, such as wood preserving, leather tanning, alloy production, pigment manufacturing and electroplating processes (1). In nature, chromium exists mostly in two different oxidation states, Cr(III) and Cr(VI). The oxidation state is mainly determined by the acidity, redox potential and other coexisting species in the environment (2)(3).

The toxicity of chromium is well known to be depending on its oxidation states. Cr(III) is proved to be biologically essential and related to human glucose tolerance factor (4)(5). No reports of oral toxicity of Cr(III) have ever been reported. However, dissolved Cr(VI) species are corrosive and toxic (6). The mechanism of toxicity of Cr(VI) is not yet well understood, but it seems to interfere with the enzymatic sulphur uptake of the cell (7)(8)(9). Airborn particulates containing Cr(VI) can be carcinogenic, and it can affect the lungs, liver and kidney.

Four different methods were approved by US EPA for chromium determination: (a) total chromium measurement using atomic absorption spectroscopy, (b) determination of Cr(VI) using coprecipitation followed by subsequent AA determination, (c) photometric measurement of Cr(VI) using 1,5-diphenylcarbazide (1,5-DPC) at 540 nm, (d) complexation of Cr(VI) with ammonium pyrrolidine dithiocarbamate followed by solvent extraction and AA determination (10-14). The speciation of

Cr(III) and Cr(VI) is normally done by indirectly procedure. The quantity of Cr(III) is differentiated by subtraction of Cr(VI) from total chromium determination.

In this study, both Cr(III) and Cr(VI) in aqueous solution can be speciated directly and determinated simultaneously with minimum sample pretreatment. The use of atomic absorption as chromatographic detector allows selective detection, and spectral interference from sample matrices is therefore minimized.

EXPERIMENTAL

I. REAGENTS

Reagent water is obtained by purifying distilled water with Milli-RO 60 water purification system and Milli-Q reagent water system. Both systems are products of Millipore.

Cr(III) and Cr(VI) standard solutions are prepared daily by dilution of 1000 ppm stock solutions which are prepared from analytical grade potassium perchromate ($K_2Cr_2O_7$), and chromium nitrate ($Cr(NO_3)_3$) with over 99.5% purity. Both chemicals are purchased from Kanto, Japan and Ferak, Germany, respectively.

The EDTA disodium salt is from E.Merck, Germany with purity over 99%. It is dissolved into an aqueous solution which has a pH of 5.00. The pH of this 0.01 M EDTA solution is adjusted using an acetic acid/sodium acetate buffer. Both chemicals for this buffer solution are E. Merck products with nearly 100% purity.

The eluent used for ion chromatographic system is 0.3 M aqueous sodium nitrate ($NaNO_3$) solution prepared from E. Merck product with purity better than 99.5%. All standards and samples injected onto ion chromatograph are subjected to membrane filtration. This is completed by using 0.45 um HVLP membrane from Millipore.

II. EQUIPMENT

The chromatographic system contains a Kratos Spectroflow 400 solvent delivery pump, Rheodyne 7125 and 7000 loops with volumes of 20 and 1000 ul respectively for injection and preconcentration. Anion exchange column, Ion-110 with length 25 cm, is purchased from Interaction, Inc. A separate 5 cm column with same packing material is used for preconcentration purpose, which is connected with the separation unit with Rheodyne switching valves as shown in figure 1.

Detection of the chromium species is accomplished by using two detectors, an ERC-7211 UV detector from Japan and Perkin-Elmer 2280 atomic absorption spectrometer with D_2 background corrector. The interface between the chromatographic system and the atomic absorption unit is facilitated with a piece of Tygon and a glass capillary tubing. The schematic of this interface is shown in figure 2.

A Hitachi U-2000 spectrophotometer is used to scan and select monitoring wavelengths for chromium species in $NaNO_3$ eluent.

III. PROCEDURE

The chromium species in aqueous samples are reacted with 0.01 M EDTA solution (pH 5) at 60° C for one hour for the complexation of

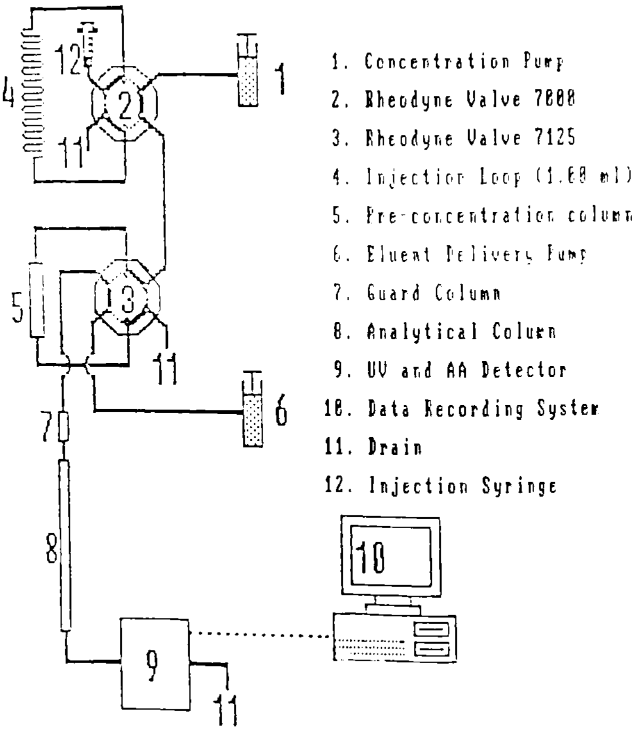

Fig. 1. Ion Chromatography - AA system with on-line pre-concentration unit

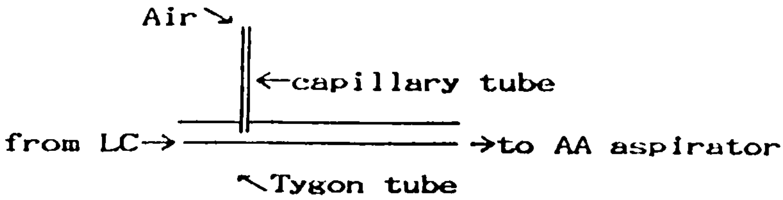

Fig. 2. Schematic illustration of the Tygon interface between ion chromatograph and flame AA detector.

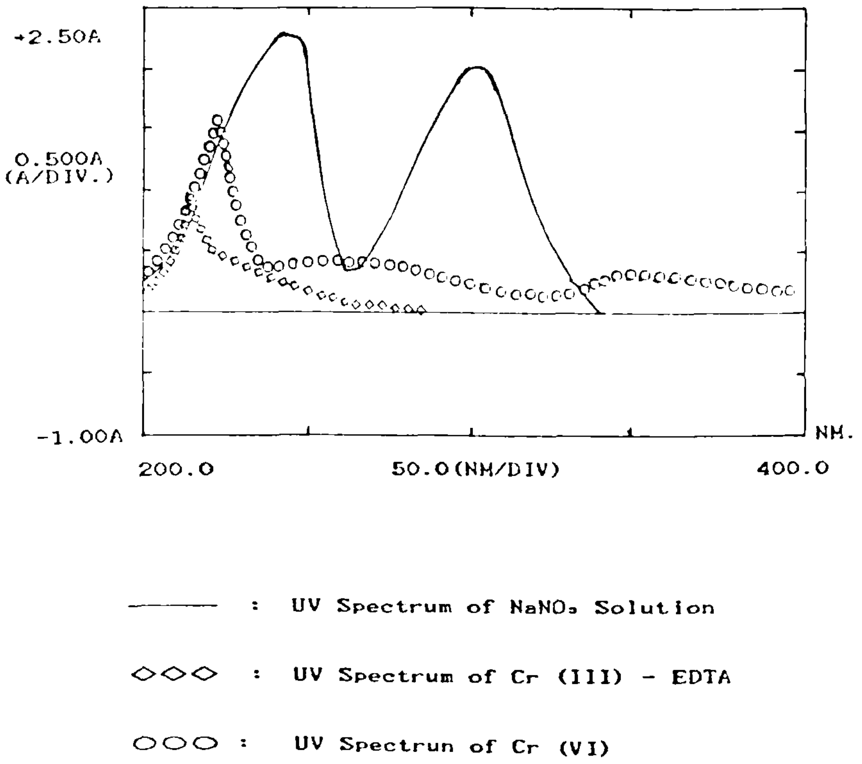

Fig. 3. UV spectra for $NaNO_3$ eluent, Cr(III) and Cr(VI) species after reaction with EDTA.

Cr(III), while the Cr(VI) remains unchanged. The complexed Cr(III) gives a color of purple. The reacted solution is injected into the chromatographic system with the on-line preconcentration unit, as illustrated in figure 1. A 0.3 M $NaNO_3$ solution with flow rate of 0.75 ml/min is applied for separation. Chromium species are preconcentrated at a pre-column at a flow-rate of 1.0 ml/min using a separate pump. The ERC UV detector is set at wavelength 257.0 nm which is the optimum for Cr(VI) species without interference from $NaNO_3$ in the mobile phase. The separated chromium species are subsequently monitored by the atomic absorption spectrometer at 357.9 nm with air-acetylene flame.

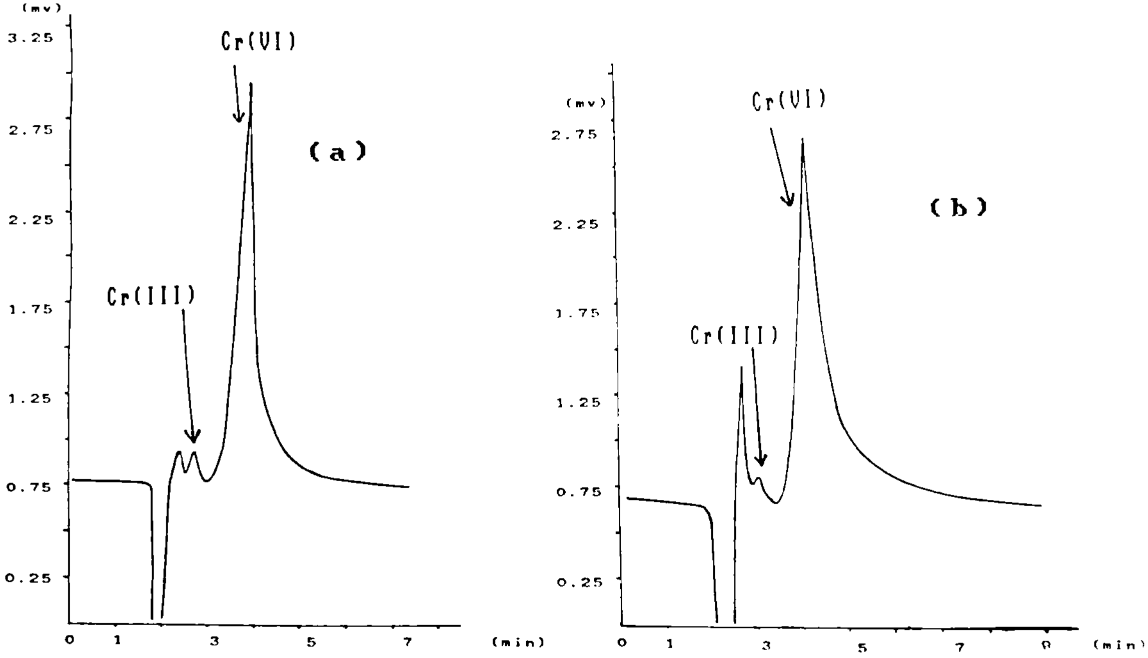

Fig. 4. (a) Ion chromatogram of 50.0 ppm Cr(III) and Cr(VI) using UV detection at 257.8 nm.
(b) Ion chromatogram of 1.00 ppm Cr(III) and Cr(VI) using UV detection after preconcentration.

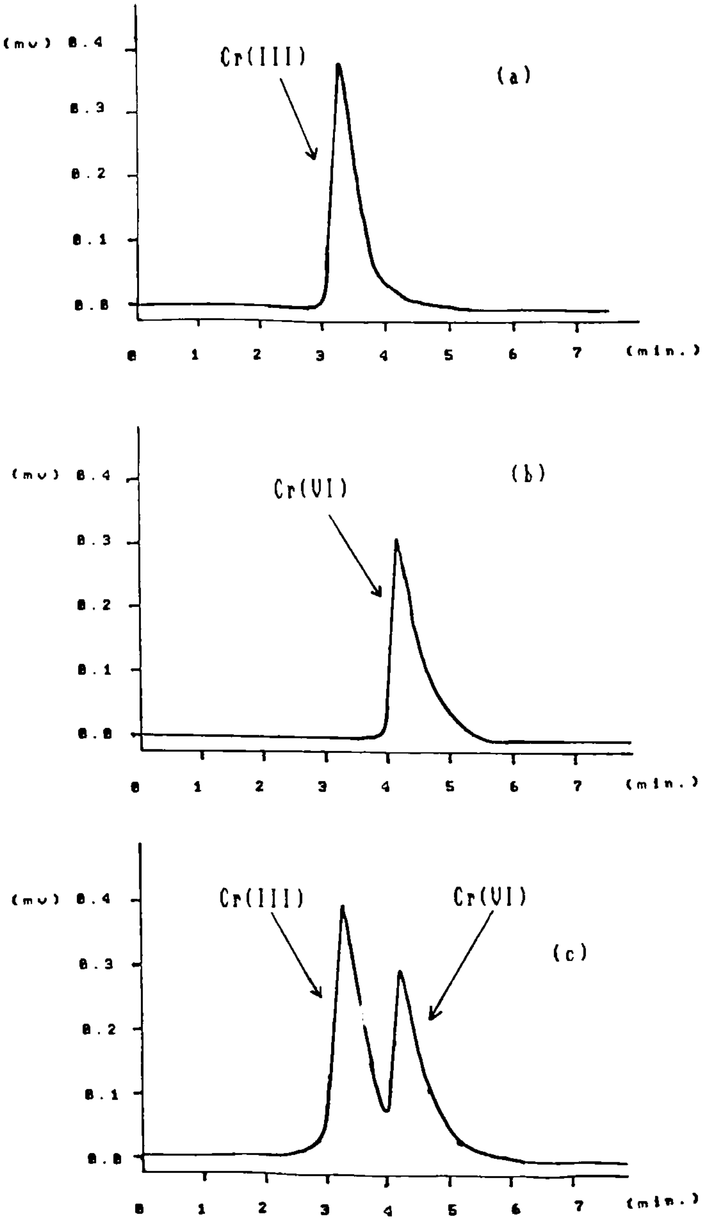

Fig. 5. Ion chromatograms of Cr(III), Cr(VI) and the mixture using AA detector. (a) Chromatogram of 25.0 ppm Cr(III); (b) Chromatogram of 25.0 ppm Cr(VI); (c) Chromatogram of the mixture.

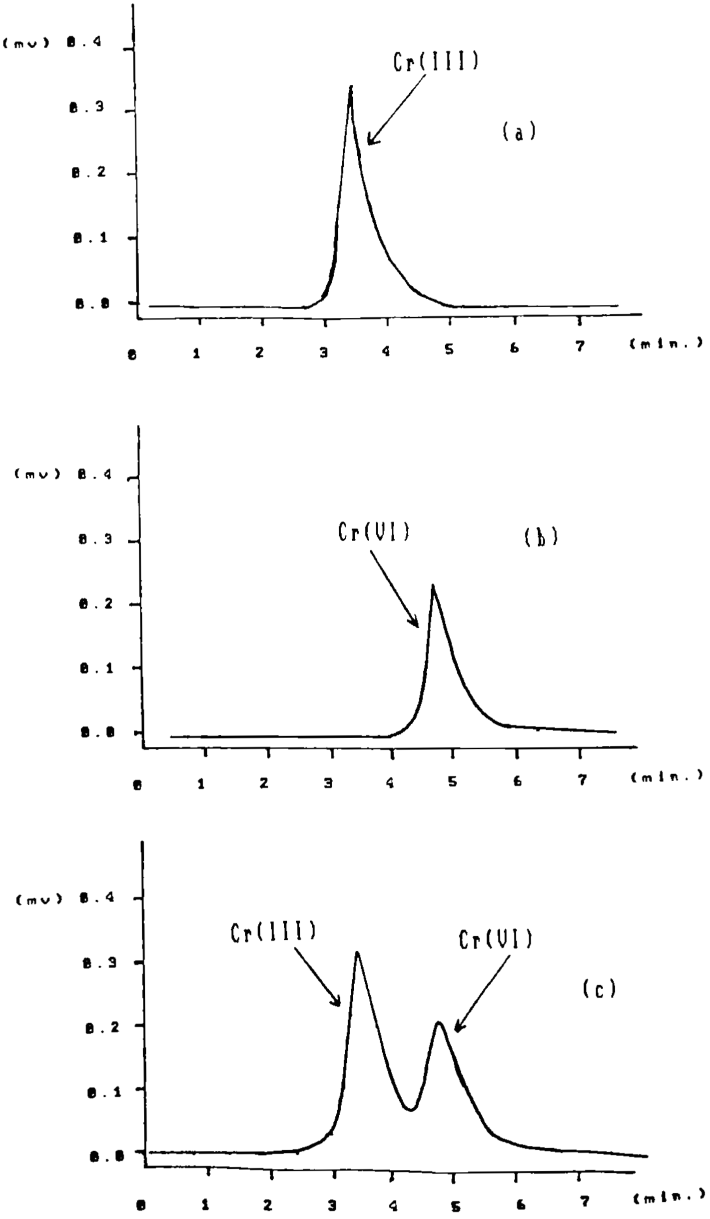

Fig. 6. Ion chromatograms of 0.50 ppm Cr(III), Cr(VI) and the mixture using AA detector. (a) Cr(III); (b) Cr(III); (c) the mixture.

Table 1. Percent recovery of preconcentration

	Concentration Injected	Concentration Calculated*	% Recovery
Cr(III)	0.50 ppm	0.42 ± 0.02 ppm	84.0
Cr(VI)	0.50 ppm	0.45 ± 0.06 ppm	90.0

* Calculated from five consecutive injections.

RESULTS AND DISCUSSION

I. CHROMATOGRAPHIC SEPARATION

The ion chromatography for anion separation is utilized as the separation mode for both Cr(VI) and Cr(III), since Cr(VI) exists predominantly as anion in aqueous solution(5), Cr(III) is complexed with EDTA. Although carbonate and bicarbonate solutions are common eluents for the separation of anions, pH of the mobile phase is more difficult to be controlled. A 0.3 M solution of $NaNO_3$ is found to be pertinent to differentiate chromium species in this system.

II. UV SPECTRA AND DETECTION

The use of UV detector for the speciation of metal compounds suffers the lack of specificity and is hampered by interferences in most cases. However, it can be used as a supplemental detection mode before the metal-specific detector, such as AA, is used. This is beneficial during the stage of method development. Figure 3 shows the UV spectra of solutions of $NaNO_3$, Cr(III) and Cr(VI) after their reactions with EDTA. Due to the strong absorption of $NaNO_3$, the wavelength 257.8 nm is selected for UV detection.

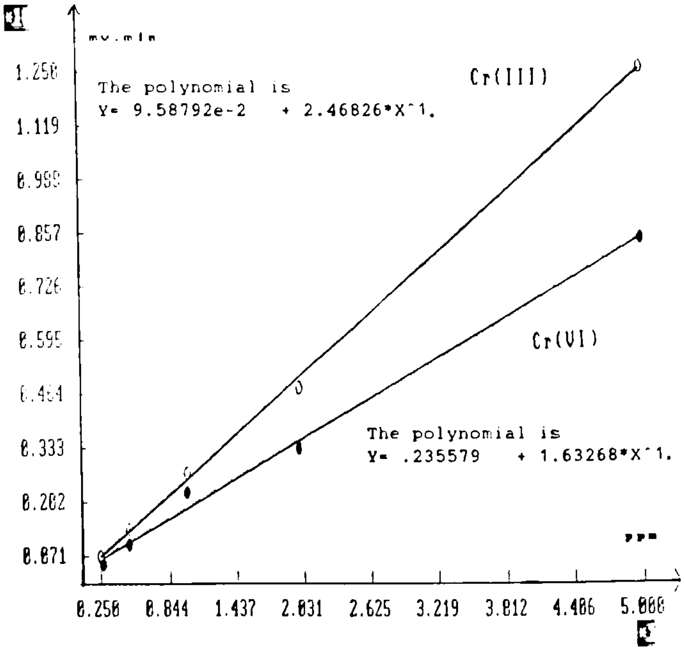

Fig. 7. Calibration lines for Cr(III) and Cr(VI) using the ion chromatography - AA system with on-line preconcentration.

The chromatograms for chromium species using UV detector is shown in figure 4. Part (a) in figure 4 is for 50.00 ppm Cr(III) and Cr(VI) each, after reaction with EDTA, and part (b) is obtained with 1.00 ppm Cr(III) and Cr(VI) after preconcentration 1.00 ml of sample. The poor sensitivity for Cr(III) is attributed to the UV wavelength selection.

III. ATOMIC ABSORPTION DETECTION

Atomic absorption detection followed by chromatographic separation of metal species enhances the monitoring specificity and facilitate quantification(15). The interface between ion chromatograph and the atomic absorption unit is achieved by a piece of Tygon tubing with a capillary side-arm to balance the high intake flow rate of AA nebulizer with air, which is also used as oxidant in AA processes. Chromatograms of chromium(III), chromium(VI) and the mixture of both are shown in in figure 5.

Table 2. Results for synthetic sample analyses

	Concentration in synthetic sample	Concentration * determined	% Recovery
Cr(III)	2.00 ppm	1.62 ± 0.03 ppm	81.0%
Cr(VI)	2.00 ppm	1.76 ± 0.07 ppm	88.0%

* Results is based on seven consective analyses of the prepared synthetic sample of river water.

Although the use of AA detection obviously improves the monitoring specificity, sensitivity is hampered by dilution effect from mobile phase and air flow drawn from the interface. The on-line preconcentration unit is applied to overcome this effect. Figure 6 illustrates chromatograms of Cr(III), Cr(VI) and the mixture, 0.50 ppm each, with AA detection after concentraing 1.00 ml of standard solutions. The preconcentration efficiency is affected by the intake flow rate of sample. The optimum flow rate is found to be around 1.00 ml/min. The preconcentration recovery is shown in table 1. The recovery may be increased with the use of a longer concentration column, but this effect is not investigated.

IV. SYNTHETIC SAMPLE ANALYSIS

To study the feasibility of this method, samples of river water are collected from Hsin Dan river, Taipei, and their total chromium contents are determined with flame AA technique. However, no chromium

is detected. Therefore, synthetic sample is prepared using filtered river water (pH 7.35). This sample contains 2.00 ppm of both Cr(III) and Cr(VI), and is subjected for multiple analyses. The contents of chromium are determined using working curve shown in figure 7.
A discrepancy of sensitivity, in term of slope of calibration line, is noticed between Cr(III) and Cr(VI), indicating possible chemical interference in flame AA detection process for Cr(VI); however, this phenomenon is not further studied and shows not effect on quantification. Results of determinations are in table 2, with calculated recoveries. The limits of detection are obtained from three times the standard deviation of seven consecutive injections of a synthetic sample with 0.50 ppm Cr(III) and Cr(VI), and they are determined to be 0.08 ppm and 0.20 ppm respectively.

ACKNOWLEDGEMENT

Financial support from the National Science Council of the Republic of China is gratefully acknowledged.

REFERENCES

1. Goldberg, A. J.; "A Survey of Emissions and Controls for Hazardous and Other Pollutants" US Environmental Protection Agency, Washington, D. C., 1973, Feb.
2. Rao, V. M.; Sastri, M. N., Talanta, 1980, 27, 771.
3. Rao, V. M.; Sastri, M. N. J. Sci. & Ind. Res., 1982, 41, 607.
4. Volkovic, V.; "Trace Elemental Analysis", Tailor and Francis Ltd., London, 1975, 107.
5. Schwarz, K.; Mertz, W., Archs Biochem. Biophys., 1959, 86, 202.
6. Gafefer, G.; "Health Workers in Chromate Producing Industries" Division of Occupational Health, US Public Health Service Publication 1953, 192.
7. Forstner, V.; Muller. G., "Schwer Metalle in Flussen und Scon" Springer-Verlag Publisher, Berlin, 1974, 24.
8. Fiabane, A. M.; Williams, D. R., "The Principle of Bioinorganic Chemistry" Chemical Society Publication, London, 1977, 42.
9. Mertz, W. Physiol. Rev., 1969, 49, 163.
10. "Test Method for Evaluating Solid Waste --- Physical/Chemical Methods" US Environmental Protection Agency, Washington, D. C., 1982.
11. Bubnis, B. P.; Straka, M. R.; Pacey, G. E. Talanta, 1983, 30(11), 841.
12. Lynch, T. P.; Kernoghan, N. J.; Wilson, J. N., Analyst, 1984, 109, 839.
13. Ruz, J.; Rios, A.; Luque de Castro, M. D.; Valcarcel, M., Anal. Chim. Acta, 1986, 186, 139.
14. Rus, J.; Rios, A.; Luque de Castro, M. D.; Valcarcel, M., Talanta, 1986, 33(3), 199.
15. Wu, J. C.; Robinson, J. W. Spectroscopy Letters, 1986, 19(1), 62.

Date Received: 10/31/90
Date Accepted: 11/28/90