



Perconcentration of Trace Cr(III) using Octadecyl Silica Membrane Modified N,N-Disalicylideneethylenediamine

ALI MOGHIMI^{1,*} and MOHAMMAD JAVAD POURSHARIFI²

¹Department of Chemistry, Islamic Azad University Varamin (Pishva) Branch, Tehran, Iran

²Department of Chemistry, Islamic Azad University Saveh Branch, Saveh, Iran

Corresponding author: E-mail: alimoghimi@iauvaramin.ac.ir

(Received: 23 August 2010;

Accepted: 9 May 2011)

AJC-9923

A novel and selective method for the fast determination of trace amounts of Cr(III) ions in water samples has been developed. The procedure is based on the selective formation of chromium N,N-disalicylideneethylenediamine (NNDED) complexes at optimum pH by elution with organic eluents and determination by atomic absorption spectrometry. The method is based on complex formation on the surface of the ENVI-18 DISK™ discs followed by stripping of the retained species by minimum amounts of appropriate organic solvents. The elution is efficient and quantitative. The effect of potential interfering ions, pH, ligand amount, stripping solvent and sample flow rate were also investigated. Under the optimal experimental conditions, the break-through volume was found to be about 1000 mL providing a preconcentration factor of 500. The maximum capacity of the discs was found to be $389 \pm 4 \mu\text{g}$ for Cr^{3+} . The limit of detection of the proposed method is 5 ng per 1000 mL. The method was applied to the extraction and recovery of chromium in different water samples.

Key Words: Cr(III), Solid phase extraction, Octadecyl silica disks, AAS, N,N-Disalicylideneethylenediamine.

INTRODUCTION

Toxicological studies have proved that the degree of toxicity of an element directly depends on the species in which it is present. Cr(III) is considered as an essential micronutrient for humans and mammals in order to maintain glucose metabolism, where as Cr(VI) is a potentially carcinogenic agent¹. The significant drawbacks of Cr(VI) are breathing disturbances, liver and digestion malfunctions, dermal corrosion and skin allergies². Therefore, it is necessary to control the level of chromium in industrial effluent, natural and drinking waters. Speciation of chromium in environmental samples is of prime importance.

There are numerous methods and techniques concerning chromium speciation and determination including liquid-liquid extraction after complex formation^{3,4}, solid-liquid extraction⁵⁻⁸, LC-AAS^{9,10}, FIA-AAS^{11,12}, spectrophotometric^{12,13}, ICP-AES¹⁴ and NAA¹⁵. However, some of these techniques are currently, time consuming and have elaborate sample preparation steps and low enrichment factors.

Solid phase extraction (SPE) methods are the best alternatives for traditional classic methods due to selective removal of trace amounts of metal ions from their matrices. Solid phase extraction determinations can be carried out on different efficient ways. One of the most appropriate performance features of SPE is achieved by using octadecyl silica membrane

discs. Solid phase extraction reduce the use of toxic solvent, disposal costs and extraction time^{16,17}. The octadecyl silica membrane discs involves shorter sample processing time and decreased plugging due to the large cross-sectional area of the disc and small pressure drop which allows higher flow-rates; reduced channeling resulting from the use of sorbent with smaller particle size and a greater mechanical stability of the sorbent bed¹⁸.

In our previous attempts, we modified SPE membrane discs with suitable compounds for selective determination of chromium¹⁹⁻²¹ and lead²². Meanwhile, other investigators have successfully utilized these sorbents for quantitative extraction and monitoring trace amounts of lead²³⁻²⁵, copper²⁶⁻²⁸, silver^{29,30}, mercury^{31,32}, cadmium³³, palladium³⁴, Ce³⁵ and UO_2 ³⁶.

In the present report, we wish to describe a proper concentration method for assessment of trace levels of chromium in different water samples. To the best of our knowledge, octadecyl silica membrane discs modified by the introduced symmetrical Schiff's base (NNDED) (Fig. 1) have not been used for chromium isolation and preconcentration. This study reports, the development of a rapid, efficient and highly sensitive method for selective extraction and concentration of ultra trace amounts of Cr^{3+} ions from aqueous media using octadecyl silica membrane modified by N,N-disalicylideneethylenediamine and AAS determination.

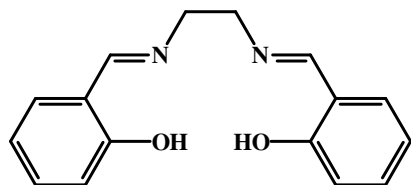


Fig. 1. Molecular structure of N,N-disalicylideneethylenediamine

EXPERIMENTAL

All acids were of the highest purity available from Merck and were used as received. Methanol and chloroform were of HPLC grade from Merck. Analytical grade nitrate salts of lithium, sodium, potassium, magnesium, calcium, strontium, barium, zinc, cadmium, lead, nickel, cobalt(II) and Cr(III) were of the highest purity. Ultra pure organic solvents were obtained from E. Merck, Darmstadt, Germany and high purity double distilled deionized water was used throughout the experiments.

The stock standard solution of Cr^{3+} was prepared by dissolving 0.1000 g of the copper powder in 10 mL concentrated nitric acid and diluted to 1000 mL with water in a calibrated flask. Working solutions were prepared by appropriate dilution of the stock solution.

The procedure for preparation of N,N-disalicylideneethylenediamine (NDEED) is as follows: A mixture of 0.002 mol salicylaldehyde and 0.001 mol of ethylene diamine in 10 to 15 mL of absolute methanol was refluxed in a round bottom flask for 1 h. The solvent was then evaporated and the residue was crystallized from 95 % ethanol as a yellow precipitate. The precipitate was thereafter recrystallized in absolute ethanol and finally dried in vacuum.

The specifications of the yellow crystals obtained as product were: m.p. 126-128 °C; IR (KBr, ν_{max} , cm^{-1}): 3050, 2932, 2901, 2870, 1636, 1497, 1283, 1149, 1042, 1021, 857, 749, 741; MS, m/z (%): 268 (M^+ , 23); Anal. calcd. for $\text{C}_{16}\text{H}_{16}\text{N}_2\text{O}_2$ (268.31): C, 71.62; H, 6.01; N, 10.44. Found: C, 71.8; H, 6.05; N, 10.3 %. $^1\text{H NMR}$ (250.1 MHz, DCCl_3): δ 3.9 (s, 4H, CH_2), 6.8 (m, 4H), 7.3 (m, 4H), 8.3 (s, 2H), 13.2 (brs, 2H, Ar-OH).

Determination of Cr^{3+} contents in working samples were carried out by a Varian spectra A. 200 model atomic absorption spectrometer equipped with a high intensity hollow cathode lamp (HI-HCl) according to the recommendations of the manufacturers. These characteristics are tabulated in Table-1.

TABLE-1
OPERATIONAL CONDITIONS OF FLAME
FOR DETERMINATION OF Cr(III)

| Parameters | Chromium |
|---|-----------|
| Hollow cathode lamp current (mA) | 7.0 |
| Wavelength (nm) | 357.9 |
| Slit width (nm) | 0.2 |
| Background correction | BC off |
| Measurement mode | Integrate |
| Air flow rate (L min^{-1}) | 13.50 |
| Acetylene flow rate (L min^{-1}) | 2.90 |

Solid phase extractions were carried out by glassy membrane discs, ENVI-18DISK™ 47 mm diameter \times 0.6 mm thickness containing octadecyl silica bonded phase (30 μm particles, 70 Å pore size) obtained from Supelco in conjunction with a

standard Millipore 47 mm filtration apparatus equipped with a vacuum pump. The pH measurements were carried out by an ATC pH meter (EDT instruments, GP 353).

Sample extraction: Extraction were performed with glassy membrane discs, ENVI-18 DISK™ 47 mm diameter \times 0.6 mm thickness containing octadecyl silica bonded phase (30 μm particles, 70 Å pore size) from Supelco. The discs were used in conjunction with a standard Millipore 47 mm filtration apparatus connected to water aspirator³⁷.

Sample treatment: The water samples were filtered through 45 μm nylon filters. Sampling vessels were polyethylene bottles soaked in 1 mol L^{-1} HNO_3 overnight and rinsed twice with deionized water. The analysis must be done within 2 days of sample collection to limit the risk of interconversion of Cr(III). Then, 5 mL of methanol was added to a 90 mL portion of each before analysis. The surface of the ENVI-18 DISK™ discs is not modified with NNDED and therefore could not retain Cr^{3+} ions properly. Instead, 10 mg of NNDED was dissolved in an appropriate volume of an organic solvent (5 mL) miscible with water. The most suitable solvent under the experimental conditions was acetone. The NNDED solution was added to aqueous solution of Cr^{3+} and the mixture was stirred gently.

Disc cleaning and conditioning: A disc was placed in the apparatus and was washed with 10 mL of methanol to remove all contaminants arising from the manufacturing process and the environment. Then, the disc was dried by passing air through it for several minutes. To ensure optimal extraction of the analytes of interest, the disc was again washed with 10 mL of methanol, immediately followed by 10 mL of water, without letting the surface of the disc dry. This step pre-wets the disc surface prior to extraction. Improper performance of this step causes slow flow-rate and poor analyte recoveries. It is important to avoid any air contact with the surface of the disc before the addition of the sample.

Sample addition: After complete homogenization, accurate volumes of the sample solutions (100 mL portions) were transferred to the top reservoir of the disc apparatus. At the same time, the solution was drawn through the disc by applying a mild vacuum. Application of vacuum was continued until the disc was completely dry (about 5 min).

Analyte elution: In order to elute the analyte selectively, exactly 5 mL of acidified solvents 0.1M HCl in methanol was passed through the disc and collected into a 5.0 mL volumetric flask under the extraction funnel. It was found that ultra pure alcoholic organic solvents were the best eluting agents. The concentration of Cr(III) in the eluates were then determined by FAAS using an external calibration graph.

RESULTS AND DISCUSSION

Evaluation of the role of the ligand: Some preliminary experiments were performed for investigation of absence or presence of NNDED on the quantitative extraction of Cr(III). It was concluded that the membrane disc itself does not show any tendency for the retention of Cr(III), but introduction of 100 mL portions of aqueous Cr(III) samples containing 10 μg of Cr(III) and 10 mg of NNDED leads to satisfactory its retention (Table-2). The latter case is most probably attributed to the existence of a considerable interaction between Cr(III)

TABLE-2
EFFECT OF PRESENCE OF NNDED ON
EXTRACTION PERCENT OF Cr(III)^a

| NNDED | pH | Extraction per cent of Cr(III) |
|----------|-----|--------------------------------|
| Absence | 2-6 | 0.03 (6.7) ^b |
| Presence | 2-6 | 98.6 (2.7) to 65 (2.8) |

^aInitial samples contained 10 µg of Cr(III) in 100 mL of water.

^bValues in parentheses are RSDs based on five individual replicate analyses.

and the NNDED. It should be mentioned that formation of stable complexes between Cr(III) and NNDED at pH = 2 is probably due to an ion pair formation mechanism. However, at pH higher than 2 the retention and percentage recovery of Cr(III) are negligible.

Choice of eluent: In order to select the most appropriate eluent for the quantitative stripping of the retained Cr(III) on the discs, 5 mL of various non organic (each containing 10 % v/v methanol) and different organic solvents were tested (Table-2). As can be seen, the best eluting solvents were found to be 5 mL of methanol or ethanol, resulting in quantitative elution of Cr(III) from the disc. It should be emphasized that presence of methanol in any kind of employed solvents helps to better the contact of eluent with hydrophobic surface of the disc.

Effect of the pH: The pH of the sample solutions were adjusted to different values between 2-9 by addition of hydrochloric acid or a suitable buffer such as sodium acetate-acetic acid or sodium dihydrogen phosphate-disodium hydrogen phosphate and then solutions passed through the discs.

Eventually, the metal ions were stripped by pure methanol or ethanol solutions followed by flame atomic absorption determination of the eluted Cr(III). Then, percentage recovery at various pH values was determined (Fig. 2). According to the results shown in Fig. 2 up to pH 4.0-4.5, complete recoveries are obtained. However, at higher pH values, percentage recovery decreases. This is due to fact that in an acidic solution the protonation of NNDED occurs and there is a weak tendency for retention between Cr(III) and NNDED, whereas at higher values (pH > 5), Cr(III) reacts with hydroxide ions to produce Cr(OH)₃. Therefore, sodium acetate-acetic acid buffer with pH = 4.5 was used for the preconcentration step. Other solvents used for dissolving NNDED were methanol and ethanol. The influences of these solvents on the recoveries as a function of pH are compared and shown in Fig. 2. Mean while, other organic solvents were not tested because of their restricted solubility and formation of two phases with aqueous solutions and incompatibility with flame higher pH values (> 7) were not tested because of the possibility of the hydrolysis of octadecyl silica in the discs³⁸. Cr(III) ions can be retained quantitatively by the modified membrane disc through the pH range from 4.0 to 4.5. However, at lower pH (< 4.0), nitrogen atoms of the NNDED could be protonated and the stability of complex is reduced.

Effect amount of counter anion: In order to investigate the effect of counter ion on the recovery Cr³⁺ ions by the modified discs, different counter anions were tested (Table-4). It is obvious that the nature of the counter anion strongly influences the retention of chromium ions by the disc. The results revealed that the NNDED behaves as a neutral ionophore in the pH range 4.0-4.5 49,50 so that the chromium ions are

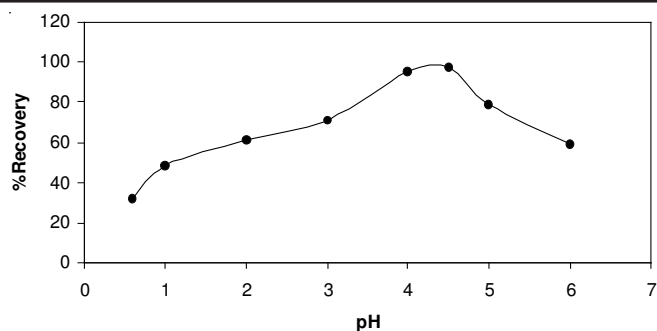


Fig. 2. Influence of sample pH and dissolving solvent of NNDED on the percentage recovery of Cr(III)

TABLE-3
EFFECT OF DIFFERENT ELUTING SOLVENTS ON PER
CENTAGE RECOVERY OF Cr(III) ADSORBED ON THE DISC^a

| Stripping solution | Recovery (%) | | |
|----------------------------------|-------------------------|------------|------------|
| | 2 mL | 5 mL | 10 mL |
| Methanol | 82.0 (2.6) ^b | 92.5 (2.6) | 98.0 (2.7) |
| Acidified methanol ^c | 54.2 (2.3) | 83.2 (2.2) | 83.9 (1.7) |
| Ammoniacal methanol ^d | 53.1 (2.5) | 87.5 (2.6) | 86.9 (2.2) |
| Ethanol | 82.1 (1.7) | 99.6 (1.5) | 99.8 (2.3) |
| Acetonitrile | 36.5 (4.8) | 46.5 (5.5) | 69.0 (3.0) |
| Formic acid (1M) | 55.0 (1.2) | 68.3 (2.0) | 71.5 (2.2) |
| 10 % v/v methanol | | | |
| Hydrochloric acid (1M) | 52.0 (1.9) | 92.0 (2.7) | 90.2 (2.9) |
| 10 % v/v methanol | | | |
| Hydrochloric acid (1M) | 51.4 (2.5) | 84.0 (2.6) | 97.4 (1.7) |
| 10 % v/v methanol | | | |
| Nitric acid (2M) | 52.8 (1.9) | 85.2 (2.2) | 85.4 (2.0) |
| 10 % v/v methanol | | | |
| Nitric acid (1M) | 64.0 (2.5) | 85.2 (2.3) | 84.9 (1.7) |
| 10 % v/v methanol | | | |
| Ethanol | 85.1 (2.8) | 95.5 (2.0) | 98.0 (2.9) |

^aInitial samples contained 10 µg of each copper in 100 mL water.

^bValues in parentheses are RSDs based on five individual replicate analysis.

^cAcidified solvents obtained by addition of 0.1M HCl.

^dAmmoniacal solvents obtained by addition of 0.1M NH₃.

TABLE-4
PER CENT RECOVERY OF CHROMIUM FROM THE
MODIFIED MEMBRANE DISC IN THE PRESENCE OF
0.01 M OF DIFFERENT COUNTER ANIONS^a

| Counter anion | Recovery (%) |
|-------------------------------|--------------|
| Cl ⁻ | 21.5 |
| Br ⁻ | 20.8 |
| ClO ₄ ⁻ | 35.9 |
| SCN ⁻ | 45.0 |
| Picrate | 74.6 |
| Acetate | 96.3 |

^aInitial samples contained 10 µg of Cr(III) in 100 mL of water.

retained as ion pair complexes by the membrane discs. As seen, acetate ion is the most efficient counter anion for the SPE of Cr(III) ions. The influence of the concentration of sodium acetate ion on chromium recovery was investigated and the results are shown in Table-4. As seen, the per cent recovery of Cr³⁺ increased with the acetate concentration until a reagent concentration of about 0.1 M is reached, beyond which the recovery remained quantitative.

Moreover, acetate ion acts as a suitable buffering agent, while it effectively contributes to the ions-pair formation. Thus,

in the SPE experiments, there was no need for the addition of any buffer solution.

Influence of flow-rate: One of the most important parameters affecting solid phase extraction is the speed of the process. Hence, the effect of flow-rates on extraction efficiencies was investigated. It was found that in the range of 10-100 mL min⁻¹, the retention of Cr(III) was not considerably affected by the sample solutions flow-rates and leads to reproducible and satisfactory results (Fig. 3). Thus, the flow-rate was maintained at 89 mL min⁻¹ throughout the experiment.

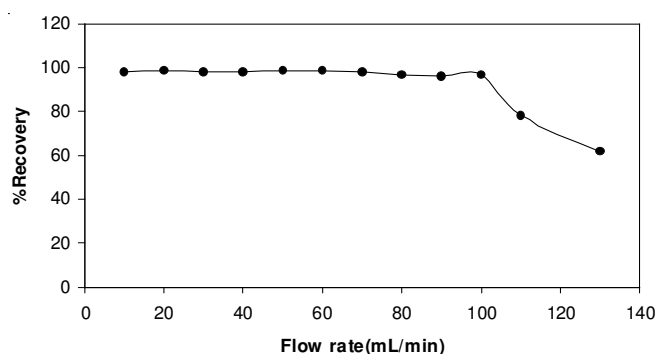


Fig. 3. Effect of the flow-rate on extraction percent of Cr(III)

Quantity of the NNDED: The optimum amount of NNDED for the quantitative extraction of Cr(III) was also investigated by adding various amounts of it to solution (between 2-20 mg). The results are listed in Table-5. The experimental results revealed that the extraction of Cr(III) was quantitative using a sample solution containing more than 10 mg NNDED. Hence, subsequent extractions were performed with 15 mg of NNDED.

TABLE-5
INFLUENCE OF THE NNDED AMOUNT ON
THE RECOVERY OF Cr(III) IONS^a

| NNDED amount (mg) | Recovery (%) of Cr(III) |
|-------------------|-------------------------|
| 2 | 39.0 (2.7) ^b |
| 5 | 44.0 (2.5) |
| 8 | 85.0 (2.4) |
| 10 | 96.8 (2.2) |
| 15 | 98.0 (2.6) |
| 20 | 98.0 (2.5) |

^aInitial samples contained 10 µg of each copper in 100 mL water.
^bValues in parentheses are RSDs based on five individual replicate analysis.

Disc efficiency: One of the major parameters affecting in the SPE determinations is the efficiency of the used membrane discs. Under the optimum experimental conditions, it was found out that each ENV-18 DISKTM disc could perform at least 14 replicate analyses if organic eluting solvents are used. On the other hand, acidic, eluents practically decrease the number of time a disc could be used to 10 replicates. These observations are represented in Fig. 4.

Analytical performance: When solutions of 10 µg chromium in 10, 50, 100, 500, 1000, 2000, 2500 and 3000 mL solutions under optimal experimental conditions were passed through the discs, the Cr(III) was quantitatively retained in all cases. Thus, the breakthrough volume for the method must be greater

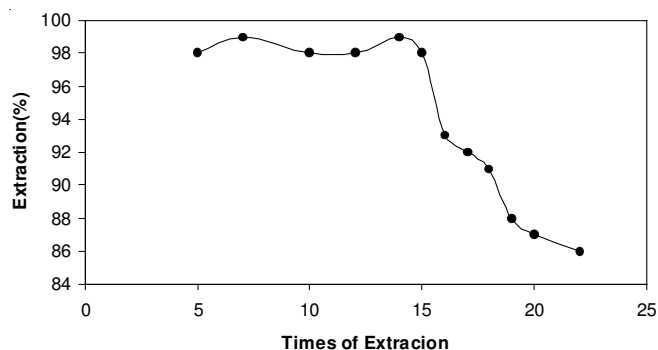


Fig. 4. Influence of eluent (5 mL of methanol) type on disc efficiency

than 2500 mL, providing a concentration factor of > 500. The limit of detection (LOD) of the method for the determination of Cr(III) was studied under the optimal experimental conditions. The LOD based on 3σ of the blank (5 mL of methanol) is 5 ng per 1000 mL.

The capacity of modified discs (5 mg NNDED) was determined by passing 50 mL portions of sample solutions containing 8 mg of chromium and 0.1M sodium acetate-acetic acid buffer with pH 4.0-4.5, followed by the determination of the retained metal ions in the eluting solution using AAS. The maximal capacity of the disc obtained from three replicate measurements was 389 ± 4 µg of Cr³⁺ on the disc.

In order to investigate the selective separation and determination of Cr³⁺ ions from its binary mixtures with various metal ions, an aliquot of aqueous solutions (50 mL) containing 10 µg of Cr³⁺ and mg amounts of other cations was taken and the recommended procedure was followed. The results are summarized in Table-6. The results show that the Cr(III) ions in binary mixtures are retained almost completely by the modified disc, even in the presence of up to about 100 mg of various ions. Meanwhile, retention of other cations by the disc is very low and they can separated effectively from the Cr³⁺ ion. It is interesting to note that, in other experiments, it is found that

TABLE-6
SEPARATION OF CHROMIUM FROM BINARY MIXTURES^a

| Diverse ion | Amount taken (mg) | Found (%) | Recovery (%) of Cr(III) ion |
|------------------|-------------------|-------------------------|-----------------------------|
| Na ⁺ | 92.4 | 1.15 (2.4) ^b | 98.5 (2.8) |
| K ⁺ | 92.5 | 1.32 (2.3) | 98.5 (2.2) |
| Mg ²⁺ | 14.5 | 0.7 (1.2) | 98.5 (1.7) |
| Ca ²⁺ | 26.3 | 2.25 (3.0) | 98.5 (1.8) |
| Sr ²⁺ | 2.45 | 2.85 (2.1) | 98.4 (2.0) |
| Ba ²⁺ | 2.66 | 3.16 (2.1) | 98.7 (2.3) |
| Mn ²⁺ | 2.66 | 1.75 (2.2) | 96.3 (2.8) |
| Co ²⁺ | 2.13 | 6.4 (2.3) | 99.1 (2.9) |
| Ni ²⁺ | 1.67 | 2.0 (2.4) | 98.5 (2.4) |
| Zn ²⁺ | 2.78 | 4.97 (2.1) | 98.6 (2.2) |
| Cd ²⁺ | 2.58 | 2.9 (2.0) | 98.2 (2.8) |
| Pb ²⁺ | 0.54 | 2.7 (1.9) | 97.8 (2.4) |
| Hg ²⁺ | 0.43 | 2.81 (2.1) | 97.7 (2.8) |
| Ag ⁺ | 2.67 | 3.45 (2.9) | 98.6 (2.3) |
| Cu ²⁺ | 1.76 | 49.92 (2.3) | 97.3 (2.4) |
| UO ²⁺ | 2.86 | 2.8 (2.1) | 98.3 (2.7) |

^aInitial samples contained 10 µg Cr³⁺ and different amounts of various ions in 100 mL water (0.1 M acetate ion).

^bValues in parentheses are RSDs based on five individual replicate analysis.

in the presence of high enough concentrations $\text{NH}_2\text{OH}\cdot\text{HCl}$ as a suitable reducing agent ($> 0.5 \text{ M}$)³⁹.

Analysis of water samples: To assess the applicability of the method to real samples, it was applied to the extraction and determination of copper from different water samples. Tap water (Tehran, taken after 10 min operation of the tap), rain water (Tehran, 26 January, 2010), Snow water (Saveh, 6 February, 2010) and Sea water (taken from Caspian sea, near the Mahmoud-Abad shore) samples were analyzed (Table-7). As can be seen from Table-4 the added chromium ions can be quantitatively recovered from the water samples used. As is seen, the recovered copper ion reveals that the results are quite reliable and are in satisfactory agreement with those obtained by ICPAES.

TABLE-7
RECOVERY OF COPPER ADDED TO 1000 mL OF
DIFFERENT WATER SAMPLES (CONTAINING
0.1M ACETATE at pH = 4.0-4.5)

| Sample | Cr ³⁺ added (μg) | Cr ³⁺ determined (ng mL^{-1}) | ICP-AES |
|------------|---|--|--------------|
| Tap water | 0.0 | 1.74 (1.8) ^a | Not detected |
| | 10.0 | 11.94 (2.6) | 11.6 |
| Snow water | 0.0 | 4.85 (2.5) | Not detected |
| | 10.0 | 14.98 (2.7) | 14.4 |
| Rain water | 0.0 | 2.66 (2.3) | Not detected |
| | 10.0 | 12.86 (2.4) | 12.4 |
| Sea water | 0.0 | 12.97 (2.7) | 12.4 |
| | 10.0 | 22.78 (2.5) | 23.6 |

^aValues in parentheses are % RSDs based on five individual replicate analysis.

Conclusion

Results presented in this work demonstrate well the tremendous possibilities offered by the solid phase extraction of trace amounts of Cr(III) in water samples using octadecyl silica membrane discs modified by N,N-disalicylideneethylenediamine and its determination by FAAS. The method developed was simple, reliable and precise for determining copper in water. The proposed method was also free of interference compared to conventional procedures to determine chromium⁴⁰⁻⁴⁴. The method can be successfully applied to the separation and determination of chromium in binary mixtures.

ACKNOWLEDGEMENTS

The author wish to thank the Chemistry Department of Varamin (Pishva) branch Islamic Azad University and East Tehran branch Islamic Azad University for financial support.

REFERENCES

- J.O. Nriagu and E. Nicboer, Chromium in the Natural and Human Environment, New York (1988).
- V. Camel, *Spectrochim. Acta*, **58B**, 1177 (2003).
- E.B. Gonzalez, J.B. Garcia, P.B. Barrera and A.B. Barrera, *Fresenius J. Anal. Chem.*, **344**, 301 (1992).
- K.S. Subramanian, *Anal. Chem.*, **60**, 11 (1988).
- R.M.C. Romero, M.C.Y. Biurrun, M.P.B. Barrera, *Anal. Chim. Acta*, **327**, 37 (1996).
- M.C. Pannain and R.E. Santelli, *Talanta*, **42**, 1609 (1995).
- B. Pasullean, C.M. Davidson and D. Little John, *J. Anal. Atom. Spectrom.*, **10**, 241 (1995).
- M.S. Jimenez, I. Martin, J.M. Mir and J.R. Castillo, *Atom. Spectrosc.*, **17**, 201 (1996).
- A. Gaspar, J. Posta and R. Toth, *J. Anal. Atom. Spectrom.*, **11**, 1067 (1996).
- J. Posta, A. Gaspar, R. Toth and L. Ombodi, *Fresenius J. Anal. Chem.*, **355**, 719 (1996).
- C.J. Krueger and J.A. Fild, *Anal. Chem.*, **67**, 3363 (1995).
- K.Z. Taylor, D.S. Waddell and E.J. Reiner, *Anal. Chem.*, **67**, 1186 (1995).
- H.D. Revanasiddappa and T.N.K. Kumar, *Talanta*, **60**, 1 (2003).
- S. Hirata, Y. Umezaki and M. Ikeda, *Anal. Chem.*, **58**, 2602 (1986).
- R.R. Greenberg, R. Ziesler, H.M. Kingston and T.M. Sullivan, *Fresenius J. Anal. Chem.*, **332**, 562 (1988).
- R.E. Majors, *LC-GC*, **4**, 972 (1989).
- D.F. Hagen, C.G. Markell, G.A. Schmitt and D.D. Blevins, *Anal. Chim. Acta*, **236**, 157 (1990).
- C.F. Poole, S.K. Poole, D.S. Seibert and C.M. Chapman, *J. Chromatogr. B*, **689**, 245 (1997).
- M. Mohammadhosseini, Ph.D. Thesis, Islamic Azad University, Science and Research Campus, Unpublished Results, Tehran, Iran (2004).
- M.S. Tehrani, A.A. Ebrahimi and F. Rastegar, *Ann. Chim. (Rome)*, **94**, 429 (2004).
- J. Pawliszyn, Solid-Phase Microextraction, Theory and Practice, Wiley-VCH, New York (1997).
- M. Mohammadhosseini, K. Zare and M.S. Tehrani, *J. Phys. Theo. Chem. I.A.U. Iran*, **1**, 149 (2004).
- O.R. Hashemi, F. Raoufi, M.R. Ganjali, A. Moghimi, M. Kargar-Razi, H. Aghabozorg and M. Shamsipur, *Anal. Sci.*, **16**, 1221 (2000).
- M. Shamsipur, F. Raoufi and H. Sharghi, *Talanta*, **52**, 637 (2000).
- O.R. Hashemi, M. Kargar-Razi, F. Raoufi, A. Moghimi, H. Aghabozorg and M.R. Ganjali, *Microchem. J.*, **69**, 1 (2001).
- M. Shamsipur, A. Avanes, M.K. Raoufi, H. Sharghi and G. Aghapour, *Talanta*, **54**, 863 (2001).
- M. Shamsipur, A.R. Ghiasvand, H. Sharghi and H. Naeimi, *Anal. Chim. Acta*, **408**, 271 (2000).
- M.R. Ganjali, M.R. Pourjavid, L.H. Babaei and M.S. Niasari, *Quim. Nova*, **27**, 213 (2004).
- M. Shamsipur, M. Javanbakht, Z. Ghasemi, M.R. Ganjali, V. Lippolis and A. Garau, *Sep. Purif. Technol.*, **28**, 141 (2002).
- L.H. Babaei, Z. Ghasemi, F. Darciche, M. Shamsipur, F. Raoufi and M.R. Ganjali, *Anal. Sci.*, **17**, 1305 (2001).
- M. Shamsipur, A. Shokrollahi, H. Sharghi and M.M. Eskandari, *J. Hazard. Mater.*, **117**, 129 (2005).
- Z. Chen, G. Yang, Q. Hu, J. Yin and Q. Su, *J. Chin. Chem. Soc.*, **51**, 297 (2004).
- H. Cesur and B. Bati, *Turk. J. Chem.*, **26**, 29 (2002).
- K. Farhadi and G. Teimouri, *Talanta*, **65**, 925 (2005).
- M. Shamsipur, M. Yousefi, Z. Ghasemi, L.H. Babaei and M.R. Ganjali, *Sep. Sci. Technol.*, **37**, 3525 (2002).
- M. Shamsipur, A.R. Ghiasvand and Y. Yamini, *Anal. Chem.*, **71**, 4892 (1999).
- D.F. Hagen, C.G. Mrkell, G.A. Schmitt and D.D. Blevins, *Anal. Chim. Acta*, **236**, 157 (1990).
- Y. Yamini, N. Alizadeh and M. Shamsipur, *Anal. Chim. Acta*, **355**, 69 (1997).
- Y.P. de Pena, M. Gallego and M. Valcarcel, *Anal. Chem.*, **67**, 2524 (1995).
- Y.S. Choi and H.S. Choi, *Bull. Korean Chem. Soc.*, **24**, 222 (2003).
- E. Matoso, L.T. Kubota and S. Cadore, *Talanta*, **60**, 1105 (2003).
- B. Purachat, S. Liawruangrath, P. Sooksamiti, S. Rattanaphani and D. Buddhasukh, *Anal. Sci.*, **17**, 443 (2001).
- A.A. Ensafi, S. Abbasi, H.R. Mansour and I.M. Pour Baltork, *Anal. Sci.*, **17**, 609 (2001).
- M.S. Tehrani, F. Rastegar, A. Parchehbab and Z. Rezvani, *Chin. J. Chem.*, **23**, 1437 (2005).