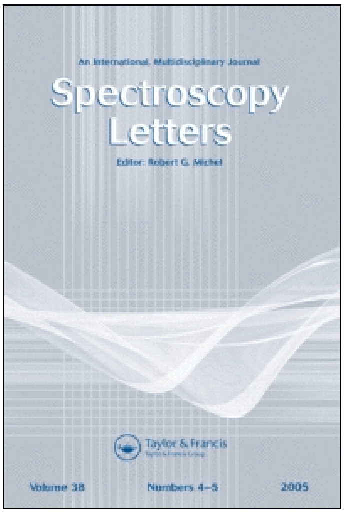
This article was downloaded by:
On: *30 January 2011*
Access details: *Access Details: Free Access*
Publisher *Taylor & Francis*
Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



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

SIMULTANEOUS ENRICHMENT OF Cd, Pb, Ni, AND Al AND THEIR DETERMINATION IN WATER BY STAT-FAAS

Mehmet Yaman[a]
[a] Science and Arts Faculty, Department of Chemistry, Firat University, Elazig, Turkey

Online publication date: 31 December 2001

To cite this Article Yaman, Mehmet(2001) 'SIMULTANEOUS ENRICHMENT OF Cd, Pb, Ni, AND Al AND THEIR DETERMINATION IN WATER BY STAT-FAAS', Spectroscopy Letters, 34: 6, 763 — 773
To link to this Article: DOI: 10.1081/SL-100107898
URL: http://dx.doi.org/10.1081/SL-100107898

PLEASE SCROLL DOWN FOR ARTICLE

Full terms and conditions of use: http://www.informaworld.com/terms-and-conditions-of-access.pdf

This article may be used for research, teaching and private study purposes. Any substantial or systematic reproduction, re-distribution, re-selling, loan or sub-licensing, systematic supply or distribution in any form to anyone is expressly forbidden.

The publisher does not give any warranty express or implied or make any representation that the contents will be complete or accurate or up to date. The accuracy of any instructions, formulae and drug doses should be independently verified with primary sources. The publisher shall not be liable for any loss, actions, claims, proceedings, demand or costs or damages whatsoever or howsoever caused arising directly or indirectly in connection with or arising out of the use of this material.

SPECTROSCOPY LETTERS, 34(6), 763–773 (2001)

SIMULTANEOUS ENRICHMENT OF Cd, Pb, Ni, AND Al AND THEIR DETERMINATION IN WATER BY STAT-FAAS

Mehmet Yaman

Firat University, Science and Arts Faculty,
Department of Chemistry, Elazig, Turkey

Downloaded At: 03:10 30 January 2011

ABSTRACT

Toxic metals such as Cd, Pb, Ni and Al were determined in drinking, dam lake, stream and lake water by using flame atomic absorption spectrometry (FAAS) after enrichment. In the enrichment procedure, their chelates with cupferron were preconcentrated on activated carbon. For increasing the sensitivity of cadmium and lead, slotted tube atom trap (STAT) was used as accessory in the FAAS. 150 fold preconcentration was achieved.

Key Words: Cadmium; Lead; Nickel; Aluminium; Water; AAS; Enrichment

Copyright © 2001 by Marcel Dekker, Inc. www.dekker.com

INTRODUCTION

The determination of toxic metals such as cadmium, lead, nickel and aluminum in drinking water is becoming increasingly important. Although reports of weak carcinogenity activity of Cd are inconclusive[1], measurements of this element in food, biological and environmental samples is still used for exposure monitoring because of its very toxic effects. Because the highly toxic cumulative poison of Pb in humans and animals[2], the allergenic and in some of its compounds even a carcinogenic effects of Ni[3] and the potential link between high Al contents in tissue and various neurodegenenerative disorders such as Alzheimer's disease[4], the determination of these metals in the water, food and other environmental samples is of considerable current interest. They may enter the organism via the alimentary and/or respiratory tract[5], so the main non-occupational sources of these metals are food, drinking water and air. On the other hand, the concentration of these toxic metals in natural waters such as sea, river and lake is also important as these elements at high concentrations may affect health, and can become concentrated in fish and mollusks, both important components of human diet. Even the concentrations of these elements were very low, their determinations are still important because they will accumulate in the receiver ambience with time. Therefore, analytical control of these elements in natural and polluted water is becoming a popular topic.

The most frequently used analytical method for these elements is probably electrothermal atomic absorption spectrometry (ETAAS)[6]. But, the necessity of the chemical modifier use because of interference problems in ETAAS has drawn much attention to the use of atom trapping techniques to increase the sensitivity of conventional atomic absorption spectrometry (AAS)[7–9].

Solvent extraction is widely used in AAS when the concentration of the analyte element is too low to permit direct determination or when the matrix is very complex and the resulting interference cannot be controlled. But the phase separations were unsatisfactory for a ratio greater than 30 and the procedure was, therefore, of restricted use[10]. Chelation and adsorption on activated carbon do not have these limitations and the separation efficiency is high[11–18].

In this study, toxic metals described above were determined in drinking, dam lake and lake water by using flame atomic absorption spectrometry (FAAS) after enrichment. For Cd and Pb determination, Slotted Tube Atom Trap (STAT)-FAAS was used. In the enrichment procedure, the chelates of metals with cupferron were preconcentrated on activated carbon.

Downloaded At: 03:10 30 January 2011

EXPERIMENTAL

Apparatus and Reagents

An ATI UNICAM 929 Model flame atomic absorption spectrophotometer (AAS) equipped with ATI UNICAM Hollow cathode lamps was used for the determinations. The optimum conditions for FAAS are given in Table 1. A slotted tube atom trap (STAT) was used to increase the sensitivity of FAAS. The pH was measured with an EDT GP 353 ATC pH meter. In the enrichment procedure Snijders magnetic stirrer with heater and a Hettich EBA III centrifuge were used.

Unless stated otherwise, all chemicals used were of high-purity reagent grade. Throughout all analytical work, doubly distilled water was used. All glass apparatus have been kept permanently full of 1 M nitric acid when not in use. Concentrated nitric acid (65%, Merck) was used for elution of metals on the activated carbon. Stock solutions of metals ($1000\,\mathrm{mg\,L^{-1}}$) were prepared by dissolving their nitrate compounds in $1.0\,\mathrm{mol\,L^{-1}}$ nitric acid. A solution of 1% m/v $LaCl_3$ was used as the STAT coating material.

A buffer solution of pH 5.0 ± 0.2 was prepared by adding $0.1\,\mathrm{mol\,L^{-1}}$ NaOH solution to $0.1\,\mathrm{mol\,L^{-1}}$ sodium citrate solution. A solution of 0.3% N-nitrosophenylhydroxylamine (cupferron) was prepared by dissolving 0.3 g of reagent in 100 ml of ethyl alcohol. Preparation of activated carbon suspension was described elsewhere[14].

Procedure

Four tap, one lake, one dam lake and two stream water samples were collected in sealed polyethylene containers which were washed in 1% HNO_3

Table 1. Operating Parameters for FAAS

Parameter	Pb	Al	Ni	Cd
Wavelength, nm	217.0	309.3	232.0	228.8
HCL current, mA	9.5	9.5	14.5	7.5
N_2O flow rate, L/min	–	4.7	–	–
Acetylene flow rate, L/min	0.6	4.2	0.6	0.6
Air flow rate, L/min	4.0	–	4.0	4.0
Slit, nm	0.5	0.5	0.2	0.5

Downloaded At: 03:10 30 January 2011

Downloaded At: 03:10 30 January 2011

solution. After filtration, if necessary, 2 ml of concentrated HNO_3 was added to each one samples. A 300 ml portion of water sample was transferred to the beaker. For the chelation and adsorption on activated carbon, the steps of enrichment were as follows:

The pH was adjusted to 5.0 ± 0.2 by adding HNO_3 and NaOH at the necessary concentrations. The buffer solution of 40 ml, cupferron solution of 40 ml and the activated carbon suspension of 5 ml were added and the pH of the solution was adjusted again, as necessary. The mixture was stirred mechanically for 45 minutes and filtered through a filter paper (Advantec Toyo 5B white ribbon). The residue was dried at 105℃ for 1 h. Concentrated nitric acid (5 ml) was added to the residue in a glass beaker and evaporated to dryness. Then, 2.0 ml of 1.5 mol L^{-1} HNO_3 was added and, after centrifuging twice, the clear solution was separated for measurements. The Cd, Pb, Ni and Al content of the solutions obtained was determined by means of the STAT-FAAS (for Cd and Pb) and FAAS. So, 150 fold enrichment was achieved.

RESULTS AND DISCUSSION

The parameters that are thought to affect the enrichment and measurement steps in the analytical scheme were taken from the previous work[14,17–18] as described above at heading "Procedure". In these papers[14,17–18], cupferron had been found as the best chelating reagent, and optimum pH had been found to be 5.0 ± 0.2

Chelation and adsorption on activated carbon was chosen as an enrichment method because high separation efficiency is obtained when the metal ions were encapsulated in organic structures prior to the adsorption step. Particularly, if the complexing agent has an aromatic structure, π-orbital overlap interaction between the aromatic structures of the molecule and the activated carbon surface is possible, resulting in larger adsorption energy. Therefore, cupferron, which has an aromatic structure, was used as a chelating reagent.

Calibration curves for Cd, Pb, Ni and Al was obtained by using 300 ml of solutions in concentration ranges of 0.05–0.8, 1.0–10.0, 1.0–15 and 4.0–50 μg L^{-1}, respectively. To identity of calibration solutions to water matrix, major components of the water were added to the calibration solution as 50 mg l^{-1} for Ca and 25 mg l^{-1} for Mg. The optimised enrichment procedure (from the Ref. 14, 17–18) was applied to these solutions (at pH 5.0 ± 0.2). The clear solutions were analysed by means of STAT-FAAS for Cd and Pb and direct FAAS for Ni and Al. The graphs obtained were rectilinear in the concentration range of described above and the equations of the curves was as follows:

$$Y = 78.441X + 0.0833 \quad R^2 = 0.99 \quad \text{for Cd}$$

$$Y = 8.4023X + 0.9492 \quad R^2 = 0.99 \quad \text{for Pb}$$

$$Y = 5.7077X + 0.7538 \quad R^2 = 0.99 \quad \text{for Ni}$$

$$Y = 0.5803X + 0.3868 \quad R^2 = 0.99 \quad \text{for Al}$$

Accuracy and Applications

To establish the validity of the method, recoveries of the studied metals from water samples fortified with these elements were determined. It was found that the added Cd, Pb, Ni and Al were recovered at least 86% 92%, 91% and 94%, respectively. The effect of contamination was eliminated by subtracting the values obtained for blanks. Adsorption loss can be excluded as the procedure was followed in exactly the same way, using the same glassware and the same reagents that were used throughout. Therefore, the effect of contamination or adsorption may be reliably overlooked.

In addition, to overcome enhancement or suppression due to the presence of major components of the water matrix, calibration solution were performed within the sample matrix itself. Standard additions of Cd, Pb, Ni and Al to a water sample were made and the samples were analysed by using STAT-FAAS and FAAS after enrichment procedure. The slopes of the calibration graphs obtained using Cd, Pb, Ni and Al standard solutions were compared with the slopes obtained by the standard additions method. The results are shown in Figs. 1, 2, 3 and 4. These results indicate the absence of chemical interferences, hence it is not necessary to apply the standard additions method to water samples, when the proposed enrichment method was used for the studied elements in natural water.

The proposed enrichment method was applied to six tap, one lake, one dam lake and two stream water samples. The results obtained were given in Table 2. The given values are the means of four separate portion of the same sample obtained from different location.

The mean Cd concentration for all studied water was in the range of 0.06–0.22 μg l^{-1}. The mean values for Pb, Ni and Al concentrations of all studied waters were in the range of 1.1–6.0; 1.0–15; 20–130 μg l^{-1}, respectively.

Downloaded At: 03:10 30 January 2011

Downloaded At: 03:10 30 January 2011

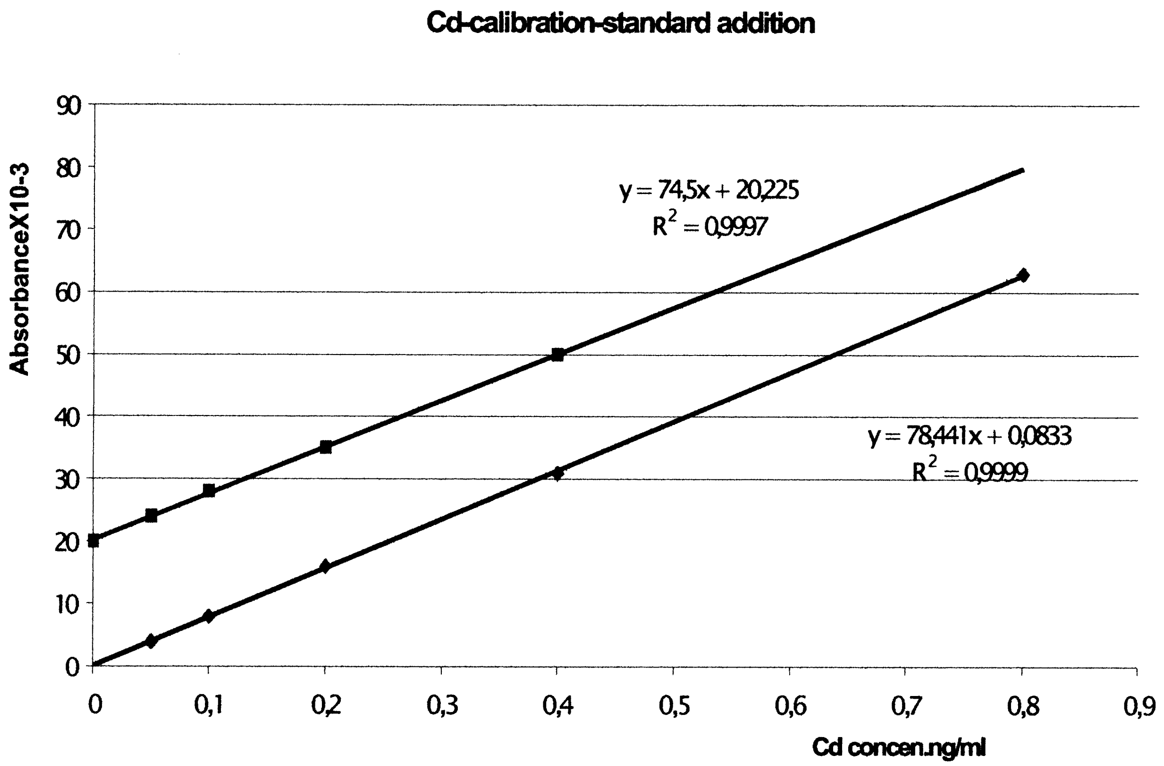


Figure 1. Calibration graphs obtained with the standard additions method (■) and with standard + major compounds of water (◆). A 300 ml volume of Cd solution was taken to a 2 ml final volume.

Downloaded At: 03:10 30 January 2011

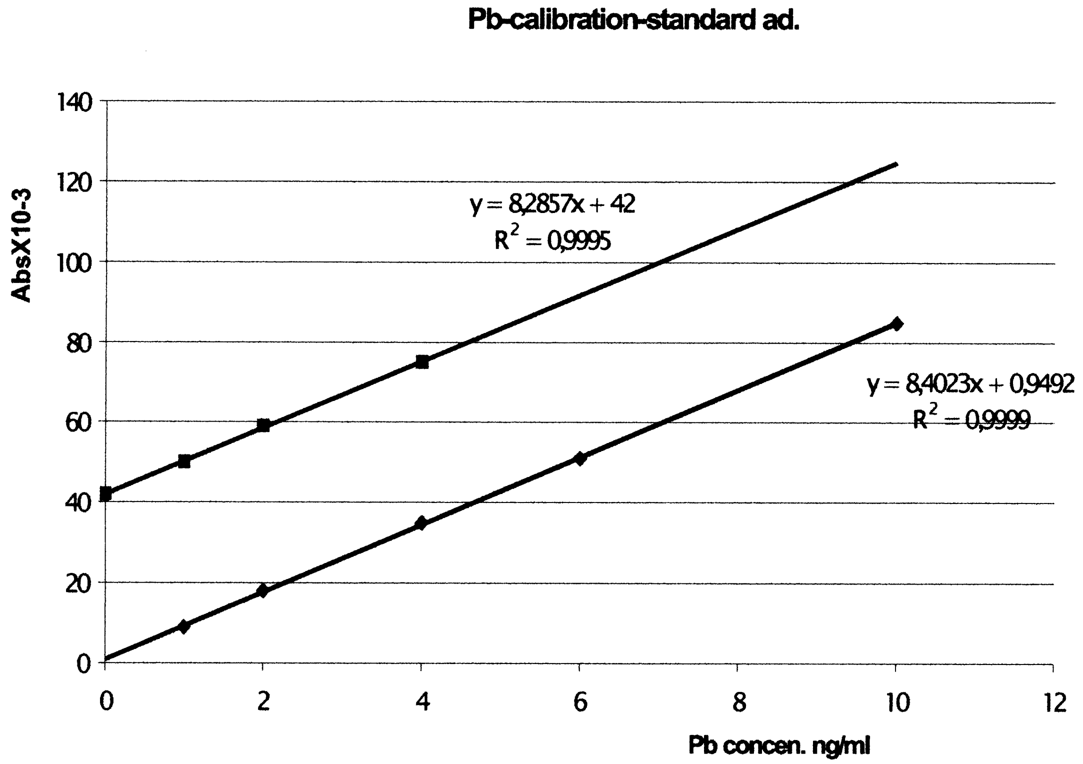


Figure 2. Calibration graphs obtained with the standard additions method (■) and with standard + major compounds of water (◆). A 300 ml volume of Pb solution was taken to a 2 ml final volume.

Downloaded At: 03:10 30 January 2011

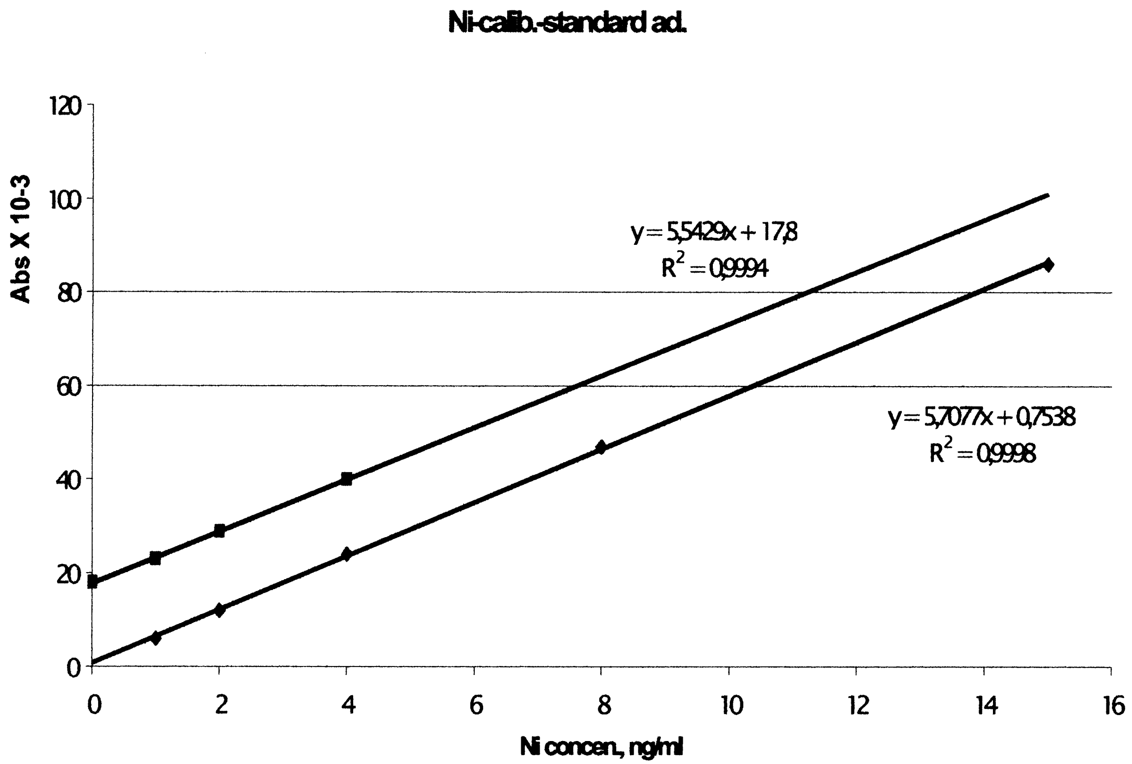


Figure 3. Calibration graphs obtained with the standard additions method (■) and with standard + major compounds of water (◆). A 300 ml volume of Ni solution was taken to a 2 ml final volume.

Downloaded At: 03:10 30 January 2011

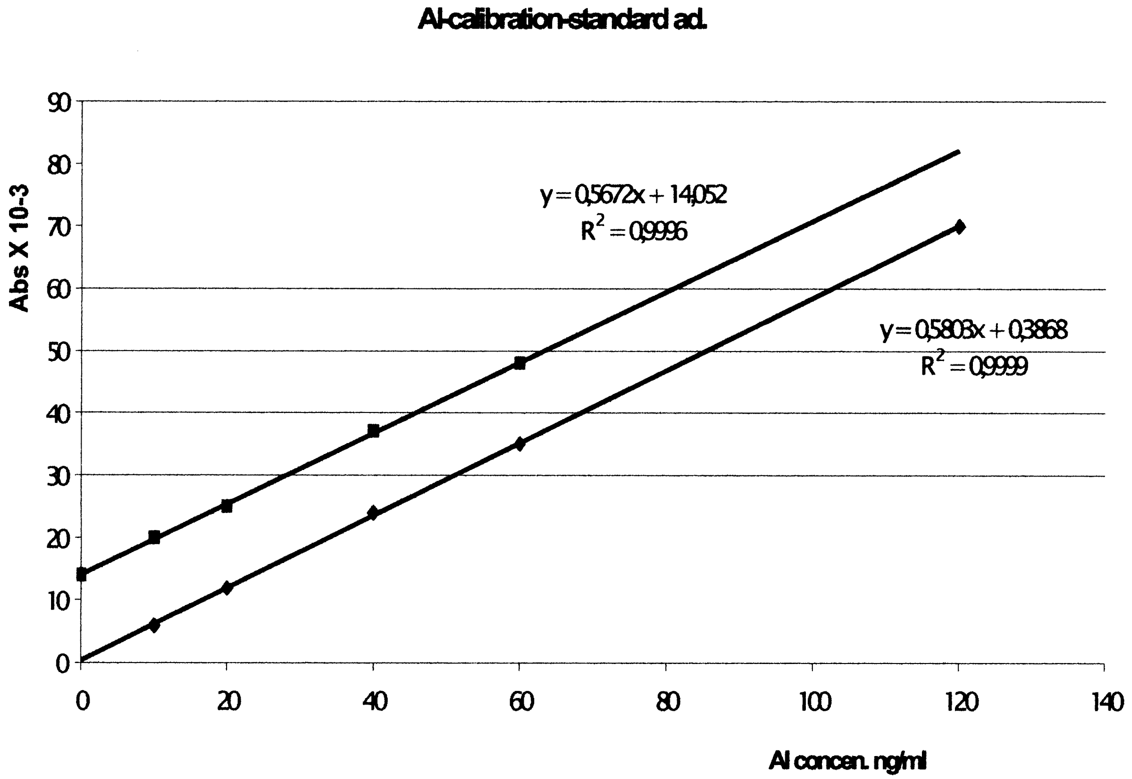


Figure 4. Calibration graphs obtained with the standard additions method (■) and with standard + major compounds of water (◆). A 300 ml volume of Al solution was taken to a 2 ml final volume.

Table 2. Concentrations of Cd, Pb, Ni, and Al in Various Natural Waters

Source of Water	Cd	Pb	Ni	Al
Hazar lake	0.06 ± 0.01	1.5 ± 0.20	15 ± 1.4	55 ± 2.8
Keban dam lake	0.06 ± 0.01	1.5 ± 0.16	2.0 ± 0.2	20 ± 1.8
Sakabasi stream	0.06 ± 0.01	2.6 ± 0.24	1.0 ± 0.15	130 ± 9
Sivrice stream	0.1 ± 0.02	2.4 ± 0.21	8.0 ± 1.1	75 ± 6
Karaçali potable	0.06 ± 0.01	1.1 ± 0.18	5.0 ± 0.9	80 ± 6
Elazig tap	0.06 ± 0.01	1.1 ± 0.19	5.0 ± 0.8	25 ± 2.0
University tap	0.22 ± 0.02	6.0 ± 1.0	5.0 ± 1.0	29 ± 2.1
Sakabasi tap	0.06 ± 0.01	2.6 ± 0.25	1.0 ± 0.16	50 ± 3.5

The results are mean values as $\mathrm{ngml^{-1}}$; $\mathrm{n^{-4}}$.

Downloaded At: 03:10 30 January 2011

CONCLUSION

An attempt was made to simultaneous enrichment of Cd, Pb, Ni and Al in water and their determination by STAT-FAAS and FAAS. The obtained Cd and Pb concentrations in studied waters were significantly lover than the maximum admissible concentrations of 50 and $5\,\mu\mathrm{g l^{-1}}$ in potable waters, respectively[19]. Because the tendency is for a reduction of these limits, the more sensitive analytical techniques must be developed. In this study 150 fold preconcentration was achieved and this rate can increased depending on first and final volume.

ACKNOWLEDGMENT

This work was supported by the Scientific and Technical Research Council of Turkey (TBAG-AY/108).

REFERENCES

1. IPCS Environmental Health Criteria 134: Cadmium, World Health Organization, Geneva, 1992.
2. Tsuchiya, K. Lead In: *Handbook on the Toxicology of Metals*; Friberg, L., Nordberg, G.F., Vouk, V.B., Eds.; Amsterdam: Elsevier, 1986; Vol. II.
3. International Committee on Nickel Carcinogenesis in Man, Scand. J. Work, Environ. Health. **1990**, *16*, 1.

4. Massey, R.C.; Taylor, D. (Eds.). *Aluminum in Food and the Environment*; Royal Society of Chemistry: London, 1991.
5. Seiler, et al., H.G. *Handbook on Toxicity of Inorganic Compounds*; Marcel Dekker: New York, 1988.
6. Cimadevilla, E.A.C.; Wrobel, K.; Medel, A.S. J. Anal. At. Spectrom. **1995**, *10*, 149.
7. Hallam, C.; Thompson, K.C. Analyst **1985**, *110*, 497.
8. Ellis, R.A.; Roberts, D.J. J. Anal. At. Spectrom. **1996**, *11*, 259.
9. Yaman, M. J. Anal. At. Spectrom. **1999**, *14*, 275.
10. Sturgeon, R.E.; Berman, S.S.; Desaulnlers, A.; Russel, D.S. Talanta **1980**, *27*, 85.
11. Wanderboght, B.M.; Van Grieken, R.E. Anal. Chem. **1977**, *49*, 311.
12. Gucer, S.; Yaman, M.J. Anal. At. Spectrom. **1992**, *7*, 179.
13. Yaman, M.; Gucer, S. Fresenius. J. Anal. Chem. **1994**, *350*, 504.
14. Yaman, M.; Gucer, S. Analyst. **1995**, *120*, 101.
15. Yaman, M.; Gucer, S. Analusis **1995**, *23*, 168.
16. Yaman, M. Chem. Anal. (Warsaw) **1997**, *42*, 79.
17. Yaman, M.; Gucer, S. Ann. Chim. (Rome) **1998**, *88*, 555.
18. Yaman, M. Mikrochim. Acta **1998**, *129*, 115.
19. EC Directive Relating to the Quality of Water Intended for Human Consumption, 80/778/EEC, Off. J. Eur. Commun., July 1980; OJL 229, 30th August 1980.

Received January 14, 2001
Accepted July 10, 2001

Downloaded At: 03:10 30 January 2011