Transactions C: Chemistry and Chemical Engineering
Vol. 17, No. 2, pp. 144–151
© Sharif University of Technology, December 2010

Research Note

Separation and Preconcentration of Ultra Traces of Some Heavy Metals in Environmental Samples by Electrodeposition Technique Prior to Flame Atomic Absorption Spectroscopy Determination (ED-FAAS)

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Abstract. *In this approach, electrodeposition was developed for separation of ultra traces of some heavy metals from the complex matrices prior to determination by flame atomic absorption spectroscopy. The electrodeposition is carried out at optimized parameters of pH and temperature of electrolyte, voltage and duration time of deposition. The calculated LOD for ED-FAAS for the interested elements was found as follows: 1.27 ng mL^{-1} for Co, 0.14 μg mL^{-1} for Re, 1.56 ng mL^{-1} for Ni, 1.84 ng mL^{-1} for Au, 0.02 μg mL^{-1} for Pt and 6.67 ng mL^{-1} for In. Characteristic concentration for Co, Re, Ni, Au, Pt and In in ED-FAAS technique are 1.72, 660, 2.67, 2.99, 30 and 9.60 ng mL^{-1} with %RSD as 1.54, 2.69, 2.45, 2.77, 2.38 and 2.55, respectively. These elements were measured in some environmental samples. Concentration of Co and Ni in a mineral water are 12.46 and 21.43 ng mL^{-1}, respectively, concentration of Re in a molybdenum mineral concentrate is 4.65 μg mL^{-1}, concentration of Au in a geological samples is 6.00 ng mL^{-1}. It was also found that the recovery test for spiked Pt and In to a waste water samples is promising using the proposed technique.*

Keywords: *Heavy metal; Environmental sample; Electrodeposition; Preconcentration; Flame atomic absorption spectroscopy*

INTRODUCTION

The monitoring of levels of trace metals in environmental samples is an important part of analytical chemistry due to their positive and/or negative influences on the human body [1-3]. Some metals including manganese, iron, copper, zinc and cobalt are essential micronutrients that have a variety of biochemical functions in all living organisms. While these elements are essential, they can be toxic when ingested in excess [2-4]. However, some metals like lead and cadmium are non-essential metals as they are toxic, even in traces [3-5]. Various techniques have been reported for the determination of trace metals in environmental samples. Flame Atomic Absorption Spectrometry (FAAS) has been widely used for the determination of trace metal ions.

However, the use of this technique is restricted, not only by inadequate sensitivity, but also by matrix interferences [6]. The direct determination of trace elements in geological or environmental samples by this technique might be difficult because of their low concentration and the complexity of the matrix, which may cause serious interferences. Preconcentration and separation of trace analyte from interfering concomitants could solve these problems and enable sensitive and accurate determination.

In trace analysis, therefore, preconcentration leads to simplify trace metal determination. Several

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Received 3 May 2010; received in revised form 14 June 2010; accepted 17 August 2010

methods of preconcentration include solvent extraction [7,8], adsorption [9,10], membrane extraction [11], coprecipitation [12-14], ion-exchange [15,16] and cloud point extraction [17,18]. Among these methods reductive electrolysis is well established for certain metal recovery applications [19]. Electrodeposition is an attractive method for both the separation and preconcentration of the analyte from the interfering matrix prior to FAAS analysis. The theory of electrolytic reduction (i.e. electrodeposition) is basically an oxidation reduction reaction that takes place at the surface of conductive electrodes in a chemical medium under the influence of an applied potential [20]. It has many advantages in terms of the sample size required, the degree of preconcentration, simplicity and freedom from contamination. Also the removal of a metal by electrodeposition at source seems to be attractive due to the potential for a one-step clean method of metal recycle. Electrolysis can generally be performed with constant current (galvanostatic arrangement) or constant potential (potentiostatic arrangement) [21].

The author and coworkers in our laboratory developed a combination technique of electrodeposition with some atomic spectroscopy method for separation of analytes from their interfering contaminations prior to determination by AAS technique [22-27].

In this approach, an experimental design methodology, using 2^4 full factorial design, also has been applied to optimize the electrodeposition parameters such as pH and temperature of electrolyte, voltage and time of duration of deposition of the interested elements from environmental samples.

The developed simple and convenient electrodeposition method at optimized parameters has been applied for separation and preconcentration of ultra traces of Co, Re, Ni, Au, In and Pt elements in the environmental samples prior to determination by FAAS.

EXPERIMENTAL

Reagents

Deionoized water was used and all reagents were of analytical reagents grade. All acids used, namely HCl, $HClO_4$, H_2SO_4 and HNO_3 were analytically pure. NH_3 solution was also analytical pure. All analyte standard solutions were prepared in 1% v/v HNO_3, by diluting stock solutions of 1000 μg mL^{-1} standard solutions of Merck titrasol for AAS.

Instrumentation

A Perkin-Elmer model AAnalyst 560 flame atomic absorption spectrometry equipped with deuterium background correction system was used for Co, Re, Ni, Au, In and Pt determinations. Hollow cathode lamps of Co, Re, Ni, Au, In and Pt were used as a primary source and the operating conditions were those recommended by manufacturer. The flame composition was acetylene-nitrous oxide for Re and acetylene-air for Co, Ni, Au, In and Pt. Electrolysis system was consist of a 8 cm Pt rod as anode and the furnace as cathode were connected to a DC power supply (0-30 V). A magnetic stirrer model Heidolph MR 3001 K and a pH meter model Metrohm 691 for adjusting the pH of solutions was also used.

Procedure

The aliquots of 250 mL of standard solution with different concentrations of metal ions as well as the acidic solution of blank (the same solution without analytes) were prepared. The electrodeposition conditions, such as pH, temperature, voltage and time of deposition should be optimized. In the electrodeposition, 250 mL standard solution of 40 ng mL^{-1} of Co, Ni and Au, 0.20 μg mL^{-1} of In, 0.60 μg mL^{-1} of Pt and 2.00 μg mL^{-1} of Re were electrolyzed. Afterwards, the retained metal ions were eluted with 10 mL of 1 mol/L HNO_3 solution. The analyte in the eluent was determined by FAAS. Table 1 shows the optimum conditions of FAAS.

RESULTS AND DISSCUSION

Optimization of the Experimental Conditions

The electrodeposition technique was optimized to ensure a virtually complete deposition of the analyte on

Table 1. Optimum conditions of FAAS for determination of Co, Ni, Au, In, Pt and Re.

Elements	Wavelength (nm)	Slit (nm)	Light Source	Oxidant/Fuel
Co	240.7	0.2	HCL	Air-Acetylene
Ni	232	0.2	HCL	Air-Acetylene
Au	242.8	0.7	HCL	Air-Acetylene
In	303.9	0.7	HCL	Air-Acetylene
Pt	265.9	0.7	HCL	Air-Acetylene
Re	346.0	0.2	HCL	Nitrous Oxide-Acetylene

cathode electrode. The optimizations of the variables were performed in a univariate and factorial design methods, by maximizing the integrated absorbance of a standard solution.

Effects of pH

The pH to which the sample is buffered proved to be very important. It was demonstrated that pH of the solution and the potential voltage have an important effect on the deposition efficiency in that they influence the vigor of hydrogen evolution [28]. The influences of pH on the deposition recovery of 250 mL standard solutions of 40 ng mL^{-1} of Co, Ni and Au, 0.20 μg mL^{-1} of In, 0.6 μg mL^{-1} of Pt and 2 μg mL^{-1} of Re were investigated at a voltage of 8 V for 4 h. The effect of the pH was studied by adjusting with ammonium sulfate buffer solutions for Co and Ni [29,30], 1M HCl for Au and In [31], 1 M H_2SO_4 for Re [32,33] and 1 M $HCLO_4$ for Pt [34,35]. In electrodeposition of Ni and Co, an increase in the pH causes an increase in its NH_3 concentration and ion complex [30]. Therefore, the efficiency of deposition is increased. Quantitative recoveries were obtained in the pH range 9-11 for Co and Ni, 0.9-2 for In, and pH < 1 for Au, Re and Pt. The results for the effect of pH on the absorbance of these elements are shown in Figure 1.

Effects of Deposition Time

Another important factor that controls the degree of deposition of reduced metal is time of deposition. The analyte electrodeposition efficiency was tested at various times, within an interval of 60-240 min. The effect of the electrolysis time on the absorbance of elements is shown in Figure 2. According to this figure, the selected electrodeposition times were: 120 min for Ni, 150 min for Pt and In, and 180 min for Au and Re. The absorbance of elements increased with electrodeposition time and after the optimum time, then reached a plateau.

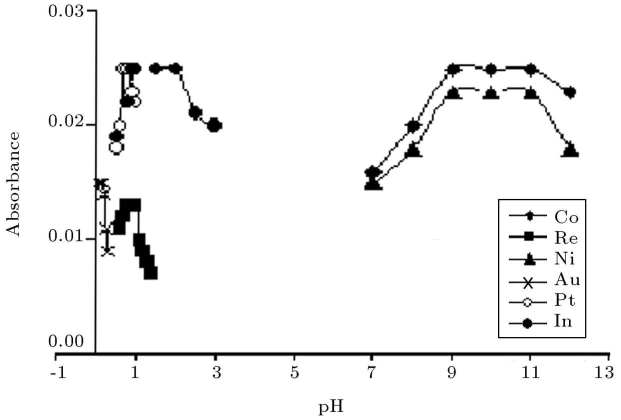

Figure 1. The effect of the pH on the electrodeposition signal of elements.

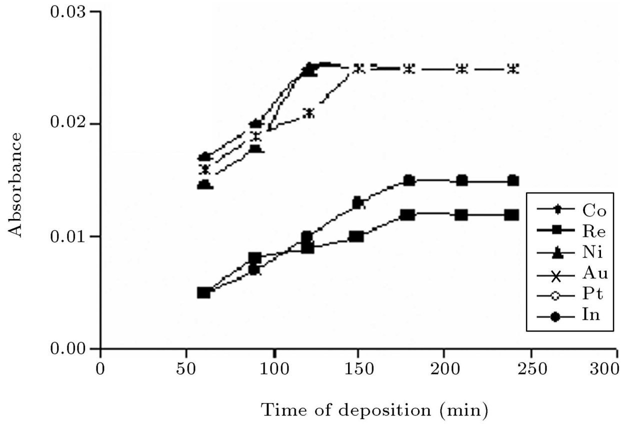

Figure 2. The effect of the electrolysis time on the electrodeposition signal of elements.

Effects of Electrolyte Temperature

Increasing of temperature usually causes to increasing of electrolyte conductivity and diffusion rate. According to Gibbs-Helmholts' law, a rise in temperature will decrease ΔG to increasingly negative values, and the reaction is completed more readily. As shown in Figure 3, the proper and optimum electrolyte temperatures were: 60-75°C for Co, Ni and Au, 70-80°C for Re and Pt, and 45-50°C for In.

Effects of Electrodeposition Voltage

The most important variable for the deposition is the applied potential to the electrolysis cell. The standard reduction potentials (E^o_{RED}) of Co, Ni, Au, In, Re and Pt are -0.28, -0.25, 1.50, -0.35, 0.30 and 1.20 V, respectively. Figure 4 shows the plot of AA signal foe elements versus the applied voltage. The results show that as the applied voltage increases, the AA signals

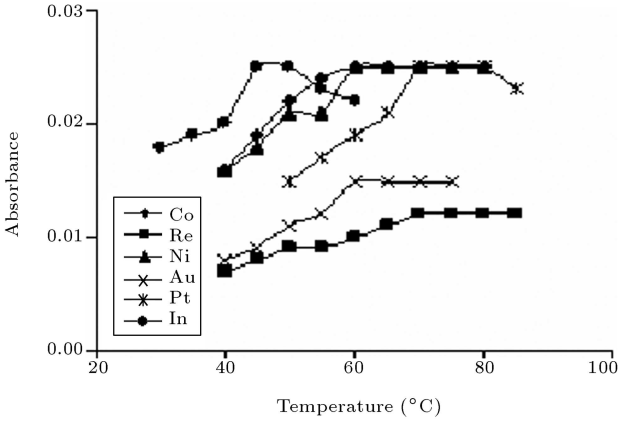

Figure 3. The effect of the electrolyte temperature on the electrodeposition signal of elements.

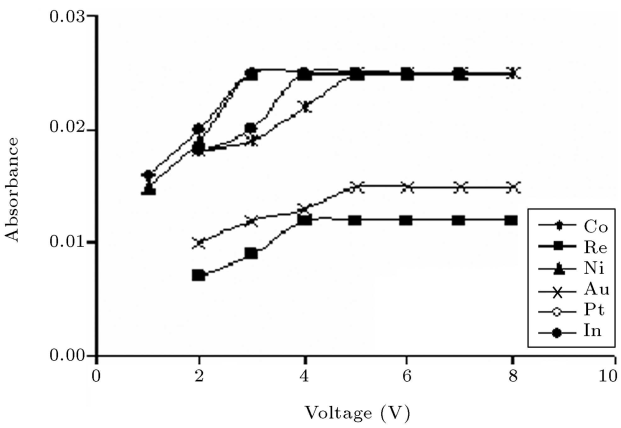

Figure 4. The plot of AA signal foe elements versus the applied voltage.

increase. the higher applied voltage cause more current and hence more gas evolution through the sample drop causes more agitation which in turn should improve the efficiency of deposition. The optimum voltage was selected 3V for Co and Ni, 5V for Au and Pt, 4V for In and Re. As it was shown, in higher than optimum voltages, the AA signal were been straight line.

Full Factorial Design

The statistical design of experiments is used when the effect of several factors are to be studied in order to determine the main and interaction effects. The effect of a variable is the change in response produced by varying the level of the factor. When the effect of a factor depends on the level of another factor, the two factors are said to interact. In the present work, a full factorial design for Co was performed, with four factors at two levels. The four variable parameters were: pH, temperature, voltage and time of deposition. The two levels of variation for these factors were selected from previous experiments on “one variable at a time” and are presented in Table 2. The designs matrix for four factors at two levels were made and 2^4 experiments at a random order were carried out; the higher and the lower levels of the variables were noted by (+) and (−). The main and interaction estimated effect have been calculated by using the Yates algorithm for non-linear regression [36-38]. A quick method of calculating the effects in factorial design has been provided by Yates, who developed an algorithm which is applicable to both complete and factorial design. According to these estimations, the deposition potential and time of duration are the most important main parameters in electrodeposition. In addition, four second-order interaction of AB, AD, BD and CD and a third-order interaction of ABD also show a potential effect on the efficiency of electrodeopsition. This means that the other variables have no significant effect on the response and their effects could be neglected.

Analytical Figures of Merit

Calibration curves were prepared under the optimum determined conditions in ranges of 0.01-0.05 μg mL^{-1} for Co in solution of 1M HNO$_3$ after 100-fold pre-concentration. The Limits Of Detection (LOD) and characteristic concentration (C$_0$) for the measurement of Co by conventional FAAS are compared with those by ED-FAAS. The detection limit was determined as three times the standard deviation divided by the (3 S_b/m) of the concentrations measured in 15 analytical blanks. The S_b and m are standard deviation of blank and calibration curve slope, respectively. The limit of detection of ED-FAAS is better than those obtained with FAAS method. This can be ascribed to an increase in the analyte signal due to preconcentration. The ED-FAAS technique, because the analyte is separated by deposition from the interfering matrix, also shows an improvement in the slope of the calibration curves and in the characteristic concentrations for this technique in the measurement of Co. In this way, calibration curve for other elements were plotted and other evaluation parameters determined. The measurements of LOD, C$_0$ and RSD% of all elements, for ED-FAAS technique, are shown in Table 3. The characteristic concentration for this technique in the measurement of Co is 1.72 ng mL^{-1}. For evaluation of the performance of the ED-FAAS technique in the measurement of traces of elements, the application of this method was tested on real samples.

Analysis of Environmental Samples

The optimized preconcentration method (ED) was used and applied to preconcentrate Co and Ni ions in

Table 2. The selected maximum and minimum values of the four influence variables in absorbance signal of Co in FAAS.

Factors	Low Level	High Level
A. pH	7	11
B. duration of time of electrodeposition (min)	60	240
C. temperature (°C)	40	75
D. voltage of electrodeposition (V)	1	7

Table 3. The amounts of LOD, C_0 and RSD% of ED-FAAS technique for Co, Re, Ni, Au, Pt and In.

Elements	**LOD**	$\mathbf{C_0}$	**RSD%*** $(n = 6)$
Co	1.27 ng mL^{-1}	1.72 ng mL^{-1}	1.54
Re	0.14 μg mL^{-1}	0.66 μg mL^{-1}	2.69
Ni	1.56 ng mL^{-1}	2.67 ng mL^{-1}	2.45
Au	1.84 ng mL^{-1}	2.99 ng mL^{-1}	2.78
Pt	0.02 μg mL^{-1}	0.03 μg mL^{-1}	2.38
In	6.67 ng mL^{-1}	9.60 ng mL^{-1}	2.55

*: The relative standard (RSD) deviation is calculated in C_0 measurement for each element.

mineral water samples collected from Sabalan (North of Iran), followed by their determination by FAAS. The determination of these metal ions concentration were performed, with and without standard addition, by electrodeposition of 250 mL of water sample. The closeness of results of direct and standard addition method indicates the reliability of present results of good agreement obtained between the direct and standard addition methods indicating the reliability of the proposed method for metal analysis in the water samples. The concentration of Co in a typical mineral water is obtained by 100 times preconcentration as 12.46 ng mL^{-1} with 1.54% RSD ($n = 6$). The concentration of Ni in the same mineral water sample is also obtained by 75 times preconcentration as 21.43 ng mL^{-1} with 2.45% RSD ($n = 6$).

The electrodeposition coupled with FAAS was applied to determine Re in a mine samples collected from Sarcheshmeh (Iran). The solid samples were digested to obtain the solution sample prior to preconcentration by electrodeposition of the Re from these solutions, followed by FAAS determination using the standard addition technique. The concentration of Re in this sample by 25 times preconetration is obtained as 4.65 μg mL^{-1} with 2.69% RSD ($n = 6$).

The concentration of Au was determined in a geological sample, after digestion in a 1:3 ratio of HNO_3:HCl solution. The concentration of Au in the geological sample after 100 times preconcetration was obtained 6 ng mL^{-1} with 2.77% RSD ($n = 6$).

The selected quantities of Pt and In samples was spiked into a typical waste water prior to analysis by the proposed technique. The calibration curve was established with and without standard addition by electrodeposition of 250 mL of spiked sample. The evaluated concentration of the waste water sample solution, using the preconcentration method, was found to be 0.15 μg mL^{-1} for Pt and 50 ng mL^{-1} for In. The precision of the measurements (RSD%), examined by 6 replicates in measurements, were found to be 2.38% for Pt and 2.547% for In. A comparison of the represented method with other approaches reported in the literature [3,7,9] is given in Table 4.

Addition/Recovery Tests

In order to estimate the accuracy of the presented preconcentration procedure, different amounts of the investigated metal ions were spiked in real samples. The results are summarized in Table 5. The recoveries values were often greater than 95%. A good agreement was obtained between the added and measured analyte amounts. It shows that the presented method can be applied for preconcentration of analyte ions in the real samples.

CONCLUSION

In conclusion, the metal contents at ng mL^{-1} levels were determined easily. The other main advantages of the method include simplicity, time saving, no requirements of sophisticated instruments and cost effectiveness. The present study shows that the eletrodeposition can serve as a preconcentration and matrix separation procedure prior to the FAAS determination. The detection limits improve, and the sensitivities of determination increase.

Table 4. Characteristic performance data obtained by using ED-FAAS and other preconcentration techniques.

Method	**Reference**	**LOD (ng mL^{-1}), RSD (%)**					
		Co	**Re**	**Ni**	**Au**	**Pt**	**In**
SPE-FAAS	3			0.92, -			
Preconcentration-FAAS	7				0.003, 3.4%		
Silica gel-FAAS	9	0.45, -		0.90, -			
ED-FAAS	This work	1.27, 1.54%	140, 2.69%	1.56, 2.45%	1.84, 2.77%	20, 2.38%	6.67, 2.55%

Table 5. The determined recovery% from addition of standard elements to real samples and blanks.

Elements	Re Samples	Added Standard (ng mL^{-1})	Real Sample (Absorbance)	Blank (Absorbance)	Recovery %
Co	Mineral water of Sabalan	0	0.031	-	-
		10	0.052	0.023	91.3
		20	0.083	0.053	98.11
		30	0.108	0.078	98.71
		40	0.138	0.107	100
Ni	Mineral water of Sabalan	0	0.034	-	
		13.4	0.055	0.022	95.45
		26.7	0.076	0.042	100
		40.0	0.099	0.066	98.48
		53.4	0.119	0.086	98.83
Au	Geological sample	0	0.008	-	-
		10	0.021	0.014	92.85
		20	0.036	0.029	96.55
		30	0.054	0.047	97.87
		40	0.067	0.06	98.33
In	Waste water	0	-	-	-
		50	0.022	0.023	95.65
		60	0.026	0.027	96.29
		70	0.031	0.032	96.87
		80	0.035	0.036	97.22
Pt	Waste water	0	-	-	-
		0.15	0.022	0.023	95.65
		0.20	0.030	0.031	96.77
		0.25	0.040	0.040	100
		0.30	0.048	0.048	100
Re	Mine sample in Sarcheshmeh	0	0.031	-	-
		2000	0.043	0.013	92.30
		4000	0.056	0.026	96.15
		6000	0.069	0.04	95.00
		8000	0.084	0.055	96.36

REFERENCES

1. Tautkus, S., Steponeniene, L. and Kazlauskas, R. "Accumulation of cadmium and zinc in bottom sediments of different waters of Lithuania", *J. Serb. Chem. Soc.*, **72**, pp. 579-583 (2007).

2. Afridi, T.H.I., Kazi, G., Jamali, M.K., Kazi, G.H., Arain, M.B., Jalbani, N., Shar, G.Q. and Sarfaraz, R.A. "Evaluation of toxic metals in biological samples (scalp hair, blood and urine) of steel mill workers by electrothermal atomic absorption spectrometry", *Toxicol. Ind. Health*, **22**, pp. 381-393 (2006).

3. Xie, F., Lin, X., Wu, X. and Xie, Z. "Solid phase extraction of lead (II), copper (II), cadmium (II) and nickel (II) using gallic acid-modified silica gel prior to determination by flame atomic absorption spectrometry", *Talanta*, **74**, pp. 836-843 (2008).

4. Ensafi, A.A. and Shiraz, A.Z. "On-line separation and preconcentration of lead(II) by solid-phase extraction using activated carbon loaded with xylenol orange and its determination by flame atomic absorption spectrometry", *J. Hazard. Mater.*, **150**, pp. 554-559 (2008).

5. Shokrollahi, A., Ghaedi, M., Niband, M.S. and Rajabi, H.R. "Selective and sensitive spectrophotometric method for determination of submicro-molar amounts of aluminium ion", *J. Hazard. Mater.*, **151**, pp. 642-648 (2008).
6. Balcerzak, M. "Sample digestion methods for the determination of traces of precious metals by spectrometric techniques", *Anal. Sci.*, **18**, pp. 737-750 (2002).
7. Carasek, E. "A low-cost flame atomic absorption spectrometry method for determination of trace metals in aqueous samples", *Talanta*, **51**, pp. 173-178 (2000).
8. Shukla, R. and Rao, G.N. "Solvent extraction of metals with potassium-dihydro-bispyrazolyl-borate", *Talanta*, **57**, pp. 633-639 (2002).
9. Goswami, A. and Singh, A.K. "Silica gel functionalized with resacetophenone: synthesis of a new chelating matrix and its application as metal ion collector for their flame atomic absorption spectrometric determination", *Anal. Chim. Acta*, **454**, pp. 229-240 (2002).
10. Yraide, H. and Hori, M. "Enrichment of metal-APDC complexes on admicelle-coated alumina for water analysis", *J. Anal. Sci.*, **15**, pp. 1055-1058 (1999).
11. Ghiasvand, A.R. and Ghaderi, R. "Selective preconcentration of ultra trace mercury(II) in aqueous samples using membrane disks modified by dithizone and its direct spectrophotometric determination", *Asian J. Chem.*, **17**, pp. 1376-1384 (2005).
12. Santelli, R.E., Gallego, M. and Valcarcel, M. "Atomic absorption determination of copper in silicate rocks by continuous precipitation preconcentration", *Anal. Chem.*, **61**, pp. 1427-1430 (1989).
13. Elci, L. and Saracoglu, S. "Applying magnesium hydroxide coprecipitation method for trace analysis to dialysis concentrate", *Talanta*, **46**, pp. 1305-1310 (1998).
14. Kagaya, S., Araki, Y. and Hasegawa, K. "Flame atomic absorption spectrometric determination of lead in waste water and effluent after preconcentration using a rapid coprecipitation technique with gallium phosphate", *Fresenius' J. Anal. Chem.*, **366**, pp. 842-845 (2000).
15. Kovacheva, P. and Djingova, R. "Ion-exchange method for separation and concentration of platinum and palladium for analysis of environmental samples by inductively coupled plasma atomic emission spectrometry", *Anal. Chim. Acta*, **464**, pp. 7-13 (2002).
16. Kubova, J., Neveral, V. and Stresko, V. "Determination of rare-earth elements in mineral waters by inductively-coupled plasma-atomic emission-spectrometry", *J. Anal. At. Spectrom.*, **9**, pp. 241-243 (1994).
17. Silva, E.L., Roldan, P.S. and Gine, M.F. "Simultaneous preconcentration of copper, zinc, cadmium, and nickel in water samples by cloud point extraction using 4-(2-pyridylazo)-resorcinol and their determination by inductively coupled plasma optic emission spectrometry", *J. of Hazard. Mater.*, **171**, pp. 1133-1138 (2009).
18. Matos, G.D., dos Reis, E.B., Costa, A.C.S. and Ferreira, S.L.C. " Speciation of chromium in river water samples contaminated with leather effluents by flame atomic absorption spectrometry after separation/preconcentration by cloud point extraction", *Microchem. J.*, **92**, pp. 135-139 (2009).
19. Najafi, N.M., Eidizadeh, M., Seidi, Sh., Ghasemi, E. and Alizadeh, R. "Developing electrodeposition techniques for preconcentration of ultra-traces of Ni, Cr and Pb prior to arc-atomic emission spectrometry determination", *Microchem. J.*, **93**, pp. 159-163 (2009).
20. Scott, K., *Electrochemical Processes for Clean Rechnology*, The Royal Society of Chemistry, UK (1995).
21. Vydra, F., Štulík, K. and Juláková, E., *Electrochemical Stripping Analysis*, Ellis Horwood, Chichester (1977).
22. Ghasemi, E., Najafi, N.M., Seidi, Sh., Raofie, F. and Ghassempour, A. "Speciation and determination of trace inorganic tellurium in environmental samples by electrodeposition-electrothermal atomic absorption spectroscopy", *J. Anal. At. Spectrom.*, **24**, pp. 1446-1451 (2009).
23. Najafi, N.M., Ghasempour A.R. and Sepehri, R. "Development of hyphenated techniques with ETAAS for determination of ultra-traces of manganese and vanadium and their speciation in environmental samples", *Scientia Iranica*, **14**, pp. 96-105 (2007).
24. Najafi, N.M., Massumi A. and Shafaghizadeh, M. "In-situ digestion of serum samples in graphite furnace prior to determination by ETAAS", *Scientia Iranica*, **12**, pp. 324-328 (2005).
25. Najafi, N.M. and Manouchehri, N. "Development of a new microelectrolysis system for in-situ electrodeposition of ultra-traces of gold prior to measurement by ETAAS", *Anal. and Bioanal. Chem.*, **376**, pp. 460-466 (2003).
26. Najafi, N.M. "Elimination of chemical and spectral interferences in measurement of trace elements in urine and blood by combined ED-ETAAS", *Iran. J. Chem. and Chem. Eng.*, **21**, pp. 80-89 (2002).
27. Najafi, N.M. "Electrodeposition techniques for interference control in electrothermal atomic absorption spectrometry", *Scientia Iranica*, **9**, pp. 181-186 (2002).
28. Chong. N.S., Norton, M.L. and Anderson, J.L. "Multielement trace-metal determination by electrodeposition, scanning electron-microscopic X-ray-fluorescence, and inductively coupled plasma mass-spectrometry", *Anal. Chem.*, **62**, pp. 1043-1050 (1990).
29. Peters, D., Hayes, J. and Hieftje, G.H., *A Brief Introduction to Modern Chemical Analysis*, W.B. Saunders Co. (1976).
30. Vogel, A.I., *Quantitative Inorganic Analysis*, Longmans (1961).
31. Sun, Y.C., Hsieh, C.H., Lin, T.S. and Wen, J.C. "Determination of trace impurities in high purity gold by inductively coupled plasma mass spectrometry with prior matrix removal by electrodeposition", *Spectrochim. Acta*, **55B**, pp. 1481-1489 (2000).

32. Szabo, S. and Bakos, I. "Electroreduction of rhenium from sulfuric acid solutions of perrhenic acid", *J. Electrochem. Chem.*, **492**, pp. 103-111 (2000).

33. Schrebler, R., Cury, P., Orellana, M., Gomez, H., Cordova, R. and Dalchiele, E.A. "Electrochemical and nanoelectrogravimetric studies of the nucleation and growth mechanisms of rhenium on polycrystalline gold electrode", *Electrochim. Acta*, **46**, pp. 4309-4318 (2001).

34. Gloaguen, F., Leger, J.M., Lamy, C., Marmann, A., Stimming, U. and Vogel, R. "Platinum electrodeposition on graphite: electrochemical study and STM imaging", *Electrochim. Acta*, **44**, pp. 1805-1816 (1999).

35. Kelaidopoulou, A., Kokkinidis, G. and Milchev, A. "Nucleation and growth of metal catalysts. Part I. Electrodeposition of platinum on tungsten", *J. Electroanal. Chem.*, **444**, pp. 195-201 (1998).

36. Morgan, E., *Chemometrics: Experimental Design*, Wiley, London (1991).

37. Davies, L. "Efficiency in research, development, and production. The statistical design and analysis of chemical experiments", *The Royal Society of Chemistry*, Cambridge, UK, p. 180 (1993).

38. Bereton, C., *Chemometrics, Applications of Mathematics and Static to Laboratory Systems*, Ellis Horwood (1990).

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Parmis Shakeri. Her biography was not available at the time of publication.

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