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Determination of Trace Elements in Leach Solution by Flame Atomic Absorption Spectrometry After Pre-Concentration on Amberlite XAD-4

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A multi-elements pre-concentration method was proposed for determination of Cu, Ni, Co, Mn, Pb, Zn and Cr from leaching solutions by flame atomic absorption spectrometry (FAAS). It has been investigated the enrichment performance of the three complexing reagents *i.e.*, [8-hydroxyquinoline (8-HQ), dithizone (DT) and sodium diethyldithiocarbamate (NaDDTC)] on Amberlite XAD-4 resin of the mentioned elements which are at or below the detection limits in FAAS. The aliquots of (5 or 10 g) fly ash were leached with 500 or 1000 mL chelating solutions at optimum pHs (8 for 8-HQ and DT and 4 for NaDDTC) for 15 min under magnetic stirring conditions. Then the leachates were passed through preconcentration column and eluted the elements 15 mL 1.0 M HNO_3 in water:water (1:2) and determined the elements by FAAS. The satisfactory recoveries had been obtained from the multi-element pre-concentration studies with dithizone on Amberlite XAD-4. The recoveries Pb, Co and Zn were higher than 90 %, while acceptable for other elements (82, 77 and 72 % for Cu, Ni and Mn, respectively) except Cr (46 %) with acceptable precisions [RSD under 10 % (N = 5)].

Key Words: Solid phase extraction, Pre-concentration, Amberlite XAD-4, Leaching solutions.

INTRODUCTION

Trace analysis is an analytical procedure which requires frequently pre-concentration of analytes and matrix modification of samples. Solid phase extraction (SPE) has advantages such as reducing of solvent consumption and exposure, disposal costs and extraction time of sample preparation for these purposes[1].

Various adsorbents, ion exchangers and chelating agents have been investigated so far for the recovery of different elements from different materials using solid phase extraction technique. Macro porous hydrophobic resins of the Amberlite XAD series are good supports for developing chelating

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matrices. Organic origins synthetic Amberlite resins can be classified into two groups as ion-exchanger and adsorbent on the basis of usage and formation. Amberlite XAD-1, XAD-2, XAD-4 and XAD-16 are polystyrene-divinyl benzene (PS-DVB) resins with a high hydrophobic character and have no ion-exchange capacity. Due to the hydrophobic character of PS-DVB, retention of trace elements on such sorbents requires the addition of a ligand to the sample. Inorganic ligands may be used, but organic ligands are preferred, such as ammonium pyrrolidine dithiocarbamate (APDC), 8-hydroxyquinoline (8-HQ) or diphenylcarbazide (DPC). Alternately, ligands may be attached to the PS-DVB by physical adsorption such as dithizone (PDT, 3-(2-pyridyl)-5,6-diphenyl-1,2,4-triazine), tropolone, PAN (1-(2-pyridylazo)2-naphthol), DDQ (7-dodecenyl-8-quinlinol), APDC or 5-BrPA-DAP (2-(5-bromo-2-pyridylazo)-5-(diethylamino)phenol)[2-18].

An effective multi-elements pre-concentration method is aimed for determination of some metals in leach solution of fly ash by FAAS in this study.

EXPERIMENTAL

Determination of the metals was performed on a Perkin Elmer 2380 Model flame atomic absorption spectrometer (FAAS). The average absorption data obtained was evaluated in the basis of the least square calibration graphs. The pH measurements were done by using HANNA 8521 pH-meter.

The analytical grade reactants were used in all the experiments and the solutions were prepared in double distilled water. Suitable blanks were formed for each stage of the leaching process and all of the data were corrected for blanks results.

The resin used was Amberlite XAD-4. It was purchased as 20-60 mesh (surface area: 725 m^2 g^{-1}, pore diameter: 40 Å) from Sigma. In order to remove organic and inorganic contaminants, after shaking with methanol for a period of 0.5 h, it was filtered through gooch crucible. It was washed successively with water, 1 mol/L HNO_3 in acetone, water, 1 mol/L NaOH, water, acetone, respectively (stirring with glass rod). It was dried at 105 ºC for 1 h in an oven and kept in desiccator.

Buffers: The buffers used were phthalic acid/potassium hydrogen phthalate (prepared from potassium hydrogen phthalate and HCl) for pH 4, potassium dihydrogen phosphate/potassium monohydrogen phosphate (prepared from potassium dihydrogen phosphate/NaOH) for pH 8.

Chelating solutions: The chelating agents were 8-hydroxyquinoline (8-HQ), dithizone (1,5-diphenlythiocarbazone) (DT) and sodium diethyldithiocarbamate (NaDDTC).

0.002 % solution of 8-HQ was prepared in a water/ethanol (75/25, v/v) mixture. 1 mmol/L dithizone solution was prepared in acetone, while 10 mmol/L NaDDTC solution was prepared in water.

Elution solution: 1 mol/L HNO_3 in acetone.

Pre-concentration experiments

Preconcentration procedure was carried out in seven groups of solutions that the details of it were given below.

Synthetic Cu, Ni, Co, Mn, Pb, Zn, Cr solutions (S_{00}): 1000 mL standard synthetic solution containing 0.5 µg/mL Cu, Ni, Co, Mn, Pb, Zn, Cr was prepared by using 1% HCl as solvent (pH = 1.20).

The elemental Cu, Ni and Zn (Merck) and nitrate salts of Co, Mn, Pb and Cr (Merck) were dissolved in 2 % HNO_3 and 1000 µg/mL stock solution were prepared for each element. Solution of 0.5 µg/mL was prepared by diluting these stock solutions.

The time dependent water leach of fly ash: 10 g Fly ash was leached with 1 L water using magnetic stirring, filtered by gooch crucible (N-4). The basic leachates ($11.48 < pH < 12.09$) were acidified. The procedure was repeated for three leaching times *i.e.*, 0.5, 1.0 and 1.5 h and the leachates were coded S_{10}, S_{20} and S_{30}, respectively.

Ultrasonic leaching: 5 g Fly ash samples and 500 mL water aliquots were used and two parallel experiments were carried out for the periods of 10 and 20 min and the leachates were coded U_{10} and U_{20}, respectively. The solutions were filtered by using gooch crucible (N-4) and each parallel experiment was mixed. The average mass losses after the leaching procedures were 9.93 and 11.00 %, respectively.

H_2SO_4 leach (Acid leach-AL_{10}): Pre-concentration experiments were carried out for leach solution produced by Sengul[19] during H_2SO_4 column leach experiments.

Solution was basic (pH = 9.0) and therefore it was made acidic (pH = 1.56) (due to high Ca concentration) and stored for pre-concentration.

Waste water of Kangal Power-Plant: Waste water (WW_{10}) samples (pH = 9.24) taken from the pond of the ash stock of Kangal Power-Plant on December 2, 1999 were used for pre-concentration experiments.

Spiking of the leach solutions: Since the elements in leach solutions could not be determined by FAAS directly (that is under detection limits), 0.5 µg/mL Cu, Ni, Co, Mn, Pb, Zn, Cr elements were spiked to the previously prepared leach solutions and the new solutions were coded S_{11}, S_{21}, S_{31}, U_{11}, U_{21}, AL_{11}, WW_{11}. Thus, it was aimed to determine % recoveries at the same time.

Pre-concentration columns: Micro filter crucible (4.5 × 1.1 cm) with G_3 filter was used as column for pre-concentration experiments. Column was prepared by putting 0.3 g Amberlite XAD-4 slam into micro crucible.

It was conditioned with the buffer solution used for the sample prior to percolation. After elution, the packed Amberlite XAD-4 is regenerated with a large volume of eluent (1 mol/L HNO_3 in acetone).

Procedures for extraction studies: The steps on the flow chart (Fig. 1) conducted as pre-concentration procedures and determinations of the elements.

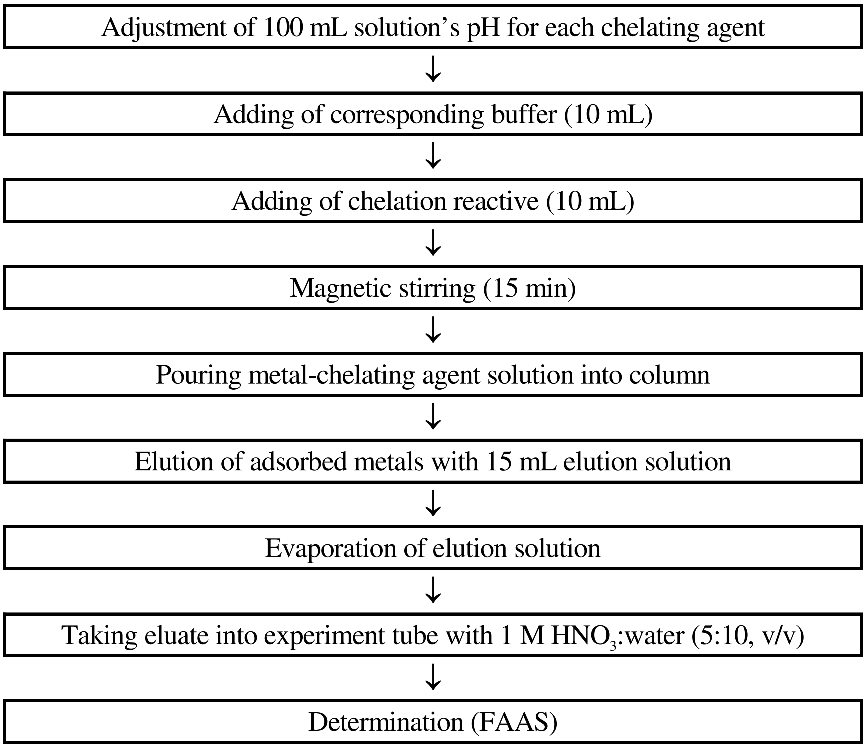

Fig. 1. Flow chart of metal determination in leaching solutions by the proposed method

pH of the sample solutions were adjusted predetermined pHs (8 for 8-HQ and DT and 4 for NaDDTC) for each chelating agent by corresponding buffers before solid phase extraction. The absorbances of the eluents were measured by FAAS for each of the analyte elements. Pre-concentration conditions were optimized by considering the literature data and carrying out pre-experiments.

The pre-concentration experiments were carried out on the standard synthetic Cu, Ni, Co, Mn, Pb, Zn, Cr solution and the leach solutions. Eluent volume was chosen to be 15 mL.

RESULTS AND DISCUSSION

The results of FAAS analysis of the spiked leach solutions are given in Table-1.

TABLE-1
RESULTS OF FAAS ANALYSIS OF LEACH SOLUTIONS
BEFORE PRE-CONCENTRATION EXPERIMENTS

Leach solutions	Element concentration (μg/g)						
	Cu	Pb	Co	Mn	Ni	Cr	Zn
S_{11}	0.642	0.815	0.899	0.769	0.693	0.962	1.014
S_{21}	0.662	0.738	0.854	0.769	0.693	0.962	1.006
S_{31}	0.662	0.815	0.854	0.769	0.693	0.865	0.997
U_{11}	0.642	0.738	0.809	0.747	0.693	0.962	1.006
U_{21}	0.662	0.738	0.809	0.769	0.646	0.962	1.007
AL_{11}	0.642	0.661	0.854	0.769	0.646	0.962	1.006
WW_{11}	0.297	0.354	0.764	0.791	0.599	0.865	0.824

The results of FAAS analysis obtained leach solutions before the pre-concentration experiments were under dedection limit of the analysis method. Recovery factor determined for the evaluation of pre-concentration experiments is defined as follows on synthetic standard solutions.

$$\% \text{ Recovery} = \frac{Q}{Q_o}100$$

where, Q_o = amount of element in the standard; Q = amount of element after pre-concentration.

Pre-concentration experiments were carried out for each solution by using three different chelating agent (8-HQ, DT, NaDDTC) on the Amberlite XAD-4.

The results of solutions obtained after preconcentration 8-HQ, DT and NaDDTC on the Amberlite XAD-4 are given in Table-2 for comparison.

TABLE-2
ELEMENT RECOVERIES OF THREE
PRE-CONCENTRATION PROCEDURES

Element	Recovery (%)		
	8-HQ on Amberlite XAD-4	DT on Amberlite XAD-4	NaDDTC on Amberlite XAD-4
Cu	3.0	82.3	57.0
Pb	67.0	93.8	52.8
Co	40.5	96.6	53.4
Mn	40.0	72.0	< DL
Ni	52.4	77.3	56.1
Cr	25.5	46.6	12.1
Zn	86.0	106.3	61.9

Conclusion

Levels of trace metals in the fly ash have been determined on another study as Cu 55 ± 3, Ni 342 ± 12, Co 75 ± 3, Mn 138 ± 3, Pb 52 ± 5, Zn 412 ± 35, Cr 176 ± 13 (at µg/g unit, as average of 17 experiments with 95 % confidence interval)[20].

In order to optimize pre-concentration procedure for Cu, Ni, Co, Mn, Pb, Cr, Zn, a series of experiments were designed and performed for nine different solutions by using three different chelating agents on Amberlite XAD-4 as adsorbent. The per cent recoveries of pre-concentration were determined on the synthetic 0.5 µg/mL Cu, Ni, Co, Mn, Pb, Cr and Zn solution since those elements in the leachats are below the limit of detection. The results drawn from those experiments are given below:

(a) The recoveries of Ni, Pb and Zn were over 50 % when preconcentration experiments were carried out by using 8-hydroxyquinoline. (b) The recovery of 6 elements was high except Cr when preconcentration experiments were carried out by using dithizone. The recovery of Pb, Co and Zn was over 90 %. Recovery was 70-80 % for Cu, Mn, Ni. (c) The recovery of Cr was 12 %, Cu, Pb, Co, Ni and Zn was 50-60 %, a no recovery was recorded for Mn when experiments were completed by using NaDDTC.

According to above results, the optimum recovery for 7 elements was obtained from the preconcentration experiments by using dithizone. Particularly Pb, Co and Zn recoveries were satisfactory (over 90 %) and acceptable for these investigations.

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