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Determination of Cd, Cu, Pb and Sb in environmental samples by ICP-AES using polyaniline for separation

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Abstract The anion exchange properties of polyaniline for Cd, Cu, Pb and Sb in potassium iodide were studied. The analytes converted into anionic complexes by KI (0.03–0.96 mol/L) in HCl were adsorbed on polyaniline and eluted with HNO₃. The optimum conditions for adsorption and elution were determined. Quantitative recoveries were obtained for Cd, Cu and Pb, whereas, the recoveries for Sb were about 75%. This separation procedure was used with subsequent ICP-AES determination for Cd, Cu, and Pb in NIST-coal fly ash (1633b) and a sea plant with an R.S.D of 5% ($n = 5$).

1 Introduction

Inductively coupled plasma – atomic emission spectrometry (ICP-AES) is a powerful tool for multi element analysis [1]. The detection limits achievable lie well below µg/g levels in aqueous solutions [2]. However, in complex matrices with a high salt content, matrix interferences have deleterious effects on the limit of detection. Samples such as coal fly ash, urban dust, soil, biological samples etc., containing a high salt content hamper the analysis of low level constituents. Such samples can be brought into the solution using alkali fusion, to ensure complete dissolution. The analysis of samples fused with sodium hydroxide, sodium carbonate etc., by ICP-AES is impeded due to the presence of large amounts of sodium in the solution requiring excessive dilution resulting in a decrease of sensitivity. In such sample solutions the excess of sodium has to be removed prior to analysis [3]. Some biological samples like sea plants also contain large amounts of sodium leading to the interferences mentioned above. Hence, in such situations, removal of sodium salts from the sample solution facilitates the study of toxic ele-

ments like Cd, Cu, Pb and Sb in the environmental samples to assess the release of toxic elements due to anthropogenic causes [4–6].

The separation of elements like As, Bi, Cd, Cr, Cu, Pb, Sb and Zn using ion exchangers like Chelex-100, Dowex-50, K-U-2-8 etc [7–10] have often been used for trace / matrix separations. Recently the anion exchange behavior of the above elements in the presence of 0.5–5 mol/L KI solution on AG1-X8 resin was also reported [11]. Polyaniline has recently been used as an anion exchanger for separation of halide ions and Pt, Pd, Ir and Au, which form stable anionic chloro complexes [12–14].

In the present work, the anion exchange capability of polyaniline towards Cd, Cu, Pb and Sb in the KI medium was studied. The optimized separation procedure has been applied for the determination of Cd, Cu, Pb and Sb in NIST-coal fly ash (1633b) and sea plant samples.

2 Experimental

2.1 Reagents

All reagents used were of analytical grade (AR). High purity water was prepared by a Millipore Q system. Eppendorf micro pipettes and PFA containers were used throughout. All containers were cleaned by soaking 20% (V/V) nitric acid and rinsing with high purity water before use.

2.2 Standard solutions

Stock standard solutions of 1 mg/mL were prepared by dissolving high-purity metals (obtained from Special Material Plant, Nuclear Fuel Complex, India) of Cd, Cu, and Pb in nitric acid and Sb in aqua regia (nitric acid was evaporated and solved, in HCl).

2.3 Apparatus and operating parameters

An inductively coupled plasma – atomic emission spectrometer (JY-38, France) equipped with 56 MHz R.F generator (Durr-JY) was used for trace determinations. The operating parameters are: Output power 1.7 kW, Plasma gas flow 18 L/min, Slit width 10 µm/10 µm, Integration time 0.3 s.

Wavelengths (nm): 327.396 (Cu), 214.438 (Cd), 220.353 (Pb) and 206.833 (Sb).

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2.4 Preparation of polyaniline

Doubly distilled aniline, 15.35 g (0.33 mol/L) was dissolved in 500 mL of 1 mol/L HCl, 36.5 g (0.32 mol/L) of ammonium peroxodisulfate was added and stirred for 1 h. The insoluble precipitate of polyaniline thus obtained was filtered, washed thoroughly with deionized water followed by acetonitrile and dried. The dried powder was ground and sieved to about 200 mesh. The dried polyaniline was found to be adequately stable and could be reused if the HNO₃ used for elution is removed by repeated washings with high purity water.

2.5 Adsorption studies

A column of 10 mm diameter and 1.5 cm long was prepared with 200 mg of polyaniline and was washed with 20 mL of deionized water. A mixed standard solution containing 50 µg each of Cd, Cu, Pb and Sb in 10 mL of 0.5 mol/L HCl were taken and treated with 0.4 g of KI. This solution was passed through the column at a flow rate of about 0.5 mL/min. The column was again washed with 10 mL of high purity water to remove any traces of KI from the column. The analytes separated were eluted with 20 mL of 1.6 mol/L HNO₃ and made up to 25 mL. For the assessment of analyte recoveries, the eluate was compared with a standard solution containing 50 µg of the analyte in 25 mL of 1.6 mol/L HNO₃ using ICP-AES.

2.6 Determination of distribution coefficients

The distribution coefficients, K_d , of the amount of metal per g of resin to the amount of metal per ml of solution were found to be 5×10^5 for Cu and Cd; 1.6×10^3 for Pb and 2×10^2 for Sb (for 200 mg of resin and 50 µg/10 mL of element).

2.7 Sample dissolution

2.7.1 Coal fly ash. NaOH (AR) (6 g) was taken in a zirconium crucible and melted on a Bunsen burner. After cooling, 500 mg of coal fly ash (NIST-1633b) was added and fused for about half an hour. The fused sample was dissolved in 40 mL of 2.5 mol/L HCl and made up to 50 mL. A process blank solution was prepared similarly.

2.7.2 Sea plant. A 750 mg of the sea plant sample (obtained from IAEA) was taken in a 100 mL round bottomed flask and 4 mL of conc. HNO₃ was added and digested using a Bethge's apparatus for about half an hour. After cooling it sufficiently, 2 mL of conc. H₂SO₄ was added and refluxed again for another half an hour. The reflux was cooled and made up to 50 mL. A process blank was also made as mentioned above.

2.8 Analytical procedure

A sample aliquot of 10 mL was taken in a 50 mL beaker, to which 0.4 g of KI (1.2 g in case of Sb) was added. The solution was loaded on to the column filled with 200 mg of polyaniline, with a flow rate of 0.5 mL/min. Then, the column was washed with 10 mL of high purity water. The analytes separated were eluted with 20 mL of 1.6 mol/L HNO₃ and made up to 25 mL. Sample aliquots with known amounts of mixed standards were also treated in a similar fashion, for obtaining a standard addition calibration plot. Process blanks were also obtained as mentioned above. The above solutions were analyzed by ICP-AES and the amounts of Cd, Cu, Pb and Sb were determined based on the standard addition calibration plot. This procedure was adopted on both the coal fly ash and sea plant samples.

3 Results and discussion

The adsorption of Cd, Cu, Pb and Sb in HCl and H₂SO₄ media were studied in the concentration range of 0.1 to 0.5 mol/L and 0.36 to 1.8 mol/L, respectively. The recoveries in HCl medium were found to be rather poor (30% for Cd and 0–15% for other elements). In H₂SO₄ medium, the elemental recoveries were determined to be < 10%. In order to obtain higher recoveries for the elements considered, it is necessary to ensure their conversion into anionic complexes. Hence KI was added to the sample solution which converts them into stable iodide complexes. The adsorption property of polyaniline in this medium

Fig. 1 Recovery of Cd, Cu, Pb and Sb as a function of the concentration of KI (in 0.5 mol/L HCl)

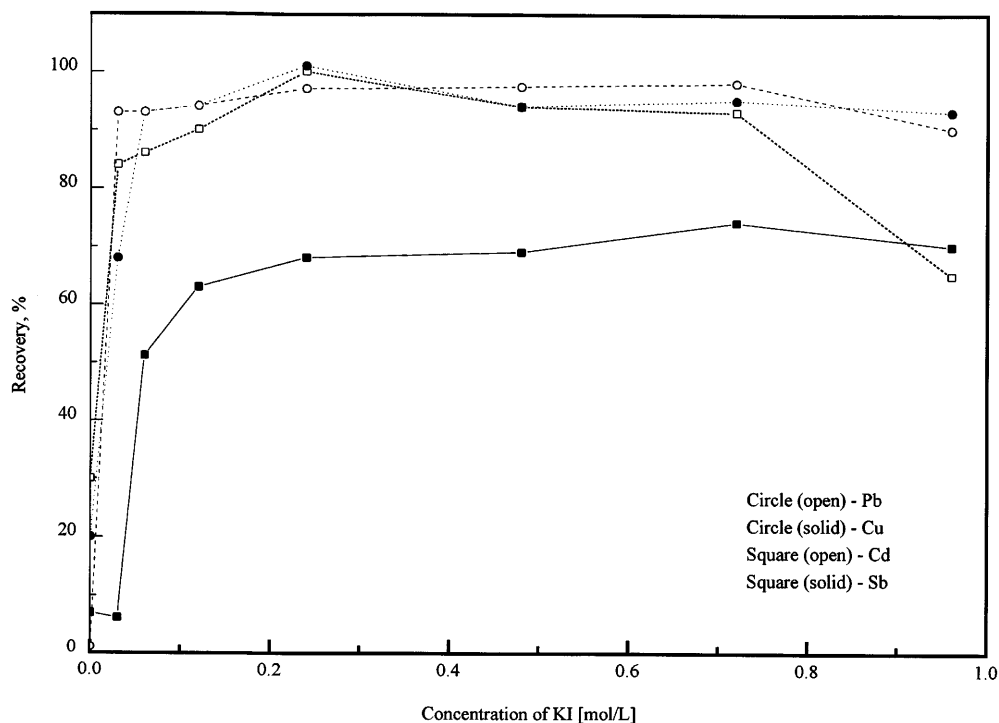
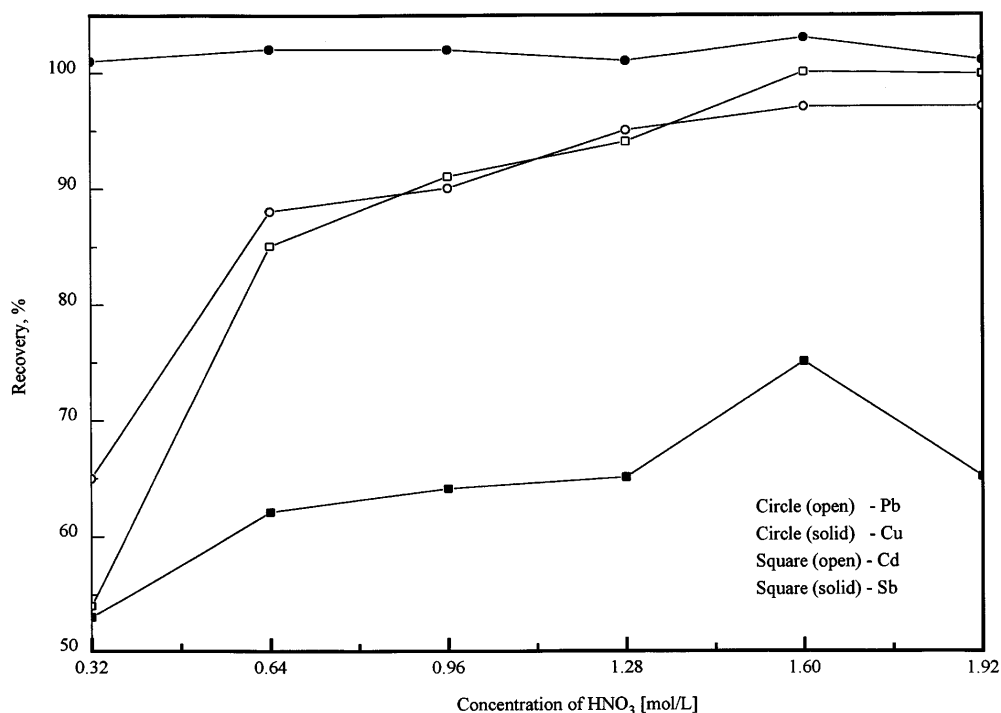


Fig. 2 Elution of Cd, Cu, Pb and Sb depending on the concentration of HNO₃



was studied using known amounts of analytes. The recoveries obtained for Cd, Cu and Pb were found to be > 97% except for Sb where the recoveries were determined to be 75%. Hence, polyaniline could be used as an alternative anion exchanger for these elements which readily form anionic complexes. However, it is necessary to optimize the experimental conditions in order to improve the efficiency of the separation procedure.

The optimization of experimental parameters i.e., the amount of KI, concentration of HCl for quantitative adsorption; and the optimum concentration of HNO₃ for elution were carried out. First, the concentration of HCl was kept constant (0.5 mol/L) and the amount of KI was varied from 0 to 0.96 mol/L (10 mL solution). The adsorption could be increased with an increase of KI up to 0.24 mol/L (0.72 mol/L in case of Sb) (Fig. 1). At higher concentrations, the percentage of adsorption remains constant except for Cd. In case of Cd, the recoveries were reduced when the concentration of KI is increased beyond 0.24 mol/L. This could be due to the conversion of cadmium from [CdI₄]²⁻ to [CdI₅]³⁻ at higher concentrations of KI [15]. The HCl concentration was varied from 0.1 to 0.7 mol/L keeping the KI concentration (0.24 mol/L) constant, for optimizing the adsorption conditions. The concentration of HCl was found to have little influence on the adsorption of analytes. For these studies, elution of the adsorbed elements has been carried out using 1.6 mol/L HNO₃. Since the recovery of the analytes has a significant dependence on the strength of HNO₃ used for elution, the concentration of HNO₃ was varied with in the range 0.3 to 1.6 mol/L (Fig. 2). The percentage of recovery was found to increase with the concentration of HNO₃. A complete recovery was obtained at 1.6 mol/L HNO₃ for Cd, Cu and

Pb. However, at such concentrations of HNO₃ the recovery of Sb was merely about 75%. The probable reason for relatively poor recoveries of Sb was due to incomplete conversion into a stable anionic complex under the optimized experimental conditions. The poor recoveries of Sb could be attributed to the probable lower percentage of adsorption, as Sb is known to exist in both anionic and cationic forms upon treatment with KI [16]. Hence the recoveries cannot be further improved by increasing the concentration of HNO₃.

After optimizing the separation and elution conditions, the percentage recoveries were determined for NIST-coal fly ash (1633b) and sea plant (IAEA) samples. At concentration of 2 µg/mL (5 µg/mL in case of Sb) the percentage recoveries were found to be quantitative and adequate for efficient separations (Table 1). The results obtained using the method were in good agreement with the certified values (Table 2). However, a small discrepancy in the value of Cu has been found which was lower than the certified value. In order to establish the source of such discrepancy, an alternate microwave digestion procedure [17] has been adopted for the determination of the Cu content in the coal

Table 1 Percentage recoveries of Cd, Cu, Pb and Sb from coal fly ash (100 mg) and sea plant (150 mg) after digestion ($n = 5$)

Element	Percentage recovery (%)	
	Coal fly ash	Sea plant
Cd	100	95
Cu	85	89
Pb	100	95
Sb	60	62

Table 2 Cd, Cu, Pb and Sb determined in NIST-Coal Fly Ash (1633b) ($n = 5$)

Element	Certified ($\mu\text{g/g}$)	Obtained ($\mu\text{g/g}$)
Cd	0.784 ± 0.006	0.9 ± 0.25
Cu	112.8 ± 2.6	102.0 ± 1.0
Pb	68.2 ± 1.1	69.5 ± 2.0
Sb	6.0^a	< 10

^arecommended by NIST

Table 3 Process blank and limit of detection values for coal fly ash and sea plant (A coal fly ash; B sea plant)

Element	Blank (ng/mL)		LOD (ng/mL)	
	A	B	A	B
Sb	< 20	< 20	< 20	< 20
Cd	20	10	4	5
Pb	57	35	30	25
Cu	35	5	22	10

fly ash sample. The Cu content was determined to be $101.5 \mu\text{g/g}$ which is in good agreement with our value. In case of the sea plant sample, the concentration of the analytes could not be determined as they were below the detection limits, the only exception being Cu. The value of Cu obtained by ICP-AES ($29 \pm 1.0 \mu\text{g/g}$) was cross validated with the values obtained by GFAAS ($30 \pm 1.0 \mu\text{g/g}$).

The values of process blanks and limits of detection (L.O.D.) are tabulated in Table 3. The L.O.D. values were computed as three times of the standard deviation of the repeated measurements of the process blank values ($n = 5$). The higher blank values of coal fly ash could possibly be attributed to the NaOH used for fusing the sample.

4 Conclusion

A new separation procedure has been developed for the determination of Cd, Cu, Pb and Sb in silicate and biolog-

ical matrices containing high sodium concentrations, using polyaniline as an anion exchanger in KI medium. Since polyaniline can be readily prepared in the laboratory, this can be used as an alternative, cost effective anion exchanger. Under the optimized conditions, polyaniline was exhibited to be an effective anion exchanger for the determination of Cd, Cu, Pb and Sb in coal fly ash and sea plant samples.

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