

Flame Atomic Absorption Spectrometric Determination of Trace Lead after Solid-Liquid Extraction and Preconcentration Using 1-(2-Pyridylazo)-2-naphthol

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An atomic absorption spectrometric method for the determination of trace amounts of lead after adsorption of its 1-(2-pyridylazo)-2-naphthol (PAN) complex on microcrystalline naphthalene has been developed. This complex was adsorbed on microcrystalline naphthalene in the pH range 8.4–11.5 from large volumes of aqueous solutions of various alloys and biological samples. After filtration, the solid mass consisting of the complex and naphthalene was dissolved with 5 ml of dimethylformamide and the metal was determined by flame atomic absorption spectrometry. Lead was alternatively quantitatively adsorbed on [1-(2-pyridylazo)-2-naphthol]-naphthalene adsorbent packed in a column and determined similarly. In this case, 0.5 μg of lead was concentrated in a column from 500 ml of aqueous sample, where its concentration was as low as 1.0 ng ml^{-1} . Eight replicate determinations of 4.0 $\mu\text{g ml}^{-1}$ of lead gave a mean absorbance of 0.200 with a relative standard deviation of 1.5 %. The sensitivity for 1 % absorption was 88 ng ml^{-1} . The interference of a large number of anions and cations was studied and the optimized conditions developed were utilized for the trace determination of lead in various standard samples.

Key words

1-(2-pyridylazo)-2-naphthol
naphthalene
adsorbent
Pb (lead)

flame atomic absorption spectrometry

INTRODUCTION

Lead affects the physical properties of steel, alloys and high purity metals. It is highly toxic to man and animals and causes environmental diseases. Very low concentrations of this metal are present in various matrices, such as plants, soils, food and water. It is, therefore, very important to develop sensitive, selective, rapid and economical methods for quantitative determination of its trace amounts. Spectrophotometric methods are simple and economical but are not sufficiently sensitive and selective.^{1,2} Graphite furnace atomic absorption spectroscopy, neutron activation analysis, inductively coupled plasma-atomic emission spectroscopy and mass spectrometry, direct current plasma atomic emission spectrometry may be used^{3–8} but the required instruments are expensive, day-to-day maintenance cost is high and various types of inherent interferences appear.^{3–8}

The analytical use of 1-(2-pyridylazo)-2-naphthol (PAN) was studied by Cheng and Bray.⁹ Methods for quantitative determination of vanadium,¹⁰ iron,¹¹ nickel,¹² zinc,¹³ rhodium,¹⁴ palladium,¹⁵ cadmium,¹⁶ indium,¹⁷ iridium,¹⁸ and bismuth,¹⁹ were published. In the present note, a method for the preconcentration of lead from a large volume of its aqueous solutions of various reference materials using PAN as complexing agent and naphthalene as adsorbent is described.

EXPERIMENTAL

Apparatus and Reagents

A Zeiss Atom-Absorption-Spectrometer FMD 3 (Germany) was used. All absorption measurements were per-

formed under the following operating conditions: wavelength: 217.0 nm; slit setting: 0.3 mm; current: 15 mA; acetylene flow setting: 10 (pressure: 0.9 kPa cm⁻²); air flow setting: 15.5 (pressure: \approx 1.2 kPa cm⁻²). A standard lead solution ($\gamma(\text{Pb}^{2+}) = 1000 \mu\text{g ml}^{-1}$) was prepared from $\text{Pb}(\text{NO}_3)_2$ (Merck) in distilled water and standardized.²⁰ A 0.1 % solution of PAN was prepared in ethanol. Buffer solutions of pH = 3–6, 6–8 and 8–11 were prepared by mixing appropriate ratios of a 0.5 M acetic acid and 0.5 M sodium acetate solution, 0.1 M sodium dihydrogen phosphate solution and 0.1 M dipotassium hydrogen phosphate solution, and 0.5 M ammonia solution and 0.5 M ammonium acetate solution, respectively. A 20 % solution of naphthalene in acetone was used. Solutions of alkali metal salts (1 %) and various metal salts (0.1 %) were used to study the interference of anions and cations, respectively. Other apparatus, reagents and preparation of loaded PAN-naphthalene adsorbent were as those described in Ref. 13.

General Procedure for the Column Method

An aliquot of lead solution (up to 500 ml) containing 0.5–100 μg of lead was put in a beaker. The pH of this solution was adjusted to 9.5 by addition of 2 ml of buffer solution and diluted to about 20 ml with distilled water. The column loaded with the PAN-naphthalene adsorbent was conditioned to pH = 9.5 with 2–3 ml of buffer and then the metal solution was passed through the column at a flow rate of 1 ml min⁻¹. The packing was washed with a small volume of water and then aspirated strongly for a few minutes, pushing down the naphthalene material with a flat glass rod to eliminate excess water attached to the naphthalene. The solid mass, consisting of the metal complex along with naphthalene, was dissolved out of the column with 5 ml of dimethylformamide (DMF). The solution was aspirated into an air-acetylene flame and the absorbance was measured at 217.0 nm against a reagent blank. The absorbances for standard amounts of lead were measured and a calibration curve was constructed against a reagent blank prepared in a similar manner.

General Procedure for Microcrystalline Naphthalene

An aliquot of lead solution (up to 200 ml containing 0.5–100 μg) was placed in an Erlenmeyer flask with a tightly fitting stopper. Then, 1 ml of 0.1 % of the reagent (PAN) was added to it. The pH was adjusted to 9.5 with 2 ml of the buffer. The further procedure was as that described in Ref. 13. Finally, the solution was aspirated into an air-acetylene flame and the absorbance was measured at 217.0 nm against a reagent blank solution prepared in the same way. A calibration graph was prepared by taking various known amounts of lead under the conditions given above.

RESULTS AND DISCUSSIONS

Reaction Conditions

The reaction conditions were investigated with 20 μg of lead. Adsorption was carried out at different pH values, keeping the other variables constant. It was found that the lead complex was quantitatively adsorbed on naphthalene in the pH range 8.4–11.5. The further procedure was as that described in Ref. 13.

In the column method, flow rates of 0.2 to 8 ml min⁻¹ were investigated. It was found that a flow rate of 0.2–7.0 ml min⁻¹ did not affect adsorption. A flow rate of 1 ml min⁻¹ was recommended in all experiments.

The volume of the aqueous phase was varied in the range 10–700 ml under the optimal conditions, keeping the other variables constant. It was observed that the signal height was almost constant up to 200 ml (preconcentration factor of 40). However, for convenience, all the experiments were carried out with 20–40 ml of aqueous phase.

In the column method, the peak height was almost constant up to an aqueous phase volume of 500 ml. Therefore, a preconcentration factor of 100 could be achieved by the column.

Choice of Solvent

A number of solvents were used to dissolve the PAN-lead-naphthalene mixture. Since the solid mass is dissolved in a small volume (3–5 ml) of solvent, it is essential to select a solvent in which the chelate is highly soluble. The solid material is insoluble in ordinary organic solvents¹³ but soluble in dimethyl sulfoxide, DMF, and propylene carbonate. DMF was preferred because of the high solubility and stability. It was found that 2–3 ml of this solvent was sufficient to dissolve the mixture, thus enhancing further the sensitivity of the method.

Calibration and Sensitivity

Considering that it is possible to retain 0.15 μg of lead from 500 ml of aqueous solution passing through the column, the dissolution with 5.0 ml DMF gives a detection limit of 0.3 ng ml⁻¹ for lead in the first aqueous solution at the minimal instrumental settings. The linearity was maintained in the concentration range of 1.0 ng ml⁻¹ to 10.0 $\mu\text{g ml}^{-1}$ lead in aqueous solution or 0.1 to 20.0 $\mu\text{g ml}^{-1}$ lead in the final DMF solution with a correlation factor of 0.9995. Eight replicate determinations of 20.0 μg of lead in 5 ml of DMF solution gave a mean absorbance of 0.200 with a relative standard deviation of 1.5 %. The sensitivity for 1 % absorption was 88 ng ml⁻¹.

Retention Capacity of the Adsorbent

The retention capacity of the adsorbent was determined by a batch method. The experiment was performed by

TABLE I. Effect of diverse salts and metal ions

| Salt or ion | Tolerance limit |
|--|------------------------------|
| CH ₃ COONa · 3H ₂ O, KNO ₃ | 1 g |
| K ₂ SO ₄ | 250 mg |
| KI, NaF | 200 mg |
| Thiourea | 120 mg |
| NH ₄ Cl, Na ₃ PO ₄ · 12H ₂ O, K ₂ CO ₃ | 110 mg |
| Na ₂ S ₂ O ₃ | 100 mg |
| Sodium potassium tartrate | 20 mg |
| KSCN | 15 mg |
| Sodium oxalate | 12 mg |
| Trisodium citrate | 10 mg |
| Dimethylglyoxime | 9.0 mg |
| Na ₂ edta | 50 µg |
| Mg ^{II} | 80 mg |
| Ca ^{II} | 70 mg |
| Cd ^{II} | 6.0 mg |
| Sb ^{III} , Mn ^{II} | 5.0 mg |
| Ag ^I | 1.5 mg |
| Cu ^{II} | 90 µg, 1.5 mg ^(a) |
| Ti ^{IV} , Zn ^{II} | 3.5 mg |
| Cr ^{VI} , Cr ^{III} | 2.5 mg |
| Se ^{VI} , Ga ^{III} | 1.5 mg |
| U ^{VI} , Al ^{III} | 1.2 mg |
| Mo ^{VI} | 1.1 mg |
| Pd ^{II} , Te ^{IV} | 0.9 mg |
| Fe ^{III} | 80 µg, 0.9 mg ^(b) |
| Ni ^{II} | 90 µg, 1.1 mg ^(c) |
| Os ^{VIII} , Bi ^{III} | 0.9 mg |
| Rh ^{III} , V ^V | 0.7 mg |
| Co ^{II} , Ru ^{III} , Hg ^{II} | 0.6 mg |

(a) Masked with 3 ml of 1 % Na₂S₂O₃ solution.

(b) Masked with 3 ml of 5 % NaF solution.

(c) Masked with 5 ml of 0.1 % dimethylglyoxime solution.

TABLE II. Analysis of lead in standard alloys

| Sample | Composition, w / % | w(Pb) / % | |
|--------------------------------------|--|-----------------|------------------------------|
| | | Certified value | Found ^(a) |
| NKK No. 916 Aluminum alloy | Si 0.41, Fe 0.54, Mg 0.10, Cr 0.05, Ni 0.06, Ti 0.10, Sn 0.05, Zn 0.30, Sb 0.01, B 0.0006, Zr 0.05, Bi 0.03, Co 0.03, Mn 0.11, Cu 0.27, V 0.02 | 0.04 | 0.038 ± 0.003 ^(b) |
| NKK No. 1021 Al, Si, Cu, Zn alloy | Si 5.56, Fe 0.99, Mg 0.29, Cr 0.03, Ni 0.14, Ti 0.04, Sn 0.10, Zn 1.76, Sb 0.01, Zr 0.01, Bi 0.01, V 0.007, Ca 0.004, Mn 0.11, Cu 2.72, | 0.18 | 0.176 ± 0.005 ^(b) |
| NKK No. 920 Aluminum alloy | Si 0.78, Fe 0.72, Mg 0.46, Cr 0.27, Ni 0.29, Ti 0.15, Sn 0.20, Zn 0.80, Sb 0.10, Bi 0.06, Ga 0.05, Ca 0.03, Co 0.10, Mn 0.20, Cu 0.71, V 0.15 | 0.10 | 0.097 ± 0.004 ^(c) |

(a) Average of five determinations ± standard deviation.

(b) Column method was applied.

(c) Microcrystalline naphthalene method was applied.

(d) 3 ml of 5 % NaF solution, 5 ml of 0.1 % dimethylglyoxime solution and 3 ml of 1 % Na₂S₂O₃ solution were added as masking reagents.

putting 500 µg of lead, 2 ml of buffer solution (pH = 9.5) and 40 ml of water into a beaker. Following the procedure from Ref. 13, the maximum amount of lead retained was 8.6 mg g⁻¹ of PAN in the adsorbent.

Effect of Diverse Ions

Various salts and metal ions were added individually to a solution containing 20.0 µg of lead and the general procedure was applied.¹³ The tolerance limit was set as the amount of ion required to cause ±3 % error in lead determination. The results obtained are given in Table I. The proposed method is selective and can be used for lead determination in standard alloys and biological samples without any prior separation.

Analysis of Lead in Standard Alloys

The proposed method was applied to the determination of lead in Nippon Keikinzo Kogyo (NKK) CRM No. 916 and No. 920 Aluminum Alloy and NKK No. 1021, Al, Si, Cu, Zn Alloy. The procedure was as that in Ref. 13. The results obtained are given in Table II. These results are in agreement with the certified values.

Analysis of Lead in Biological Samples

The proposed method has been applied to the determination of lead in samples from National Institute for Environmental Studies (NIES) No. 1 Pepperbush; No. 5 Human hair; No. 7 Tea leaves; No. 3, Chlorella; No. 6, Mussels and No. 2, Pond sediment. A 0.1 g sample was placed in a beaker and dissolved in concentrated nitric acid (≈ 5 ml) with heating. The solution was cooled, diluted and filtered. The filtrate was made up to 100 ml with water in a calibrated flask. NIES, No. 8, Vehicle exhaust particulates (1 g) was dissolved in 18 ml of concentrated nitric acid, 18 ml of concentrated perchloric acid and 2 ml of concentrated hydrofluoric acid in a 100 ml Teflon beaker, evaporated to a

TABLE III. Analysis of lead in biological samples

| Sample | Composition; w / %, $\mu\text{g g}^{-1}$ | Pb concentration / $\mu\text{g g}^{-1}$ | |
|---|---|---|--------------------------------|
| | | Certified Value | Found ^{(a),(b)} |
| NIES, No. 1 ^(c) Pepperbush | K 1.51 ± 0.06 , Mn 0.203 ± 0.107 , Mg 0.408 ± 0.020 , Ca 1.38 ± 0.07 % Cd 6.7 ± 0.5 , Cu 12 ± 1 , As 2.3 ± 0.3 , Fe 205 ± 17 , Co 23 ± 3 , Na 106 ± 13 , Zn 340 ± 20 , Ni 8.7 ± 0.6 , Sr 36 ± 4 , Rb 75 ± 4 , Ba 165 ± 10 , P (1100), Cr (1.3), Cs (1.2), Tl (0.13), Hg (0.056) $\mu\text{g g}^{-1}$ | 5.5 ± 0.8 | 5.4 ± 0.1 ^(d) |
| NIES, No. 5 Human hair | Zn 169, Cd 0.20, Cr 1.4, Sb 0.07, Ni 1.8, Ba 2.2, Al 240, Fe 225, Na 26, Mg 208, Hg 4.4, Sr 2.3, K 34, Rb 0.19, Sc 0.05, Se 1.4, Ti 3.2, Ca 728, Cu 16.3, Co 0.10 $\mu\text{g g}^{-1}$ | 6.0 | 5.93 ± 0.08 ^(d) |
| NIES, No. 7 Tea leaves | Zn 33, Cd 0.030, Na 15.5, Sb 0.014, Ni 6.5, Sr 3.7, Cr 0.15, Al 775, Ca 3200, Mg 1530, Ba 5.7, Cs 0.221, K 18600, Sc 0.011, Mn 7.00, Co 0.12, Cu 7.0 $\mu\text{g g}^{-1}$ | 0.80 | 0.78 ± 0.03 ^(e) |
| NIES, No. 8 ^(c) Vehicle exhaust particulates | K 0.115 ± 0.008 , Ca 0.53 ± 0.02 , Mg 0.101 ± 0.005 , Al 0.33 ± 0.02 , Na 0.92 ± 0.008 , Zn 0.104 ± 0.005 % Sr 89 ± 3 , Co 3.3 ± 0.3 , Cu 67 ± 3.5 , Cd 1.1 ± 0.1 , As 2.6 ± 0.2 , Cr 25.5 ± 1.5 , V 172, Sb 6.0 ± 0.4 , Ni 18.5 ± 1.5 , Cs (0.24), Rb (4.6), Sc (0.055), La (1.2), Br (56), Ag (0.2), Se (1.3), Mo (6.4), Ce (3.1), Th (0.35), Sm (0.20), Eu (0.05), Lu (0.02) $\mu\text{g g}^{-1}$ | 219 ± 9 | 215 ± 7 ^(e) |
| NIES, No. 3 ^(c) Chlorella | K 1.24 ± 0.06 , Ca 0.49 ± 0.03 , Fe 0.185 ± 0.010 , Mg 0.33 ± 0.02 , P (1.7) % Mn 695, Sr 403, Co 0.87 ± 0.05 , Cu 3.5 ± 0.3 , Zn 20.5 ± 1.0 , Cd (0.026), Sc (0.013) $\mu\text{g g}^{-1}$ | 0.60 | 0.61 ± 0.02 ^(d) |
| NIES, No. 6 ^(c) Mussels | Na 1.00 ± 0.03 , K 0.54 ± 0.02 , Ca 0.13 ± 0.01 , Mg 0.21 ± 0.01 , P (0.77) % Mn 16.3 ± 1.2 , Fe 1588, As 9.2 ± 0.5 , Cu 4.9 ± 0.3 , Ni 0.93 ± 0.06 , Cr 0.63 ± 0.07 , Ag 0.027 ± 0.003 , Zn 1066, Cd 0.82 ± 0.03 , Al (220), Sr (17), Se (1.5), Co (0.37), Hg (0.05) $\mu\text{g g}^{-1}$ | 0.91 ± 0.04 | 0.89 ± 0.04 ^(e) |
| NIES, No. 2 Pond sediment | Fe 6.53 ± 0.35 , Al 10.6 ± 0.5 , Ca 0.81, K 0.68, Na 0.57 % Zn 343, Cu 210, Cr 75, Ni 40, Cd 0.82, Co 27, As 12 $\mu\text{g g}^{-1}$ | 105 | 102 ± 4 ^(d) |

(a) Average of five determinations \pm standard deviation.

(b) Standard addition method was applied.

(c) NIES: National Institute of Environmental Studies reference materials. NIES, No. 1, 3, 6 & 8: values in parentheses were approximate and not certified.

(d) Column method was applied.

(e) Microcrystalline naphthalene method was applied.

(f) 3 ml of 5 % NaF solution, 5 ml of 0.1 % dimethylglyoxime solution and 3 ml of 1 % $\text{Na}_2\text{S}_2\text{O}_3$ solution were added as masking reagents.

small volume, filtered through a filter paper and made up to 100 ml with distilled water. An aliquot (10–50 ml) of the sample solution was taken individually and lead was determined by the recommended procedure. The results are given in Table III and are in good agreement with the certified values.

CONCLUSION

An efficient adsorbent generated simply by mixing solutions of PAN and naphthalene has been developed and used for the preconcentration of lead from large volumes of aqueous solutions of standard reference materials using AAS. Since PAN reacts with many metal ions, a similar procedure may also be developed for other metal ions.^{10–19} It is not possible to develop selective methods for metal ions using this adsorbent in spectrophotometry since many metal-PAN complexes absorb at similar wavelengths, 550–590 nm. However, this problem can be easily solved by the use of AAS.

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SAŽETAK

Određivanje tragova olova plamenom atomskom apsorpcijskom spektrometrijom nakon ekstrakcije kruto-tekuće i koncentriranja 1-(2-piridilazo)-2-naftolom

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Razvijena je atomska apsorpcijska spektrometrijska metoda za određivanje tragova olova nakon adsorpcije njegova 1-(2-piridilazo)-2-naftol (PAN) kompleksa na naftalenu. Iz velikih volumena vodenih otopina raznih legura i bioloških uzoraka, taj je kompleks adsorbiran na mikrokristalnome naftalenu u pH području 8,4–11,5. Nakon filtracije, kruta masa koja se sastoji od kompleksa i nafatalena, otopljena je u 5 ml dimetilformamida te je metal određen plamenom atomskom apsorpcijskom spektrometrijom. Alternativno, olovo može biti kvantitativno adsorbirano na 1-(2-piridilazo)-2-naftol-naftalen adsorbentu pakiranome u kolonu i određeno na sličan način. U tome slučaju, 0,5 μg olova može biti koncentrirano u koloni iz 500 ml vodenoga uzorka u kojem je njegova koncentracija 1,0 ng ml^{-1} . Osam ponovljenih određivanje za 4,0 $\mu\text{g ml}^{-1}$ olova daje srednju apsorbanciju od 0,200 s relativnom standardnom devijacijom od 1,5 %. Osjetljivost za 1 % adsorpcije je 88 ng ml^{-1} . Proučavana je interferencija velikoga broja aniona i kationa i utvrđeni optimalni uvjeti rabljeni su za određivanje tragova olova u različitim standardnim uzorcima.