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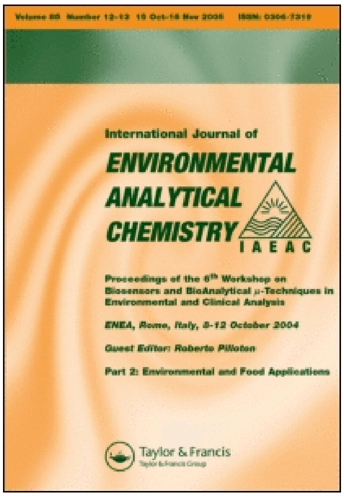

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# Determination of Lead and Cadmium in Soils by Atomic Absorption Spectrophotometry After Solvent Extraction as Iodide Complexes

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An atomic absorption spectrophotometric method has been devised for the determination of microgram quantities of lead and cadmium in soil samples. The method is based upon the solvent extraction of the two metals as iodide complexes from acid extracts (2 M HCl) of soil samples which contain 16% (w/v) potassium iodide, into methylisobutyl ketone. The ion-association complexes of lead and cadmium are atomized into an air-acetylene flame. The interference of iron has been investigated. The analytical aspects of the method are discussed.

KEY WORDS: Lead and cadmium determination; atomic absorption spectrophotometry; soil analysis; solvent extraction.

## INTRODUCTION

The United States Environmental Protection Agency has stated that lead, cadmium and nine other elements are toxic metals of which microgram quantities can cause serious damage to human life and might lead to death.[1] The detrimental effects of lead and cadmium on human health are well known, where their accumulation in man

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has been linked with many diseases. It is well known too, that cadmium in the soil is readily taken up by many cultivated crops,[2,3] where it finds its way to the food cycle. Therefore, there is a continuing need to determine lead and cadmium in soils at trace levels. Methods were devised and used by independent workers to meet this challenge for determining microgram quantities of these two metals. Information about some of these methods is given in Table I.

TABLE I

Methods for the determination of lead and cadmium in soils

| Element | Method | Comment | Reference |
|---|---|---|---|
| Pb | 1) D.C. arc-emission spectrography. Direct analysis of solid samples (50 mg)<br>2) Flame atomic absorption spectrophotometry, after digestion of the samples in hot concentrated nitric acid. | The differences of results obtained by the two techniques varies between −29% and +26%. | 4 |
| Pb | Flame atomic absorption spectrophotometry after both acid and acetate extractions of soils. | The acid extraction gave consistently much higher results than did acetate; the method is slow and time consuming. | 5 |
| Cd | Atomic absorption spectrophotometry, using conventional flame atomization and Delves Cup Technique atomization after both acid and acetate extraction of soils. | | |
| Cd | Atomic absorption spectrophotometry with carbon furnace atomization after chelation by ammonium pyrrolidine dithiocarbamate (APDC) and solvent extraction into MIBK. | The pH of the solutions must be rigidly controlled to eliminate the interference of Fe(III). | 6 |

Preliminary studies by the authors revealed that lead and cadmium can be extracted as iodide complexes from acid solutions containing 8–20% (w/v) potassium iodide, into methylisobutyl ketone (MIBK). Good recoveries for both metals were obtained after back extraction into the aqueous phase followed by atomization into an air-acetylene flame. The proposed method was used for determining lead and cadmium in soil samples, after the optimum conditions of the method were obtained. The limits of detection for Pb and Cd in soils are $0.30\,\mu g\,g^{-1}$ and $0.015\,\mu g\,g^{-1}$, respectively. The method, results and the analytical aspects are presented and discussed in this paper.

## EXPERIMENTAL

### Apparatus

A Varian Model AA-475 double-beam atomic absorption spectrophotometer, equipped with deuterium background corrector was used with an air-acetylene flame. Varian hollow cathode lamps were used as the source of radiation. The instrumental settings are summarized in Table II, the instrumental response being optimized according to the manufacturers instructions.

TABLE II

Instrumental conditions for the determination of lead, cadmium and iron

| Element | Wave-length (nm) | Slit width (nm) | Lamp current (mA) | Gas flow rates ($l\,min^{-1}$) | | Scale expansion |
|---|---|---|---|---|---|---|
| | | | | $C_2H_2$ at 12 psi | Air at 60 psi | |
| Lead | 217.0 | 0.5 | 5 | 2 | 8 | ×5 |
| Cadmium | 228.8 | 0.2 | 4 | 2 | 8 | ×5 |
| Iron | 372.0 | 0.2 | 5 | 2 | 8 | ×1 |

### Materials

Six soil samples were provided by the Botany Department of this University, which were collected from Makkah (Mecca) and Riyadh, from different depths according to the recommended methods of

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sampling. These soil samples were ground with a mortar and pestle to pass a 2 mm sieve, and oven-dried at 105°C for 24 h.

## Reagents

Analytical-reagent grade reagents were used. Hydrochloric acid of density 1.18, and nitric acid of density 1.42, were used.

Standard lead nitrate solution ($1000\,\mu g\,ml^{-1}$ of lead). Dissolve 1.599 g of $Pb(NO_3)_2$ in 100 ml of 1% nitric acid and dilute to 1 l with 1% nitric acid.

Standard cadmium nitrate solution ($1000\,\mu g\,ml^{-1}$ of cadmium). Dissolve 2.744 g of $Cd(NO_3)_2.4H_2O$ in 100 ml of 1% nitric acid and dilute to 1 l with 1% nitric acid.

Standard ferric nitrate solution ($1000\,\mu g\,ml^{-1}$ of iron). Dissolve 7.231 g of $Fe(NO_3)_3.9H_2O$ in 100 ml of 1% nitric acid and dilute to 1 l with 1% nitric acid.

Potassium iodide solution, 40% (w/v). Prepare daily a solution containing 40% (w/v) of KI in 2 M HCl.

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## Analysis of the soil samples

To 2 g of soil sample in a 100 ml beaker, add 25 ml of 2M HCl. Cover the beaker with a watch glass and boil for 30 min on a water bath. Cool and then filter the acid extract into a separating funnel. Wash with 5 ml 2M HCl and make up the volume to about 30 ml with 2M HCl. Add 20 ml of 40% KI solution and then pipette 10 ml of MIBK into the separating funnel. Shake for about 1 min and then allow the two layers to separate. Drain off the aqueous layer and discard it. Transfer the organic layer into a 15 ml stoppered bottle. Atomize this organic extract which contains the ion-association complexes of lead and cadmium into an air-acetylene flame. Read off the lead and cadmium contents of the soil sample from the calibration graphs of the two metals.

## Preparation of calibration graphs

Prepare a $10\,\mu g\,ml^{-1}$ lead solutions and a $1\,\mu g\,ml^{-1}$ cadmium solution by a series of appropriate dilutions of the standard lead and cadmium solutions with 2M HCl. Pipette 0, 1, 2, 3, 4 and 5 ml of the $10\,\mu g\,ml^{-1}$ lead solution and the $1\,\mu g\,ml^{-1}$ cadmium solution into separate 150 ml separating funnels. Make up the volumes to about 30 ml with 2M HCl and continue as described above.

## RESULTS

Calibration graphs of Pb and Cd were obtained from the standard solutions as described above. The lead calibration graphs were constructed first, by atomizing the standard solutions and measuring absorbances versus concentration, followed by atomizing and measuring the absorbances of the sample solutions. Then the calibration graphs of cadmium were obtained in the same manner. The background corrector was switched on during all runs, in order to correct for molecular absorption and/or scattering of light that might occur in the regions of the 217.0 nm and 228.8 nm resonance lines.

The calibration graphs of cadmium were straight lines through the origin. The concentration of cadmium which gives 1.0% absorption was about 0.0024 $\mu$g ml$^{-1}$ Cd. The calibration graphs of lead were straight lines but they did not pass through the origin, intercepting the absorbance axis at about 0.10 absorbance unit which indicates that the reagents contain small amounts of lead. This absorbance corresponds to a blank concentration of 0.70 $\mu$g ml$^{-1}$ Pb. Therefore, all absorbances of standard and sample solutions were corrected for the blank value. The concentration of lead which gives 1.0% absorption was about 0.03 $\mu$g ml$^{-1}$ Pb.

Six soil samples were analyzed according to the described method, in order to obtain their lead and cadmium contents. The results are shown in Table III.

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## DISCUSSION

It is well-known that Pb(II) and Cd(II) form iodide complexes in acid solutions containing iodide. Preliminary investigations have shown that these complexes, tetraiodoplumbate(II) and tetraiodocadmate(II), can be extracted into MIBK as ion-association complexes. Good recoveries were obtained for both metals, when these complexes were destroyed and the two metals back-extracted into the aqueous phase. The results were encouraging and consequently, optimum solvent extraction conditions were established (cf. above).

TABLE III
Determination of lead and cadmium in soils

| Soil sample | Lead found ($\mu g\, g^{-1}$) | Cadmium found ($\mu g\, g^{-1}$) |
|---|---|---|
| 1 | 7.3 | 0.19 |
| 2 | 4.0 | 0.16 |
| 3 | 3.3 | 0.16 |
| 4 | 2.5 | 0.16 |
| 5 | 2.2[a] | 0.10[a] |
| 6 | 4.3 | 0.10 |

[a] Average of 10 determinations. Other quoted results are the average of 2 determinations.

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## Acid recovery

A set of 10 sample solutions containing $3\,\mu g\, ml^{-1}$ Pb and $0.2\,\mu g\, ml^{-1}$ Cd was subjected to the analytical procedure as described. Instead of atomizing the organic layers which contain the lead and cadmium complexes into the flame, a 10 ml portion of a (1:1) mixture of conc. $HNO_3$ and conc. HCl was used to destroy the complexes, and the metals were back-extracted into the aqueous phase. Then the aqueous solutions were atomized into the flame; the recoveries are shown in Table IV. Initially, 10 ml of conc. HCl was used for this purpose, but then the recovery for cadmium was low, while with lead the results were satisfactory. This observation indicates that the ion-association complex of cadmium is strong and stable, which was confirmed when the time stability of the two ion-association complexes was investigated.

## Stability of the ion-association complexes

Two 100 ml test solutions containing $3\,\mu g\, ml^{-1}$ lead and $0.02\,\mu g\, ml^{-1}$ cadmium were prepared and subjected to the analytical procedure using 20 ml MIBK for the extraction. The organic extracts were atomized into the air-acetylene flame, and the absorbances of lead and cadmium were read at varying times after the extraction. The results are shown in Fig. 1.

It is clear that the ion-association complex of cadmium is very stable. It does not dissociate even after 5 h from the extraction time.

TABLE IV

Recovery of 3 μg ml$^{-1}$ Pb and 0.2 μg ml$^{-1}$ Cd added

| Sample number | Pb found (μg ml$^{-1}$) | Cd found (μg ml$^{-1}$) |
|---|---|---|
| 1 | 2.5 | 0.19 |
| 2 | 2.4 | 0.20 |
| 3 | — | 0.19 |
| 4 | 2.8 | 0.18 |
| 5 | 2.5 | 0.21 |
| 6 | 2.3 | 0.20 |
| 7 | 2.4 | 0.19 |
| 8 | 2.8 | 0.21 |
| 9 | 2.5 | 0.20 |
| 10 | 2.8 | — |
| Mean value | 2.6 | 0.20 |
| Recovery | 86.7% | 100% |

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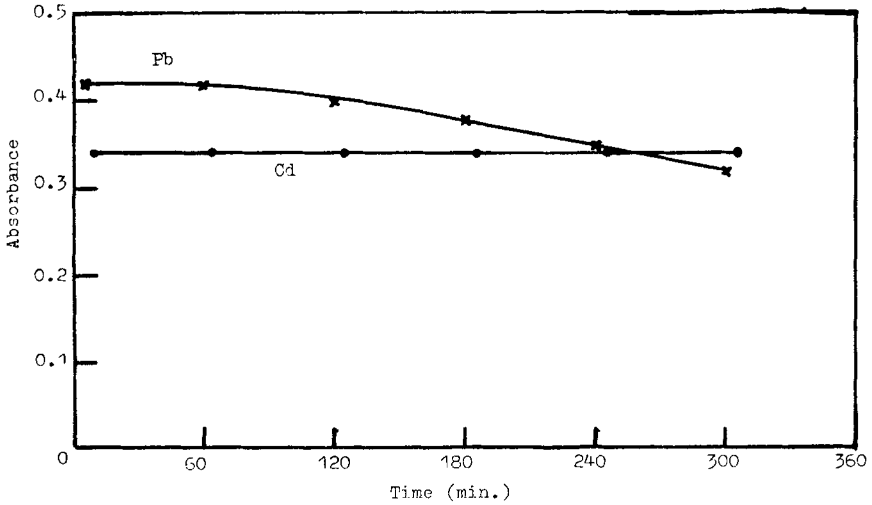

FIGURE 1. Stability of the ion-association complexes of lead and cadmium.

The lead complex is stable during 1 h. Subsequently it starts to dissociate: after 2 and 3 h there is a 5 and 10% reduction in signal intensity, respectively. This investigation confirmed the stability of the cadmium complex.

The stability constants[7] of $PbI_4^{2-}$ and $CdI_4^{2-}$ are $8.3 \times 10^3$ and $1.4 \times 10^6$, respectively. It is believed that the stability of such ion-association complexes depends upon the stability constants of their iodide complexes. This hypothesis has not been reported in the literature before, and studies are being carried out by the present authors to prove it.

## Interference of iron

Fe(III) interferes in the determination of many metals by solvent extraction with atomic absorption spectrophotometry. Firstly, Fe(III) affects the efficiency of the solvent extraction of the metals,[6,8] because it is hydrolyzed at about pH 4.0 where ions of interest coprecipitate with the hydrated Fe(III). The proposed method does not suffer from this kind of interference, because the solutions are too acidic and, therefore, the possibility of hydrolysis is ruled out. Secondly, extraction of a solution containing lead and iron (60% steel) caused[9] a severe depression of the absorbance of lead. The solvent extraction separation of iron from HCl solutions is well documented.[10,11] Ascorbic acid was used by Headridge and Sowerbutts[12] and Burke[13] to reduce Fe(III) to the non-extractable Fe(II), before the solvent extraction of some metals in steel alloys.

The possibility of the depression of the lead and cadmium absorbances by the extractable Fe(III) was investigated by adding 1 g of ascorbic acid to each acid extract of the soil samples (2 g), followed by adding the KI solution and the extraction into MIBK. The results of lead and cadmium contents are similar to those reported in Table III, which indicates that the concentration of Fe(III) which was extracted from the aqueous solutions of the soil samples does not decrease the absorbances due to lead and cadmium. However, it was necessary to determine the iron contents of the six soil samples to find out the highest concentration of iron in these soil samples, and then to establish that there is no interference from Fe(III) at this level.

## Determination of iron in the soil samples

The sample solutions were prepared by adding 50 ml of 2 M HCl to 1 g of soil sample in a 250 ml beaker and boiling for 30 min on a water bath. The solutions were left to cool and then filtered. The

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filter papers were washed with 10 ml of 2 M HCl and then the acid extracts were transferred to 100 ml volumetric flasks and the volumes made up to the mark with 2 M HCl. Seven 100 ml solutions containing 0–150 $\mu$g ml$^{-1}$ Fe prepared by appropriate dilution of the standard iron solution using 2 M HCl.

The calibration graph of iron passed through the origin and was slightly curved at the upper end. The concentration of iron which gives 1% absorption was 0.65 $\mu$g ml$^{-1}$ Fe. The iron content of the soil samples was deduced from the calibration graph (Table V).

TABLE V
Determination of iron in soils

| Soil samples | Iron found ($\mu$g g$^{-1}$) | Percentage of iron in soil samples |
|---|---|---|
| 1 | 1,000 | 0.10 |
| 2 | 2,100 | 0.21 |
| 3 | 3,900 | 0.39 |
| 4 | 9,200 | 0.92 |
| 5 | 6,000 | 0.60 |
| 6 | 13,500 | 1.35 |

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It can be concluded that iron levels of between 0.1 and 1.4% do not interfere with the determination of cadmium and lead using the proposed method.

## Precision, detection limits and accuracy

Soil sample No. 5 was analyzed ten times according to the proposed method, in order to establish the precision and detection limit (cf. Table III). The rel. S.D. of the method is 7.1% for lead and 8.9% for cadmium. The detection limits taken as twice the standard deviation for soil sample No. 5—for lead and cadmium are 0.30 $\mu$g g$^{-1}$ 0.015 $\mu$g g$^{-1}$, respectively.

Aziz-Alrahman and Headridge[14] have reported on the calculation of the detection limit of eight elements in irons and steels, based upon the concentration of these elements which give 1.0% absorption and the precision of the method. The detection limits for lead and cadmium in soils calculated according to that method, were

0.15 μg g$^{-1}$ and 0.012 μg g$^{-1}$, respectively, which is in good agreement with the actual detection limits.

## CONCLUSION

The proposed method is fast, reliable and accurate, gives reproducible results for lead and cadmium in soils, and is free from the interference of Fe(III). 40–50 soil samples can be analyzed in 4–5 h, when using a microprocessored atomic absorption spectrophotometer equipped with a deuterium background corrector and an auto sampler. The results can be obtained directly from the read-out device after calibrating the instrument, using 3 different concentrations for each element. The method is also applicable for the determination of lead and cadmium in minerals, rocks, sea-water and beverages, and in plants, food and meat after ashing and dissolution in an acid.

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