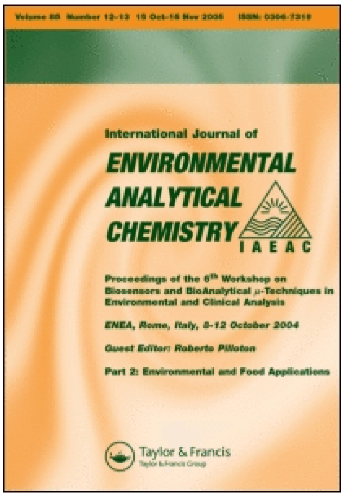

International Journal of Environmental Analytical Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713640455

Extraction and Spectrophotometric Determination of Arsenic in the Environment

Y. K. Agrawal[a]; S. K. Patke[a]
[a] Analytical Laboratories, Pharmacy Department, Faculty of Technology and Engineering, M.S. University of Baroda Kalabhavan, Baroda, India

To cite this Article Agrawal, Y. K. and Patke, S. K.(1980) 'Extraction and Spectrophotometric Determination of Arsenic in the Environment', International Journal of Environmental Analytical Chemistry, 8: 3, 157 — 162

To link to this Article: DOI: 10.1080/03067318008071496

URL: http://dx.doi.org/10.1080/03067318008071496

Intern. J. Environ. Anal. Chem. 1980, Vol. 8, pp. 157–162
0306-7319/80/0803-0157 $6.50/0

Printed in Great Britain

Extraction and Spectrophotometric Determination of Arsenic in the Environment

Y. K. AGRAWAL and S. K. PATKE

Analytical Laboratories, Pharmacy Department, Faculty of Technology and Engineering, M.S. University of Baroda, Kalabhavan, Baroda—390 001, India.

(*Received March 3, 1980*)

KEY WORDS: Arsenic; PBHA; extraction; photometric; plants; soil; industrial effluents.

A simple, sensitive and selective method for the determination of microamounts of arsenic (III) in the environment is described. Arsenic forms a yellow coloured complex with N-phenylbenzo-hydroxamic acid (PBHA) at pH 4.5–5.2 which can be extracted from chloroform. The effective molar absorptivity of As-PBHA extract is $1.1 \times 10^{-4}\,\mathrm{l\,mol^{-1}\,cm^{-1}}$ at 410 nm. Many common ions associated with arsenic do not interfere. The effect of pH, reagent concentration and solvent is described. The arsenic in trace quantities is estimated in the industrial effluents, soil and glass samples.

INTRODUCTION

Arsenic and arsenical compounds are reported as waste products of the metallurgical, glass, ceramic, dyes, and pesticide industries. Insecticide industries discharge 362 mg/litre of arsenious oxide as waste products.[1] Arsenic is a toxic element and can produce dermatitis, mild bronchitis and upper respiratory tract irritation. Maximum limits in whole blood and urinary levels are about 100 and 15 mg/litre respectively.[2] According to an I.S.I. report 0.2 mg/litre is the tolerance limit for marine disposal.[3] Various reagents like halides, triphenylstanoammonium etc. were used for extraction and spectrophotometric determination of arsenic, but extraction is incomplete.[4–5] Diethyl ammonium diethyl-dithiocarbamate was also used as an extracting reagent for arsenic[6–7] with Bi^{3+}, Pb^{2+}, Zr^{4+}, Th^{4+} and Ag^{+} interfering. A preliminary distillation is also required prior to the extraction and diethylammonium diethyldithiocarbamate gets oxidised.

Hydroxamic acids are potential analytical reagents used for the determination of several metal ions.[8] The N-phenyl-benzohydroxamic acid (PBHA) has been used as an analytical reagent for the extraction and spectrophotometric determination of arsenic in the environment. The advantage of this method is that no primary separation is required and that few interferences are encountered.

EXPERIMENTAL

All the chemicals used were of AnalaR and G.R. grades of B.D.H. or E. Merck unless otherwise specified.

A buffer solution of pH 4.7 is prepared from sodium acetate and acetic acid (1:1 of 0.01 M).

The N-phenylbenzohydroxamic acid is synthesised as described elsewhere.[9] Its purity was checked by mp, elemental analysis, TLC, IR and UV spectra. A 0.05 M solution was prepared in chloroform.

A VSU2-P spectrophotometer is used for spectral measurements. A Systronics digital pH meter equipped with glass and calomel electrodes was used for pH measurements.

Procedure: Take 2 ml of arsenic solution (1.1×10^{-3} M) and dilute to 10 ml with water; adjust pH 4.7 with buffer (acetic acid and sodium acetate). Transfer this solution into 100 ml separatory funnel. Add 10 ml reagent solution, shake for 5 min and allow the phases to separate. Separate the yellow coloured chloroform layer and transfer to a 25-ml volumetric flask after drying over anhydrous sodium sulphate. Extract in aqueous layer with 5 ml of reagent solution to ensure the complete recovery of arsenic extract. Wash the anhydrous sodium sulphate with 2 ml of chloroform and finally dilute to 25 ml. Measure the absorbance against reagent as blank at 410 nm.

Plot a calibration curve by taking arsenic concentration between 0.38 to 8.00 ppm for As-PBHA complex.

Determination of Arsenic from Industrial Effluent: 100 ml of industrial effluents were transferred into the 250-ml separatory funnel after adjusting its pH 4.7 with the buffer solution. To this add 10 ml reagent solution followed by each 5 ml solutions of ascorbic acid (1 %), sodium fluoride (0.5 %) and dimethylglyoxime (DMG) (1 %) were added and the contents were shaken for 10 minutes. The organic layer was separated and absorbance measured at 410 nm. The concentration of arsenic was calculated from the calibration curve.

Determination of Arsenic from Plant and Soil Samples: Depending upon the concentration of arsenic in the plants or soils, about 10 to 15 g of samples were digested with excess of hydrochloric acid (and 10 ml of perchloric acid). The filtrate was evaporated and diluted to 100 ml with 0.1 N HCl. The arsenic was determined as above and its concentration was calculated from the calibration curve.

RESULTS AND DISCUSSION

The yellow coloured complex of As-PBHA in chloroform gives no λ_{max}, but measurements are reproducible at 410 nm. Hence all the measurements are made at 410 nm. The As-PBHA complex is extracted at the pH range 3–8 and the optimum pH for the extraction is pH 4.5–5.2. The data are summarised in Table I.

TABLE I

Spectral characteristic of arsenic-N-phenylbenzohydroxamate complex extracted in chloroform.

Colour of the complex—Yellow
Wavelength—410 nm

Arsenic conc (ppm)	pH	Absorbance	Molar absorptivity ($l\,mol^{-1}\,cm^{-1}$)
3.74	3.0	0.249	5.0×10^3
3.74	4.0	0.374	7.5×10^3
3.74	4.5	0.549	1.1×10^4
3.74	4.7	0.549	1.1×10^4
3.74	4.7	0.550	1.1×10^4
3.74	4.7	0.550	1.1×10^4
7.48	4.7	1.099	1.1×10^4
1.87	4.7	0.275	1.1×10^4
3.74	5.2	0.550	1.1×10^4
3.74	5.5	0.475	9.5×10^3
3.74	6.0	0.350	7.0×10^3
3.74	7.0	0.325	6.5×10^3
3.74	8.0	0.310	6.2×10^3
3.74	9.0	0.300	6.0×10^3

Beer's law

A yellow coloured As-PBHA extract in chloroform obeys Beer's law within the range 0.37–8.0 ppm of arsenic. The molar absorptivity is worked out to be $1.1 \times 10^4\,l\,mol^{-1}\,cm^{-1}$ at 410 nm.

Effects of solvents

As-PBHA complex is extracted with various solvents viz chloroform, carbon tetrachloride, iso-butylmethyl ketone and isomayl alcohol etc. Chloroform is found the most suitable solvent for extraction of arsenic (Table II).

TABLE II

Effect of solvents on the extraction of arsenic with PBHA

Arsenic conc = 7.0 ppm λ max = 410 nm

pH = 5.0 Colour = Yellow

Solvents	% recovery	Molar absorptivity ($l\,mol^{-1}\,cm^{-1}$)
Chloroform	100.00	1.1×10^4
Carbon tetrachloride	77.3	8.5×10^3
Isobutylmethylketone	86.3	9.5×10^3
Isoamyl alcohol	68.1	7.5×10^3

Effect of reagent concentration

Trivalent arsenic is extracted with PBHA with varying volumes and reagent concentrations at pH 5.0. Results indicate that single extraction with 10 ml of 0.05 M of reagent is adequate for quantitative extraction of arsenic. Extraction is incomplete with lower concentration of the reagent but a large excess of reagent can be used without any difficulty.

Synergestic extraction of arsenic with PBHA-Dithizone

The use of dithizone favours extraction of As-PBHA and molar absorptivity increases to $1.9 \times 10^{-4}\,l\,mol^{-1}\,cm^{-1}$ at 530 nm.

Effects of diverse ions

7.0 ppm of arsenic is extracted in presence of 40 mg of the following ions: Bi^{3+}, Cd^{2+}, Mg^{2+}, Ca^{2+}, Ba^{2+}, Sr^{2+}, Pb^{2+}, Be^{2+}, Nb^{5+}, Ag^{+}, Zr^{4+}, Mo^{6+}, Pd^{2+}, Sn^{2+}, Al^{3+}, V^{5+}, F^{-}, Br^{-}, I^{-}, SO_4. Of these Fe^{3+} Cu^{2+} interfere and can be eliminated by masking with ascorbic acid. Ni^{2+} and Ti^{4+} are masked with DMG and NaF respectively.

Determination of arsenic in various samples

The data on the determination of concentration of arsenic in standard samples, industrial effluents, plants and soil samples are given in Tables III and IV. The data are in good agreement with standard values.

TABLE III

Analytical data on extraction of arsenic in standard steel samples

Sample	Certified values %	Arsenic found %			
		Present method	% Standard deviation ($n=6$)	DDDTC[a]	AAS[b]
NBS 1155E	0.008	0.010	0.2	0.011	0.009
NBS 1174A	0.022	0.020	0.2	0.023	0.020
BCS 169	0.031	0.030	0.2	0.032	0.030
BCS 169	0.013	0.015	0.3	0.011	0.015

[a]Diethylammonium diethyldithiocarbamate.
[b]Atomic absorption spectrophotometer at the wavelength 1937 A°.

TABLE IV

Concentration of arsenic in industrial effluents, plants and soils

Sample	Arsenic found [a]ppm	
	Present method	AAS
Soil sample	200–500	190–480
Plant sample	160–485	150–480
Cabbage	2.5–5.0	2.5–5.0
Apple	1.5–3.0	1.5–3.0
Industrial effluents	60–1000	50–1000
Phosphorus pentaoxide	100–150	95–150
Super phosphate	30–60	25–55
Insecticide	300–400	300–400
Sulphuric acid	18–55	20–55
Glass	0.5–30	0.4–25
	0.05–6.0	0.05–7.0

[a]Average of eight determinations.
Ranges for highest and lowest concentrations found.

Acknowledgement

The financial assistance given by C.S.I.R. New Delhi is gratefully acknowledged.

References

1. S. N. Cherkinski and F. I. Genzburg, "*Water Pollution Abstr*", **14,** 315 (1941).
2. F. S. Lisella, K. R. Long and H. G. Scott, *J. Environ. Health* **34,** 511 (1972).
3. I.S.I. Report "Standards for the Disposal of Industrial Effluents" *IS:* **7968** (1976).
4. R. Bock, H. T. Niederaure and K. Z. Behrends, *Anal. Chem.*, **190,** 33 (1962).
5. S. Kitahara, *Bull. Inst. Phys. Chem. Res. Tokyo,* **25,** 165 (1949).
6. C. L. Luke and M. E. Campbell, *Anal. Chem.*, **25,** 1588 (1953).
7. G. Delorak and M. G. Mellon, *Anal. Chem.*, **25,** 1803 (1953).
8. Y. K. Agrawal, *Rev. Anal. Chem.*, In Press.
9. U. Priyadarshini and S. G. Tandon, *J. Chem. Eng. Data,* **12,** 143 (1967).