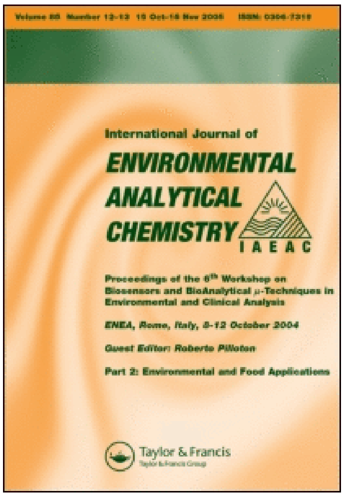

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Extraction-Spectrophotometric Determination of Arsenic in Environmental Samples with Iodide and Amidines

M. K. Deb[a]; C. Agarwal[a]; K. S. Patel[a]; R. K. Mishra[a]
[a] Department of Chemistry, Ravishanker University, Raipur, M.P., India

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ANALYTICAL DATA

EXTRACTION-SPECTROPHOTOMETRIC DETERMINATION OF ARSENIC IN ENVIRONMENTAL SAMPLES WITH IODIDE AND AMIDINES

M. K. DEB, C. AGARWAL, K. S. PATEL and R. K. MISHRA

Department of Chemistry, Ravishanker University, Raipur-492 010, M.P., India

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A simple and rapid method for the spectrophotometric determination of traces of total arsenic present in industrial waste waters is described. It is based on the reaction of As(III) with I^- in 5–6 M HCl, and extraction of the iodo-arsenite complex formed into chloroform with amidines. The molar absorptivity of AsI_4^- with 11 different amidines is in the range $(3.9–7.9) \times 10^3 \, l \, mol^{-1} \, cm^{-1}$ at $\lambda_{max} = 380–395$ nm; the simplest compound, N,N′-diphenylbenzamidine (DPBA) has been chosen for further studies. The limit of detection with DPBA is 0.1 μg As/ml. The method is highly selective with almost no interference from all anions and cations tested.

KEY WORDS: Arsenic(III), extraction, N,N′-diphenylbenzamidine, spectrophotometry, industrial waste water.

INTRODUCTION

Molybdenum blue and diethyldithiocarbamate methods are commonly employed for the colorimetric determination of arsenic; they require prior separation of the analyte.[1] Many dyes are claimed to considerably enhance the sensitivity of heteropolyacid methods, but their selectivity often is insufficient.[2,3]

In the present investigation, N,N′-diphenylbenzamidine and ten of its derivatives were tested for use in the extraction spectrophotometric determination of As(III) in the presence of iodide for the determination of the analyte in environmental samples.

EXPERIMENTAL

Standard solutions of As(III) were prepared by dissolving a weighed amount of As_2O_3 in alkaline solution (0.1 M) and diluting to 1 litre with deionised water. Fresh solutions of ascorbic acid (10%, w/v) and potassium iodide (80%, w/v) were used. A 10 M HCl solution was employed for extraction work. The various amidines tested were synthesized according to the literature;[4] they were used as 0.2% (w/v) solutions in chloroform. All chemicals were of analytical grade (E. Merck).

An ECIL UV-VIS spectrophotometer GS-865 matched with 1-cm quartz cells was used for absorbance measurements.

Procedure

An aliquot of the solution containing up to 200 μg As(III) and 1 ml ascorbic acid is transferred to a 100-ml separatory funnel held in a thermostat at 18 ± 2 °C. The analyte is treated with 5.5 ml of the HCl and 2 ml of the KI solution and diluted to 10 ml with deionized water. The aqueous solution is shaken with 10 ml amidine solution in chloroform for 2 min at room temperature and washed three times with fresh 2-ml portions of chloroform.

The combined extracts are dried over anhydrous sodium sulphate (2 g) in a 25-ml beaker and transferred to a 25-ml volumetric flask, which is filled to the mark with chloroform. The absorbance of the extract is measured at the λ_{max} of the complex against the reagent blank.

RESULTS AND DISCUSSION

The absorption spectrum of the As(III)-I^--DPBA complex measured against the reagent blank in chloroform has its absorption maximum at 395 nm. In this region, the reagent blank exhibits high absorption; hence, it was used as a reference for all measurements. Various solvents like 1-pentanol, MIBK, ethyl acetate, chloroform, benzene and toluene were tested for the extraction of the metal. They all quantitatively extracted the complex. Of these, chloroform was selected as extraction solvent because of the high colour intensity and stablity of the complex and the relatively high distribution of the reagent.

Ascorbic acid was used as a reducing agent to convert As(V) into As(III). The amount of ascorbic acid added is not critical over a wide range. The quantitative extraction of the analyte as its complex into chloroform is achieved with 5–6 M HCl or 2.5–3.5 M H_2SO_4. At least 0.75–1.25 M KI and 0.0014–0.006 M DPBA in chloroform are required for the maximum and constant colour development of the complex. The order in which the reagents are added is not critical. Varying the volume of the aqueous phase from 2:1 to 2:5 V_{org}:V_{aq}) or the temperature from 10 to 30 °C did not affect the absorbance of the extract. A shaking period of 2 min is sufficient for full colour development of the extract and the extract is stable for at least 2 h at room temperature (23 ± 2 °C). The molar absorptivities of the complex with the 11 amidines tested are in the range of $(3.9–7.9) \times 10^3 \, l \, mol^{-1} \, cm^{-1}$ at $\lambda_{max} = 380–395$ nm in chloroform (Table 1). The detailed study was carried out with the simplest compound, N,N′-diphenylbenzamidine (DPBA). The limit of detection is 0.1 μg As/ml. The RSD of the method for 10 replicate measurements at the level of 4 ppm As(III) in the organic solution was ±1.3%. The system obeys Beer's law for 0.5–8 μg As/ml with DPBA. The stoichiometry of the complex was determined by plotting $\log D_{As}$ versus log molar concentration of the amidine (HA) in chloroform. The data obtained show the involvement of 4 I^- and 2 HA for each As(III) to give the chloroform-extractable ion-pair complex, $H[As(I)_4].(HA)_2$.

The effect of diverse ions on the determination of 0.1 mg of arsenic were studied using the above procedure. Most anions and cations tested do not interfere, especially because some metal ions are masked by the iodide added in large excess.

Table 1 Spectral data of iodoarsenite complexes with various amidines in chloroform

Amidine	*λ_{max} (nm)*	*ε ($l\ mol^{-1}\ cm^{-1}$)*
N,N'-diphenylbenzamidine	395	7850
N-(2-chlorophenyl)-N'-phenylbenzamidine	390	3900
N-(3-chlorophenyl)-N'-phenylbenzamidine	380	4900
N-(4-chlorophenyl)-N'-phenylbenzamidine	390	6550
N-(2-methylphenyl)-N'-phenylbenzamidine	395	7900
N-(3-methylphenyl)-N'-phenylbenzamidine	395	6400
N-(4-methylphenyl)-N'-phenylbenzamidine	395	6400
N-(2,5-dichlorophenyl)-N'-phenylbenzamidine	390–395	5250
N-(2,5-dimethylphenyl)-N'-phenylbenzamidine	385–390	6750
N-benzyl-N'-phenylbenzamidine	380	5250
N-octyl-N'-phenylbenzamidine	390	7500

Table 2 Determination of total arsenic in industrial waste waters

Sample	*As added (ppm)*	*As content (ppm)*	*RSD (%)*[a]
A	5	0.23	1.1
B	4	0.50	1.3
C	4	0.55	1.2
D	3	1.17	1.1
E	2	1.75	1.2

[a] $n = 5$.

A and B, effluent from gas cleaning plant and blast furnace, respectively, obtained from Bhilai Steel Plant, Bhilai, India.

C, D and E, waste water obtained from Bhilai Steel Plant, Bhilai, M.P. Metals, Raipur and Adwani Oerlikon, Raipur, respectively.

The tolerance limit of various ions (in mg) causing an error of less than 2% (in parentheses) are as follows: Sb^{3+} (0.3); Cu^{2+}, Pd^{2+}, Se^{4+}, Mo^{6+}, Re^{7+} (0.5); Hg^{2+} (0.75); Nb^{5+} (1); Ag^{+}, Sn^{4+} (1.5); Bi^{3+}, Zr^{4+} (2.5); Pb^{2+} (3); Al^{3+} (4); Be^{2+}, La^{3+}, NO_3^- (5); Fe^{3+}, V^{5+} (7.5); U^{6+} (12); Cd^{2+}, Ti^{4+}, W^{6+} (15); EDTA (20); Ni^{2+} (22); Mn^{2+}, Co^{2+} (30); $C_2O_4^{2-}$ (35); F^- (100).

The present method has been used for the recovery of the analyte from industrial waters (Table 2). A known volume of the waste water (400 ml) is taken and evaporated to about 20 ml and made up to 25 ml in the volumetric flask. 2–3 millilitre of this solution are taken and the analyte content is determined by a standard addition following the above procedure.

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