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SHORT PAPER

Determination of arsenate and phosphate in rainwater: preconcentration by membrane filtration

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A simple and rapid method for the determining arsenate and phosphate in rainwater is proposed. These compounds form molybdoarsenate– and molybdophosphate–Malachite Green aggregates with Mo–MG reagent (Mo–MG = a mixture of ammonium molybdate and Malachite Green). The aggregates were first collected on a nitrocellulose membrane filter (pore size 3 μm) and then dissolved with the filter in a small amount of 2-methoxyethanol. Absorbance (627 nm), denoted as A(As + P), was found to be proportional to the sum of the arsenate and phosphate concentrations with a molar absorptivity of $2.8 \times 10^5 (\text{mol dm}^{-3})^{-1} \text{cm}^{-1}$. Following the addition of *thiosulphate, an agent which reduces arsenate, the* absorbance *A*(P) was measured as described above. *A*(P) corresponded to the concentration of phosphate alone and *A*(As + P) − *A*(P), to arsenate concentration only. This method is shown to be a rapid and highly accurate means for determining arsenate and phosphate levels within the 1–150 nmol dm^{-3} concentration range

Keywords: Arsenate, phosphate, rainwater, membrane filter, molybdoarsenate, molybdophosphate, Malachite Green, preconcentration, spectrophotometric determination

INTRODUCTION

The toxicity and accumulation of arsenate (AsO_4^{3-}) in biological material have made necessary its careful measurement in rainwater and a simple, rapid and economical method for this is essential.

A simple and rapid preconcentration technique by which molybdoarsenate– and molybdophosphate–Malachite Green (As–Mo–MG and P–Mo–MG) aggregates are collected on a membrane filter for the determination of arsenate and phosphate was proposed in a previous study. By this technique, aggregates are dissolved in a small volume of 2-methoxyethanol along with the membrane filter, followed by measurement of solution absorbance.[1]

The technique was also used in this study to determine trace arsenate and phosphate in rainwater. A 25-fold enrichment of the aggregates was possible and absorbance was measured with a molar absorptivity of $2.8 \times 10^5 (\text{mol dm}^{-3})^{-1}$ cm^{-1}. This method is thus shown to be effective for quickly and accurately determining arsenate and phosphate at nanomoler levels.

EXPERIMENTAL

Reagents

All chemicals were of analytical reagent grade and were used without further purification.

Malachite Green solution (2×10^{-3} mol dm^{-3}) was prepared by dissolving 0.976 g of bis(*p*-dimethylaminophenyl)phenylmethane trioxalate, $C_{52}H_{54}N_4O_2$ in one litre of water.

Ammonium molybdate solution (0.0971 mol dm^{-3}) was prepared by dissolving 120 g of $(NH_4)_6Mo_7O_{24} \cdot 4H_2O$ in one litre of water.

Molybdate-Malachite Green (Mo-MG) reagent was prepared by mixing together 300 cm^3 of ammonium molybdate solution, 250 cm^3 of Malachite Green solution and 47 cm^3 of concentrated sulphuric acid. The mixture was allowed to stand for about 30 min and then filtered through a

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0.45-μm pore size membrane filter. The filtrate thus obtained served as the Mo–MG reagent.

Phosphate standard solution (2.00×10^{-3} mol dm^{-3}) was prepared by dissolving 0.2722 g of potassium dihydrogen orthophosphate in one litre of water.

Arsenate standard solution (1.00×10^{-2} mol dm^{-3}) was prepared by dissolving 0.3120 g of disodium hydrogen orthoarsenate in 100 cm^3 of water.

Apparatus

Absorbance was measured with a Jasco Uvidec 660 double-beam spectrophotometer, using 1-cm cuvettes.

Determination procedure

To 100 cm^3 of a rainwater sample, 1 cm^3 of standard phosphate solution (2×10^{-5} mol dm^{-3}), 1 cm^3 of 7.5 mol dm^{-3} sulphuric acid and 8 cm^3 of Mo–MG reagent were added. The solution was then filtered through a nitrocellulose 3-μm pore size membrane filter (Toyo Roshi Co. Ltd, Japan) to collect the As–Mo–MG and P–Mo–MG aggregates which were subsequently dissolved in 4 cm^3 of 2-methoxyethanol along with the membrane filter. Absorbance, $A(\mathrm{As}+\mathrm{P})$, was measured at 627 nm with a reagent blank serving as the reference. To a different 100 cm^3 sample of rainwater, 1 cm^3 of 7.5 mol dm^{-3} sulphuric acid, and 1 cm^3 of 20 mmol dm^{-3} sodium thiosulphate (to reduce arsenate to arsenite) were added and the solution was allowed to stand for 30 min at room temperature. Absorbance, $A(\mathrm{P})$, of the solution was measured after obtaining an aggregate by the Mo–MG reagent. Arsenate concentration was readily given as $A(\mathrm{As}+\mathrm{P}) - A(\mathrm{P})$.

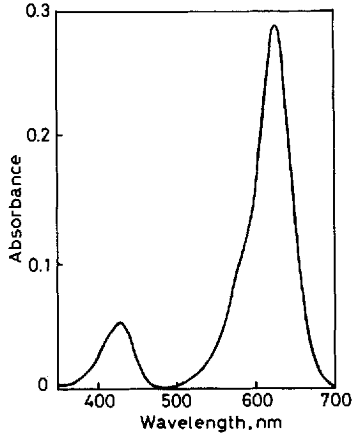

Figure 1 Absorption spectrum of the molybdoarsenate–Malachite Green aggregate in 2-methoxyethanol. Concentration of arsenate 1×10^{-6} mol dm^{-3}.

RESULTS AND DISCUSSION

Optimum conditions

The As–Mo–MG aggregate obtained by the Mo–MG reagent was collected on a membrane filter and then dissolved with it in methylcellosolve. The absorption spectrum of this aggregate in methylcellosolve is shown in Fig. 1. Its molar absorptivity was 2.8×10^5 (mol dm^{-3})$^{-1}$ cm^{-1} at 627 nm.

In the absence of phosphate, the response of arsenate was less than half that of the final response even after standing for two hours, whereas in the presence of 2×10^{-7} mol dm^{-3} phosphate, detection exceeded 98% within 30 min. Standard phosphate solution was thus added to each sample solution at a concentration of 2×10^{-7} mol dm^{-3}.

The molybdophosphate–Malachite Green aggregate spectrum was essentially the same as that for the As–Mo–MG aggregate.[1] This means that

Table 1 Effect of foreign substances on the determination of phosphate and arsenate[a]

Cation added	Concentration (mol dm^{-3})	PO_4^{3-} and AsO_4^{3-} found (%)[b]	Anion added	Concentration (mol dm^{-3})	PO_4^{3-} and AsO_4^{3-} found (%)[b]
Ca^{2+}	1×10^{-3}	101.1	AsO_3^{2-}	4×10^{-6}	100.5
Fe^{3+}	4×10^{-7}	120.0	Cl^-	2×10^{-1}	100.2
	1×10^{-7}	105.0	SiO_3^{2-}	2×10^{-5}	105.0
	4×10^{-8}	100.5		4×10^{-6}	101.1
K^+	1×10^{-1}	100.2	SO_4^{2-}	1	100.0
Na^+	1×10^{-1}	100.0	NO_3^-	2×10^{-4}	100.0

[a] Concentrations of phosphate and arsenate present, 2×10^{-7} mol dm^{-3}. [b] As percentage of added concentration.

Table 2 Concentrations arsenate and phosphate in rainwater[a]

Date	As(V) (nmol dm^{-3})	P(V) (nmol dm^{-3})	Date(nmol dm^{-3})	As(V) (nmol dm^{-3})	P(V) (nmol dm^{-3})
25 Jun. 1989	0.0	0.8	18 Oct. 1989	0.8	0.0
26 Jun. 1989	0.2	1.6	31 Oct. 1989	0.0	1.2
27 Jun. 1989	0.8	0.6	31 Oct. 1989	0.3	5.0
25 Jul. 1989	2.9	13.5	1 Nov. 1989	1.1	0.0
26 Jul. 1989	0.3	5.4	13 Nov. 1989	0.0	30.0
7 Oct. 1989	1.4	25.0	15 Nov. 1989	0.3	27.4
16 Oct. 1989	0.0	27.0	17 Nov. 1989	0.6	14.9

[a] The rainwater was sampled in Tokyo, Japan.

in order that arsenate and phosphate in the same sample solution can each be determined separately and distinctly, an appropriate agent is essential. The addition of thiosulphate (2×10^{-4} mol dm^{-3}) to a sample solution reduces arsenate to arsenite, which does not form an aggregate, while leaving the P–Mo–MG aggregate unchanged. Without thiosulphate, the absorbance, $A(P + As)$, was proportional to the sum of the arsenate and phosphate in concentration in a test solution with a molar absorptivity of 2.8×10^5 (mol dm^{-3})$^{-1}$ cm^{-1}. Absorbance, A (P), due to phosphate alone was determined for a separate portion of the test solution after the arsenate had been reduced to arsenite by thiosulphate. The arsenate concentration was subsequently given as $A(As + P) - A(P)$.

To obtain a constant and maximum absorbance, the final concentrations of molybdate, Malachite Green and sulphuric acid before filtration were adjusted to 4×10^{-2} mol dm^{-3}, 1×10^{-4} mol dm^{-3} and 0.45 mol dm^{-3}, respectively, to ensure the optimum conditions recommended by Motomizu *et al.* in determining phosphate in an aqueous solution.[2]

The membrane filter (3-μm pore size) was used since it was most suitable for the purposes of the present study.

The present procedure for determining arsenate and phosphate was decided upon after a consideration of the above experimental results. Calibration curves for arsenate and/or phosphate were essentially linear in the test range of 0.1–14 nmol dm^{-3}.

Interference problems

Table 1 lists the effects of various extraneous ions. Except for iron (III), none of the ions caused on error of more than 5% even when present at concentrations exceeding 10 times that of arsenate. By passing the sample through a column packed with cation-exchange resin (Dowex 50 WX-80), the effect of iron (III) was avoided.

Determination of arsenate and phosphate in rainwater

The results for determining arsenate and phosphate in real rainwater samples by the present method are shown in Table 2. Arsenate and phosphate at nanomolar levels were determined in a short time, the analysis of 20 samples requiring only 60 min.

Analytical recoveries of arsenate and phosphate in the range of 1–2 nmol per 100 cm^3 rainwater were between 86 and 95%.

The results presented above demonstrate the present method to be a sensitive, rapid and economical means for determining arsenate and phosphate content in rainwater.

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