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Extractive Fluorimetric Determination of Methoxyethylmercury Chloride in Environmental Samples

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A sensitive, extractive fluorimetric method for the determination of trace levels of methoxyethylmercury chloride is described. The method is based on the decomposition of methoxyethylmercury chloride under acidic condition and bromination to form tetrabromomercurate(II) anion. The resulting anion is reacted with rhodamine 6G, a cationic fluorescent dye and the resulting ion pair is extracted into toluene. The fluorescence of the organic layer is measured at 560 nm after excitation at 536 nm. The method is extended to the determination of methoxymercury chloride in environmental samples. The method is compared with reported spectrophotometric method and found to be more sensitive.

Key Words: Fluorimetric determination, methoxyethylmercury chloride.

INTRODUCTION

Methoxyethylmercury chloride which is a contact fungicide is widely applied against various plant fungus diseases like flag smut of wheat, pyriculiariosis and other diseases of cereals and cotton[1-3]. It is highly toxic to human beings and causes mutagenic, tetratogenic and embryotoxic effects. Long exposure causes mental disorder, impairment of memory, numbness, awkwardness of gait and blurring of vision[4-6]. Because of wide application as fungicide, it finds its way into different agricultural products and natural water bodies thrcugh agricultural run off. In view of this, it is necessary to determine its concentration in water bodies, agricultural products to assess the potential toxicity by these compounds.

Various spectrophotometric methods[7-9], GC[10], GLC[11], HPLC[12] and flow injection ICP-MS[13] have been reported for its determination. But the spectro-fluorimetry which offers high sensitivity and selectivity has not been employed for the determination of methoxyethylmercury chloride.

EXPERIMENTAL

A Hitachi 650-10S fluorescence spectrophotometer with 10 mm glass cell and xenon source was used. An Elico model LI-129 pH/ion meter with combined glass electrode was used for pH measurements.

All chemicals used were of AnalaR grade and deionized doubly distilled water

was used throughout the experimental study. Methoxyethylmercury chloride (100 mg) was dissolved in 100 mL ethanol. Working standard was prepared by progressive dilution from stock solution with water. Freshly prepared a saturated aqueous solution of bromine daily and stored in a chemical-resistant dark glass bottle. Rhodamine 6G (2.0 g) was dissolved in 100 mL of distilled water.

Sulphosalicylic acid: Sulphosalicylic acid (1.0 g) was dissolved in 100 mL of distilled water.

Buffer solution pH 6: Concentration sulphuric acid (1.7 mL) was added to the 125 mL of distilled water in a 250 mL flask. Monosodium dihydrogen orthophosphate dihydrated (15.7255 g) was added and the flask was shaken until dissolution was compete and finally diluted to 250 mL.

General Procedure

(a) Preparation of calibration plot: 3.0 to 25 μg of standard methoxyethylmercury chloride solution was taken in a 50 mL calibrated tube and decomposed in boiling water bath (*ca.* 100°C) for 10 min using with 30% sulphuric acid. The solution was allowed to cool at room temperature. 0.3 mL of bromine water was added and vigorously shaken for 3 min. Excess bromine was removed by 1% sulphosalicylic acid added slowly. The solution was transferred in a separatory funnel and 25 mL water was added. To this 5 mL of rhodamine 6G and 10 mL toluene were added and shaken vigorously[9]. The organic layer was collected in a polyethylene bottle and drived over anhydrous sodium sulphate, then transferred into the spectrofluorimetric cell. The fluoroscence of the organic layer was measured at 560 nm after excitation at 536 nm. Calibration plot was constructed by using fluorescence readings against concentration of methoxyethylmercury chloride.

(b) Recovery of methoxyethylmercury chloride from spiked water samples: 50 mL each of the water was spiked with known amounts of the methoxyethylmercury chloride standards and allowed to stand overnight and determined as described in general procedure (a). The results are presented in Table-1.

TABLE-1
RECOVERY OF METHOXYETHYLMERCURY CHLORIDE FROM SPIKED WATER SAMPLES

Amount added (μg/50 mL)	Proposed method			Reported method[9]		
	Amount found (μg/50 mL)	Recovery* (%)	RSD* (%)	Amount found (μg/50 mL)	Recovery* (%)	RSD* (%)
3.0	2.93	97.66	5.63	2.89	96.33	5.92
5.0	4.93	98.60	4.12	4.86	97.20	4.57
10.0	9.84	98.40	4.53	9.68	96.80	4.96
15.0	14.74	98.26	4.89	14.51	96.73	5.12
20.0	19.72	98.60	4.12	19.32	96.60	4.53
25.0	24.48	97.92	5.37	24.13	96.52	5.64

*% recovery and % RSD for four independent determinations

(c) Determination of methoxyethylmercury chloride in various cereals: Various samples of cereals were collected, known amounts of methoxyethylmercury chloride were added and stored over a period of 7 d. 100 g of sample was taken, blended in a mixer with 50% ethanol and then filtered through a thin cotton cloth. The filtrate was centrifuged for 10 min. Aliquots of supernatant were taken and analyzed. The results are shown in Table-2.

TABLE-2
RECOVERY OF METHOXYETHYLMERCURY CHLORIDE FROM CEREALS

Sample*	Amount added (μg/50 mL)	Proposed method			Reported method[9]		
		Amount found (μg/50 mL)	Recovery† (%)	RSD† (%)	Amount found (μg/50 mL)	Recovery† (%)	RSD† (%)
Rice	5.0	4.83	96.6	5.71	4.79	95.8	5.88
	10.0	9.79	97.9	4.62	9.68	96.8	5.53
Wheat	5.0	4.89	97.8	5.12	4.82	96.4	5.32
	10.0	9.84	98.4	4.27	9.79	97.9	4.86

*Amount of sample = 100 g (free from methoxyethylmercury chloride)
†% recovery and %RSD for four independent determinations

(d) Determination of methoxyethylmercury chloride in water: Agriculture runoff water samples were collected from different sources of agricultural fields, which had been sprayed with methoxyethylmercury chloride. The samples were stored in 1 L stoppered polyethylene bottles. 50 mL of water sample was taken and filtered through a Whatmann No. 40 filter paper, decomposed with 30% sulphuric acid and determined by following the procedure described in general procedure (a). The results are represented in Table-3.

TABLE-3
DETERMINATION OF METHOXYETHYLMERCURY CHLORIDE IN WATER SAMPLES

Sample No.	Concentration of methoxyethylmercury chloride (μg/50 mL)
1.	5.13
2.	10.21
3.	7.83
4.	11.34
5.	8.75

RESULTS AND DISCUSSION

Choice of the solvent for extraction of ion pair: The fluorescence spectra of tetrabromomercurate(II) and rhodamine 6G ion pair extracted into toluene is shown in Fig. 1. The extraction of ion pair was carried out in several organic solvents, *viz.*, *n*-hexane, cyclohexane, toluene and CCl_4. It was found that maximum ion pair recovery was obtained in toluene which is stable for several hours.

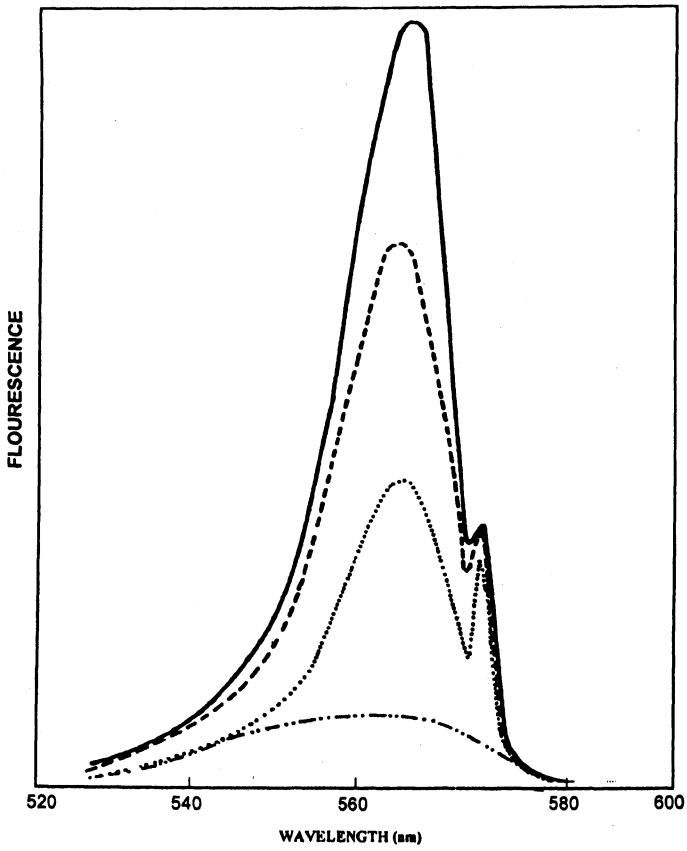

Fig. 1. Fluorescence spectrum of ion pair (tetrabromomercurate(II)-rhodamine 6G) extracted in toluene with different concentrations of methoxyethylmercury chloride

Spectral characteristics of the ion pair: Tetrabromomercurate(II) anion and rhodamine 6G ion pair extracted in toluene showed excitation wavelength at 536 nm and emission wavelength at 560 nm. All the spectral measurements were carried out against the reagent blank. The intensity of fluorescence was linear over the range of 3.0–25.0 μg of methoxyethylmercury chloride in 50 mL of final solution.

Effect of pH: The extraction of tetrabromomercurate(II) and rhodamine 6G was carried out in pH range of 4.0 to 10.0. The maximum extraction was obtained at pH 6.0. Hence, the extraction was carried out at pH 6.0 using buffer.

Effect of foreign species: The effect of foreign species and other pesticides on the determination of methoxyethylmercury chloride were studied. Known amounts of foreign species and pesticides were added prior to decomposition to a standard solution containing 20 μg of methoxyethylmercury chloride in 50 mL of solution and the solution was analyzed by proposed method. Results showed that foreign species and pesticides do not interfere in the analysis under reported condition. Tolerance limits for foreign species and pesticides are given in Table-4.

TABLE-4
EFFECT OF FOREIGN SPECIES AND PESTICIDES

Foreign species	Concentration of methoxyethylmercury chloride (20 μg/50 mL)		
	Tolerance limit (μg/50 mL)	Pesticides	Tolerance limit (μg/50 mL)
Ni^{2+}, Pb^{2+}, Mn^{2+}	550	BHC	600
Cd^{2+}, Al^{3+}	450	Phenol	550
Zn^{2+}	400	Carbaryl	500
NH^{4+}, Fe^{2+}	350	DDT, malathion	450
Ca^{2+}, Mg^{2+}, Cu^{2+}	250	Ethyl parathion	550
CO_3^{2-}	300	Quinolphos	300
SO_4^{2-}	200		
Cl^-	400		

Application: The method has been applied to the determination of methoxyethylmercury chloride in water samples and environmental samples. Known amounts of methoxyethylmercury chloride were added to the environmental samples like water and cereals, analyzed by the proposed method and the data compared with reported spectrophotometric method[9]. The results are presented in Tables 1 and 2. These results indicate that recovery is more than 97.66% for water samples and above 96.6% for cereals. The method has good precision with RSD of 4.12 to 5.63% for water samples and 4.27 to 5.71% RSD for cereals. The comparison with reported spectrophotometric method shows that the fluorimetric method is more sensitivie than the spectrophotometric methods for the determination of methoxyethylmercury chloride in environmental samples.

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