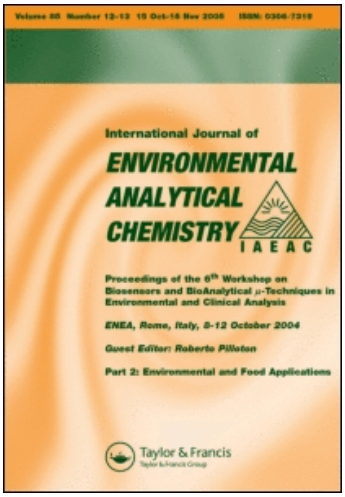

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SPECTROPHOTOMETRIC DETERMINATION OF FERBAM USING SODIUM SELENITE

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A procedure has been developed for the microdetermination of ferbam (ferric dimethyldithiocarbamate) after extraction of its selenium dimethyldithiocarbamate complex into chloroform. The maximum absorbance is at 430 nm; Beer's law is obeyed over the ferbam concentration range of 1.0–28.0 $\mu g\ ml^{-1}$ in the extract. The method is sensitive, selective and can be safely employed for the determination of ferbam in commercial samples, and synthetic mixtures containing nabam, zineb and maneb.

KEY WORDS: Ferbam determination, sodium selenite, spectrophotometry, commercial samples.

INTRODUCTION

Dithiocarbamates have found a variety of applications in agriculture as pesticides and in the rubber industry as vulcanisation accelerators and anti-oxidants. The toxicity of the dithiocarbamates is increased when a heavy metal ion is present in the molecule. The dithiocarbamates are generally determined on the basis of their decomposition by hot mineral acid to the amine and carbon disulphide. The conditions for the acid digestion have been investigated by a number of workers. Callan and Strafford[1] first devised the acid hydrolysis method using 7.5 N H_2SO_4. Most of the analytical methods in general use are based on the Clarke method[2] in which the dithiocarbamate is destroyed in acid solution to give carbon disulphide (CS_2). The latter is absorbed in methanolic potassium hydroxide and the potassium methylxanthate so formed is then titrated iodimetrically. Dithiocarbamate pesticide residues, however, have been determined[3–12] by spectrophotometric measurement of the CS_2 released. Petrascu[13] has modified the Viles–Clarke–Lowen method. Hall[3] has reported on a collaborative study of the determination of dithiocarbamates by modified versions of the methods of Clarke *et al.*[2] and Rosenthal *et al.*[4]. Dithiocarbamates have been determined from vegetable foodstuffs using high-performance liquid chromatography[14], titrimetry[15] and extraction voltammetry[16]. Dithiocarbamate fungicides are also determined in air[17] by head-space gas chromatography of the CS_2 evolved under controlled conditions from collected air-borne dust and from water samples on acid hydrolysis of the pesticide using a Hall detector[18].

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However, most of these methods are non-specific since all dithiocarbamate pesticides (thiram, ziram, nabam, etc.) yield carbon disulphide on digestion in acid medium, and the sensitivity of most methods is low. Ferbam is also determined by converting it into a molybdenum-containing complex[19] in acid medium, but the extraction is not rapid and requires multistage extractions for the complete extraction of the complex. Most of these methods are indirect, time-consuming and not too sensitive. Here we present a relatively simple, sensitive and selective method by converting ferbam into a selenium dimethyldithiocarbamate complex which is then extracted into chloroform.

EXPERIMENTAL

Equipment All absorbances were measured with a SP-20 Spectronic spectrophotometer. The pH measurements were carried out with an ECIL pH meter.

Reagents All solvents and reagents were of analytical reagent grade.

Ferbam solution, 1.0%. Ferbam was prepared by a method published in the literature[20] and its purity was checked by elemental analysis. The iron content was checked by decomposing it with concentrated nitric acid and complexometric titration using Variamine Blue B as indicator[21]. A stock solution (0.1%) of ferbam was prepared by dissolving 100 mg in acetonitrile, standardisation and further dilution as required.

Sodium selenite solution, 1.0% A 1% solution of sodium selenite (JMC Industrial Chemicals, England) in distilled water was prepared.

Acetate buffer solution, 1 M. pH 5.8 Dissolve 68 g of sodium acetate trihydrate in 400 ml of water, mix with 25 ml of glacial acetic acid, adjust the pH to 5.8 and dilute to 500 ml.

Salts. Stock solutions of various salts were prepared by dissolving them in water or in suitable solvents. Synthetic samples were prepared by mixing the appropriate solutions to give the required composition.

General procedure

To a known volume ($\leqslant 1$ ml) of sample containing 5–140 μg of ferbam taken in a beaker, 2.0 ml of 1.0% sodium selenite solution and 1.5 ml of acetate buffer (pH = 5.8) were added and the volume was made up to 5.0 ml with distilled water. This solution was transferred to a separatory funnel along with 5.0 ml of chloroform and shaken for 2 min. The organic phase was transferred to a dry tube containing anhydrous calcium chloride. A preliminary study confirmed that the extraction was complete in one step. Therefore, the absorbance of the first extract was measured at 430 nm against a reagent blank.

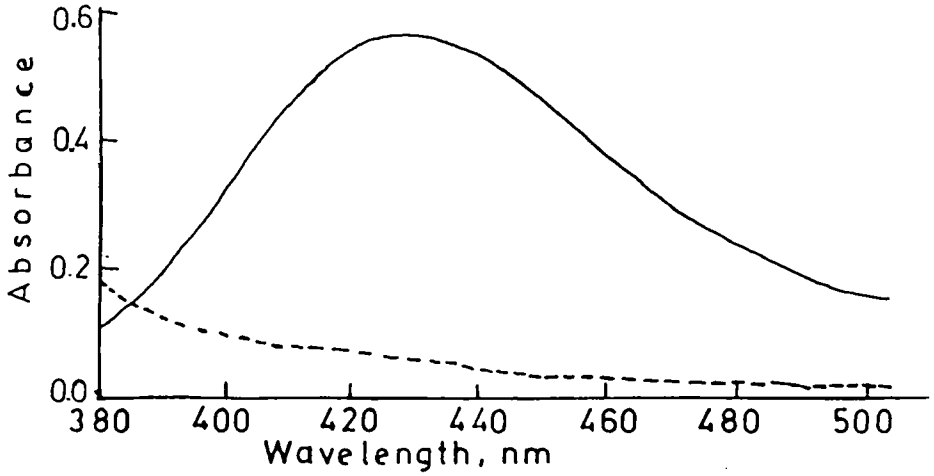

Figure 1 Absorption spectra of ferbam (----) against chloroform and of the ferbam-selenium complex (——) in chloroform against the reagent blank. Ferbam: 80 μg; sodium selenite: 2.0 ml of 1.0% solution; pH; 5.8.

RESULTS AND DISCUSSION

The absorption spectrum of the selenium dimethyldithiocarbamate complex in chloroform was recorded against a reagent blank. The complex absorbs strongly at 430 nm (Figure 1). Maximum absorbance was observed when the pH of the aqueous phase was 4.0–8.0 (Figure 2) and 1.5–2.0 ml of 1.0% sodium selenite were used. The ferbam complex can be extracted into *n*-butyl acetate, amyl acetate, diethyl ether, butan-2-one, ethyl acetate, isobutyl alcohol, isobutylmethyl ketone and chloroform.

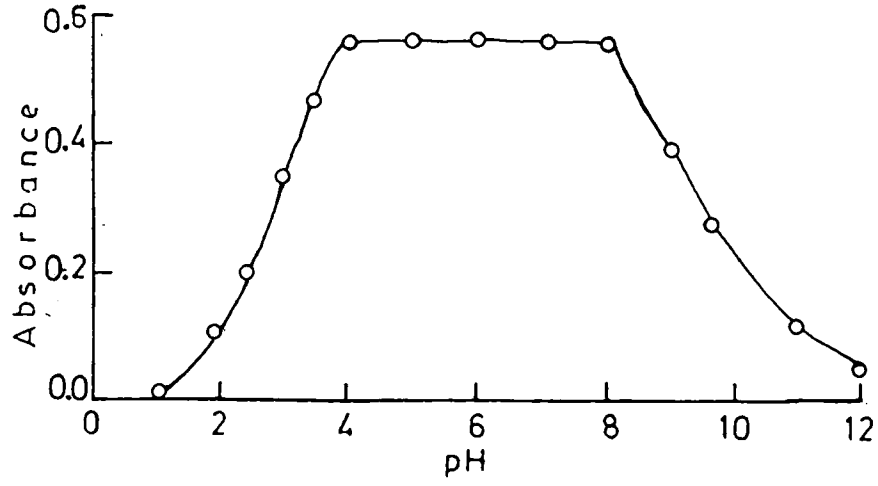

Figure 2 Effect of pH on absorbance: ferbam 80 μg; sodium selenite: 2.0 ml of 1.0% solution; wavelength: 430 nm; reference: reagent blank.

Maximum absorbance was observed in chloroform; hence, this solvent was selected. The absorbance of the complex remained essentially constant for more than 12 h.

Under the optimum conditions described above, a calibration graph for ferbam constructed at 430 nm was linear over the concentration range 1.0–28.0 μg ml^{-1} of ferbam. Ten replicate determinations on sample solutions containing 80 μg of ferbam gave a mean absorbance of 0.56 with an RSD of 1.4%. The molar absorptivity and Sandell's sensitivity (for an absorbance of 0.001) are 1.46×10^4 l mol^{-1} cm^{-1} and 0.028 μg cm^{-2}, respectively.

Interferences

The effect of various ions on the extraction of the selenium dimethyldithiocarbamate complex and on the determination of 10 μg of ferbam in 5 ml of final solution was studied. The following foreign ions (amounts in parentheses) did not interfere : acetate, fluoride, bromide, iodide, nitrate, sulphate (25 mg each); chloride (20 mg); citrate (3 mg); orthophosphate (2 mg); oxalate (700 μg); thiosulphate and metabisulphite (2.5 mg); EDTA (10 mg); Pb(II) and Cd(II) (260 μg each); Zn(II) (50 μg); Fe(III) and Bi(III) (20 μg). Copper interfered but could be tolerated up to 200 μg provided it was masked with 5–10 mg of EDTA during extraction. The effect of various ions on the determination of ferbam are given in Tables 1 and 2.

Interference due to the presence of other dithiocarbamates and xanthates was also studied. Disodium ethylenebisdithiocarbamate (nabam), manganese ethylenebisdithiocarbamate (maneb), zinc ethylenebisdithiocarbamate (zineb), tetramethylthiuram disulphide (thiram), sodium *N*-methylanilinecarbodithioate, ethyl xanthate, isopropyl xanthate and butyl xanthate could be tolerated up to 2 mg in the determination of 50 μg of ferbam in 5 ml of final solution, because nabam, maneb, zineb, thiram, sodium *N*-methylanilinecarbodithioate and the xanthates do not yield complexes with sodium selenite under these conditions. Nabam, sodium monomethyldithiocarbamate (vapam), sodium dimethyldithiocarbamate (dibam), sodium diethyldithiocarbamate and potassium morpholine-4-carbodithioate can be separated by pre-extraction of ferbam into chloroform; the other compounds remain in the aqueous phase, and the chloroform can be removed by evaporation. Ziram is also extracted into chloroform, if present with ferbam, and hence interferes in its determination.

Determination of ferbam in synthetic mixtures and in commercial samples

Mixtures of ferbam with nabam, zineb, maneb, thiram and with xanthates in various proportions were prepared and determined by the general procedure. The results are given in Table 3. Simultaneous determination of ferbam and other water-soluble dithiocarbamates is indeed possible. The method was applied for the determination of ferbam in the commercial sample 'Ferbam 75% W. P' containing 75% as active ingredient. Table 4 shows the results of five dilutions of stock solutions prepared from a pure and a commercial sample. The results of the present method are compared with those obtained by the method of Clarke *et al.*[2], and the result is seen to be fully satisfactory.

Table 1 Effect of diverse anions on ferbam determination*.

Salt added	*Anion added (mg)*	*Absorbance at 430 nm*
No addition	—	0.35
Sodium acetate	25	0.35
Sodium chloride	20	0.35
Sodium fluoride	25	0.35
Potassium bromide	26	0.35
Potassium iodide	25	0.35
Potassium nitrate	25	0.35
Sodium sulphate	35	0.35
Sodium citrate	5	0.32
	3.5	0.35
Sodium oxalate	5	0.33
	1	0.35
Sodium orthophosphate	20	0.27
	10	0.32
	5	0.34
	3	0.35
Sodium metabisulphite	20	0.08
	10	0.17
	5	0.31
Sodium thiosulphate	15	0.23
	5	0.29
EDTA (Disodium)	20	0.32
	10	0.35

* 50 μg of ferbam in 5 ml final solution; 2.0 ml of 1% sodium selenite, pH 5.8.

Table 2 Effect of diverse cations on ferbam determination*.

Metal salt added	*Metal added (mg)*	*Absorbance at 430 nm*
No addition	—	0.35
Leas(II) nitrate	0.50	0.35
Zinc(II) nitrate	0.15	0.35
Iron(III) chloride	0.17	0.35
Cadmium(II) acetate	0.42	0.35
Bismuth(III) nitrate	0.05	0.35
Copper(II) sulphate**	0.25	0.35

* For conditions, see Table I.
** Determination in presence of 1.0 ml of 1.0% EDTA.

Table 3 Determination of ferbam in synthetic mixtures.

No.	*Composition and percentage*	*Amount of ferbam (μg)*		
		taken	*found*	*rel. error (%)*
1	Ferbam: 40 Nabam: 20 Thiram: 20 Zineb: 10 Maneb: 10	30.0	30.2	0.7
2	Ferbam: 50 Thiram: 50	40.0	40.3	0.7
3	Ferbam: 40 Ethyl xanthate: 20 Isopropyl xanthate: 20 Butyl xanthate: 20	50.0	50.3	0.5
4	Ferbam: 50 Dibam: 20 NaDDC*: 15 Vapam: 15	50.0	50.3	0.6

* Sodium diethyldithiocarbamate

Table 4 Determination of ferbam in a commercial sample.

Ferbam	*Ferbam present (%)*	*Ferbam found**	
		Proposed method	*Clarke method*
Ferbam (pure)	0.10	0.098	0.099
	0.20	0.199	0.199
	0.40	0.399	0.398
	0.60	0.599	0.598
	0.80	0.799	0.798
Ferbam (75% W.P.)	0.10	0.096	0.098
	0.20	0.198	0.199
	0.40	0.399	0.398
	0.60	0.598	0.599
	0.80	0.798	0.796

* RSD, 1.3–2.3% ($n = 10$)

Table 5 Determination of ferbam in crops.

Crop	*Amount of ferbam (μg)**	
	taken	*found*
Apples	40.0	39.9
	50.0	49.0
Grain	40.0	38.0
	50.0	49.5

* $n = 3$; 20 g of crops taken.

Determination of ferbam in crops

The procedure was applied for the determination of ferbam in grain and apples. A known amount of ferbam was crushed with 20 g of the crops and shaken mechanically with 100 ml of chloroform for 1 h. The mixture was filtered and the residue in the funnels washed with three 10 ml portions of chloroform. The extracts were evaporated down to 2.0 ml and the remaining solvent was removed by blowing a current of dry air at room temperature. The residue was dissolved in acetonitrile and ferbam determined by the general procedure. The results are given in Table 5.

CONCLUSIONS

The present method is selective for the determination of ferbam in the presence of dithiocarbamates like thiram, nabam, zineb, maneb, and xanthates like ethyl, isopropyl and butyl xanthate. The sensitivity of the present method is better than that of the methods of, e.g., Lowen[12], Cullen[22] and Chmiel[23]. According to Lowen, a minimum of 10 μg of CS_2 and according to others—a minimum of 20 μg of CS_2 evolved can be determined. However, with the present method, a minimum of 5.0 μg of ferbam can be determined which is equivalent to 2.73 μg of evolved CS_2. Although the gas chromatographic methods are more sensitive than the present one, they lack the selectivity since all dithiocarbamate pesticides liberate CS_2 on acid hydrolysis. The wide applicability, simplicity and selectivity of this method make it preferable to others.

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