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Spectrophotometric Determination of Sodium N-Methylpiperazinecarbodithioate by Extraction of its Chromium Complex into Chloroform

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A microprocedure has been developed for the determination of sodium N-methylpiperazinecarbodithioate by converting into chromium complex which is then extracted into chloroform and measured at 420 nm against a reagent blank. Beer's law is obeyed over the concentration range 6.0–110.0 μg in 5 ml of final solution. Interference of various ions and dithiocarbamates has been studied in detail.

INTRODUCTION

Dithiocarbamates have found a variety of applications in agriculture as pesticides and in rubber industry as vulcanisation accelerators and anti-oxidants. 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]. Dithiocarbamate pesticides residues, however, have been determined[3–8] by spectrophotometric measurement of the carbon disulphide released. Petrascu[9] has modified the Viles-Clarke-Lowen methods. 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] However, these methods are non-specific since any dithiocarbamate pesticides e.g. tetramethylthiuram disulphide, zinc dimethyl dithiocarbamate or disodium ethylenebisdithiocarbamate, yield carbon disulphide on digestion in acidic medium and sensitivity of these methods is very low. Dithiocarbamates have also been determined from vegetable food stuffs using high performance liquid chromatography[10], titrimetric[11] and extraction voltametry[12]. Most of these methods are found to be indirect and time consuming. It is considered of interest to determine these by a simple, direct and rapid spectrophotometric method. Here we present a more simple, sensitive and selective method for the determination of sodium N-methylpiperazinecarbodithioate by extraction of its chromium complex into chloroform.

EXPERIMENTAL

A digital pH meter and a SP–20 spectronic spectrophotometer were used. Sodium N-methylpiperazinecarbodithioate was prepared by the method of Macrotrigiano[13]. The purity of the sample was checked by elemental analysis. Solution (0.1%) of sodium N-methylpiperazinecarbodithioate was prepared in distilled water and standardised by adding excess standard copper(II) solution and titration of the excess copper with EDTA using pyrocatechol as indicator[14] and buffering with pyridine. Further dilutions were carried out with distilled water as required. A 0.5% solution of chromium acetate[15] in distilled water was prepared. Stock solutions of cations, anions and other elements (whose interferences are to be studied) were prepared by dissolving suitable salts in water or in a suitable solvent. Synthetic samples were prepared by mixing solutions of the dithiocarbamates to give the required composition.

Procedure

To a known volume ($\leq$ 1 ml) of sample containing 6.0–110 μg of sodium N-methylpiperazinecarbodithioate in a beaker, 2.0 ml of 0.5% chromium acetate and 2 ml of acetate buffer (pH = 2.5) were added and the volume was made up to 5.0 ml with distilled water. This solution was transferred into a separatory funnel and shaken with an exact volume 5 ml of chloroform for 1 min. The organic phase was transferred into a dry tube containing anhydrous calcium chloride. A second extraction was carried out with another 5.0 ml of chloroform and the organic phase gave negligible absorbance. So the absorbance of the first extract was measured at 420 nm against a reagent blank.

RESULTS AND DISCUSSION

The absorption spectrum of chromium N-methylpiperazinecarbodithioate complex in chloroform was recorded against a reagent blank. The complex absorbed strongly at 420 nm. The absorbance of the extract remained constant in the pH range 3.0–4.0 and when 1.5–2.0 ml of 0.5% chromium acetate solution were used. The complex was not extractable into benzene, carbon tetrachloride, toluene and hexane but could be extracted with amyl acetate, chloroform, butane-2-one, ethyl acetate, *iso*butanol and *iso*butylmethyl ketone. Maximum absorbance was observed with chloroform, and hence it was used in this method. The absorbance of the complex remained practically constant for 4 hrs.

Under optimum conditions described above a calibration curve was constructed at 420 nm and Beer's law being obeyed in the concentration range 6.0–110.0 μg per 5 ml of the final solution. The moral absorptivity and Sandell's sensitivity (for an absorbance of 0.001) were calculated to be 0.516×10^4 l/mol/cm and 0.038 μg/cm^2, respectively at 420 nm. Ten replicate determinations containing

100 μg of sodium N-methylpiperazinecarbodithioate gave mean absorbance of 0.52 with a relative standard deviation of 1.43%.

Composition of chromium N-methylpiperazinecarbodithioate complex was studied by Job's method of continuous variation and mole ratio method and was found to be 1 : 3. This suggested the extraction of $Cr(C_6H_{11}N_2S_2)_3$ complex under these conditions.

Interferences

Sample solutions containing upto 100 μg of sodium N-methylpiperazinecarbodithioate and various amounts of different alkali metal salts or metal ions were prepared and sodium N-methylpiperazinecarbodithioate was determined by general procedure in the presence of various ions. The following foreign ions (mg amount in parentheses) did not interfere in the determination of 100 μg of sodium N-methylpiperazinecarbodithioate in 5 ml of final solution: Pb^{II} (1.251), Zn^{II} (0.500), Cd^{II} (0.870), Fe^{III} (0.6892), Mn^{II} (0.649) . Cu^{II} interfered strongly, but it can be masked with 1.0 ml of 1.0% EDTA solution. Bromide (26), iodide (30), chloride (9.75), nitrate (24), citrate (36), sulphate (27) and EDTA (1) did not interfere, but thiosulphate and metabisulphite interfered strongly.

Synthetic mixtures of sodium N-methylpiperazinecarbodithioate with disodium ethylenebisdithiocarbamate (nabam), zinc ethylenebisdithiocarbamate (zineb), manganese ethylenebisdithiocarbamate (maneb), sodium dimethyldithiocarbamate (dibam), zinc dimthyldithiocarbamate (ziram), ferric dimthyldithiocarbamate (ferbam), sodium monomethyldithiocarbamate (vapam), tetramethylthiuram disulphide (thiram) and sodium dimethyldithiocarbamate in various proportions were prepared. Taking advantage of the solubility difference ziram, ferbam, zineb, maneb and thiram were extracted into chloroform while sodium N-methylpiperazinecarbodithioate remains in the aqueous phase and is then determined by the general procedure.

Application

The applicability of the method was tested by analysis of variety of mixtures containing up to 110.0 μg of sodium N-methylpiperazinecarbodithioate in the aliquots taken. The method is selective for the determination of sodium N-methylpiperazinecarbodithioate in the presence of nabam, zineb, maneb, ethyl xanthate, *iso*-propyl xanthate and butyl xanthate. It is one of the most sensitive methods available for sodium N-methylpiperazinecarbodithioate determination and could be used for the analysis of commercial samples of dithiocarbamates and good recoveries were obtained from food stuffs (95–95.5%). Table 1 shows typical results of five dilutions of stock solutions prepared from a sample of sodium N-methylpiperazinecarbodithioate. Results obtained are compared with the Clarke *et al.*[2] method.

TABLE 1
ANALYSIS OF DILUTIONS OF SODIUM N-METHYL-PIPERAZINECARBODITHIOATE STOCK SOLUTION

Amount taken %	Amount found %	Clarke et al.[22] method %
0.100	0.099	0.097
0.250	0.249	0.247
0.500	0.498	0.497
0.800	0.798	0.796
0.900	0.899	0.898

Comparison of sensitivity

The sensitivity of the present method is better than the methods of Lowen[16], Cullen[17], Chmiel[18] and many other methods reported in literature. According to Lowen the minimum of 10 μg evolved CS_2 and according to others a minimum of 20 μg CS_2 evolved can be determined. But according to the present method, a minimum 6.0 μg of sodium N-methylpiperazine carbothioate equivalent to 2.3 μg of evolved CS_2 can be determined, respectively.

The wide applicability, simplicity and selectivity of this method makes it a choice amongst the known methods.

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