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EXTRACTIVE PHOTOMETRIC DETERMINATION OF TRITHIOCARBONATES AND MERCAPTANS (THROUGH TRITHIO CARBONATE FORMATION) WITH COBALT(II)

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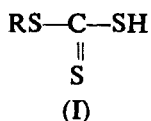
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A new and rapid extractive photometric method for the microdetermination of trithiocarbonates and mercaptans (through trithiocarbonate formation) with cobalt(II), has been described. Chloroform has been found to extract the precipitated complex quantitatively in the presence of excess reagent in the pH range 1-6. The absorbance of the yellow brown solution is measured using 420nm filter against a reagent blank. The concentration ranges for each trithiocarbonate and mercaptan over which the Beer's law is obeyed, are listed. The method is accurate, widely applicable and may be used for routine analysis.

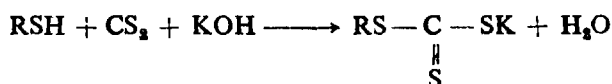
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INTRODUCTION

ORGANOTRITHIOCARBONATES may be considered as the salts of the corresponding trithiocarbonic acids (I). The compounds



find considerable applications (Reid, 1962; and Karchmer, 1972) in medicine, agriculture and industry. Consequently, the determination of these compounds is of great interest and value. The present communication reports a new and rapid extractive photometric method for their determination at micro level using cobalt (II) reagent. Chloroform has been found to extract the precipitated complex quantitatively in the presence of excess reagent in the pH range 1-6. The absorbance of the yellow brown solution is measured using 420nm filter against a reagent blank. The method has been successfully used for the determination of mercaptans after their quantitative transformation into the corresponding trithiocarbonates through reaction with carbon disulphide and alkali.



This reaction forms the basis of a general and convenient method for the preparation of organotrithiocarbonates from mercaptans. The concentration ranges for each trithiocarbonate and mercaptan over which the Beer's law is obeyed, have been listed. The proposed method is accurate, reliable, widely applicable and may be used for routine analysis.

MATERIALS AND METHOD

Organotrithiocarbonates were prepared and purified as described earlier (Verma & Sharma, 1976; and Reid, 1962). The purity of the compounds was checked by iodimetric method (Verma & Sharma, 1976). The mercaptans were distilled before use. Acetate buffer, 4.99, was prepared by mixing 2M solutions of acetic acid and sodium acetate in the ratio 3 : 7 (v/v). All other reagents used in this investigation were of guaranteed quality.

Systronics colorimeter (Type 101) was used for absorbance measurements. Digital pH meter equipped with glass-calomel combination electrode was used for pH measurements.

Procedure

(a) *Determination of Trithiocarbonates* — Aliquots (0.1 to 1.0 ml) of the solutions in water of each trithiocarbonate were transferred with shaking to cobalt(II) chloride hexahydrate solution (1ml, 0.1M) and acetate buffer (1ml, pH 4.99) added. The volume of each solution was made to 10ml with water. Chloroform (10ml) was added and the two phases thoroughly equilibrated for 1min. and then allowed to settle for 1min. The absorbance of the organic phase was measured using 420nm filter against a reagent blank, which was similarly prepared. A calibration curve was prepared in each case.

(b) *Determination of Mercaptans* — To aliquots (0.1 to 1.0ml) of the solutions in acetonitrile were added potassium hydroxide solution (2ml, app. 0.05M in water) and carbon disulphide solution (0.5ml, app. 1M in acetonitrile). The solution thus obtained was neutralised with acetic acid (app 0.1M in water) and to it were added with shaking cobalt(II) chloride hexahydrate solution (1ml, 0.1M in water) and acetate buffer (1ml, pH 4.99). The volume of each solution was made to 10ml with water. Chloroform (10ml) was added and the two phases thoroughly equilibrated for 1min. and then allowed to settle for 1 min. The absorbance of the organic phase was measured using 420nm filter against a similarly prepared reagent blank and calibration curve prepared in each case.

RESULTS AND DISCUSSION

The pH-absorbance profiles have shown that the precipitated complex is quantitatively extracted in the pH range 1-6. Shaking for one minute was required for maximum colour development in the organic phase. The colour of the extract was found to be stable for at least 24 hours. The composition of the complex was established spectrophotometrically by the method of continuous variation and mole ratio method. The

studies showed that 1:2 metal-ligand complex is formed. The concentration range per ml of each trithiocarbonate solution over which the Beer's law is obeyed, is given in Table I. Urea, acetate, sulphate, and carbon disulphide do not cause any interference even when present in upto tenfold excess relative to trithiocarbonate. Xanthates, dithiocarbamates, amines and thioureas, however, interfere.

TABLE I
Concentration ranges over which Beer's law is obeyed

Compounds	Concentration range (per ml of sample solution)
<i>Trithiocarbonates (TTC)</i>	
Potassium ethyl TTC	8-135 μg
Potassium benzyl TTC	6-150 μg
Potassium n-butyl TTC	5-125 μg
Potassium isobutyl TTC	5-125 μg
Potassium n-hexyl TTC	5-135 μg
Potassium dodecyl TTC	9-250 μg
<i>Mercaptans</i>	
Ethyl mercaptan	2-50 μg
Benzyl mercaptan	4-98 μg
n-Butyl mercaptan	3-70 μg
Isobutyl mercaptan	3-90 μg
n-Hexyl mercaptan	6-130 μg
Dodecyl mercaptan	9-230 μg

The method has been successfully extended to the micro determination of mercaptans after their transformation into the corresponding trithiocarbonates through reaction with carbon disulphide and alkali. That this transformation is rapid and quantitative, has already been shown (Verma & Sharma, 1976 ; and Verma & Kumar, 1978). The presence of excess of carbon disulphide (added for transformation) does not interfere in the analysis of mercaptans by this method. The concentration range per ml of the mercaptan solution over which the Beer's law is obeyed, is also given in Table I. Chloride, bromide, iodide and ethyl acetate even when present in upto tenfold excess relative to the mercaptan, do not interfere. Urea, dimethyl disulphide and bromobenzene, on the other hand, can be tolerated if present in upto fivefold excess. Xanthates, dithiocarbamates, acrylonitrile, benzaldehyde and glucose however interfere seriously.

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