

## QUANTITATIVE ANALYSIS OF ORGANIC MIXTURES : DETERMINATION OF MERCAPTANS IN ADMIXTURE WITH XANTHATES, ORGANO-TRITHIOCARBONATES, DITHIOCARBAMATES OR THIOUREAS

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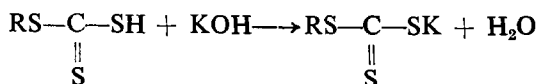
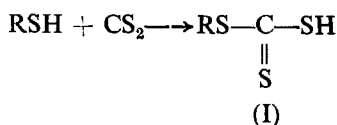
Simple, accurate and reliable methods possessing wide applicability have been developed for the analysis, on the same sample solution, of mercaptan-xanthate, mercaptan-organotrithiocarbonate, mercaptan-dithiocarbamate and mercaptan-thiourea mixtures.

**Keywords:** Mercaptans; Xanthates; Trithiocarbonates; Dithiocarbamates

### INTRODUCTION

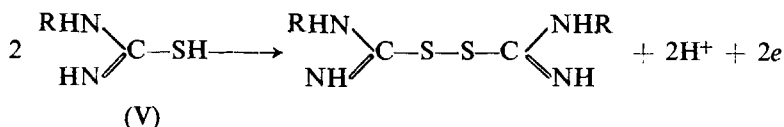
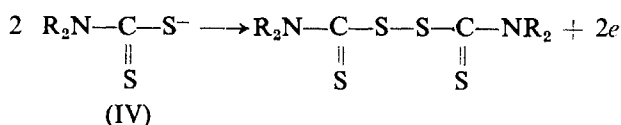
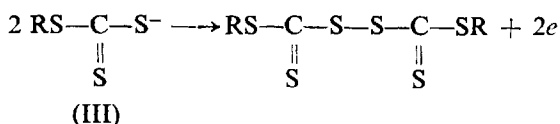
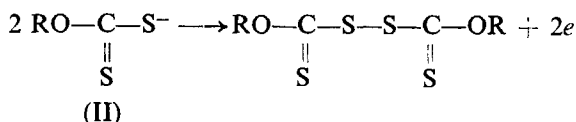
THE analysis of organic compounds by functional groups is of great value in industry and research. Though methods are available for application to the analysis of pure samples of compounds belonging to the same functional group, the analysis of mixtures of compounds belonging to different functional groups has only received scant attention, despite the fact that such mixtures are frequently encountered. In our laboratory, we have been able to evolve simple procedures for the analysis of organo-isothiocyanate-organoisocyanate, organo-isothiocyanate-thiourea, primary/secondary amine-tertiary amine, amine-thiourea, amine-dithiocarbamate, thiourea-xanthate and thiourea-formamidine disulphide mixtures with a single sample solution in each case (Verma & Kumar, 1973, 1974, 1976, 1977). The present communication reports simple and accurate methods of wide applicability for the analysis, on the same sample solution, of mercaptan-xanthate, mercaptan-organotrithiocarbonate, mercaptan-dithiocarbamate and mercaptan-thiourea mixtures. The methods are based on the following observations:

(a) Mercaptans react with carbon disulphide in tert.-butanol to form the corresponding organotrithiocarbonic acids(I) which can be titrated with standard aqueous alkali visually using phenolphthalein indicator or pH metrically. This affords us an alkalimetric method (Verma & Kumar, 1978) for the determination of mercaptans.



Mercaptans are thus quantitatively transformed to alkali organotrithiocarbonates under these conditions.

(b) Xanthates(II), organotrithiocarbonates(III), dithiocarbamates(IV) and thioureas(V) can be titrated with iodine/iodine monochloride which oxidise them smoothly, rapidly and quantitatively to the corresponding disulphides.



The end points can be detected visually by the appearance of yellow colour due to iodine (or blue colour if starch is used as indicator) or potentiometrically.

The mixture solution is reacted with carbon disulphide in tert.-butanol and the resulting organotrithiocarbonic acid (obtained from mercaptan) titrated with standard aqueous alkali visually using phenolphthalein indicator or pH metrically. The alkalimetric titration gives the amount of mercaptan (present in the mixture), which is now quantitatively transformed to alkali salts of the corresponding organotrithiocarbonates. The titrated solution containing xanthate, organotrithiocarbonate, dithiocarbamate or thiourea in addition to alkali organotrithiocarbonate (obtained from alkalimetric titration) is titrated with iodine or iodine monochloride visually to the appearance of yellow colour. The oxidimetric titration corresponds to the amount of alkali organotrithiocarbonate (obtained from alkalimetric titration) and consequently of the mercaptan plus xanthate, organotrithiocarbonate, dithiocarbamate or thiourea present in the mixture. The amount of xanthate, organotrithiocarbonate, dithiocarbamate or thiourea is found by difference. Hence the alkalimetric titration followed by oxidimetric titration enable each mixture to be analysed for both components.

#### MATERIALS AND METHOD

Xanthates (Rao, 1971), organotrithiocarbonates (Reid, 1962), dithiocarbamates (Klopping & Kerk, 1951; and Isoire & Musso, 1960) and thioureas (Drake, 1941)

were prepared and purified by reported methods. Mercaptans were distilled before use. Iodine monochloride, 0.05N in ethanol, was prepared by dissolving a little more than the calculated amount of the compound in ethanol. The solution was standardised iodometrically in aqueous acidic medium. Iodine and potassium hydroxide (both 0.05N in water) were prepared and standardised as usual.

Potentiometric titrations were performed with a Toshniwal CLO6 potentiometer using bright platinum wire indicator electrode and saturated calomel reference electrode. Digital pH meter equipped with glass-calomel combination electrode was used for pH titrations.

#### *Procedure*

Aliquots of solutions in acetonitrile, ethanol, isopropanol, or tert.-butanol of synthetic mixtures with various proportions of mercaptans and xanthates, organotrithiocarbonates, dithiocarbamates or thioureas were taken in titration flasks and mixed with 30–40 ml of tert.-butanol. Each solution was mixed with 1 ml of carbon disulphide, 1–2 drops of phenolphtholein (0.5% in tert.-butanol) and titrated at room temperature (26 °C) with standard (0.05N) aqueous sodium hydroxide to a colour change from yellow to yellow-pink or pH metrically.

In case of mercaptan-xanthate, mercaptan-organotrithiocarbonate and mercaptan-thiourea mixtures, the solution obtained after alkalimetric titration was diluted with 50–60 ml of water, neutralised with very dilute solution of acetic acid (the solution reverts to straw yellow colour) and titrated with standard iodine (iodine monochloride in case of mercaptan-thiourea mixture) to a sharp colour change from straw yellow to deep yellow. Amylose may also be used as an indicator; the solution turns blue at the end-point. The end points were also detected potentiometrically.

In case of mercaptan-dithiocarbamate mixtures, the solution obtained after alkalimetric titration was mixed with 20ml of water, neutralised with dilute solution of acetic acid (the solution reverts to straw yellow colour) and titrated with iodine to the appearance of deep yellow colour or potentiometrically.

Whereas the alkalimetric titration gives the amount of mercaptan, the oxidimetric titration gives the amount of mercaptan plus xanthate, organotrithiocarbonate, dithiocarbamate or thiourea present in the mixture. The amount of xanthate, organotrithiocarbonate, dithiocarbamate or thiourea is found by difference. The results of analysis of synthetic mixtures of n-butyl mercaptan and potassium n-butyl xanthate; isopropyl mercaptan and potassium isopropyl trithiocarbonate; ethyl mercaptan and sodium diethyl dithiocarbamate; and n-butyl mercaptan and n-butyl thiourea, as representative of the sets of mixtures under investigation, are given in Table I.

### RESULTS AND DISCUSSION

The proposed methods for the determination of mercaptan-xanthate, mercaptan-organotrithiocarbonate, mercaptan-dithiocarbamate and mercaptan-thiourea mixtures besides being simple, accurate and reliable have the added advantage that the analysis can be conducted on a single sample thus resulting in saving of time and effort.

TABLE I

Assay results of synthetic mixtures containing a mercaptan and a xanthate, organotrithiocarbonate, dithiocarbamate or thiourea

Mixture	Values are means of ten determinations with standard deviation ( $\pm$ )					
	Amount taken mg	Ratio	Amount found mg	Amount taken mg	Ratio	Amount found mg
<i>n</i> -Butyl mercaptan	10.00		10.11 $\pm$ 0.066	40.00		39.69 $\pm$ 0.092
Pot. <i>n</i> -butyl xanthate	40.00	1:4	40.38 $\pm$ 0.101	10.00	4:1	9.91 $\pm$ 0.063
Isopropyl mercaptan	8.00		8.03 $\pm$ 0.039	32.00		32.28 $\pm$ 0.062
		1:4			4:1	
Pot. isopropyl trithiocarbonate	32.00		32.33 $\pm$ 0.076	8.00		8.07 $\pm$ 0.058
Ethyl mercaptan	10.00		10.06 $\pm$ 0.042	40.00		39.72 $\pm$ 0.108
		1:4			4:1	
Sod. diethyl dithiocarbamate	40.00		39.59 $\pm$ 0.097	10.00		9.93 $\pm$ 0.057
<i>n</i> -Butyl mercaptan	5.00		5.04 $\pm$ 0.039	20.00		20.22 $\pm$ 0.063
		1:4			4:1	
<i>n</i> -Butyl thiourea	20.00		20.19 $\pm$ 0.072	5.00		5.01 $\pm$ 0.036

For the determination of mercaptan content of each mixture, carbon disulphide is added to transform each mercaptan to its corresponding trithiocarbonic acid and its excess does not interfere in any way in the analysis of mixtures. During the alkalimetric titration of the trithiocarbonic acid, the solution becomes yellow since alkali salts of organotrithiocarbonic acids are yellow coloured. The colour change from yellow to yellow-pink is due to the imposition of the pink colour of the basic form of phenolphthalein on the yellow of trithiocarbonate. The end-point is extremely sharp. In the analysis of mercaptan-thiourea mixtures, the solution after alkalimetric titration is not titrated with iodine since the reaction of thiourea with iodine does not give clear stoichiometry (Karchmer, 1972) unless extremely dilute solutions are used and even under these conditions, the end-point is difficult to locate. It is however titrated with iodine monochloride since thioureas are smoothly and quantitatively oxidised to the corresponding disulphides with iodine monochloride (Singh *et al.*, 1962).

The results recorded in Table I for the analysis of synthetic mixtures of *n*-butyl mercaptan and potassium *n*-butyl xanthate; isopropyl mercaptan and potassium isopropyl trithiocarbonate; ethyl mercaptan and sodium diethyl dithiocarbamate and *n*-butyl mercaptan and *n*-butyl thiourea, with the ratios of mercaptan and xanthate, organotrithiocarbonate, dithiocarbamate or thiourea in the range of 1:4 to 4:1 can be analysed with a maximum average standard deviation of less than 0.8 per cent. The method has been applied to several synthetic mixtures such as *n*-propyl mercaptan/potassium *n*-propyl xanthate, ethyl mercaptan/potassium ethyl

xanthate, benzyl mercaptan/potassium benzyl xanthate (in case of mercaptan-xanthate mixtures); n-propyl mercaptan/potassium n-propyl trithiocarbonate; benzyl mercaptan/potassium n-benzyl trithiocarbonate; n-butyl mercaptan/potassium n-butyl trithiocarbonate (in case of mercaptan-organotrithiocarbonate mixtures); n-propyl mercaptan/sodium diethyl dithiocarbamate, benzyl mercaptan/sodium dibenzyl dithiocarbamate (in case of mercaptan-dithiocarbamate mixtures) and n-propyl mercaptan/n-propyl thiourea; n-amyl mercaptan/n-amyl thiourea and isobutyl mercaptan/isobutyl thiourea (in case of mercaptan-thiourea mixtures); the results agree well with those of the respective tabulated mixtures.

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