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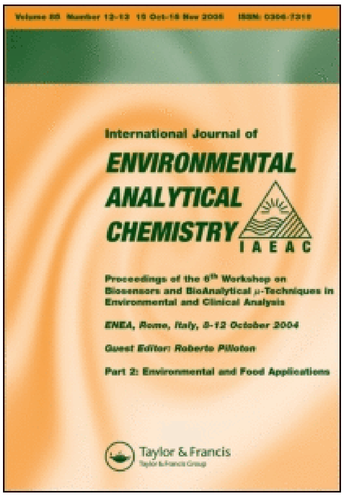

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Gas Chromatographic Determination of Sodium N,N-dialkyl Dithiocarbamates such as their S-*n*-propyl Esters in Industrial Wastewater

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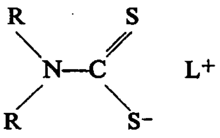
(*Received August 23, 1972*)

KEY WORDS: gas chromatography; alkylation; water-soluble N,N-dialkyl dithiocarbamates; wastewater; quantitative analysis.

A gas chromatographic method for the determination of N,N-dialkyl dithiocarbamates in industrial wastewater at the nanogram level is described. The sample is freeze-dried, extracted with ethanol and then esterified with l-iodopropane. The method is sensitive, specific, and free from interference of metals. The sensitivity of the method is in the order of 1 ng (injected).

INTRODUCTION

Dithiocarbamates are salts of the dithiocarbamic acids



where R_2N- is an ammonia or amine residue.

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The alkali and alkaline earth metal, ammonia and methylamine salts are soluble in water and are usually insoluble in organic solvents. The heavy metal salts are insoluble in water; they are coordinated compounds, some of which are soluble in organic solvents such as chloroform, benzene, and dimethylformamide.

Dithiocarbamates are widely used as fungicides, especially as their alkaline metal complexes, and are utilized in the rubber industry as vulcanization accelerators and antioxidants.

Several methods[1,2] are available for the determination of sodium N,N-dialkyl dithiocarbamates (Na-DTC). Most of the present analytical methods are based on the Clarke method[3] in which the Na-DTC are destroyed in acidic solution to give dialkylamines and carbon disulfide.

Spectrophotometric methods[4,5] have been used for the determination of dithiocarbamate pesticide residues. They are based on the released carbon disulfide. Infrared spectrometry,[6,7] polarographic methods,[8,9] separation methods,[10-12] and tandem GC-MS[13] have also been employed. Some of the methods[2-10] are inadequate for environmental investigations and are subject to interferences in industrial wastewater.

Dithiocarbamates can be readily esterified[12] with any iodoalkane, and the esters formed have sufficient volatility to permit chromatographic separation and determination.

The present paper is part of a more general investigation of the chromatographic behaviour of dithiocarbamates and describes the pre-concentration of Na-DTC from a wastewater stream and the optimum conditions for esterification to an *n*-propyl ester and subsequent quantitative chromatographic determination.

EXPERIMENTAL

Reagents

Sodium N,N-(dimethyl-, diethyl-, and di-*n*-butyl-) dithiocarbamates were UNIROYAL commercial-grade chemicals. Samples were recrystallized from methanol. Sodium N,N- (di-*n*-propyl-, and diisobutyl-) dithiocarbamates were prepared and purified at our laboratories. The 1-iodopropane was obtained from British Drug House Chemical Co., the carbon disulfide was supplied by Baker Chemical Co., and the absolute ethanol was from Consolidated Alcohols Ltd. (min. 99.5%).

Storage of samples

From other experiments carried out at our laboratories[14] it was observed that Na-DTC stability is strictly dependent on pH. It is therefore recommended that samples should be filtered and neutralized immediately after collection.

Pre-concentration procedure

Fifty millilitre of water containing various amounts of Na-DTC was frozen in a 125-ml Erlenmeyer flask of known weight. Periodic swirling of the flask created an enlarged surface area necessary to reduce freeze-drying time to a minimum. The sample was put into a Vir Tis Freeze-Drier, Model Unitrap D-7100, and freeze-dried at −50°C and 0.01 Torr.

S-*n*-Propylation procedure

A freeze-dried sample was dissolved in 25 ml of absolute ethanol and filtered through Whatman No. 1 filter paper. Half a millilitre of 1-iodopropane was added to the filtrate and the mixture was maintained at 50°C for 1 hr. Solvent removal was effected by vacuum distillation. To the residue in the flask a known amount of carbon disulfide was added. Once thoroughly mixed the solution of S-*n*-propyl dialkyl dithiocarbamate in carbon disulfide was diluted to obtain samples of various concentration. The procedure is summarized as follows: The sample (1 gallon) was filtered as soon as possible after collection through a 0.45-micron membrane filter and neutralized with 50% sodium hydroxide solution. A 50-ml sample was freeze-dried. The residue was extracted with two 25-ml portions of absolute ethanol. The solution was transferred into a 100-ml flask. Half a millilitre of 1-iodopropane and a known amount of sodium N,N-di-*n*-propyl dithiocarbamate were added. The mixture was esterified as described above. The excess of 1-iodopropane and ethanol was evaporated on a water bath (at 50°C) and then reduced to dryness under vacuum. The residue was taken up in 500 mcl of CS_2 and 2 mcl was injected on to the column.

Equipment

A Varian Aerograph, Model 1800 dual-column gas chromatograph equipped with a flame ionization detector (FID) and a Model 20 Varian recorder, was used for the study. The stainless steel column of 365 cm length and 2.1 mm i.d., was packed with 10% Apiezon L on Varaport 60 (80–100 mesh). The following chromatographic parameters were used: helium flow rate, 30 ml/min; hydrogen flow rate, 30 ml/min; air flow rate, 300 ml/min; injection port temperature, 270°C; column temperature, 250°C; detector temperature, 250°C. A disc chart integrator, which was built into the recorder, was used to measure the peak areas.

RESULTS AND DISCUSSION

As the concentration of Na-DTC in the industrial wastewater is expected to be in the mcg/l range, a concentration process is necessary prior to their determination. The procedure employed was reported by Sapiro[15] and Kobayashi and Lee.[16] The technique of freeze-drying the industrial waste water as a means of concentrating inorganics and non-volatile organics has been used successfully. This method should effect complete solute recovery in sufficient quantity, without alteration. This criterion essentially dictates that the method be evaluated in terms of the efficiency of recovery with respect to initial solute concentration and degree of preconcentration (Table I).

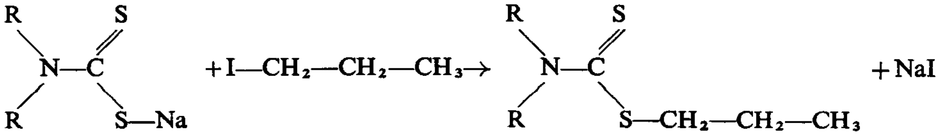
TABLE I

Efficiency of the recovery of Na-DTC by freeze-drying determined by weighing the residue and by gas chromatography

Sample	Known amount (mg)	By weight (mg)	By GC (mg)	Recovery (%) W	Recovery (%) GC
1	1.0	1.05[a]	1.02	105	102
2	1.0	1.03[a]	1.06	103	106
3	5.0	5.1	5.04	102	100.9
4	5.0	5.0	5.02	100	100.5
5	10.0	10.1	10.00	101	100
6	10.0	10.8	10.42	108	104
7	25.0	24.9	25.08	99.6	100.4
8	25.0	24.8	25.08	99.5	100.4
9	50.0	49.9	50.07		100.2
10	50.0	51.0	50.05		100.2

[a] The last decimal place was estimated.

S-*n*-propylation of Na-DTC was studied in order to obtain S-*n*-propyl N,N-dialkyl dithiocarbamates which are volatile and hence can be determined by gas chromatography. The use of 1-iodopropane as the alkylating agent for the preparation of S-substituted *n*-propyl N,N-dialkyl dithiocarbamates is described by the following reaction:



Present work is concerned with the quantitative aspects of this reaction and it will be demonstrated that the reaction proceeded on a stoichiometrically reproducible basis.

It has been reported by Halls[17] that Na-DTC are stable in neutral and alkaline solution but that N-monoalkyl dithiocarbamates may react with hydroxyl ions. The initial step in the decomposition of Na-DTC is therefore the transfer of a proton between the nitrogen and sulphur atoms, as follows:

$$R_2NCS_2^- + H^+ \longrightarrow R_2NH + CS_2$$

The effect of pH of the wastewater during the esterification process was investigated by adjusting the standard 50 ml/l of each Na-DTC to various pH values before freeze-drying. Quantitative recoveries were obtained in the pH range of 6 to 11. At pH 5, the recovery dropped off markedly (Table II).

TABLE II

Effect of pH of water on recovery of Na N,N-dimethyl dithiocarbamate[14]

	pH						
	2	4	5	6	7	8	10
τ^a (min)	0.10	1.33	9.0	34.0	2075	6520	56,000
Recovery (%)	0.10	0.10	32.0	92.0	98	100	100

[a] Half-life time (τ) was calculated from the equation:

$$\tau = \frac{2{,}303}{K} \log 2$$

Effect of pH of industrial wastewater on recovery of Na-DTC esterification yield at various levels was studied by esterifying various amounts of Na-DTC (from 0.1 ppm to 100 ppm) and comparing their corresponding yields. The yield was consistent over the range of 1 ng to 100 ng of injected DTC expressed on the starting concentration. The structure of the ester formed in the reaction was studied by infrared, n.m.r. and mass spectrometry. The characteristic values for S-*n*-propyl N,N-dialkyl dithiocarbamates are given in Table III.

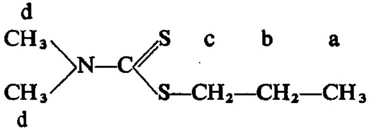
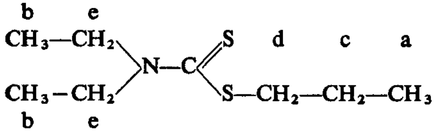
Results obtained for the optimum time at 50°C for the esterification showed that 60 min is sufficient for the esterification (Table IV).

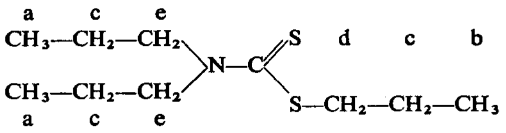
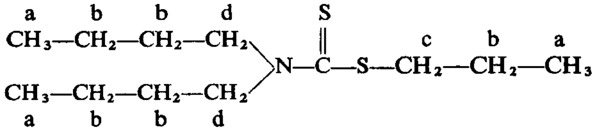
Gas chromatographic separation

The S-*n*-propyl N,N-di-*n*-propyl dithiocarbamate known to be absent in the mixture of the industrial wastewater was chosen as an internal standard. It was expected that thiuram and metallic complexes of DTC such as iron(III),

TABLE III

Analytical properties of S-propyl, N,N-dialkyl dithiocarbamates

Compound	Infrared (cm^{-1})	n.m.r. (δ)	m/e	MS % RI	%Σ
S-Propyl, N,N-dimethyl dithiocarbamate	1510	a = 1.01 (tr)[a]	15	5.1	2.1
	965	b = 1.4–2.0 (mu)	42	7.6	3.1
		c = 3.25 (tr)	74	5.7	2.4
		d = 3.48 (p.r.)	88	100.0	40.1
			119	25.3	10.3
			163	24.6	10.1
S-Propyl, N,N-diethyl dithiocarbamate	1505	a = 0.01 (tr)	29	37.6	5.7
	975	b = 1.28 (tr)	41	12.0	1.8
		c = 1.5–2.0 (mu)	88	62.4	9.4
		d = 3.26 (tr)	116	100.0	15.1
		e = 3.5–4.2 (p.r.)	149	33.9	5.1
			191	27.3	4.1

S-Propyl, N,N-di-*n*-propyl dithiocarbamate 	1505 1000	a = 0.94 (tr) b = 1.02 (tr) c = 1.4–2.1 d = 3.26 (tr) e = 3.4–4.1 (ur)	42 44 61 103 145 178 219	32.1 100.0 19.8 27.3 37.8 15.3 9.4	8.3 25.9 5.1 7.0 9.8 7.0 2.4
S-Propyl, N,N-di-*n*-butyl dithiocarbamate 	1505 1000	a = 0.8–1.2 b = 1.2–2.0 c = 3.27 (tr) d = 3.4–4.2 (pr)	41 43 57 172 205 247	54.1 51.1 69.9 100.0 34.5 30.0	6.6 6.2 8.5 12.2 4.2 3.6

[a] tr —triplet
mu —multiplet
p.r. —poorly resolved
ur —unresolved.

TABLE IV
Effect of time for esterification of DTC

Time (min)	DMDTC (mg)	DEDTC (mg)
19.5	47.4	43.3
34.0	51.0	43.3
47.5	52.3	43.2
62.0	51.4	43.3
125.0	51.5	43.4
Theoretical yield	52.0	45.0
Per cent (related to 62 min)	98.9	96.2

zinc(II), and copper(II) could also be concentrated by the present procedure, and therefore their interferences were studied. No interference was noted for the thiuram. However, Fe(III), Zn(II), Cu(II), and K^+ metallic complexes of DTC and its ammonium salt will be replaced by the same aklylation process as the sodium salt.

Figure 1 illustrates the relative retention of the *n*-propyl esters of DTC. Detector responses have been reasonably linear to the amount of DTC ester up to at least 100 mcg. Since the esterification gave a consistent yield over the range studied, the peak areas were found to be satisfactory, after a correction

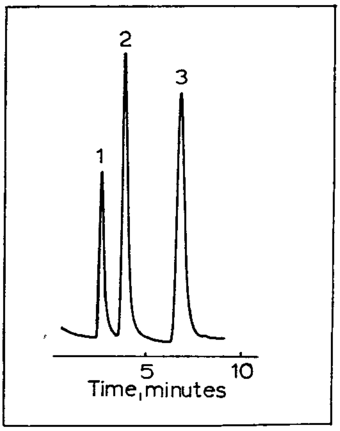


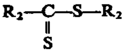
FIGURE 1 Typical chromatogram showing separation of S-propyl esters of dithiocarbamates at the 5-ppm level. 1, N,N-dimethyl dithiocarbamate; 2, N,N-diethyl dithiocarbamate; 3, N,N-di-*n*-butyl dithiocarbamate.

of the area by relative weight response factor (RWR) of each DTC. S-*n*-propyl N,N-di-*n*-propyl dithiocarbamate was assumed to be equal to 1. RWR factors are given with the Kováts retention indices in Table V.

TABLE V

Kováts' retention indices for S-alkyl N,N-dialkyldithiocarbamates, separated on an Apiezon L column[a]

Sample	R_1	R_2	I^{250}	RWR
1	$(CH_3)_2N$-	*n*-C_3H_7	1492	0.482
2	$(C_2H_5)_2N$-	-C_3H_7	1569	0.680
3	*n*-$(C_3H_7)_2N$-	-C_3H_7	1750	1.000
4	iso-$(C_4H_9)_2N$-	-C_3H_7	1786	—
5	*n*-$(C_4H_9)_2N$-	-C_3H_7	1867	1.235
6	$(CH_3)_2N$-	-C_2H_5	1177	
7	$(C_2H_5)_2N$-	-C_2H_5	1257	
8	*n*-$(C_4H_9)_2N$-	-C_2H_5	1541	
9	$(CH_3)_2N$-	-CH_3	1082	
10	$(C_2H_5)_2N$-	-CH_3	1116	
11	*n*-$(C_4H_9)_2N$-	-CH_3	1418	

[a] General structure 

$R_2{-}\underset{\underset{S}{\|}}{C}{-}S{-}R_2$

Accuracy and precision

The precision test[18] of the methods was evaluated from the results of five replicate analyses of a 1000-ml sample to which a known amount of each DTC was added (Table VI). The DTC's injected were equivalent to 1 ng. At this level the standard deviation calculated was lower than 1 and the coefficient of variation ± 4%.

TABLE VI

Precision test of the method for various amounts of dithiocarbanates

	Na-DMDTC (mg/l)			Na-DEDTC (mg/l)		
Sample	added	found[a]	S.D.	added	found[a]	S.D.
1	102.00	98.660	0.766	144.00	135.20	2.980
2	51.00	48.760	0.986	72.00	69.38	1.082
3	10.20	9.880	0.083	14.40	13.66	0.207
4	5.10	4.680	0.363	7.20	6.92	0.130
5	1.02	0.938	0.122	1.44	1.34	0.063

[a] Mean of 5 replicate determinations.

Acknowledgements

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