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Short Communication

Direct gas chromatographic analysis of O,O-dimethyl- and O,O-diethyldithiophosphoric acids and identification of their by-products

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ABSTRACT

Direct gas chromatographic methods for the quantitative analysis of O,O-dimethyl- and O,O-diethyldithiophosphoric acids using a 5% SE-30 column and flame ionization detection are described. The separation and identification of by-products were performed by spiking with known standards. The minimum detectable levels were 17.5 ppm for O,O-dimethyl- and 15.5 ppm for O,O-diethyldithiophosphoric acids.

INTRODUCTION

The commercial applications of O,O-dialkyldithiophosphoric acids as raw materials for producing pesticides, lubricant additives and plastic stabilizers are widely known. In spite of these applications, limited information is available regarding their analyses. Methods of analysis which have been applied include acidimetric titration [1–3], colour comparison after alkali decomposition [4,5] and infrared and NMR spectrometry [6,7]. Moreover, two publications have described gas chromatography (GC) after esterification by either diazoalkane [8,9] or trialkyl phosphites [10], since the acids could not be analysed owing to their decomposition at high temperatures.

As we are involved in the synthesis of O,O-dimethyldithiophosphoric acid (DMDTPA) by the reaction of methanol with phosphorus pentasulphide, efforts were directed to developing a GC method for the assay of DMDTPA after distillation. Since our objective was to develop a simple and fast GC method for analysing direct DMDTPA test samples, we carried out thermal stability studies on DMDTPA and O,O-diethyldithiophosphoric acid (DEDTPA) in normal air and in inert helium under fixed time and temperature conditions; these studies indicated they are safe and stable materials. The stationary liquid phase SE-30 was selectively found to be suitable for the separation and identification of by-products of DMDTPA and DEDTPA by spiking, after priming the column for optimization [11].

The GC determinations of DMDTPA and DEDTPA with flame ionization detection (FID) gave reproducible results. To our knowledge, this is the first report on the direct GC analysis of intact, underivatized O,O-dialkyldithiophosphoric acids. The method described here is rapid, sensitive and convenient for monitoring.

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EXPERIMENTAL

Materials

Analytical-grade dichloromethane and absolute ethanol were obtained from Frutarom, Israel. Standard and technical grades of DMDTPA, DEDTPA and by-products, such as O,O,O-trimethylphosphorothioate (TMPT), O,O,S-trimethylphosphorodithioate (TMPDT), O,O-diethylphosphoroite (DEPT) and O,O,S-triethylphosphorodithioate (TEPDT) were supplied by Makhteshim Chemical Works; O,O-dimethylphosphoroite (DMPT) was supplied by Cheminova, Lenwig Denmark. All stationary liquid phases and supports used in this investigation were obtained from Alltech Assoc. All other chemicals were of analytical grade.

Chromatographic conditions

A Varian Model 3700 gas chromatograph with a flame ionization detector equipped with a 4 ft. × 3 mm I.D. glass column packed with a 5% SE-30 on Gas Chrom Q (80–100 mesh) support was used. The column temperature was maintained at 75°C for DMDTPA and at 85°C for DEDTPA, the injector port at 120°C and the detector at 240°C. The carrier gas was helium at a flow-rate of 65 ml/min. A 5-μl sample was injected each time by means of a 10-μl Hamilton syringe. Chromatograms and peak areas were recorded on a Spectra-Physics Model 4290 integrator. For the titrimetric method, a Metrohm Model E-415 semiautomatic titrator and Model 691 pH meter were used.

Titrimetric method

Weigh accurately about 4–5 g of DMDTPA or DEDTPA sample into a 100-ml beaker containing a magnetic stirrer and add 10 ml of absolute ethanol. Titrate with 1 *M* sodium hydroxide solution to pH 3.5.

DMDTPA or DEDTPA (%) = [ml of 1 *M* sodium hydroxide × mol.wt. of DMDTPA (or DEDTPA)]/(weight of sample × 10)

Stability studies

About 10–12 g of technical-grade DMDTPA (or DEDTPA) were placed in a 100-ml, two-neck, round-bottom, quick-fit flask fitted with a condenser carrying a calcium chloride drying tube on the top. A helium gas bubbling tube was fixed to the second neck of the flask. After flushing the helium through the system for 5 min, the flask was immersed in a water bath preheated to 95°C and heating continued. At intervals of 10 and 30 min, the flask was removed and cooled in ice-water and the sample was removed for weighing. The concentration of this sample was determined by the titrimetric method described above. Similar experiments were carried out without bubbling the helium gas. The results obtained are shown in Table I.

Column priming for optimization

First set all the GC conditions as described above. Before starting the routine analysis, load the column by injecting large quantities (10–15 × 5 μl) of a concentrated solution (15%) of DMDTPA (or DEDTPA). Continue operating the system until the baseline reaches its normal position, which takes about 30–40 min.

Using this treatment, optimization is expressed in terms of the ability of the stationary phase to elute free acids with good peak symmetry.

TABLE I

TITRIMETRIC RESULTS OF STABILITY STUDIES ON DMDTPA AND DEDTPA IN AIR AND HELIUM

Average values obtained from duplicate analyses.

Dithiophosphoric acid	Original concentration (%)	Concentration at 95°C (%)		
		In normal air For 10 min	In inert helium	
			For 10 min	For 30 min
DMDTPA	97.33	96.91	97.10	97.06
DEDTPA	98.70	98.37	98.43	98.08

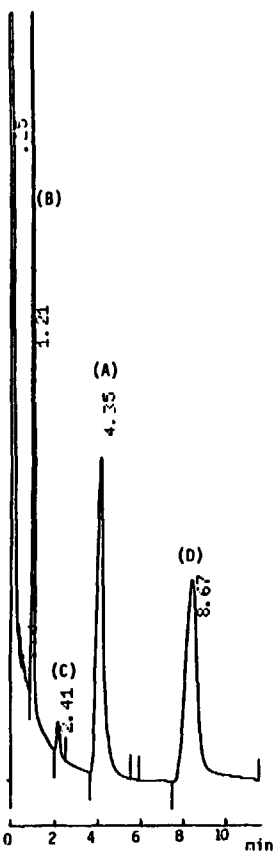

Fig. 1. Chromatogram for comparison with Fig. 2 after spiking with known standards of by-products such as: (A) DMDTPA, (B) O,O-dimethylphophorothioite (DMPT) [$(CH_3O)_2PSH$], (C) O,O,O-trimethylphosphorothioate (TMPT) [$(CH_3O)_3PS$] and (D) O,O,*S*-trimethylphosphorodithioate (TMPDT) [$(CH_3O)_2PS \cdot SCH_3$].

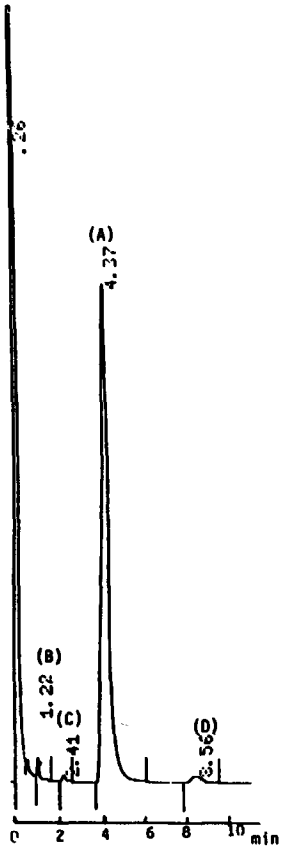

Fig. 2. Chromatogram showing the separation of O,O-dimethyldithiophosphoric acid (DMDTPA) [$(CH_3O)_2PS \cdot SH$], peak A, which contains small impurities of by-products B, C and D in standard material.

Calibration curves

Standard solutions for linearity six different concentrations in the range 50–450 mg for DMDTPA and 50–405 mg for DEDTPA were prepared, dispensed into 100-ml volumetric flasks and dissolved in dichloromethane.

Sample preparation for GC assaying

For regular analysis, duplicate weights of standard (*ca.* 250 mg) and sample (*ca.* 300 mg) were placed in 100-ml volumetric flasks and dissolved in dichloromethane. Injections of 5 μl each were made in the sequence standard then sample.

Identification of by-products by spiking

A 5-ml sample of a 0.1% solution in dichloromethane of each known by-product, such as TMPT, TMPDT and DMPT, was spiked with 25 ml of 0.3% DMDTPA in dichloromethane and injected to detect the elution of spiked peaks. Fig. 1 shows the general profile of the three by-products obtained, and their identity was confirmed by comparison with known samples in Fig. 2.

Similar attempts were made to indentify two by-products observed in DEDTPA, which appeared to be DEPT and TEPDT, as shown in Fig. 3.

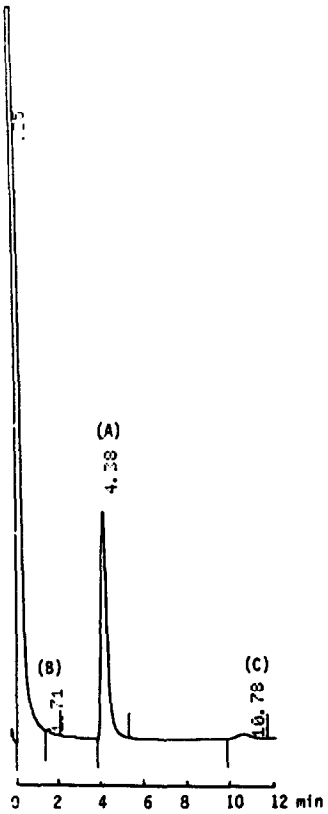

Fig. 3. Chromatogram showing the separation of standard (A) O,O-diethyldithiophosphoric acid (DEDTPA) [$(C_2H_5O)_2PS \cdot SH$] from the two small by-product impurities which were confirmed by spiking as (B) O,O-diethylphosphorothioite (DEPT) [$(C_2H_5O)_2PSH$] and (C) O,O,*S*-triethylphosphorodithoate (TEPDT) [$(C_2H_5O)_2PS \cdot SC_2H_5$].

RESULTS AND DISCUSSION

Information on stability studies by Cheminova [3] has revealed that DMDTPA decomposes by 50% and DEDTPA by 10% upon storing at 50°C for three weeks. For our purpose, it was imperative that the products could be distilled under vacuum as stable materials in order to analyse them by GC as stable materials if heated for a short time inert helium. Accordingly, the results of our stability studies also indicated that no significant changes in the concentrations of DMDTPA and DEDTPA were observed on heating at 95°C in air for 10 min and in helium for up to 30 min (Table I). These finding encouraged us to proceed to the direct GC analysis of DMDTPA and DEDTPA in inert helium under fixed time and temperature conditions for peak elutions.

TABLE II

COMPARISON BETWEEN RESULTS OBTAINED BY GC AND TITRIMETRIC METHODS

Average values obtained from duplicate analyses.

Sample No.	Concentration (%)	
	GC	Titration
DMDTPA		
1	92.81	94.53
2	91.84	94.71
3	93.27	95.02
4	97.42	96.93
5	96.02	96.48
6	96.24	96.86
DEDTPA		
1	98.43	98.51
2	98.13	98.43
3	97.87	98.27

Various stationary liquid phases for GC were examined for the separation of by-products contained in the technical DMDTPA and DEDTPA samples, for example DEGS, DC-550, OVs-17/101/210 and SE-30. Of these, the last column (5% SE-30 on Gas Chrom Q support) gave the most satisfactory separations with a good symmetry in all the peaks in less than 10–12 min, but only after the optimization of the stationary phase as described above. Using this procedure, multiple determinations of commercial DMDTPA and DEDTPA samples gave reproducible results; some of them are shown in Table II.

Since the GC method was found to be very efficient at separating the by-products from the main peaks of DMDTPA and DEDTPA, the assay results were compared with those of the titrimetric method (Table II). Most of results obtained by GC are slightly lower than those obtained by titrimetry, indicating that there was no interference from the by-products present, whereas the titrimetric results are the combined values of free acids such as DMDTPA and DMPT (or DEDTPA and DEPT) and the hydrolysis products of any included esters. The correlation coefficients for DMDTPA and DEDTPA were 0.9984 and 0.9972, respectively, and the relative standard deviations were ± 0.7% (n =

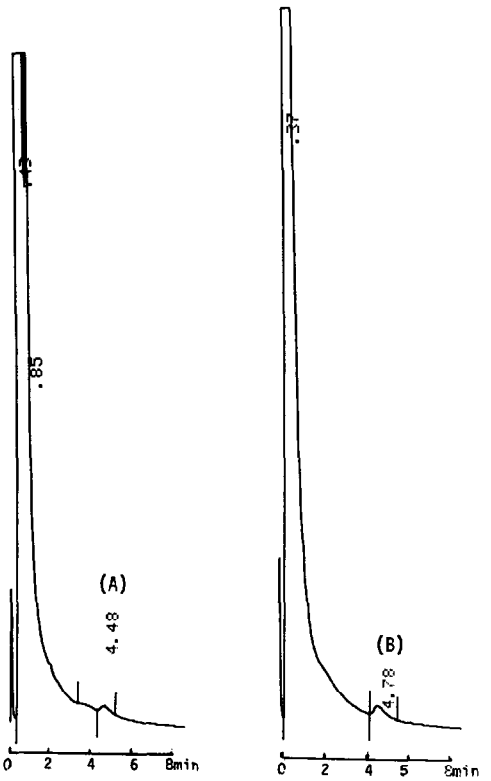

Fig. 4. Chromatogram showing the minimum detectable limit of DMDTPA (A) at 17.5 ppm ($8.5 \cdot 10^{-6}$ mg) and DEDTPA (B) at 15.5 ppm ($7.5 \cdot 10^{-6}$ mg) levels.

8) and ± 0.9% (n = 9), respectively, indicating that the GC method is precise and reproducible.

Tentative identification of the by-products of DMDTPA was accomplished by spiking the samples with known compounds and comparing the peaks obtained with those of the original impurities, as shown in Figs. 1 and 2. Similarly, two by-products in DEDTPA were also tentatively identified, as described in Fig. 3.

Determinations of DMDTPA and DEDTPA at the ppm level were achieved using FID at a sensitivity of 10^{-11}. At this sensitivity, it was possible to detect (signal-to-noise ratio > 3) 17.5 ppm ($8.5 \cdot 10^{-6}$ mg) DMDTPA and 15.5 ppm ($7.5 \cdot 10^{-6}$ mg) DEDTPA, as shown in Fig. 4, and to quantitatively analyse samples containing ppm amounts by comparing peak height measurements with standards.

In conclusion, the present GC method is reproducible and rapid, and the availability of the direct GC technique in analytical laboratories represents a valuable alternative to titrimetric and esterification procedures.

REFERENCES

1 M. I. Kabachuik and T. A. Mastryukova, *Otdel. Khim. Nauk.*, (1952) 727; *C.A.*, 47 (1953) 9909a.
2 P. F. Hu and W. Y. Chen, *Hua Hsueh Hsueh Pao*, 22 (1956) 215; *C.A.*, 52 (1958) 7186c.
3 *Commercial Data Sheets on MP-1 and EP-1*, Cheminova, Lemvig, 1980.
4 S. D. Upham, *J. Assoc. Off. Agric. Chem.*, 43 (1960) 360.
5 M. T. H. Regab, *J. Assoc. Off. Agric. Chem.*, 50 (1967) 1088.
6 N. Oi and H. Tadeka, *Bunseki Kagaku*, 16 (1967) 257, *C.A.*, 54 (1967) 96659d.
7 A. E. Lippman, *J. Org. Chem.*, 31 (1966) 471.
8 L. Nebbia and V. Belloti, *Chim. Ind.*, 52 (1970) 369, *C.A.*, 73 (1970) 72854m.
9 Z. Frobe, B. Stengl, V. Drevenkar and A. Deljac, *J. Chromatogr. Sci.*, 28 (1990) 269.
10 K. Imamura and T. Arai, *Bunseki Kagaku*, 19 (1970) 653, *C.A.*, 73 (1970) 72855n.
11 D. M. Ottenstein and W. R. Supina, *J. Chromatogr.*, 91 (1971) 119, and references cited therein.