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ETHYLATION OF INORGANIC ANIONS, PHENOLS AND CARBOXYLIC ACIDS FOR GAS CHROMATOGRAPHIC DETERMINATION

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SUMMARY

Some inorganic anions, phenols and carboxylic acids were converted into their ethyl derivatives by reaction with diethyl sulphate, and the ethyl derivatives then determined by gas chromatography with flame ionization detection. For phenols and carboxylic acids, 18-crown-6 was employed as a catalyst for the derivatization reaction. It was observed that 18-crown-6 significantly increases the derivatization yields of phenols and carboxylic acids. From a comparison of this ethylation procedure with the corresponding methylation using dimethyl sulphate, it is concluded that ethylation is more suitable for the determination of sulphide, iodide, phenols and carboxylic acids.

INTRODUCTION

Many gas chromatographic (GC) methods involve the use of derivatization prior to analysis[1–4]. Although this procedure is frequently used for the determination of compounds which are not accessible to direct GC determination, its application to the determination of inorganic anions is as yet relatively unexplored[4–6].

We have investigated the determination of inorganic anions by GC with derivatization[7–10]. In our recent study[9], some inorganic anions were converted into their methyl derivatives by reaction with dimethyl sulphate, etc., and the derivatives were determined by GC with a flame ionization detector (FID). We have also reported a method for determining cyanide (CN^-) or thiocyanate (SCN^-) at trace levels by methylation with dimethyl sulphate and flame thermionic GC[10].

It is interesting to study the ethylation of inorganic anions with diethyl sulphate for GC determination. In this paper, we describe a comparison of methylation and ethylation of some inorganic anions in order to obtain the optimum derivatization system for the GC determination.

Many methods have been published for the GC determination of phenols and carboxylic acids[1–4]: methylation with diazomethane, silylation and acylation have frequently been used. Crown ethers have been used as phase transfer catalysts in the derivatization of organic substances[11–13]. We have also investigated the GC determi-

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nation of phenols and carboxylic acids by using dimethyl or diethyl sulphate and 18-crown-6. The effect of 18-crown-6 on the methylation or ethylation is also reported in the present paper.

EXPERIMENTAL

Apparatus

A Yanagimoto G-180 gas chromatograph equipped with a dual FID (Yanagimoto, Kyoto, Japan) was used. The column and column temperature employed were dependent on the ethyl derivative of the anion; details are given in Table I. The column packing materials, Porapak Q (80–100 mesh) and T (80–100 mesh), were purchased from Waters Assoc. (Milford, MA, U.S.A.), and 5% PEG-HT on Uniport HP (60–80 mesh) and 10% dinonyl phthalate on Chromosorb W (60–80 mesh) were from Gasukuro Kogyo (Tokyo, Japan). Nitrogen was used as the carrier gas at a constant flow-rate of 30 ml/min: the hydrogen and air pressures were 0.5 and 1.0 kg/cm^2, respectively. The injection port temperature was maintained at 250°C. Peak areas were measured by a Chromatopac E1A digital integrator (Shimadzu, Kyoto, Japan).

TABLE I

ETHYLATION AND GAS CHROMATOGRAPHIC CONDITIONS

Stainless-steel column (3 mm I.D.). Column packing: Q = Porapak Q (1 m); T = Porapak T (1 m); PEG = PEG-HT (2 m); DNP = dinonyl phthalate (2 m).

Anion	*Ethyl derivative*	*Extraction (or reaction) solvent*	*Column*	*Column temp. (°C)*
CN^-	C_2H_5CN	Dichloromethane	PEG	60
SCN^-	C_2H_5SCN	Dichloromethane	PEG	100
I^-	C_2H_5I	1,2-Dichloroethane	T	175
Br^-	C_2H_5Br	1,2-Dichloroethane	Q	150
S^{2-}	$(C_2H_5)_2S$	Chloroform	Q	200
C_6H_5OH	$C_6H_5OC_2H_5$	(1,2-Dichloroethane)	PEG*	110*
C_3H_9COOH	$C_3H_9COOC_2H_5$	(Acetonitrile)	DNP*	110*

* In the determination of other phenols or carboxylic acids, the column and column temperature used are shown in Figs. 2 and 3.

Materials

All reagents were of analytical reagent grade and were used without further purification unless otherwise stated. Diethyl sulphate and dimethyl sulphate were commercial grade reagents (Tokyo Kasei Kogyo, Tokyo, Japan). Deionized water, dichloromethane, chloroform, 1,2-dichloroethane and acetonitrile were distilled before use for analysis. All phenols and carboxylic acids were purified by distillation or recrystallization. Solutions of inorganic anions were prepared by dissolving their potassium or sodium salts in water.

Procedure

Determination of inorganic anions. The procedure is analogous to that using

dimethyl sulphate[9], unless otherwise stated. The concentrations of KOH aqueous solutions (0.5 ml) which were added before the diethyl sulphate were 0.5 *M* in the determination of CN^- and 4.0 *M* in that of sulphide (S^{2-}). The extraction solvents employed in each case are given in Table I.

Determination of phenols. To 1.0 ml of an aqueous solution of phenols in a reaction vessel were added 0.5 ml KOH (0.5 *M*) and 1.0 ml 1,2-dichloroethane solution containing diethyl sulphate (0.1 *M*) and 18-crown-6 (0.2 *M*). The vessel was shaken for 30 min in an incubator at 70°C. At the end of the reaction period, after cooling, the organic layer was separated from the aqueous layer. An aliquot (1.0 μl) of the organic layer was injected into the gas chromatograph and the resulting ethyl derivatives were determined with a FID.

Determination of carboxylic acids. A 0.1-ml volume of K_2CO_3 (0.5 *M*) aqueous solution was added to 1.0 ml of an aqueous solution of carboxylic acids. After mixing, the solution was carefully evaporated to dryness. To the residue were added 0.05 ml diethyl sulphate and 2.0 ml acetonitrile solution containing 0.05 *M* 18-crown-6. The mixture was then stirred at room temperature for 30 min. After the reaction, an aliquot (1.0 μl) of the mixture was subjected to GC analysis.

RESULTS AND DISCUSSION

Ethylation of inorganic anions

In order to obtain the optimum ethylation conditions, the effects of the concentration of KOH used, reaction temperature and reaction time on the ethylation yield were investigated for each inorganic anion. From the results, the reaction temperature and reaction time were fixed at 70°C and 30 min, respectively, for ethylation of each anion. The optimum concentration of KOH used in the ethylation of each anion was the same as that used in methylation, Table II, except for the case of S^{2-}. For the latter the optimum KOH concentration was 4.0 *M* in ethylation whereas it was 6.0 *M* (0.5 ml) in methylation. The yield of ethylation of each anion was determined as

TABLE II

DERIVATIZATION YIELDS FOR INORGANIC ANIONS

Sample: 0.10 *M* aqueous solution of inorganic anion. Yields are mean ± S.D. of five replicate analyses.

Anion	*Added KOH**	*Yield (%)*	
		Methylation	*Ethylation*
CN^-	0.5 *M*, 0.5 ml	53.5 ± 1.5	17.4 ± 0.3
SCN^-	None	104.3 ± 2.1	99.8 ± 2.6
I^-	None	73.2 ± 1.8	85.4 ± 1.8
Br^-	None	*ca.* 65**	47.2 ± 1.6
S^{2-}	6.0 *M*, 0.5 ml	42.3 ± 0.8	–
S^{2-}	4.0 *M*, 0.5 ml	–	79.8 ± 1.6

* The optimum derivatization condition is given.

** This value could not be obtained exactly because of the high volatility of the product, methyl bromide.

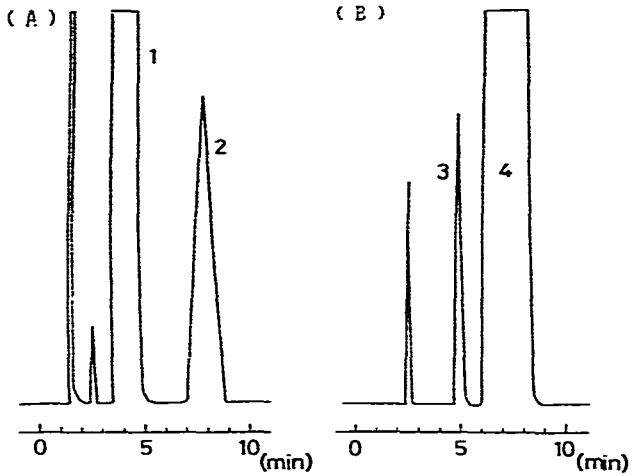

Fig. 1. Gas chromatograms of ethylation products of S^{2-} (A) and I^- (B). GC conditions as in the Experimental section and Table I. Peaks: 1 = chloroform (solvent); 2 = diethyl sulphide; 3 = ethyl iodide; 4 = 1,2-dichloroethane (solvent).

previously reported[9]. The ethylation yields and the yields of methylation using dimethyl sulphate are also given in Table II.

Some anions other than those shown in Table II are also ethylated with diethyl sulphate, for example, nitrite and chloride. However, the yields are fairly low under a variety of derivatization conditions. Ethylation reactions of these anions were not further investigasted because the low yields will not be of practical use for GC determination of the anions.

From Table II, it is seen that both methylation and ethylation of SCN^- proceed quantitatively and that the methylation yields of CN^- and bromide (Br^-) are higher than the ethylation yields of the corresponding anions. On the other hand, iodide (I^-) and S^{2-} have higher ethylation than methylation yields. Therefore, methylation is more suitable for the determination of CN^-, SCN^- and Br^-, whereas ethylation is preferred for S^{2-} and I^-.

Fig. 1 shows typical gas chromatograms of the products of ethylation of S^{2-} and I^- using diethyl sulphate under the optimum conditions described in the Experi-

TABLE III

DERIVATIZATION YIELDS OF PHENOL

Sample: phenol (0.01 *M*). Yields are mean ± S.D. of five replicate analyses.

Reaction temp. (°C)	*18-Crown-6*	*Yield (%)*	
		Methylation	*Ethylation*
70	Added	90.8 ± 1.0	92.3 ± 2.3
	–	81.7 ± 0.5	54.2 ± 0.5
Room temp.	Added	53.8 ± 1.9	2.9 ± 0.1
	–	17.6 ± 1.1	0.9 ± 0.1

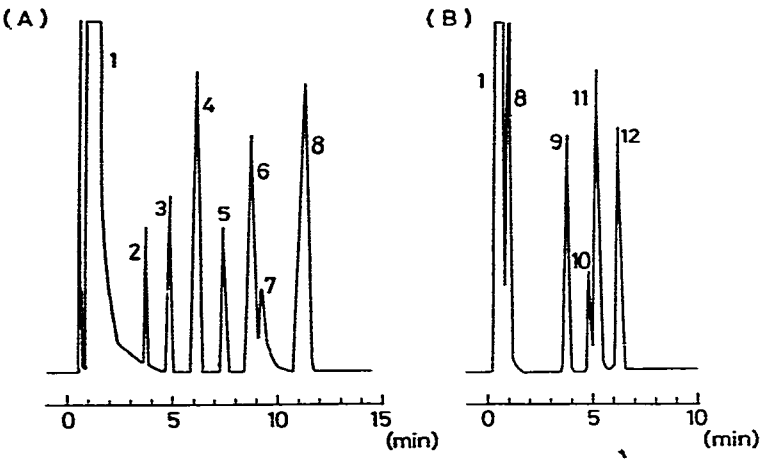

Fig. 2. Gas chromatograms of ethylation products of phenols. Column: 5% PEG-HT (2 m × 3 mm I.D.). Column temperatures: 110°C (A); 210°C (B). Peaks: 1 = 1,2-dichloroethane; 2 = phenol; 3 = *o*-cresol; 4 = *m*-, *p*-cresol and *o*-ethylphenol; 5 = 2,4-xylenol; 6 = *m*- and *p*-ethylphenol; 7 = 3,5-xylenol; 8 = diethyl sulphate; 9 = *m*-nitrophenol; 10 = *o*-nitrophenol; 11 = α- and β-naphthol; 12 = *p*-nitrophenol.

mental section. In each case, a calibration curve was constructed by plotting the peak area of the ethyl derivative *vs.* the concentration of the anion in aqueous solution. The calibration curves were straight lines in the concentration range of 0.1–1.0 mg/ml, passing through the origin.

Derivatization of phenols

In the derivatization of phenols, 18-crown-6 was used as a catalyst. Methylation and ethylation of phenol were performed in the presence and absence of 18-crown-6, both at room temperature and 70°C. The derivatization yields obtained are given in Table III. It is seen that the use of 18-crown-6 increases the derivatization yield in each case. Also ethylation using 18-crown-6 at 70°C gives the highest and most nearly quantitative yield. Therefore, the procedure described in the Experimental section was selected. Fig. 2 shows typical gas chromatograms obtained in the analysis of an aqueous mixture of several phenols. The calibration plots for phenol were linear in the range of 0.1–1.0 mg/ml.

TABLE IV

DERIVATIZATION YIELDS OF CARBOXYLIC ACID

Sample: *n*-valeric acid (0.01 *M*). Yields are mean ± S.D. of five replicate analyses.

Reaction temp. (°C)	*18-Crown-6*	*Yield (%)*	
		Methylation	*Ethylation*
60	Added	99.9 ± 3.3	99.7 ± 0.7
	–	90.3 ± 1.9	83.5 ± 18.1
Room temp.	Added	98.1 ± 2.5	99.6 ± 4.9
	–	53.9 ± 6.6	25.1 ± 2.7

Derivatization of carboxylic acids

Methylation or ethylation of carboxylic acids in aqueous solution gives fairly low yields. Therefore, the derivatization of carboxylic acids was performed in acetonitrile solution after evaporation of an aqueous alkaline solution of the acids, as described in the Experimental section. 18-Crown-6 was also used as the catalyst in these derivatizations. Derivatization yields of *n*-valeric acid were determined under various conditions. From the results in Table IV, it is apparent that 18-crown-6 improves the derivatization yields of *n*-valeric acid, and that this acid is quantitatively methylated or ethylated in the presence of 18-crown-6 even at room temperature. Fig. 3 shows typical gas chromatograms obtained by treating an aqueous mixture of carboxylic acids (C_1–C_7) according to the procedure described in the Experimental section. Higher carboxylic acids can also be detected by this GC method. The calibration plots for *n*-valeric acid were linear in the range of 0.1–1.0 mg/ml.

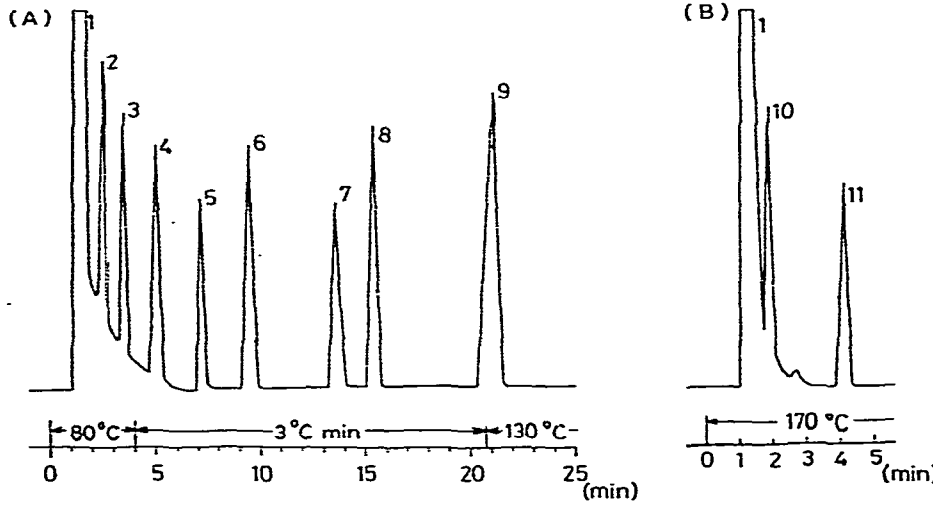

Fig. 3. Gas chromatograms of ethylation products of carboxylic acids. Columns: 10% dinonyl phthalate (2 m × 3 mm I.D.) (A); Porapak Q (1 m × 3 mm I.D.) (B). Peaks: 1 = acetonitrile; 2 = propionic acid; 3 = isobutyric acid; 4 = *n*-butyric acid; 5 = isovaleric acid; 6 = *n*-valeric acid; 7 = isocaproic acid; 8 = *n*-caproic acid; 9 = *n*-heptanoic acid; 10 = formic acid; 11 = acetic acid.

CONCLUSIONS

By ethylation and GC–FID, S^{2-}, I^-, phenol and *n*-valeric acid can be determined at concentrations of 0.1–1.0 mg/ml. It is not expected that this method can be directly applied to these species at much lower levels such as in environmental samples so long as a FID is used. The use of a more highly sensitive detector would enable the determination of S^{2-} or I^- at trace levels.

We have investigated the GC determination of S^{2-} at trace levels by use of ethylation with diethyl sulphate and a flame photometric detector (FPD), and the results will be reported in the near future[14]. Iodide at trace levels can also be determined by this derivatization and electron capture GC. Work is currently being undertaken to apply this method to the simultaneous determination of I^- and Br^- at trace levels by using an electron-capture detector (ECD).

Phenol and *n*-valeric acid are methylated or ethylated almost quantitatively in the presence of 18-crown-6. In general, methyl or ethyl derivatives of phenols and carboxylic acids have no substituents which respond to highly sensitive detectors (*e.g.*, ECD, FPD, flame thermionic detector, etc.). This method, therefore, needs a pre-concentration step in order to determine phenols or carboxylic acids at trace levels. Because certain kinds of phenols, such as nitrophenols and chlorinated phenols frequently found in the environment, have substituents yielding high ECD responses, their ethyl derivatives should be detectable at trace levels by GC–ECD.

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