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PENTAFLUOROBENZYL *p*-TOLUENESULPHONATE AS A NEW DERIVATIZING REAGENT FOR GAS CHROMATOGRAPHIC DETERMINATION OF ANIONS

KOICHI FUNAZO*

Department of Chemistry, Osaka Prefectural Technical College, Saiwai-cho 26-12, Neyagawa, Osaka 572 (Japan)

MINORU TANAKA, KAZUHIRO MORITA, MITSUO KAMINO and TOSHIYUKI SHONO

Department of Applied Chemistry, Faculty of Engineering, Osaka University, Yamada-oka, Suita, Osaka 565 (Japan)

and

HSIN-LUNG WU

School of Pharmacy, Kaohsiung Medical College, Kaohsiung 800 (Taiwan)

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SUMMARY

A new derivatizing agent, pentafluorobenzyl *p*-toluenesulphonate, has been synthesized, which is designed to enhance the volatility of analytes and introduce a detector-oriented tag into the molecules for gas chromatography (GC) with electron-capture detection. The derivatization of several inorganic anions was studied, and a new GC method for their simultaneous determination has been developed. Bromide, iodide, cyanide, thiocyanate, nitrite, nitrate and sulphide can be simultaneously derivatized to their pentafluorobenzyl derivatives using tetra-*n*-amylammonium chloride as the phase transfer catalyst. The derivatives were subsequently determined by GC with flame ionization detection. This method has also been applied to the determination of carboxylic acids or phenols, the derivatives of which were identified using mass spectrometry. The derivatives from bromide, iodide, cyanide, thiocyanate, nitrite, nitrate and sulphide were pentafluorobenzyl bromide, pentafluorobenzyl iodide, pentafluorobenzyl cyanide, pentafluorobenzyl thiocyanate, α -nitro-2,3,4,5,6-pentafluorotoluene, pentafluorobenzyl nitrate and bis(pentafluorobenzyl) sulphide, respectively. The effects of added acid or base, and of the reaction time, on the pentafluorobenzylation are discussed.

INTRODUCTION

Gas chromatography (GC) is a valuable technique for determining volatile organic and inorganic compounds because of its unmatched separating power. By use of derivatization, furthermore, this technique can be extended to the determination of non-volatile and thermally unstable compounds. Derivatization has been used not only to increase the volatility of compounds but also to introduce a detec-

tor-oriented tag into the molecules. Electron-capture detection (ECD) has been studied in conjunction with derivatization, due to its very high sensitivity¹, and various derivatizing agents have been developed for electron-capture GC.

We are interested in GC of inorganic anions, which is still a relatively new and far from thoroughly investigated discipline because of the non-volatility of inorganic anions and the failure to find suitable methods of chemical derivatization. Nevertheless, some procedures have been reported for GC of inorganic anions²⁻⁵. The majority of these procedures are for the determination of individual inorganic anions, while only a few are for their simultaneous determination. Chloride, bromide and iodide, for instance, were reported to be simultaneously determined by GC, based on the addition of hydrogen halides to epoxides^{6,7}. Silylation was also applied to the simultaneous GC determination of several inorganic oxyanions⁸⁻¹⁰. In that method, the anions were desiccated as their tetraalkylammonium salts before silylation. Faigle and Klockow¹¹ reported a procedure for the simultaneous determination of nitrate, sulphate and phosphate as their *n*-butyl esters formed by reaction with *n*-butyl iodide. MacGee and Allen¹² described the determination of four halides: they were converted into their tetraalkylammonium salts on an ion-exchange resin and then into the corresponding alkyl halides by thermal decomposition in the injection port of the gas chromatograph. This method was modified by using an alkyl sulphonate, such as *n*-butyl *p*-toluenesulphonate¹³ or *n*-decyl methanesulphonate¹⁴, as the alkylating agent. In this case, the inorganic anions must first be isolated or dried before alkylation because the derivatization takes place in the water-free organic solvent. We have improved this method, which is complicated and time-consuming: aqueous bromide, iodide, thiocyanate and nitrate were extracted into the organic layer from the aqueous one as their tetraalkylammonium salts and then *n*-butylated with *n*-butyl *p*-toluenesulphonate¹⁵.

All the methods described above are not very sensitive, because the use of flame ionization detection (FID) or thermal conductivity detection (TCD) could not be avoided, owing to the introduction of the hydrocarbon moieties from the derivatizing agents. Therefore, in order to use ECD, which is much more sensitive than FID or TCD, we have attempted pentafluorobenzoylation of inorganic anions instead of *n*-butylation in our previous method¹⁵ and synthesized a new derivatizing agent, pentafluorobenzyl *p*-toluenesulphonate (TsO-PFB). Its applicability to the simultaneous determination of inorganic anions by GC has been investigated. Organic anions, such as carboxylates and phenolates, have also been derivatized with TsO-PFB. This paper describes a preliminary study of the simultaneous determination of inorganic or organic anions at relatively high concentrations using FID. The final objective of this work is, of course, to develop a new GC method for the simultaneous determination of trace inorganic or organic anions by using ECD.

EXPERIMENTAL

Apparatus

A Yanaco G-180 gas chromatograph equipped with a dual FID system (Yanagimoto, Kyoto, Japan) was used together with a stainless-steel coiled tube (4 m × 3 mm I.D.) as separation column. The liquid phase and column temperature employed in determining each inorganic anion are given in Table I. For simultaneous

TABLE I

GC CONDITIONS AND CORRELATION COEFFICIENTS OF CALIBRATION CURVES FOR DETERMINATION OF INORGANIC ANIONS

Anion	Liquid phase	Column temp. (°C)	Internal standard and concentration (M)	Correlation coefficient	Concentration range (ppm)
Br ⁻	5% OV-225	120	Benzyl bromide (0.01)	0.9991	30-300
I ⁻	5% OV-225	120	Iodobenzene (0.05)	0.9996	50-500
CN ⁻	5% OV-225	180	Tribromobenzene (0.01)	0.9952	10-100
SCN ⁻	5% OV-225	180	Tribromobenzene (0.01)	0.9997	20-200
NO ₂ ⁻	5% DC-550	120	Iodobenzene (0.01)	0.9993	45-450
NO ₃ ⁻	5% DC-550	155	<i>p</i> -Dibromobenzene (0.01)	0.9990	25-250
S ²⁻	5% OV-225	200	Tribromobenzene (0.005)	0.9985	6.5-65
Cl ⁻	5% PEG-HT	110	<i>p</i> -Dichlorobenzene (0.05)	0.9992	35-350

determinations, the column was packed with 5% OV-225 (2.5 m) + 5% OV-210 (1.5 m). The liquid phases 5% OV-225 and 3% OV-17 were used in the determination of individual organic anions and for their simultaneous determination, respectively. The column packing materials, 5% OV-225, 5% OV-210, 3% OV-17, 5% DC-550 and 5% PEG-HT on Uniport HP (60-80 mesh) were obtained from Gasukuro Kogyo (Tokyo, Japan). Nitrogen was used as the carrier gas at a constant flow-rate of 30 ml/min. The injection port and detector temperatures were maintained at 250°C. A Shimadzu Chromatopac C-R1B data processor was used as the recorder and integrator.

A Hitachi RMU-6E mass spectrometer was employed with an ionization source temperature of 200°C, an electron energy of 70 eV and an acceleration energy of 1.8 kV.

Reagents

Analytical-reagent grade tetra-*n*-butylammonium hydrogensulphate (TBAHS) was obtained from Tokyo Kasei (Tokyo, Japan), and commercial grade tetra-*n*-amylammonium chloride (TAAC) from Wako (Osaka, Japan). The new derivatizing agent, TsO-PFB, was prepared from *p*-toluenesulphonyl chloride and pentafluorobenzyl alcohol by a modification of the literature method¹⁶ and recrystallized from methanol. It was identified by mass spectrometry and infrared spectrophotometry (Fig. 1). The inorganic anions were used as their sodium or potassium salts of analytical reagent grade. Dichloromethane and deionized water were distilled before use for analysis. All other chemicals were also of analytical-reagent grade.

Procedure

The procedure for the simultaneous determination of bromide, iodide, cyanide, thiocyanate, nitrite, nitrate and sulphide was as follows. A brown-coloured test-tube with a screw cap (*ca.* 10 ml) was used as the reaction vessel in order to protect the contents from the light. To 1.0 ml of a reference standard solution containing the seven inorganic anions were added 0.2 ml of a 0.1 M aqueous solution of TAAC and 1.0 ml of a 0.1 M solution of TsO-PFB in dichloromethane. The vessel was sealed

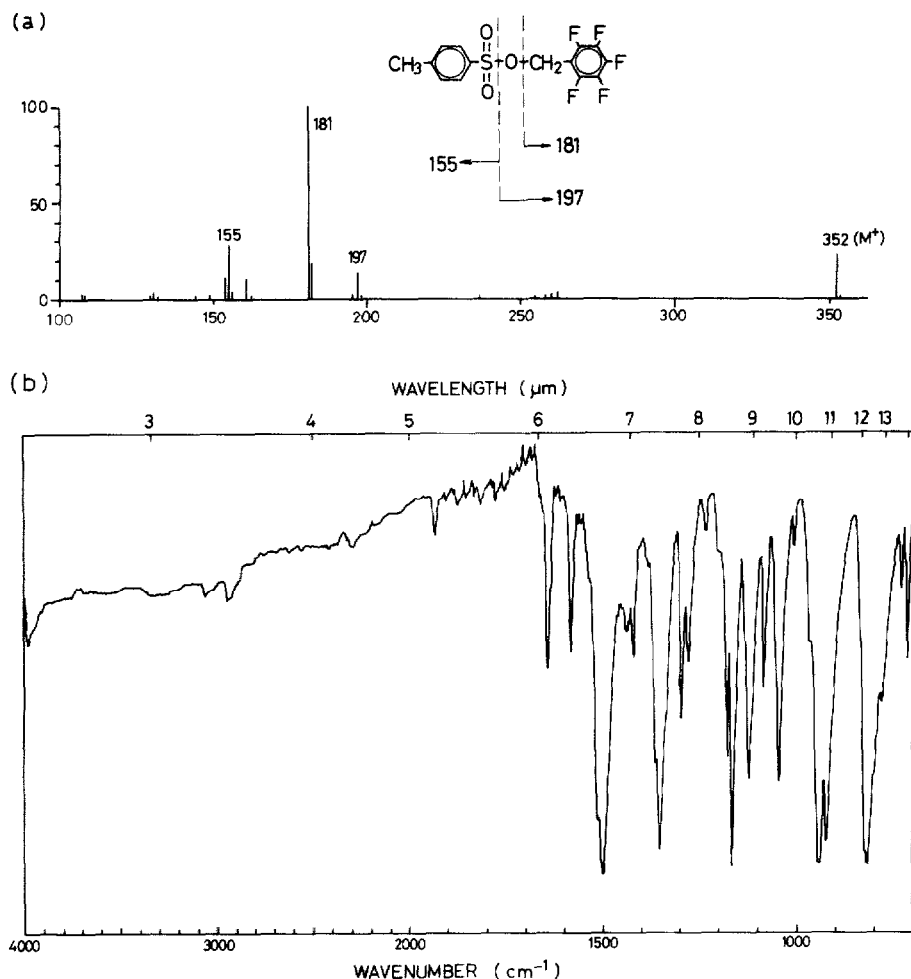


Fig. 1. Mass (a) and infrared (b) spectra of TsO-PFB.

tightly with the stopper and shaken mechanically for 30 min at room temperature. The organic layer was then separated from the aqueous one, and an aliquot of it (0.5 μ l) was injected into the gas chromatograph. For the determination of the individual anions, the dichloromethane solution of TsO-PFB contained an internal standard as listed in Table I.

The procedure for determining carboxylic acids or phenols was different from the above. To 1.0 ml of a reference standard solution containing carboxylic acids or phenols was added 0.5 ml of a 0.1 *M* aqueous solution of TAAC, 0.1 ml of a buffer solution pH 12.0 comprising 0.05 *M* disodium hydrogenphosphate and 0.0432 *M* sodium hydroxide and 1.0 ml of a 0.05 *M* solution of TsO-PFB in dichloromethane. Then the reaction vessel was shaken for 2 h (carboxylic acids) or for 1 h (phenols). For determinations of the individual carboxylic acids or phenols, 0.5 ml of dichloromethane were further added, which contained an internal standard as listed in Table II.

TABLE II

GC CONDITIONS AND CORRELATION COEFFICIENTS OF CALIBRATION CURVES FOR DETERMINATION OF CARBOXYLIC ACIDS OR PHENOLS

Internal standards: BDCB = 1-bromo-2,4-dichlorobenzene; DBB = *p*-dibromobenzene; TCB = 1,2,3,4-tetrachlorobenzene.

Carboxylic acid or phenol	Column temp. (°C)	Internal standard and concentration (mM)	Correlation coefficient
<i>n</i> -Butyric acid	160	BDCB (6.6)	0.9994
<i>n</i> -Valeric acid	170	DBB (5.0)	0.9988
Isovaleric acid	170	TCB (10.0)	0.9992
<i>n</i> -Caproic acid	170	DBB (5.0)	0.9985
Isocaproic acid	170	DBB (5.0)	0.9982
<i>n</i> -Heptanoic acid	180	TCB (8.0)	0.9993
<i>n</i> -Caprylic acid	180	TCB (8.0)	0.9987
Phenol	180	TCB (5.0)	0.9983
<i>o</i> -Cresol	180	TCB (8.0)	0.9990
<i>m</i> -Cresol	180	TCB (8.0)	0.9992
<i>p</i> -Cresol	180	TCB (8.0)	0.9983
2,4-Xylenol	190	TCB (8.0)	0.9996
2,6-Xylenol	190	TCB (8.0)	0.9986
3,4-Xylenol	190	TCB (8.0)	0.9992
3,5-Xylenol	190	TCB (8.0)	0.9995
<i>o</i> -Methoxyphenol	190	TCB (8.0)	0.9996

RESULTS AND DISCUSSION

Pentafluorobenzylation of inorganic anions

Fig. 1 shows the mass and infrared spectra of TsO-PFB synthesized. The mass peaks at *m/e* 352 and 181 correspond to the parent ion and base ion equivalent to the fragment $C_6F_5CH_2^+$, and infrared bands at 1170 and 1360 cm^{-1} are characteristic of the symmetric and antisymmetric vibrations of $S(=O)_2$, respectively.

In order to estimate the ability of TsO-PFB to pentafluorobenzylate inorganic anions, the derivatization reaction was performed as described in the Experimental section for bromide, iodide, cyanide, thiocyanate, nitrite, nitrate sulphide, cyanate, sulphate, carbonate, phosphate and phosphite. For the first seven anions from bromide to sulphide, the GC peaks seemed to correspond to the PFB derivatives of the anions. However, the other anions did not give GC peaks. Therefore, further studies were carried out only for the seven anions.

The PFB derivatives of the inorganic anions were identified as follows. An authentic sample of the PFB derivative of each anion was synthesized by scaling up the reaction and was examined by mass spectrometry after purification. From the mass spectra obtained, the PFB derivatives of bromide, iodide, cyanide, nitrite, nitrate and sulphide were assigned as pentafluorobenzyl bromide (PFB-Br), pentafluorobenzyl iodide (PFB-I), pentafluorobenzyl cyanide (PFB-CN), α -nitro-2,3,4,5,6-pentafluorotoluene (PFB-NO₂), pentafluorobenzyl nitrate (PFB-ONO₂) and bis(pentafluorobenzyl) sulphide [(PFB)₂S], respectively. From its mass spectrum, the PFB derivative of thiocyanate (Fig. 2) seemed to be pentafluorobenzyl thiocyanate (PFB-

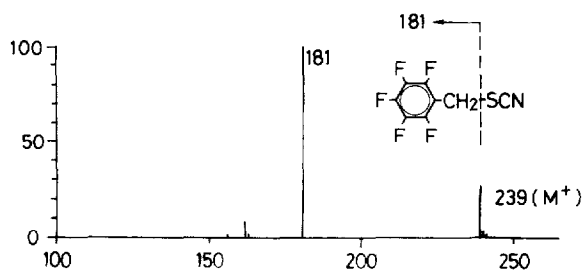


Fig. 2. Mass spectrum of the PFB derivative of thiocyanate.

SCN) or pentafluorobenzyl isothiocyanate. Based on the qualitative test of alkyl thiocyanate or isothiocyanate reported by Kemp¹⁷, the PFB derivative of thiocyanate was identified as PFB-SCN. Bromide, iodide, cyanide, nitrate and sulphide are each converted into only one PFB derivative under the various conditions tested. However, depending on the derivatization conditions, nitrite or thiocyanate gives two PFB derivatives, *i.e.*, PFB-NO₂ or PFB-ONO₂ for nitrite or PFB-SCN and/or (PFB)₂S for thiocyanate.

Optimum derivatization conditions for inorganic anions

The effect on the derivatization of added acid or base was examined using TBAHS or TAAC as the phase transfer catalyst. To 1.0 ml of a 0.05 *M* aqueous solution of each inorganic anion were added 0.5 ml sulphuric acid or potassium hydroxide at different concentrations, 0.2 ml of a 0.1 *M* aqueous solution of the phase transfer catalyst and 1.0 ml of a 0.1 *M* solution of TsO-PFB in dichloromethane. Then the derivatization was performed by shaking for 1 h. Fig. 3 shows the results; the derivatization yield (the overall yield containing the extraction yield) plotted on the ordinate was measured as follows. The peak area of the PFB derivative produced from each anion at 0.05 *M* was compared with that of a standard solution. The latter contained each authentic PFB derivative at a concentration of 0.05 *M*, corresponding to a derivatization yield of 100%.

When TBAHS is the phase transfer catalyst (Fig. 3a), nitrite is derivatized mainly to PFB-ONO₂ (●) and slightly to PFB-NO₂(○), independent of the concentration of the added acid or base. In an acidic medium, thiocyanate is derivatized to PFB-SCN (○) in quite high yield, but to (PFB)₂S (●) in relatively low yields in a basic medium. Similar behaviour for thiocyanate is also observed when using TAAC (Fig. 3b). The optimum pH for the derivatization of nitrate and sulphide was achieved by adding 8.0 *M* potassium hydroxide. However, this is not the case for the derivatization of thiocyanate. Consequently, the optimum pH for the simultaneous determination of the seven anions cannot be found when TBAHS is used as the phase transfer catalyst.

Fig. 3b shows the results of the effect of added acid or base on the derivatization with TAAC. Nitrite is derivatized to PFB-NO₂ (○) when neither sulphuric acid nor potassium hydroxide is added. Thiocyanate is derivatized to PFB-SCN (○) in an acidic or neutral medium, in quantitative yield. It is also clear that neither the addition of sulphuric acid nor potassium hydroxide leads to the optimum pH. This suggests that simultaneous determination is possible by using TAAC as the

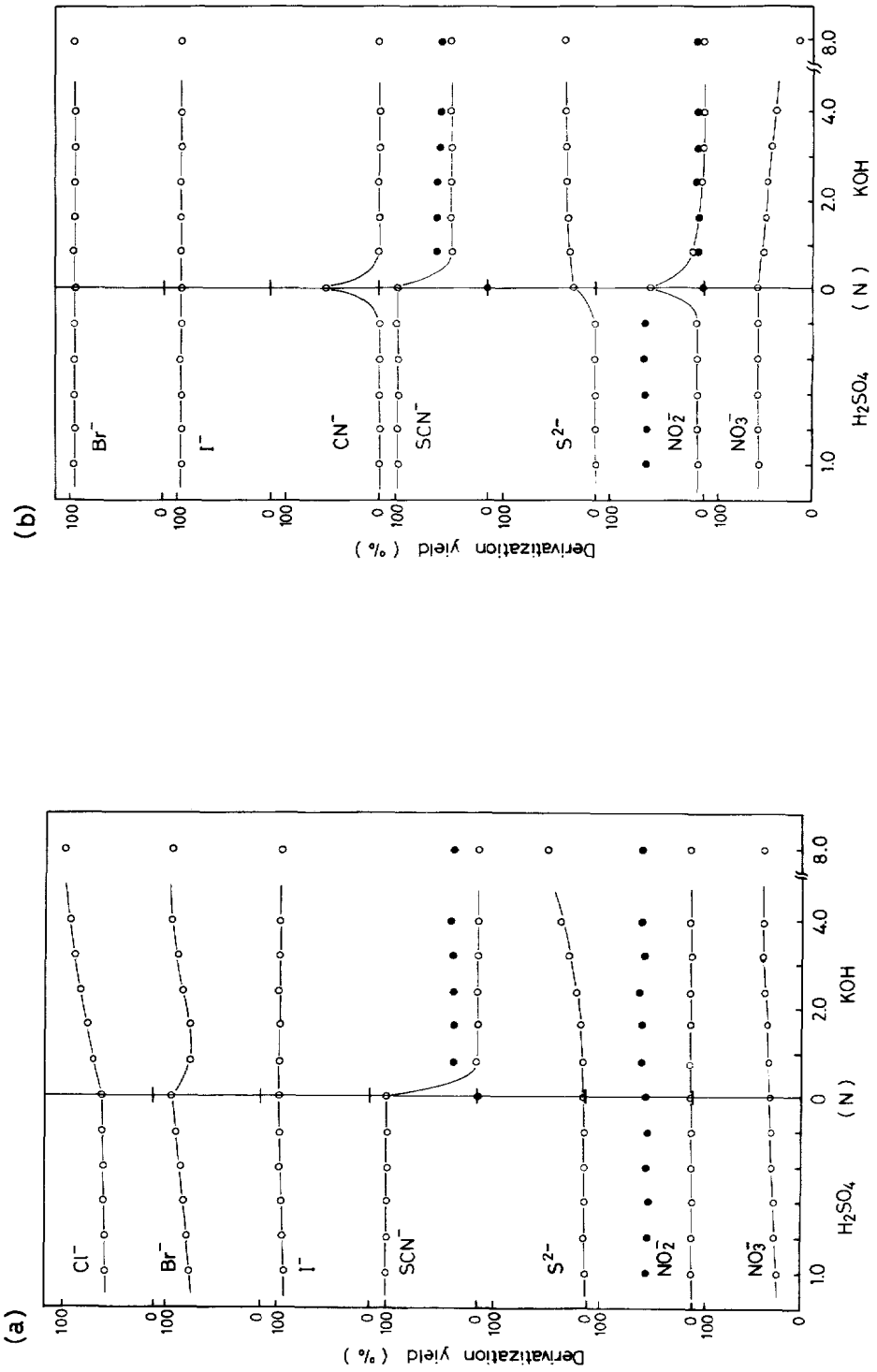


Fig. 3. Effect of added acid or base on the derivatization of inorganic anions, using TBAHS (a) or TAAC (b) as the phase transfer catalyst.

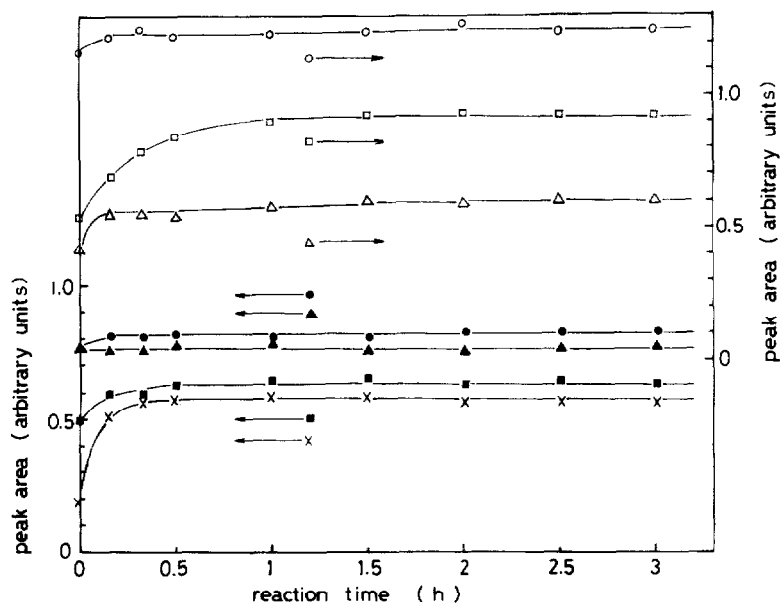


Fig. 4. Effect of reaction time on the derivatization of inorganic anions. Anions: \circ = bromide; \bullet = iodide; \triangle = cyanide; \blacktriangle = thiocyanate; \square = nitrite; \blacksquare = nitrate; \times = sulphide.

phase transfer catalyst. Therefore, further work was carried out with TAAC, adding neither the acid nor the base.

The effect of reaction time on the derivatization was also examined at the optimum pH. The results are shown in Fig. 4; about 30 min are required for plateau formation with all the PFB derivatives. A period of 30 min was therefore set as the derivatization time.

Analytical calibration and gas chromatogram

The application of the method to the determination of the seven inorganic anions was evaluated. Ten different concentrations of the reference standard solutions containing each anion were quantitated in order to construct a calibration curve

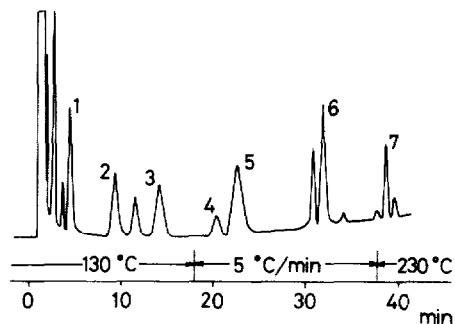


Fig. 5. Gas chromatogram for the simultaneous determination of seven inorganic anions. Peaks: 1 = bromide; 2 = iodide; 3 = nitrate; 4 = nitrite; 5 = cyanide; 6 = thiocyanate; 7 = sulphide.

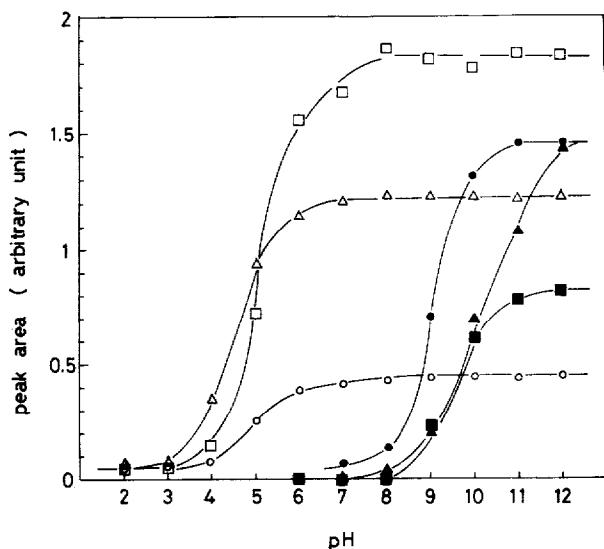


Fig. 6. Effect of pH on the derivatization of carboxylic acids or phenols. Analytes: ○ = *n*-butyric acid; △ = *n*-valeric acid; □ = isocaproic acid; ● = phenol; ▲ = *o*-cresol; ■ = 2,6-xyleneol.

of the amount of each anion *versus* the ratio of the peak area of the corresponding PFB derivative to that of the internal standard. Straight lines were obtained passing through the origin. The correlation coefficients and the determination ranges are given in Table I.

Fig. 5 shows the gas chromatogram obtained for the simultaneous determination of the seven inorganic anions. The resolution of the seven PFB derivatives is very difficult on a column containing only one liquid phase. Therefore, we used a column packed with OV-225 and OV-210, with temperature-programming. For the determination of individual anions, the organic layer is subjected to isothermal GC at the column temperature given in Table I, and the resulting PFB derivative determined by an internal standard method.

Derivatization of carboxylic acids or phenols

The derivatization method described for the inorganic anions was also applied to the determination of organic anions. In addition to the carboxylic acids and the phenols listed in Table II, formic, acetic and propionic acids were examined, but were not derivatized in relatively high yields under various reaction conditions. The derivatization was performed at various pH values by using buffer solutions, according to the procedure described in the Experimental section. Fig. 6 shows some of the results, which indicate that the derivatization yields for the carboxylic acids and the phenols become constant at pH higher than 7 and 12, respectively. Therefore, a buffer solution of pH 12 was used. The reaction time was set at 120 min for the derivatization of carboxylic acids and at 60 min for that of phenols.

Fig. 7 shows typical gas chromatograms for the mixtures of PFB derivatives obtained under the optimum reaction conditions. Good resolution of the derivatives of carboxylic acids or phenols is achieved on the column of 3% OV-17, except for

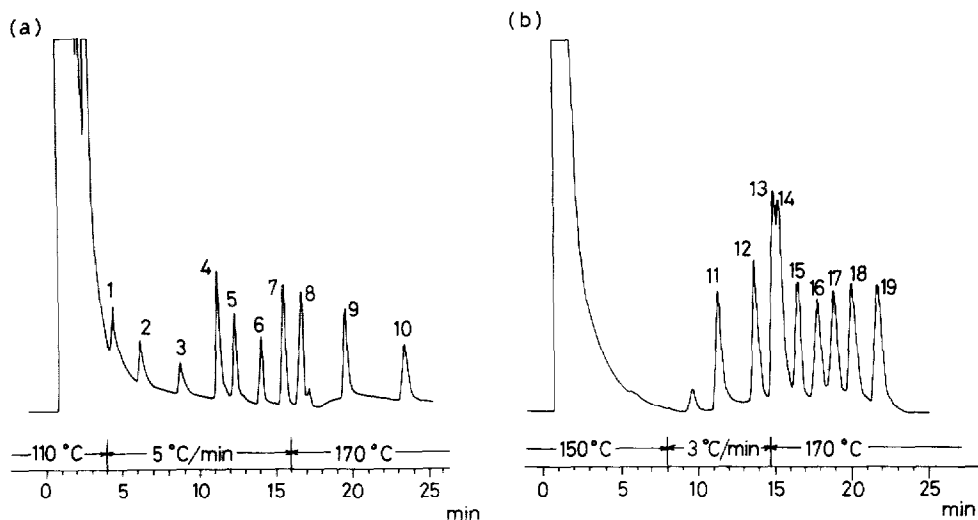


Fig. 7. Gas chromatograms for the simultaneous determination of carboxylic acids (a) and phenols (b). Peaks: 1 = formic acid; 2 = acetic acid; 3 = propionic acid; 4 = *n*-butyric acid; 5 = isovaleric acid; 6 = *n*-valeric acid; 7 = isocaproic acid; 8 = *n*-caproic acid; 9 = *n*-heptanoic acid; 10 = *n*-caprylic acid; 11 = phenol; 12 = *o*-cresol; 13 = *m*-cresol; 14 = *p*-cresol; 15 = 2,6-xyleneol; 16 = 2,4-xyleneol; 17 = 3,5-xyleneol; 18 = *o*-methoxyphenol; 19 = 3,4-xyleneol.

m- and *p*-cresol (Fig. 7b). In Fig. 7a, formic, acetic and propionic acids are included, though they give low derivatization yields. Calibration curves for all the acids (except for these three) and phenols were constructed over the concentration range 0.20–2.0 mM. They were all straight lines passing through the origin, and the correlation coefficients are given in Table II. The derivatives of carboxylic acids and phenols were also identified by mass spectrometry, as with those of inorganic anions. The carboxylic acids are derivatized as their PFB esters, and the phenols as their PFB ethers.

CONCLUSIONS

It is found that inorganic anions, *i.e.*, bromide, iodide, cyanide, thiocyanate, nitrite, nitrate and sulphide, can be simultaneously determined by pentafluorobenzoylation with TsO-PFB and TAAC followed by GC-FID. Furthermore, chloride is also pentafluorobenzoylated; however, it cannot be determined when TAAC is used as the phase transfer catalyst, because TAAC possesses chloride as a counter anion. In the determination of chloride, 8.0 M potassium hydroxide aqueous solution (0.5 ml) was added to the solution containing chloride, which was then derivatized using TBAHS instead of TAAC as described for the other seven inorganic anions. The GC conditions and the correlation coefficient of the calibration curve for chloride are also given in Table I together with those of the other inorganic anions.

The present technique based on pentafluorobenzoylation is an ECD-oriented derivatization designed to enhance the sensitivity. The development of this method for the simultaneous determination of trace inorganic or organic anions by GC-ECD is under investigation.

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