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BUTYLATION OF INORGANIC ANIONS FOR SIMULTANEOUS DETERMINATION BY GAS CHROMATOGRAPHY

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SUMMARY

Some aqueous inorganic anions were extracted into the organic layer as their tetra-*n*-butylammonium salts and then treated with *n*-butyl *p*-toluenesulphonate to yield their *n*-butyl derivatives which were determined by gas chromatography with flame ionization detection. Bromide, iodide, thiocyanate and nitrate were thereby derivatized and determined. The *n*-butyl derivatives were identified by comparison of the retention times as *n*-butyl bromide, *n*-butyl iodide, *n*-butyl thiocyanate and *n*-butyl nitrate, respectively. The effects of added base or acid, shaking time and phase-transfer catalyst on the extraction of the anions were discussed. By this method the anions could be determined simultaneously in the concentration range 10–50 mM.

INTRODUCTION

Gas chromatography (GC) is highly suited to the determination of various organic and inorganic compounds because of its excellent separating ability. Furthermore, various techniques of analytical derivatization have been developed, in order to permit the determination of thermally unstable and non-volatile compounds which would not be possible by direct GC. Many derivatization methods have been studied for organic compounds. On the other hand, a large number of inorganic cations have been determined by GC as their volatile β -diketone chelates. However, the determination of inorganic anions by GC has not been extensively studied. This is due not only to the non-volatility of inorganic anions but also to the relative lack of suitable derivatives for GC determination. In spite of the difficulties, a fair number of methods have been developed^{1,2} the majority of which are for the determination of only one or two inorganic anions; for example, the method for cyanide³ or nitrate⁴

based on the derivatization to cyanogen halide or nitrobenzene, respectively, which is subsequently detected by electron capture GC. Only a few methods are applicable to the simultaneous determination of several inorganic anions.

Silylation is a very useful method for the derivatization of several inorganic oxyanions^{5,6}, *i.e.*, borate, carbonate, oxalate, phosphite, sulphite, sulphate, arsenite, phosphate, vanadate and arsenate. The ammonium salts of the oxyanions are silylated by bis(trimethylsilyl)trifluoroacetamide or N-methyl-N-(*tert.*-butyldimethylsilyl)trifluoroacetamide in N,N-dimethylformamide. However, direct silylation in aqueous solution is impossible since the silylating agents and the resulting silyl derivatives are sensitive to water. Therefore, the inorganic oxyanions must be converted into their ammonium salts and then dried before silylation.

Alkylation has also been studied for the GC determination of inorganic anions and various reagents have been used. We have previously reported methods for direct alkylation of aqueous inorganic anions with dimethyl or diethyl sulphate^{7,8} or pentafluorobenzyl bromide⁹. Faigle and Klockow¹⁰ treated nitrate, sulphate and phosphate with *n*-butyl iodide yielding their *n*-butyl esters which were subsequently determined by GC. MacGee and Allen¹¹ studied the thermal decomposition of tetraalkylammonium halides to their alkyl halides which were determined by GC. Alkylation based on the thermal decomposition of quaternary ammonium was complete when performed with *n*-butyl *p*-toluenesulphonate¹². Faigle and Klockow¹³ reported a modified alkylation method for chloride, bromide, iodide, cyanide, thiocyanate and nitrate. In this method the aqueous inorganic anions were transferred into non-aqueous solution with tetra-*n*-butylammonium sulphate as the phase-transfer catalyst, and were alkylated with *n*-decyl methanesulphonate into their *n*-decyl derivatives which were then determined by GC. However, lyophilization of the aqueous sample is unavoidable before alkylation, and direct alkylation of the aqueous inorganic anions has not yet been studied.

The present study was undertaken to investigate the applicability of direct alkylation of aqueous inorganic anions using *n*-butyl *p*-toluenesulphonate (TsOBu) and tetra-*n*-butylammonium hydrogensulphate (TBAHS), as the alkylating agent and the phase-transfer catalyst, respectively.

EXPERIMENTAL

Apparatus

A Yanaco (Kyoto, Japan) G-180 gas chromatograph equipped with a dual flame ionization detector was used. A stainless-steel column (1 m × 3 mm I.D.) was packed with Porapak P (80–100 mesh). Nitrogen was used as the carrier gas at a constant flow-rate of 30 ml/min. The injection port temperature was maintained at 250°C. In the determination of each inorganic anion, the column temperature was kept constant at the values shown in Table I. In the simultaneous determination of bromide, iodide, thiocyanate and nitrate, the column temperature was programmed as shown in Fig. 6. The peak areas were measured by a digital integrator (Chromatopac-E1A; Shimadzu, Kyoto, Japan).

Materials

All reagents were of analytical reagent grade and were used without further

TABLE I
GC COLUMN TEMPERATURES AND INTERNAL STANDARDS

<i>Anion</i>	<i>Column temp.</i> (°C)	<i>Internal standard</i> (concentration)
Br ⁻	145	<i>n</i> -Octane (0.025 <i>M</i>)
I ⁻	180	<i>n</i> -Decane (0.020 <i>M</i>)
SCN ⁻	180	<i>n</i> -Nonane (0.025 <i>M</i>)
NO ₃ ⁻	160	<i>n</i> -Nonane (0.025 <i>M</i>)
Simultaneous determination	Programmed (see Fig. 6)	None (absolute calibration method)

purification, unless stated otherwise. Commercial grade TsOBu and tetradecyldimethylbenzylammonium chloride (TDDMBAC) were purchased from Tokyo Kasei (Tokyo, Japan) and Dojindo Laboratories (Kumamoto, Japan), respectively, and TBAHS was of analytical reagent grade from Wako (Osaka, Japan). Deionized water was distilled before use. Solutions of inorganic anions were prepared by dissolving their potassium or sodium salts in water.

Procedure

A brown coloured reaction tube (*ca.* 10 ml) with a screw cap was used as a reaction vessel in order to protect the contents from light. A suitable amount of the aqueous TBAHS solution (1.0 *M*) was added to 1.0 ml of the reference standard aqueous solution of the inorganic anion in the reaction vessel. This was followed by TsOBu (0.2 ml), 8.0 *M* KOH solution (0.5 ml) and dichloromethane containing an internal standard (1.0 ml). The volume of the TBAHS solution, the internal standard and its concentration were dependent on the inorganic anion; they are shown in Tables I and II. In the determination of iodide, KOH solution was not added. The reaction vessel was shaken for a fixed time (see Table II) in an incubator at 28°C. At the end of the reaction period, the organic layer was separated from the aqueous layer and an aliquot (0.5 µl) of the organic layer was injected into the gas chromatograph. In the simultaneous determination of the four anions, the peak areas of their butyl derivatives were measured by an absolute calibration method. On the other hand, in the case of the analysis of a solution containing only one of the anions, the peak areas were measured by an internal standard method. TDDMBAC was also used as the phase-transfer catalyst instead of TBAHS for comparison.

RESULTS AND DISCUSSION

Butylation of inorganic anions

Chloride, bromide, iodide, cyanide, thiocyanate, sulphide, nitrite and nitrate were chosen as the inorganic anions, and the butylation of each inorganic anion (0.05 *M*) was studied as described in the Experimental section. The butyl derivatives of bromide, iodide, thiocyanate and nitrate gave relatively large GC peaks. However, the nitrite derivative was always obtained in very low yield, although the butylation was performed under various conditions. Still worse, the other three anions, chloride, cyanide and sulphide, were not butylated at all, and no GC peaks of their butyl

derivatives were observed. Therefore, further studies were carried out for bromide, iodide, thiocyanate and nitrate.

Based on the paper by Moore¹², the mechanism of this derivatization of inorganic anions is as follows. The inorganic anion is extracted into the organic layer as the counter anion of a quaternary ammonium cation after reacting with the phase-transfer catalyst. Then the anion extracted is butylated by TsOBu. The butylation occurs mainly in the injection port of the gas chromatograph which is heated to high temperatures.

In our procedure the derivatization proceeds with relatively high yields only for bromide, iodide, thiocyanate and nitrate. In the similar method presented by Faigle and Klockow¹³, chloride and cyanide were derivatized as well as the above four anions by using *n*-decyl methanesulphonate. These two methods are equivalent in that the quaternary ammonium salts of the anions are alkylated by an alkyl sulphonate ester. However, they differ in that in our method the aqueous inorganic anion is extracted as the counter anion of quaternary ammonium by liquid-liquid extraction, whereas in the other method the quaternary ammonium salt from the anion is not extracted but is desiccated by freeze-drying and then dissolved in a polar organic solvent. In our method, neither chloride nor cyanide can be extracted into the organic layer as quaternary ammonium chloride or cyanide by liquid-liquid extraction and, therefore, be derivatized.

Identification of butyl derivatives of inorganic anions

The derivative of each inorganic anion, which was expected to be its butyl derivative, was identified by various methods. The butyl derivative of bromide or iodide was identified as *n*-butyl bromide or *n*-butyl iodide, respectively, by comparing the retention time of the derivative with that of an authentic sample. Because of the

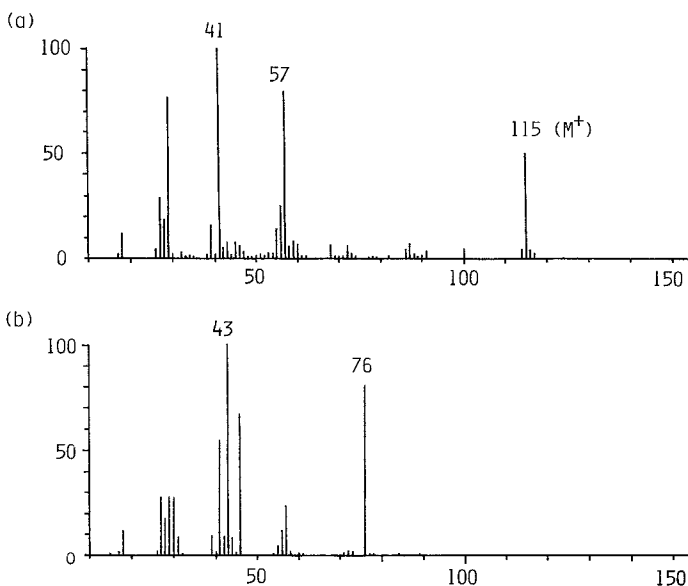


Fig. 1. Mass spectra of *n*-butyl derivatives of thiocyanate (a) and nitrate (b).

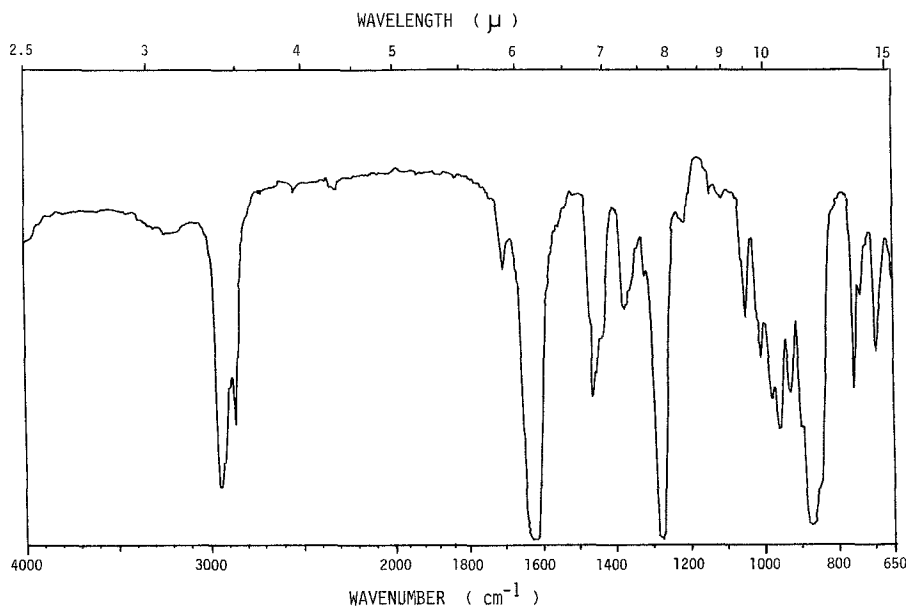


Fig. 2. IR spectrum of the *n*-butyl derivative of nitrate.

unavailability of commercial *n*-butyl thiocyanate, the butyl derivative of thiocyanate was assigned as follows. The butyl derivative was synthesized by scaling up the reaction and was examined by mass spectrometry (MS) after purification. 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. The mass spectrum obtained exhibits the parent ion at $m/e = 115$ and some other peaks (Fig. 1a). From this spectrum the derivative seems to be *n*-butyl thiocyanate or *n*-butyl isothiocyanate, but the retention time of authentic *n*-butyl isothiocyanate was not the same as that of the derivative synthesized. Furthermore, the retention time of the derivative synthesized is in agreement with that obtained from thiocyanate by analytical derivatization. Therefore, the butyl derivative of thiocyanate is reasonably assigned as *n*-butyl thiocyanate.

The butyl derivative of nitrate was also synthesized and examined by MS in the same manner. It was also analyzed by infrared (IR) spectroscopy. The mass and IR spectra are shown in Figs. 1b and 2, respectively. The mass spectrum exhibits no parent ion but two important ion peaks at $m/e = 43$ (base peak) and $m/e = 76$, which correspond to the ion fragments $C_3H_7^+$ and $CH_2=O^+-NO_2$ (Fig. 1b). This is in accord with the general tendency for α -cleavage in MS of organic nitrates. As shown in Fig. 2, the IR absorption bands at 1280 and 1620 cm^{-1} correspond to the symmetric and antisymmetric vibrations of NO_2 , respectively. From these results, the derivative synthesized is assigned as *n*-butyl nitrate. Its retention time is in good agreement with that of authentic *n*-butyl nitrate.

Optimum derivatization conditions

Moore¹² reported that the butylation occurs mainly in the injection port of

TABLE II
OPTIMUM EXTRACTION CONDITIONS AND DERIVATIZATION YIELDS

Anion	TBAHS				TDDMBAC			
	Vol. of TBAHS soln. (ml)	Added KOH (M)	Shaking time (h)	Deriv. yield (%)	Vol. of TDDMBAC soln. (ml)	Added KOH (M)	Shaking time (h)	Deriv. yield (%)
Br ⁻	0.2	8.0	1	91.5	0.1	None	2	83.6
I ⁻	0.2	None	1	99.5	0.1	None	2	87.2
SCN ⁻	0.2	8.0	1	94.7	0.2	8.0	1	85.3
NO ₃ ⁻	0.4	8.0	1	54.0	0.4	8.0	1	41.4
Simultaneous detn.	0.4	8.0	1					

the gas chromatograph and proceeds quantitatively even when the injection port temperature is 210°C. Therefore, we set the injection port temperature at 250°C.

To investigate the optimum volume of the phase-transfer catalyst required for the extraction of each inorganic anion, different volumes were tried. As shown in Table II, more than a certain volume of the solution is required to achieve a constant derivatization yield (*i.e.*, the overall yield based on the extraction and derivatization steps) of each inorganic anion by using TBAHS or TDDMBAC as the phase-transfer catalyst.

In order to perform the extraction under the optimum conditions, the effects of added base or acid and shaking time were examined. The effect of base or acid was studied as follows. To 1.0 ml of each aqueous solution of inorganic anion (0.05 M) were added 0.5 ml of sulphuric acid (H₂SO₄) or potassium hydroxide (KOH) in different concentrations. Then the extraction was performed by shaking for 1 h, and the derivatization carried out as described in the Experimental section. The results are shown in Fig. 3. The derivatization yield was measured as follows. The peak area of the butyl derivative produced from each anion (0.05 M) was compared with that from a standard solution. The latter contained each authentic butyl derivative at a concentration of 0.05 M, corresponding to a derivatization yield of 100%. With TBAHS as the phase-transfer catalyst (Fig. 3a), the extraction of iodide is almost quantitative, independently of added base or acid. However, the other three anions (bromide, thiocyanate and nitrate) are dependent on it, and the highest derivatization yields are obtained with 8.0 M KOH. On the other hand, with TDDMBAC (Fig. 3b), all derivatization yields varied with the concentration of H₂SO₄ or KOH. The highest derivatization yields for bromide and iodide are obtained when neither H₂SO₄ nor KOH is added. For nitrate and thiocyanate, the optimum yield is obtained by adding 8.0 M KOH. From these results, the simultaneous determination of the four anions can be performed by adding 8.0 M KOH and by using TBAHS as the phase-transfer catalyst. However, the simultaneous determination is impossible when TDDMBAC is used as the catalyst.

The effect of shaking time on the extraction was also examined by performing the derivatization after the extraction at each optimum pH value mentioned above (see Table II). The results are given in Fig. 4. With TBAHS, each anion is extracted

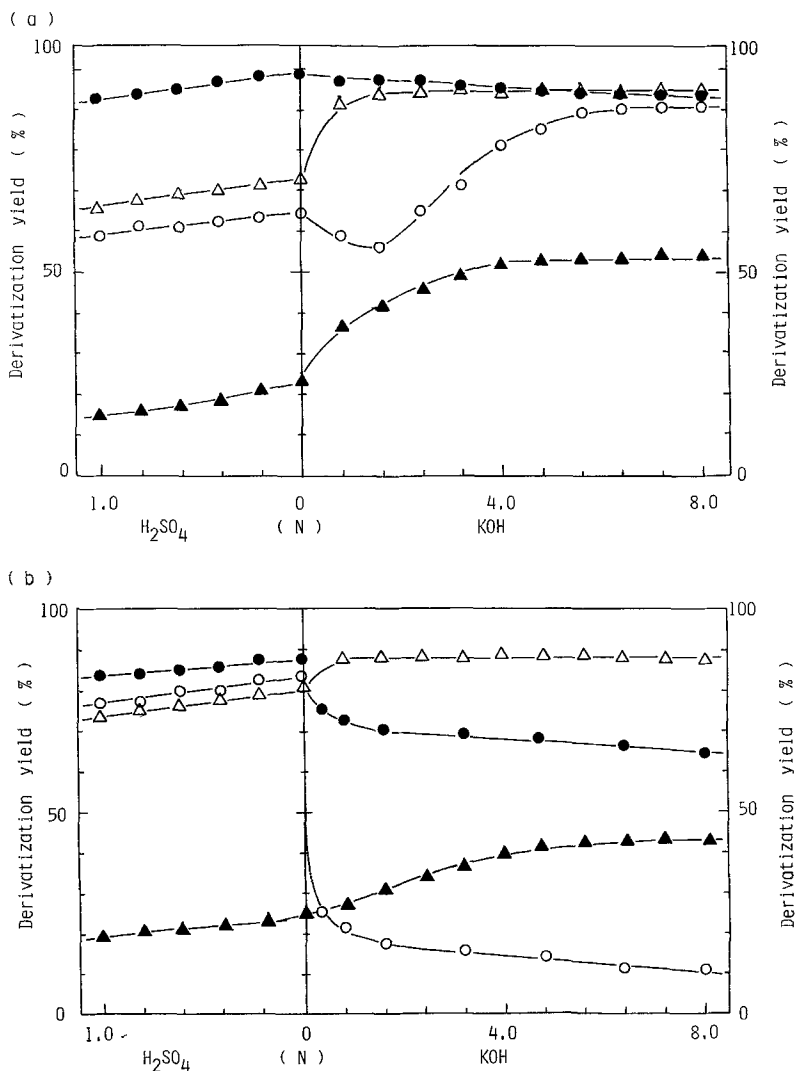


Fig. 3. Effect of added base or acid on the derivatization yields of bromide (○), iodide (●), thiocyanate (△) and nitrate (▲). Phase-transfer catalysts: TBAHS (a); TDDMBAC (b).

within 30 min. With TDDMBAC, thiocyanate or nitrate is extracted by shaking for 30 min, while bromide or iodide requires about 2 h. The overall derivatization yield for each anion (0.05 M) was measured by extracting and derivatizing under each optimum condition described in Table II, and the results are also given there. For each anion, TBAHS results in a higher derivatization yield than TDDMBAC. Thus, TBAHS is superior to TDDMBAC as the phase-transfer catalyst in this extraction. Further studies were performed by using TBAHS as the phase-transfer catalyst, with a shaking time of 1 h for the simultaneous determination of the four anions.

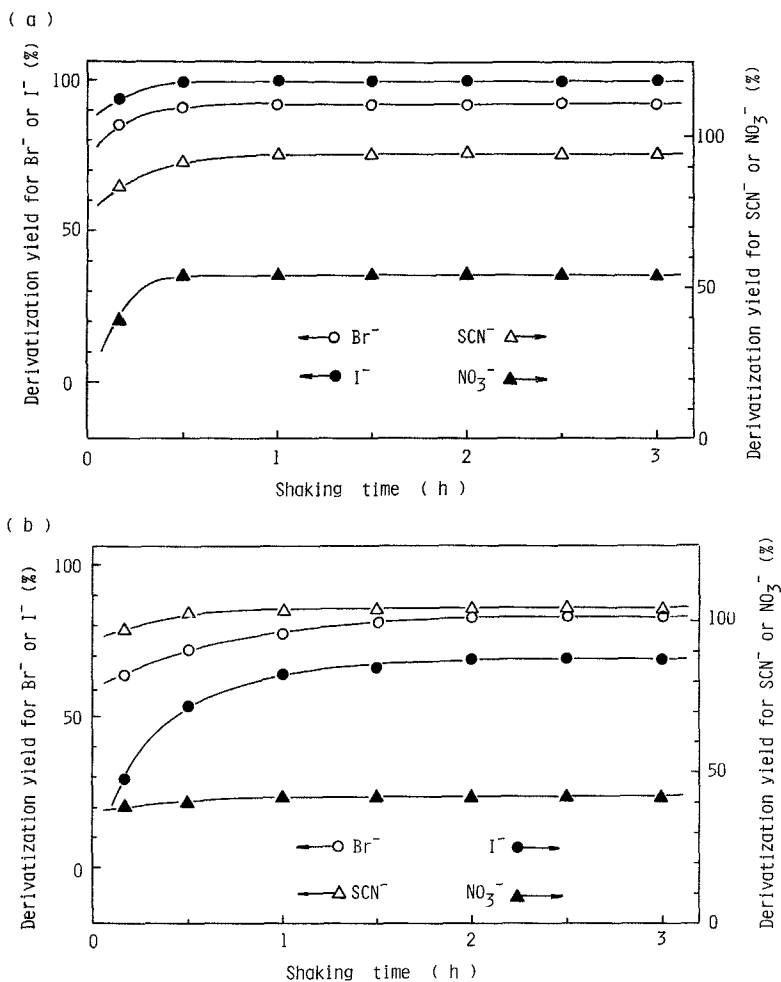


Fig. 4. Effect of shaking time on the derivatization yields. Details as in Fig. 3.

Analytical calibration and gas chromatogram

After the optimum extraction conditions for each anion had been established, the quantitative application of the method to the determination of bromide, iodide, thiocyanate and nitrate was evaluated. Fig. 5 shows the calibration curves for bromide and iodide, plotting the peak area of the butyl derivative vs. the concentration of inorganic anion in aqueous solution. The plots are straight lines passing through the origin. For thiocyanate and nitrate, good linear relationships were also observed over the concentration range 10–50 mM. Fig. 6 shows the gas chromatogram obtained for the simultaneous determination of the four anions. Good resolution of the four butyl derivatives is achieved with a temperature-programming technique. In the determination of only one anion, the reacted organic layer is subjected to isothermal GC at the column temperature shown in Table I, and the resulting butyl derivative is determined by an internal standard method.

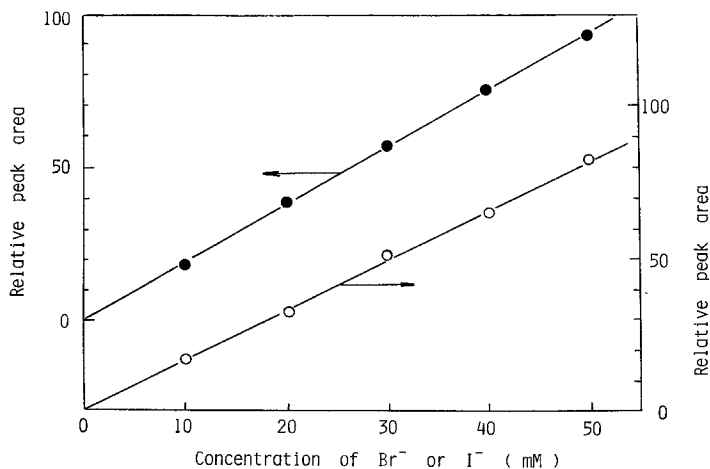


Fig. 5. Calibration curves for bromide (○) and iodide (●).

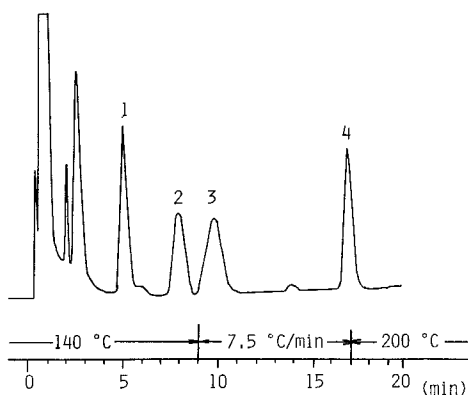


Fig. 6. Gas chromatogram obtained for the simultaneous determination. Peaks: 1 = *n*-butyl bromide; 2 = *n*-butyl nitrate; 3 = *n*-butyl iodide and 4 = *n*-butyl thiocyanate.

CONCLUSIONS

We have developed a new gas chromatographic method for the simultaneous determination of aqueous inorganic anions with direct derivatization by using TsOBu and TBAHS in a biphasic system. The aqueous inorganic anions are extracted into the organic layer and butylated with TsOBu. We have also examined butylation of aqueous inorganic anions with TsOBu in a homogeneous reaction system. The procedure is briefly as follows. To 1.0 ml of the reference standard aqueous solution of inorganic anions are added 2.0 ml of methanol and 0.2 ml of TsOBu, and then the mixture is shaken in an incubator at 28°C. After shaking, an aliquot of the reaction mixture is injected into the gas chromatograph. Sulphide, besides bromide, iodide, thiocyanate and nitrate, is derivatized to the butyl derivative (*i.e.*, di-*n*-butyl sulphide) and the simultaneous determination of the five anions is possible. However, the shaking time required is long (3 h) and the derivatization yield of each anion is

lower than the value shown in Table II. Therefore, this homogeneous method is inferior to the main method reported.

The sensitivity of the method reported is low because flame ionization detection is used. However, no detector is available which can detect all the butyl derivatives (*i.e.*, *n*-butyl bromide, *n*-butyl iodide, *n*-butyl thiocyanate and *n*-butyl nitrate) more sensitively. Therefore, we now intend to investigate methods for the simultaneous and trace determination of inorganic anions by using electron capture detection which is much more sensitive than flame ionization detection. For enhancement of the response, the use of pentafluorobenzoylation by pentafluorobenzyl *p*-toluenesulphonate instead of TsOBu is of interest.

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