

CHROM. 11,186

## GAS-LIQUID CHROMATOGRAPHIC-MASS SPECTROMETRIC DETERMINATION OF ALKYL BENZENESULPHONATES IN RIVER WATER

HIROMI HON-NAMI and TAKAHISA HANYA

*Department of Chemistry, Tokyo Metropolitan University, Setagaya-Ku, Tokyo (Japan)*

(Received April 17th, 1978)

---

### SUMMARY

Trace analysis of alkylbenzenesulphonates in river water has been investigated by combined gas-liquid chromatography-mass spectrometry. Methylene blue-alkylbenzenesulphonate complexes are first formed and then extracted with chloroform. The methylene blue is removed and the alkylbenzenesulphonates are converted to methyl sulphonate derivatives by treatment with phosphorus pentachloride and then with methanol. The individual components of the alkylbenzenesulphonate are determined separately by mass fragmentography. The reproducibility of the determination is satisfactory.

---

### INTRODUCTION

The determination of alkylbenzenesulphonates (ABS) in the environment has been carried out by the methylene blue method<sup>1,2</sup> and by infrared analysis<sup>3,4</sup>. In the former method, ABS cannot be determined precisely due to the formation of complexes of methylene blue with other organic and inorganic compounds. Although several improvements<sup>5-7</sup> have been reported which involve removal of the interfering matter, their data have been presented not in terms of ABS, but of methylene blue active substances (MBAS). The latter are troublesome, so this method is not applicable to the analysis of many samples. The development of an accurate and rapid method of analysis of ABS is thus required.

Gas-liquid chromatographic (GLC) and mass spectrometric (MS) analysis of ABS are of value in terms of the accurate determination and analysis of the individual components in a mixture and the isomers. Desulphonation<sup>8-12</sup>, alkali fusion<sup>13</sup>, thermal decomposition<sup>14-16</sup>, sulphonyl chlorination<sup>17-22</sup> and sulphonyl esterification<sup>19,23</sup> methods require at least several milligrams of ABS, and are therefore difficult to apply to the determination of ABS in the environment.

In this paper, we describe improvements of the sulphonyl chloride method<sup>21,22</sup> and of the methyl sulphonate method<sup>24</sup> for the analysis of trace amounts of ABS (several micrograms), and the analysis of ABS in river water by GLC and GLC-MS with satisfactory results.

## EXPERIMENTAL

*Apparatus*

The GC analysis was performed using a Shimadzu Type 4BM-PF chromatograph equipped with a flame ionization detector. A silanized glass column (2 m × 3 mm I.D.) was packed with 1.5% silicon OV-1 on Chromosorb W AW DMCS (80–100 mesh). Nitrogen was used as carrier gas with a flow-rate of 40 ml/min.

The GLC-MS measurements were made with a Shimadzu LKB-9000 instrument. The flow-rate of carrier gas (helium) was 30 ml/min. The chromatogram was recorded as the total ion current monitor (TICM) at 20 eV. The molecular separator and ion source were maintained at 300° and 330°, respectively. Mass spectra were taken at 70 eV with an accelerator voltage of 3.5 kV.

The reaction temperature of the sulphonyl chlorination and the methyl esterification was controlled by a constant-temperature hot-plate (Thermorine/dri bath, Sybron Co., Ltd.).

A 1-ml glass ampoule was ignited at 500° for 3 h before use.

*Chemicals*

All the organic solvents were guaranteed reagent grade and distilled. Linear alkylbenzene and linear alkylbenzenesulphonate (LAS) were supplied by Lion Fat & Oil Co., Tokyo, Japan. Sodium *p*-dodecylbenzenesulphonate (a mixture of 2-, 3-, 4-, 5- and 6- phenyldodecanesulphonate; Wako, Osaka, Japan) was used as a standard. Methylene blue was prepared as a 0.025% solution in distilled water. The solution was purified by washing with chloroform. Dowex 50W-X8 (50–100 mesh), a cation-exchange resin, was conditioned with 3 M HCl and 2 M NaCl and washed with ethanol. Silica gel (100 mesh) was ignited at 500° for *ca.* 3 h and deactivated with 5% distilled water after cooling in a desiccator.

*Procedure*

A 1-ml volume of 0.025% methylene blue solution and 10 ml of chloroform are added to a glass-stoppered 500-ml separating funnel containing a suitable volume (200–300 ml) of a sample solution. After shaking for 1 min, the chloroform layer is transferred to a 100-ml round-bottomed flask. If an emulsion is formed, it is removed by centrifugation. The extraction is repeated three times using 10 ml chloroform each time. If the blue colour of the aqueous phase becomes faint and disappears, another 1 ml of the methylene blue solution is added.

The chloroform layer containing methylene blue and methylene blue-ABS complexes is evaporated to dryness under reduced pressure. The residue is dissolved in a small amount of ethanol and passed through a column of cation-exchange resin (Dowex 50W-X8, 50–100 mesh, 50 × 10 mm I.D.; flow-rate 0.3 ml/min) for removal of methylene blue. The ethanol eluate (*ca.* 10 ml) containing ABS is then evaporated and the residue dissolved in *ca.* 20 ml of water.

The aqueous solution is washed with chloroform (3 × *ca.* 5 ml), concentrated, transferred to a 1-ml ampoule and then evaporated. After addition of *ca.* 10 mg phosphorus pentachloride the ampoule is sealed and maintained at 110° for 10 min on a hot-plate. The sulphonyl chloride derivatives produced are extracted with *n*-hexane, and the extract is transferred to another 1-ml ampoule and evaporated.

About 0.5 ml methanol are added to the ampoule, which is sealed and maintained at 70° for 20 min on a hot-plate. The methanol solution containing the methyl sulphonate derivatives produced is evaporated and the residue dissolved in *n*-hexane. The hexane solution is applied to the silica gel column (30 × 4 mm I.D.). The column is washed with three times its volume of *n*-hexane and then with one volume of *n*-hexane-benzene (1:1). The eluate, comprising eight times the column volumes of *n*-hexane-benzene (1:1), is pooled and evaporated to a definite volume.

ABS is analyzed as its methyl sulphonate derivatives by GLC and GLC-MS. The concentration of ABS is determined by measuring the peak areas on the gas chromatogram and/or the mass fragmentogram and comparing these with linear dodecylbenzenesulphonate.

### Abbreviations

The formulae of the alkylbenzenesulphonates are abbreviated by use of a numerical prefix, indicating the position of the phenyl group on the alkyl chain with the carbon number of the alkyl group indicated as C<sub>*n*</sub>.

## RESULTS AND DISCUSSION

### Extraction of MB-ABS complex with chloroform

Dodecylbenzenesulphonate (DBS) was used as a standard. The extraction of the MB-DBS complex with chloroform was carried out at various pH. A 300-ml volume of an aqueous solution containing 20 μg DBS was prepared at various pH values with 0.1 M NaOH or 0.1 M H<sub>2</sub>SO<sub>4</sub>. DBS was determined as described in the "Experimental" section. The percentage extraction of the MB-DBS complex at various pH values is shown in Fig. 1. At pH > 4.0, ca. 100% of DBS was extracted. Therefore, river water having a pH of >4.0 can be analyzed without adjusting the pH.

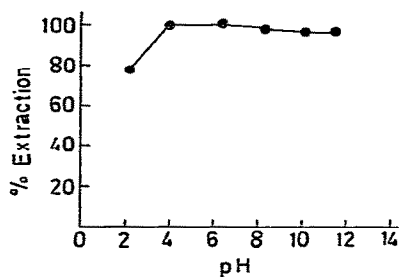


Fig. 1. Percent extraction of MB-DBS complex with chloroform at various pH values.

### Elution of DBS from cation-exchange resin

MB-DBS (20 μg) complex, dissolved in a small amount of ethanol, was applied to the column of cation-exchange resin. Ethanol eluents were fractionated in 7-ml portions and were analyzed as methyl sulphonate derivatives, respectively. All the DBS was found to be eluted in the first 7-ml portion.

### Sulphonyl chlorination

A gas chromatogram of the sulphonyl chloride derivatives of DBS used as a standard is shown in Fig. 2. Curves of peak height vs. heating time at several temperatures are shown in Fig. 3 for the reaction of DBS and phosphorus pentachloride. Under the reaction conditions of 110° for 5–15 min, 100° for 15–30 min and 90° for 60 min, the peak heights were the same. For the remainder of this study, the reaction conditions were chosen as 110° for 10 min.

Parsons<sup>21</sup> converted 0.5 g of naphthalenesulphonate and benzenesulphonate into the sulphonyl chloride derivatives by reaction with 3 g of phosphorus pentachloride in a silicone bath maintained at 110° for 1 h. Watanabe *et al.*<sup>22</sup> applied this principle to 0.5 mg of linear alkylbenzenesulphonate. In the present study, 1  $\mu$ g of DBS was determined by use of a small ampoule as a reaction tube.

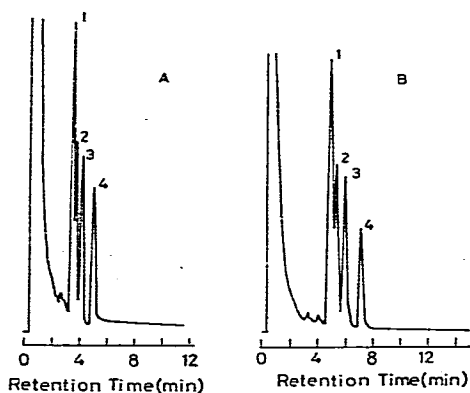


Fig. 2. Gas chromatogram of sulphonyl chloride (A) and methyl sulphonate (B) derivatives of linear dodecylbenzenesulphonate. Peaks: 1 = 5-C<sub>12</sub>, 6-C<sub>12</sub>; 2 = 4-C<sub>12</sub>; 3 = 3-C<sub>12</sub>; 4 = 2-C<sub>12</sub>. Column temperature, 220°.

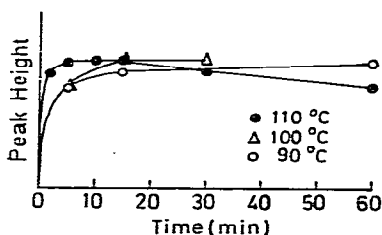


Fig. 3. Time dependence of sulphonyl chloride derivatives produced at various temperatures.

### Methyl esterification

A gas chromatogram of methyl sulphonate derivatives of DBS is shown in Fig. 2. For the mixture of DBS isomers, the peaks of 2-C<sub>12</sub> and 3-C<sub>12</sub> were separated from other isomers, but those of 4-, 5- and 6-C<sub>12</sub> were overlapped under these conditions. Curves of peak height vs. heating time at several temperatures are shown in Fig. 4. The reaction conditions were 70° for 20 min.

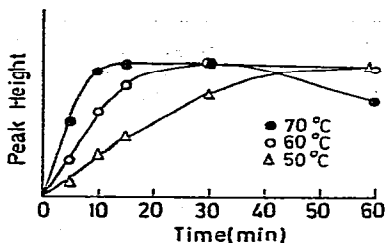


Fig. 4. Time dependence of methyl sulphate derivatives produced at various temperatures.

#### Recovery of DBS from a silica-gel column

Methyl sulphate derivatives of ABS in river water were purified through a silica-gel column. Under the elution conditions described in the Experimental, the recovery of DBS (5–25  $\mu\text{g}$ ) used as a standard from a silica-gel column was *ca.* 88.5%.

#### Calibration curve

DBS (5–25  $\mu\text{g}$ ) was analyzed by GLC after conversion into methyl sulphate derivatives by the procedure described above. The calibration curve is shown in Fig. 5. A linear relationship was obtained between the amount of DBS and the peak area on the chromatogram. The reproducibility was satisfactory. The DBS analyzed was a mixture of 2- $\text{C}_{12}$  (24.5%), 3- $\text{C}_{12}$  (19.3%) and 4-, 5-, 6- $\text{C}_{12}$  (56.2%). Using this method, more than 1  $\mu\text{g}$  of ABS was determined accurately.

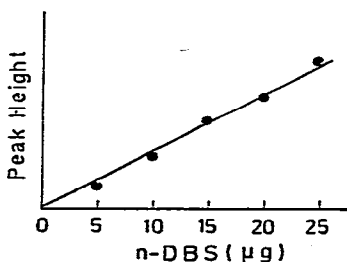


Fig. 5. Calibration curve of dodecylbenzenesulphonate.

#### Thermal decomposition

Kirkland<sup>19</sup> reported that under the conditions of gas chromatography the sulphonic esters decompose. Therefore, in this study the distribution of the individual components of a linear  $\text{C}_{10}$ – $\text{C}_{14}$  alkylbenzene were compared with those of the methyl sulphate derivatives of ABS by mass fragmentography. Mass spectra of the methyl ester gave a fragmentation pattern typical of an alkylbenzene. The mass spectrum of one of the methyl sulphate derivatives is shown in Fig. 6. The MS molecular-weight data were obtained from the molecular ions in the mass spectrum, which were prominent for this class of components. The mass fragmentography was run at the *m/e* value of the molecular ion. Table I shows that alkylbenzenes and ABS have the same distribution of individual components. Thermal decomposition products were not observed in the gas chromatogram under these conditions.

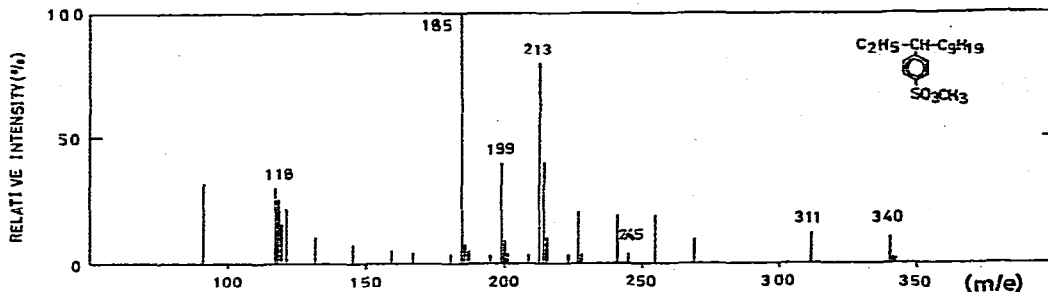


Fig. 6. Mass spectra of the methyl sulphonate derivative of dodecylbenzenesulphonate.

TABLE I

DISTRIBUTION OF INDIVIDUAL COMPONENTS OF ALKYLBENZENE AND ALKYL-BENZENESULPHONATE AS METHYL ESTERS

Isomer	Alkylbenzene (%)	Alkylbenzenesulphonate (%)
2-C <sub>10</sub>	5.3	5.4
3-C <sub>10</sub>	3.6	3.1
4,5-C <sub>10</sub>	7.1	7.3
2-C <sub>11</sub>	11.0	11.1
3-C <sub>11</sub>	7.1	6.8
4,5,6-C <sub>11</sub>	19.3	19.9
2-C <sub>12</sub>	7.0	7.7
3-C <sub>12</sub>	4.3	4.4
4,5,6-C <sub>12</sub>	15.0	15.5
2-C <sub>13</sub>	3.5	3.2
3-C <sub>13</sub>	2.1	2.2
4,5,6,7-C <sub>13</sub>	8.1	7.5
2-C <sub>14</sub>	1.4	0.8
3-C <sub>14</sub>	1.1	0.8
4,5,6,7-C <sub>14</sub>	4.1	3.4

It was concluded that the individual components of the original ABS were determined accurately by the use of the above improvement in procedure.

#### GLC and GLC-MS analysis of ABS in river water

A gas chromatogram of ABS in river water is shown in Fig. 7. The pattern of the gas chromatogram was analogous to that of the LAS standard. The assignment of the peaks was performed on the basis of the retention times and mass spectrum, and the individual components of ABS were determined by mass fragmentography. For overlapped peaks on the gas chromatogram, more than two mass spectra were recorded. The result of the GLC-MS analysis is shown in Table II. The total amounts of ABS determined by mass fragmentography were in good accord with those determined by gas chromatography. Therefore it was concluded that ABS in river water was analyzed without interferences from other organic materials. It was also found that ABS in the river water analyzed were almost linear. Table III shows the satisfactory reproducibility of the determination of ABS in river water.

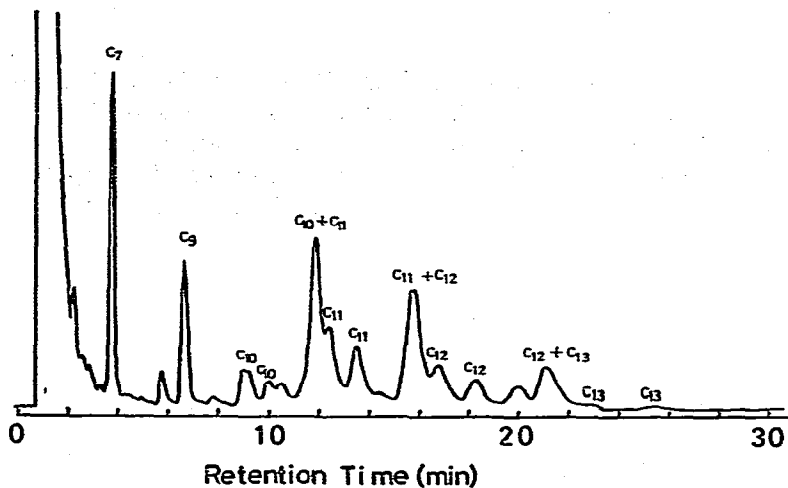


Fig. 7. Gas chromatogram of ABS as methyl esters in river water. Column temperature, 230°.

TABLE II

DISTRIBUTION OF ALKYL BENZENESULPHONATE IN RIVER WATERS

ND = Not determined.

Isomer	Tama river (Maruko) (%)	Tama river (Taishi) (%)
2-C <sub>10</sub>	4.8	4.4
3-C <sub>10</sub>	3.7	6.2
4-,5-C <sub>10</sub>	7.2	16.2
2-C <sub>11</sub>	12.2	3.9
3-C <sub>11</sub>	8.3	8.2
4-,5-,6-C <sub>11</sub>	34.7	42.7
2-C <sub>12</sub>	4.2	ND
3-C <sub>12</sub>	3.4	1.2
4-,5-,6-C <sub>12</sub>	13.7	17.1
2-C <sub>13</sub>	0.8	ND
3-C <sub>13</sub>	0.8	ND
4-,5-,6-,7-C <sub>13</sub>	6.2	ND

TABLE III

REPRODUCIBILITY OF ABS ANALYSIS IN RIVER WATERS

Sampling location	Sampling date	Concentration (ppm)		
Tama river	Aug. 3rd 1977	0.125	0.129	
Tama river	Oct. 31st 1977	0.729	0.728	0.705

CONCLUSIONS

Trace amounts of ABS in river water have been determined by GLC and GLC-MS. Passage through a silica-gel column prior to GLC enables the exclusion of some interfering organic matter. The individual components of ABS have been determined by mass fragmentography. Amounts greater than 3 µg/l of ABS in river water have been determined accurately by using this method.

## ACKNOWLEDGEMENTS

The authors wish to thank Drs. R. Ishiwatari and K. Ogura, Tokyo Metropolitan University, for valuable discussions. They also express thanks to Dr. Y. Ambe, National Institute for Environmental Studies, and Dr. T. Nakagawa, Kyoto University, for their kind advice. The linear alkylbenzenes and the linear alkylbenzenesulphonates used in this study were kindly supplied by Lion Fat & Oil Co. Ltd.

## REFERENCES

- 1 J. Longwell and W. D. Maniece, *Analyst (London)*, 80 (1955) 167.
- 2 M. C. Rand, A. E. Greenberg and M. J. Taras, *Standard Methods for the Examination of Water and Wastewater*, American Public Health Association/American Water Works Association/Water Pollution Control Federation, 14th Ed., 1975, p. 600.
- 3 M. C. Rand, A. E. Greenberg and M. J. Taras, *Standard Methods for the Examination of Water and Wastewater*, American Public Health Association/American Water Works Association/Water Pollution Control Federation, 14th Ed., 1975, p. 603.
- 4 E. M. Sallee, J. D. Fairing, R. W. Hess, R. House, P. M. Maxwell, F. W. Melpolder, F. M. Middleton, J. Ross, W. C. Wollfel and P. J. Weaver, *Anal. Chem.*, 28 (1956) 1822.
- 5 D. C. Abott, *Analyst, (London)*, 87 (1962) 286.
- 6 Y. Ambe and T. Hanya, *Bunseki Kagaku (Japan Anal.)*, 21 (1972) 252.
- 7 W. H. Hill, M. A. Shapiro and Y. Kobayashi, *J. Amer. Water Works Ass.*, 54 (1962) 409.
- 8 J. D. Knight and R. House, *J. Amer. Oil Chem. Soc.*, 36 (1959) 195.
- 9 E. A. Setzkorn and A. B. Carel, *J. Amer. Oil Chem. Soc.*, 40 (1963) 57.
- 10 E. R. Wright and A. L. Glass, *Soap Chem. Spec.*, 41 (1965) 83.
- 11 S. Lee and N. A. Puttnam, *J. Amer. Oil Chem. Soc.*, 44 (1967) 158.
- 12 I. Ötvös, B. Bartha, Z. Balthazár and G. Pályi, *J. Chromatogr.*, 94 (1974) 330.
- 13 S. Nishi, *Bunseki Kagaku (Japan Anal.)*, 14 (1965) 917.
- 14 T. H. Liddicoet and L. H. Smithson, *J. Amer. Oil Chem. Soc.*, 42 (1965) 1097.
- 15 H. L. Lew, *J. Amer. Oil Chem. Soc.*, 44 (1967) 359.
- 16 R. Denig, *Tenside Detergents*, 10 (1973) 59.
- 17 W. Davies and J. H. Dick, *J. Chem. Soc., London*, (1932) 483.
- 18 H. H. Bosshard, R. Morg, M. Schmid and H. Zollinger, *Helv. Chim. Acta*, 42 (1952) 1653.
- 19 J. J. Kirkland, *Anal. Chem.*, 32 (1960) 1389.
- 20 J. B. Himes and I. J. Dowbak, *J. Gas Chromatogr.*, 3 (1965) 194.
- 21 J. S. Parsons, *J. Gas Chromatogr.*, 5 (1967) 254.
- 22 S. Watanabe, M. Nukiyama, F. Takagi, K. Iida, T. Kaise and Y. Wada, *J. Food Hyg. Soc. Jap.*, 16 (1975) 212.
- 23 A. Heywood, A. Mathias and A. E. Williams, *Anal. Chem.*, 42 (1970) 1272.
- 24 M. Imaida, T. Sumimoto, M. Yada, M. Yoshida, K. Koyama and N. Kunita, *J. Food Hyg. Soc. Jap.*, 16 (1975) 218.