Gas Chromatographic Analysis for Alpha-olefin Sulfonate

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Abstract

The separation and determination of alkene sulfonate and hydroxyalkane sulfonate, and the carbon chain distribution of the lipophilic groups of long chain alpha-olefin sulfonates (C_{14} to C_{18}) were studied by means of gas chromatography. Samples were hydrogenated initially, and converted to sulfonyl chlorides for gas chromatographic analysis. Using a glass column, 4 mm i.d. and 2.5 m long, packed with Silicon SE-30, 3% on 60 to 80 mesh Chromosorb WAW treated with hexamethyldisilazane, a 0.3 to 0.6 μl sample, as 10% carbon tetrachloride solution, was injected directly on the column, and alkane and monochloroalkane sulfonyl chloride were determined as alkyl chloride and alkyl dichloride, respectively. Minimization of further decomposition, improvement of peak separation and reproducibility were accomplished by this procedure. The method was applied to alpha-olefin sulfonates produced commercially from C_{14} to C_{18} alpha-olefins.

Introduction

Alpha-olefin sulfonates (AOS), one of the active ingredients of some of the newer synthetic detergents, contains alkene sulfonate and hydroxyalkane sulfonate as main ingredients, and is a mixture of isomers and homologues having carbon chain distribution in the alkenyl and hydroxyalkyl groups (1–3). As a rule, alkene sulfonate is determined by measuring the degree of unsaturation and hydroxyalkane sulfonate by the hydroxyl value. Analysis is further complicated for unknown samples unless the carbon chain distribution of the original alpha-olefin is known, and due to disulfonate by-product. Measuring of hydroxyl value in AOS is not as easy as under ordinary circumstances, and the determination of hydroxyalkane sulfonate by means of formation of sultone (4) is not so desirable since sultone is also formed in part from alkene sulfonate under these conditions. In the case of alkylaryl sulfonate, desulfonated samples are analyzed by gas liquid chromatography (GLC) (5–8) but this method is not applicable to AOS. In some cases, alkyl sulfonate, alkylaryl sulfonate and naphthalene sulfonate were analyzed as sulfonyl chloride derivatives or as methylester derivatives (9,10), but they have relatively small carbon numbers which make them easier to handle. It seems that AOS, having carbon numbers of 15 to 18, is most suitable for detergent composition (1,2), hence such AOS was converted to easily decomposable sulfonyl chloride derivatives (11), and subjected to thermal decomposition gas chromatography. Because direct sulfonylization of AOS complicates the problem owing to alkene sulfonate in AOS, materials are sulfonylized after hydrogenation to yield corresponding sulfonyl chloride derivatives. It was found that side reaction products other than alkyl chloride from alkane sulfonyl chloride and alkyl dichloride from monochloroalkane sulfonyl chloride were minimized. This was accomplished by the on column method using a glass column. The carbon chain distribution of alkene sulfonate and hydroxyalkane sulfonate are determined by this method.

Experimental Procedure

Materials

Standard Sulfonates. These were synthesized in our laboratory. Several 3-hydroxy alkane sulfonates were synthesized by the Strecker reaction of 3-ketoalkyl chloride followed by reduction. C_{15}-2-alkene sulfonate was synthesized by the method of Kaiser and Püscher (12). Position of the double bond was ascertained by means of the Rudloff (13) approach. The C_{15}-2,3 and 4-alkene sulfonate components were found to be 96.1%, 3.5% and 0.4%, respectively. Oleyl sulfonate was synthesized by bromination of oleyl alcohol by means of the Colonge and Berthoux (14) method followed by the Strecker reaction. Position of the double bond was ascertained as above. The C_{18}-7,8,9,10 and 11 alkene sulfonate contents were 10.0%, 1.3%, 75.2%, 3.0% and 10.5% respectively. Properties of these sulfonates are indicated in Table I.

C_{14}, C_{16} and C_{18} AOS. Gulf's C_{14}, C_{16} and C_{18} alpha olefins were sulfonated by means of a falling film type reactor similar to Hurlbert's apparatus (15). The product was hydrolyzed with sodium hydroxide under high temperature and pressure, adjusted to proper pH and dried. Unreacted oil was removed by petroleum ether extraction, sodium sulfate was removed as 90% ethanol insoluble, and the sulfonates were dried at 70 C under reduced pressure.

C_{15} to C_{18} AOS. The above procedure was applied to Chevron's C_{15} to C_{18} alpha olefin.

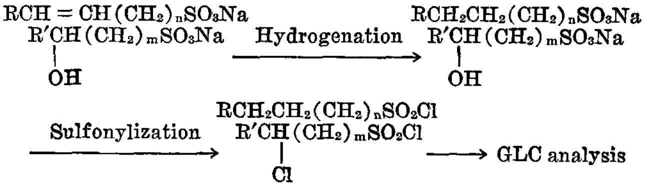
Thionyl Chloride. Kishida Kagaku Co., Special grade.

N,N-Dimethyl formamide. Kishida Kagaku Co., Special grade.

Dichloromethane. Tokyo Kasei Co., Special grade.

Apparatus. A Shimazu Model GC-1C equipped with HFID and temperature programming system was used.

Outline of Procedure.



$$\begin{matrix} RCH=CH(CH_2)_nSO_3Na \\ R'CH(OH)(CH_2)_mSO_3Na \end{matrix} \xrightarrow{\text{Hydrogenation}} \begin{matrix} RCH_2CH_2(CH_2)_nSO_3Na \\ R'CH(OH)(CH_2)_mSO_3Na \end{matrix} \xrightarrow{\text{Sulfonylization}} \begin{matrix} RCH_2CH_2(CH_2)_nSO_2Cl \\ R'CH(Cl)(CH_2)_mSO_2Cl \end{matrix} \longrightarrow \text{GLC analysis}$$

TABLE I

Properties of Standard Sulfonates[a]

Sample	OH.V.	Br.No.	Elemental analysis value, %			Active ingredient, %	Water content, %
			C	H	O		
C_{14}-3-Hydroxyalkane sulfonate	169.9(177.5)	....	53.1(53.2)	9.1(9.2)	10.1(10.1)	98.5	1.5
C_{16}-3-Hydroxyalkane sulfonate	157.6(163.0)	....	55.5(55.8)	9.4(9.6)	9.2(9.3)	98.4	1.5
C_{18}-3-Hydroxyalkane sulfonate	145.3(150.6)	....	56.3(58.1)	9.8(9.9)	8.3(8.6)	98.3	1.6
C_{15}-2-Alkene sulfonate	....	49.2(51.2)	55.4(57.7)	8.9(9.4)	9.6(10.3)	98.7	1.1
Oleyl sulfonate	....	43.9(45.1)	57.1(59.8)	9.2(9.8)	8.9(8.9)	97.8	1.2

[a] All sulfonates are sodium salt. Values in parentheses are calculated.

TABLE II

Elemental Analysis of Sulfonylized Materials

Sample	C, %		H, %		S, %		Cl, %	
	Meas.	Calc.	Meas.	Calc.	Meas.	Calc.	Meas.	Calc.
C_{18}-Alkane sulfonyl chloride	59.2	61.4	10.2	10.3	8.0	9.1	9.9	10.1
C_{18}-Monochloroalkane sulfonyl chloride	56.2	55.8	9.3	9.4	8.3	8.2	16.8	18.3

Results and Discussion

Preparation of Sample

Hydrogenation. Approximately 0.5 to 1.0 g of sample dissolved in 150 ml of 50% ethanol was placed in the reaction flask with inlet and outlet for hydrogen gas, and the same weight of Paladium (5%)/carbon catalyst was added. The flask was immersed in a 50 C water bath. Hydrogen gas was injected into the solution for 2 hr under stirring. The end-point of the reaction was judged by disappearance of 965 cm^{-1} absorption band of double bond in the IR spectrum. Alkene sulfonate not containing oleyl sulfonate was completely hydrogenated under these conditions. In oleyl sulfonate, the 965 cm^{-1} band was increased in the first hydrogenation and it disappeared in the second hydrogenation as shown in Figure 1. The reason for this is interpreted as isomerization of *cis* to *trans* occurring in the first step, while hydrogenation is then completed in the second step (16).

Sulfonylization. As sulfonylization of long chain sulfonate requires a relatively long time, it was found that during sulfonylization by the ordinary procedure oxidation may occur. In our study sulfonylization was carried out in a nitrogen atmosphere. A 0.5 to 1.0 g sample which had been hydrogenated previously, in the case of alkene sulfonate, was placed in a small round-bottom flask with attached condenser. Then 20 ml of thionyl chloride sulfonylizing agent and 0.5 g of dimethylformamide catalyst were added. The resulting solution was refluxed at 80 to 85 C under agitation and with nitrogen gas injected into the solution until the reaction was completed. If the reactant was a salt of a sulfonic acid, 20 ml of dichloromethane were added, and the sodium chloride reaction product was filtered off through a fine porosity sintered-glass filter. Excess thionyl chloride and solvent were removed by careful evaporation in a rotating vacuum evaporator. The final residue was weighed, and the relation between the time of sulfonylization and yield was examined. Finally, the residue was diluted to 10% in carbon tetrachloride for use in the GLC analysis. If insoluble matter was produced in the carbon tetrachloride solution, a small amount of sodium sulfate was added and the solids were filtered off. Yields of sulfonylized products of C_{18}-alkane sulfonate were 96.2%, 97.3% and 104.9% in reaction times of 30, 45 and 60 min, respectively. The IR spectrum of the reaction product at 60 min indicated the presence of oxidized material, but none was present at 45 min. Therefore, 45 min of reaction time was considered suitable. The same result was obtained for hydroxyalkane sulfonate. The IR spectrum and elemental analysis of sulfonylized products are shown in Figure 2 and Table II. The broad absorption band at about 1185 cm^{-1} and the sharp absorption band at about 1065 cm^{-1} based on the vibration of SO_3 in sulfonate disappeared, and sharp absorption bands at about 1150 and 1350 cm^{-1} based on the vibration of SO_2 in sulfonyl chloride appeared (17). The theoretical and the measured value of elemental analysis showed relatively good agreement. This indicates that alkane sulfonyl chloride is produced from alkane sulfonate and monochloro-alkane sulfonyl chloride from hydroxyalkane sulfonate.

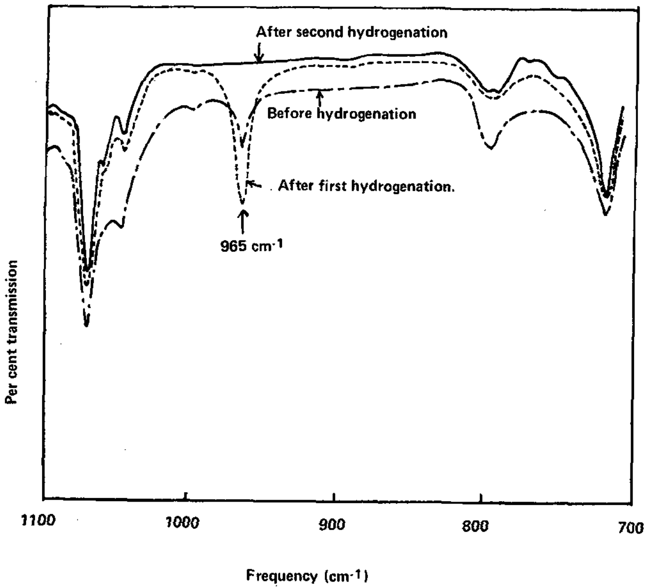


FIG. 1. IR spectra of sodium oleyl sulfonate and their hydrogenated products.

Gas Chromatographic Analysis

Examination of the Conditions of Separation. The conditions for the GLC analysis are summarized in Table III. A silicon DC-550 column was not suitable because of tailing and bad peak shape. The silicon SE-30 column in the first set of conditions gave relatively good peak shapes with a little tailing, but the separation of some peaks was troublesome. On the other hand, the application of the glass column in the second set of conditions yielded sharp peak shapes and good separation of the several peaks. The gas chromatogram of the sulfonyl chloride mixture having a carbon chain distribution (Chevron's C_{15} to C_{18} AO

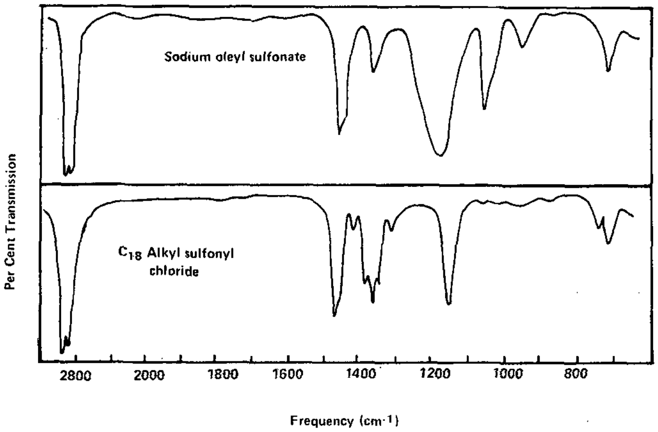


FIG. 2. IR spectra of sodium oleyl sulfonate and their sulfonylized products.

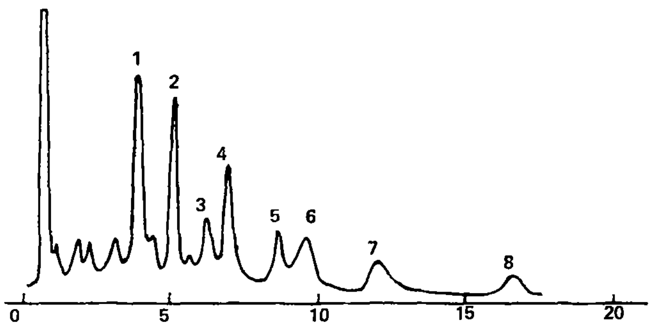


FIG. 3. Gas chromatogram of C_{15} to C_{18} sulfonyl chloride mixture.

derivative) under the second set of conditions is shown in Figure 3. It indicates that use of a glass column is suitable. By using standard sulfonates at the same conditions, it was confirmed that peaks 1, 2, 4 and 6 in Figure 3 were peaks derived from C_{15}, C_{16}, C_{17} and C_{18}-alkane sulfonyl chlorides respectively, and those numbered 3, 5, 7 and 8 were from C_{15}, C_{16}, C_{17} and C_{18}-monochloro-alkane sulfonyl chlorides respectively. Next, peaks were identified by means of GC-MS (GC connected to a Hitachi RMU-6 mass spectrometer) in several sulfonyl chlorides derived from C_{18} AOS, oleyl sulfonate and C_{18}-3-hydroxy-alkane sulfonate. Several chromatograms are shown in Figure 4. Retention time of peak 3 coincides with that of C_{18}-alkyl chloride; this result was supported by GC-MS (11). Peak 4 is presumed to be 1,3-dichloro octadecane from its mass spectrum. Retention time of peak 1 coincides with C_{18}-alpha-olefin; this result was supported by GC-MS (11). Peak 2 is presumed to be 3-chloro-1-octadecene from its mass spectrum.

Reproducibility. As sulfonyl chloride derivatives of long carbon chain sulfonates exhibit characteristic thermal decomposition as shown above, the conditions for quantitative analysis were investigated. The half width method was used to measure the peak area.

The relation between temperature of injection port and quantity of decomposed product was examined when the sample is injected into the injection port of the gas chromatograph at 200 C column temperature using C_{18} sulfonyl chloride derived from oleyl sulfonate. The result is shown in Figure 5. The quantity of olefin decreased with lowering of injection port temperature showing a minimum value at 220 C. Further lowering of temperature yielded a poorly shaped peak and tailing. With column temperature at 200 C and injection port temperature at 220 C, the reproducibility of the quantities of olefin and of alkyl chloride produced were examined in terms of the ratio of peak areas to methyl laurate area used as an internal standard. Deviation of both measured values is large as indicated in Table IV. It is presumed that these result from the indefinite amount of sample decomposition. To overcome the defects of the above-mentioned procedure, a method involving sample injection directly on the column (on-column method) was examined. In order to control the temperature of the injection port independently of the column temperature, the injection port of the column was modified as shown in Figure 6. From the relation between temperature of injection port and quantity of olefin, it was found that 225 C is a suitable injection port temperature. In a run with temperature under 225 C, the determination of peak area was not very

TABLE III
Conditions for GLC Analysis of Sulfonyl Chloride

		Condition 1		Condition 2
Column		Stainless steel (3 mm i.d. 2.4 m long)		Glass (4 mm i.d. 2.5 m long)
Liquid phase		Silicon SE-30, 3 %		Silicon SE-30, 3 %
Active solid[a]		Chromosorb W.AW (60/80)		Chromosorb W.AW (60/80)
Detector		HFID		HFID
Column temp., C		200		200
Injection port temp., C		220		220
Carrier gas	N_2	60 ml/min	N_2	60 ml/min
H_2		50 ml/min		40 ml/min
Air		0.85 Kg/cm^2		0.85 Kg/cm^2

[a] Treated with hexamethyldisilazane.

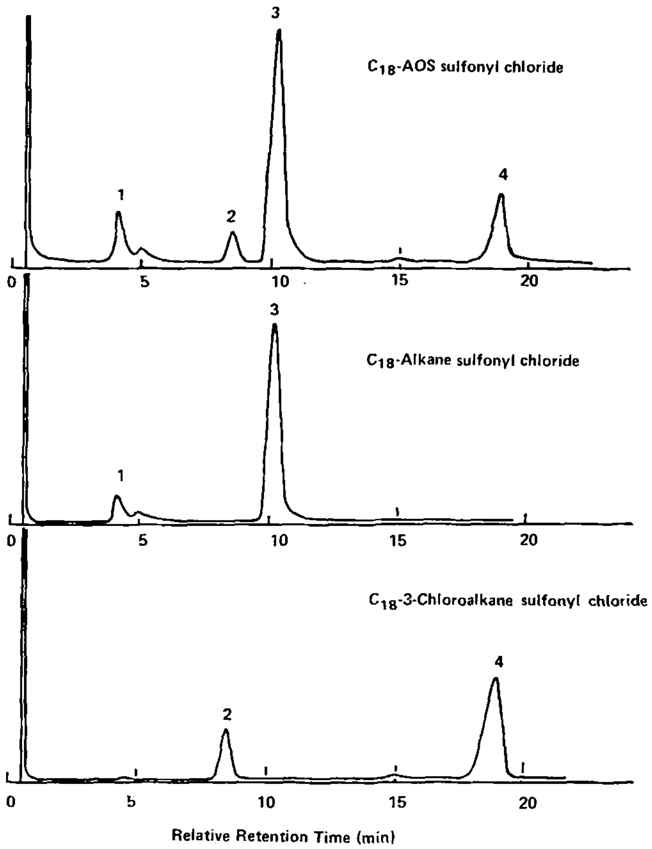


FIG. 4. Gas chromatograms of C_{18}-AOS sulfonyl chloride, C_{18}-alkane sulfonyl chloride and C_{18}-3-chloroalkane sulfonyl chloride.

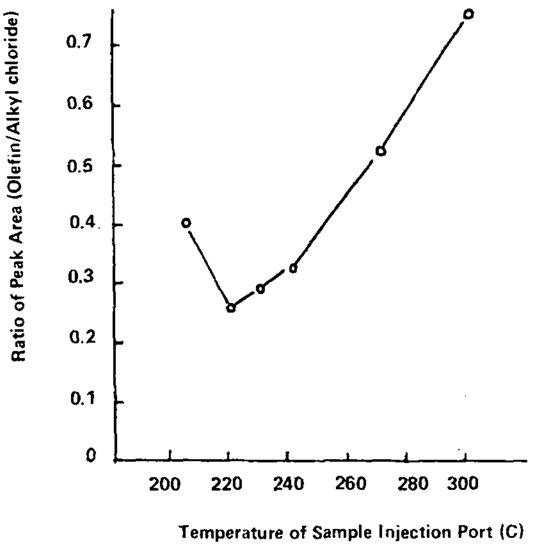


FIG. 5. Relation between temperature of sample injection port and ratio of peak area.

TABLE IV

Comparison of Reproducibility and Quantity of Olefin for Different Sample Injection Methods (C_{18} Sulfonyl Chloride)

Method	Ratio of peak area	Trials						Average	Standard deviation
		1	2	3	4	5	6		
Conventional	Olefin–C_{12} methyl ester	0.46	0.50	0.51	0.49	0.39	0.54	0.48	0.05
	Alkyl chloride–C_{12} methyl ester	1.48	1.67	1.36	2.20	2.47	1.52	1.78	0.41
On-column	Olefin–C_{12} methyl ester	0.28	0.28	0.27	0.33	0.36	0.32	0.31	0.04
	Alkyl chloride–C_{12} methyl ester	3.20	3.46	3.46	2.97	3.30	3.50	3.33	0.19

TABLE V

Comparison of Reproducibility With Respect to Quantity of Sample

Quantity of sample	Ratio of peak area	Trials										Average	Standard deviation
		1	2	3	4	5	6	7	8	9	10		
C_{15} AOS 0.1~0.2 μl	Alkyl chloride–alkyl dichloride	2.98	2.74	2.94	3.10	3.01	3.01	2.86	2.93	3.14	3.09	2.97	0.10
	Olefin and Olefin chloride–methyl ester	0.70	0.75	0.81	0.73	0.73	0.77	0.96	0.86	0.87	0.90	0.81	0.08
	Alkyl chloride–methyl ester	1.76	2.41	2.35	1.80	1.80	2.37	2.95	2.67	2.17	2.90	2.32	0.41
	Alkyl dichloride–methyl ester	0.61	0.88	0.80	0.58	0.60	0.79	1.03	0.91	0.69	0.94	0.78	0.15
C_{18} AOS 0.3~0.6 μl	Alkyl chloride–alkyl dichloride	2.81	2.95	2.93	3.04	2.99	3.00	2.93	......	......	......	2.95	0.07
	Olefin and Olefin chloride–methyl ester	0.70	0.92	1.02	0.80	1.00	0.93	0.96	......	......	......	0.90	0.11
	Alkyl chloride–methyl ester	3.64	3.33	3.72	3.41	3.41	3.19	3.13	......	......	......	3.40	0.20
	Alkyl dichloride–methyl ester	1.30	1.13	1.27	1.12	1.14	1.06	1.16	......	......	......	1.16	0.09
C_{16} AOS 0.3~0.6 μl	Alkyl chloride–alkyl dichloride	3.03	2.90	3.14	2.87	3.03	3.04	3.00	3.18	2.96	......	3.02	0.10
	Olefin and Olefin chloride–methyl ester	0.72	0.90	0.84	0.84	0.84	0.81	0.81	0.78	0.90	......	0.84	0.06
	Alkyl chloride–methyl ester	2.64	2.64	2.61	2.58	2.82	2.10	2.43	2.67	2.49	......	2.55	0.18
	Alkyl dichloride–methyl ester	0.87	0.90	0.90	0.90	0.92	0.69	0.81	0.78	0.90	......	0.84	0.06

TABLE VI

Correction Factor of C_{18}-Monochloroalkane Sulfonyl Chloride to C_{18}-Alkane Sulfonyl Chloride

Ratio	Trials									Average	Standard deviation
	1	2	3	4	5	6	7	8	9		
Mixed ratio of $R(Cl)SO_2Cl/RSO_2Cl$	3.91	3.91	1.47	1.47	1.47	0.65	0.65	0.24	0.24	......	......
Ratio of peak area	1.51	1.65	0.61	0.55	0.53	0.26	0.23	0.10	0.10	......	......
Correction factor	2.60	2.37	2.39	2.65	2.77	2.51	2.79	2.61	2.64	2.59	0.15

good because of poor peak shape and tailing. With column temperature of 200 C and 225 C on-column temperature, the reproducibility was examined by use of the same C_{18} sulfonyl chloride. Reproducibility is improved over the prior method with respect to olefin and alkyl chloride. As indicated in Table IV, the ratio of C_{18} alkyl chloride to olefin became three to one. Stated another way, the conventional VPC injection method resulted in an apparent area decomposition of alkyl chloride to olefin of approximately 21%, which was reduced 8.5% by the improved on-column injection technique. In the next test, an investigation was made of the chromatographing of a C_{18} sulfonyl chloride mixture derived from hydrogenation and sulfonylization of C_{18} AOS containing alkene sulfonate and hydroxyalkane sulfonate. At the same time, the effect of sample quantity injected onto the column was examined. As shown in Table V, an injected sample of 0.3 μl to 0.6 μl at 10% concentration in carbon tetrachloride gives better reproducibility and is prefered to a sample quantity of 0.1 μl to 0.2 μl. But the ratio of alkyl chloride to alkyl dichloride remains the same regardless of the injected sample quantity.

Another test was also carried out in the same manner, using a C_{16} sulfonyl chloride mixture derived from the same treatment. The results from the 0.3 μl to 0.6 μl injections are indicated in Table V. Good reproducibility was also gained in this case. These results indicate that it is difficult to eliminate the side reaction completely, but it was found that this procedure offers a quantitative determination with good reproducibitly.

Quantitative Analysis

Correction Factor. Relative sensitivity should be measured for the quantitative determination of a mixture of alkane sulfonyl chloride and monochloroalkane sulfonyl chloride. Standard C_{18} alkane sulfonyl chloride and C_{18} monochloroalkane sulfonyl chloride were mixed in various ratios of 20% to 80%, peak areas in the gas chromatogram were determined, and a correction factor was calculated from the ratio of the peak areas. Therefore, the correction factor in-

TABLE VII

GLC Analysis of Mixture of C_{16}- and C_{18}-Sulfonyl Chloride

Added, %		Found, %					
C_{16}	C_{18}	C_{16}-SO_2Cl	C_{16}-(Cl)-SO_2Cl	C_{16} Total	C_{18}-SO_2Cl	C_{18}-(Cl)-SO_2Cl	C_{18} Total
28.9	71.1	16.6	10.4	27.0	41.1	31.9	73.0
41.7	58.3	24.2	16.2	40.4	34.7	24.9	59.6
58.2	41.8	35.2	23.0	58.2	23.0	18.8	41.8
75.1	24.9	47.2	28.9	76.1	12.9	11.0	23.9

TABLE VIII

GLC Analysis of AOS Derived From Chevron's C_{15} to C_{18} Alpha-Olefin

Carbon chain	RSO_2Cl	$R(Cl)SO_2Cl$	Total	Original alpha-olefin[a]
C_{15}	15.5	10.5	26.0	26.7
C_{16}	18.2	10.8	29.0	27.6
C_{17}	16.1	8.8	24.9	24.6
C_{18}	14.0	6.1	20.1	18.3
Total	63.8	36.2	100.0	97.2

[a] This sample contains 2.8% olefin other than C_{15} to C_{18} olefin.

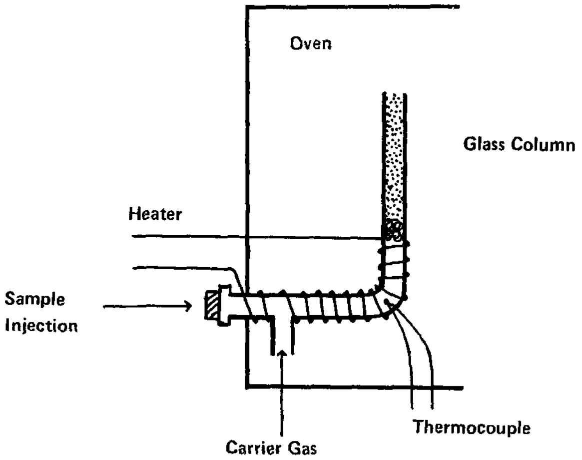


FIG. 6. Scheme of on column injection port.

dicated here involves both relative sensitivity of the sample and decomposition rate, if it differs. As shown in Table VI, the correction factor for C_{18} monochloroalkane sulfonyl chloride to C_{18} alkane sulfonyl chloride is 2.59. Conversely, when 2.59 is used as correction factor of C_{18} monochloroalkane sulfonyl chloride to C_{18} alkane sulfonyl chloride, the standard deviation of measured value from calculated value was 1.22 by means of the least squares method in the other eight measurements.

The correction factors for several carbon chain lengths were successively examined. A mixture of sulfonyl chloride derivatives of C_{18} and C_{16} AOS which contains alkene sulfonate and hydroxyalkane sulfonate was used for this purpose. The mixture was examined under the hypothesis that the correction factor of monochloroalkane sulfonyl chloride to alkane sulfonyl chloride is constant at 2.59 and is unrelated to the carbon chain length in the range of C_{14} to C_{18}. If the correction factor for C_{16} monochloroalkane sulfonyl chloride is greater than for C_{18} monochloroalkane sulfonyl chloride, the total of C_{16} monochloroalkane sulfonyl chloride and C_{16} alkane sulfonyl chloride will decrease against the total of C_{18}, and this tendency should be more pronounced with an increase of C_{16} content. As shown in Table VII, the calculated ratios of mixed sulfonyl chlorides and measured values in which 2.59 is used equally as correction factor for both C_{18} and C_{16} monochloroalkane sulfonyl chloride were in good agreement, so this hypothesis is considered suitable.

As an example of the application of this method, an AOS derived from Chevron's C_{15} to C_{18} alpha-olefin was examined. Programmed temperature GLC gave good peak separation as shown in Figure 7 compared with Figure 4. This AOS contains disulfonate as all such AOS industrial products, so these disulfonates are also hydrogenated and sulfonylized in the same way. But, since many types of decomposition products are formed in small quantities respectively, these elevate the base line as a whole. For instance, a gas chromatogram of Chevron's C_{15} to C_{18} AOS, when containing nearly 20% disulfonate, indicates a relatively elevated base line. So, to get a precise result, disulfonate should be separated by countercurrent fractionation (18) prior to the suggested procedure. As shown in Table VIII, the carbon chain distribution indicates good agreement; alkane sulfonate and hydroxyalkane sulfonate were 63.8% and 36.2% respectively. As a comparison, hydrogen value indicates the existence of 62% alkene sulfonate.

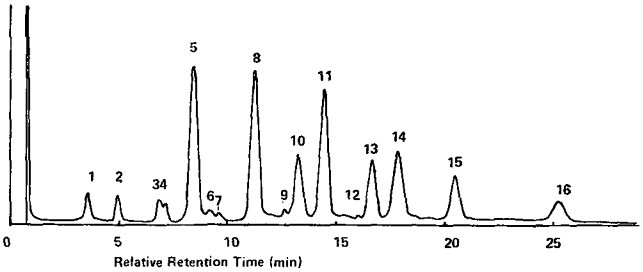


FIG. 7. Gas chromatogram of C_{15} to C_{18} sulfonyl chloride mixture by programmed temperature GLC (170C–200C, 2C/min). 1, C_{15}-alpha-olefin; 2, C_{16}-alpha-olefin; 3, C_{17}-alpha-olefin; 4, C_{15}-alpha-olefin chloride; 5, C_{15}-alkyl chloride; 6, C_{18}-alpha-olefin; 7, C_{16}-alpha-olefin chloride; 8, C_{16}-alkyl chloride; 9, C_{17}-alpha-olefin chloride; 10, C_{15}-alkyl dichloride; 11, C_{17}-alkyl chloride; 12, C_{18}-alpha-olefin chloride; 13, C_{16}-alkyl dichloride; 14, C_{18}-alkyl chloride; 15, C_{17}-alkyl dichloride; 16, C_{18}-alkyl dichloride.

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