Gas Chromatographic Analysis for Long Chain Sultones in Olefin Sulfonates

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ABSTRACT AND SUMMARY

A gas chromatographic method is described for the analysis of tetradecane-1,4-sultone (C_{14} delta sultone) and the combination of 2-chlorotetradecane-1,3-sultone (C_{14} 2-chloro gamma sultone), and 1-tetradecene-1,3-sultone (C_{14} unsaturated gamma sultone) in neutral oils isolated from olefin sulfonate. Samples of the neutral oil are diluted in hexane and injected directly into the gas chromatograph. Quantitative data are obtained by comparison to known amounts of the respective sultones. Through the use of silica gel column chromatography followed by gas chromatography of collected fractions, separation and individual quantitation of the 2-chlorotetradecane-1,3 sultone and 1-tetradecene-1,3-sultone can be obtained. Routine use for control purposes has shown the method to be reliable and interlaboratory agreement of data has been good.

INTRODUCTION

Sulfonation of alpha olefins produces primarily olefin sulfonate, but it also produces small amounts of sultones. Hydrolysis of the reaction products converts the sultones to sulfonates, but a subsequent hypochlorite bleaching step can produce additional, undesirable chlorinated and unsaturated sultones which have been indicted as skin sensitizers (1).

Because of the complexity of the mixture and the extremely low levels of sultones which may be present in olefin sulfonates, existing methods of analysis were not applicable. Gas chromatographic (GC) and thin layer chromatographic (TLC) procedures (2) for sultone analysis were investigated simultaneously in our laboratories, but it was felt that gas chromatography was a more suitable method for use in quality control laboratories. Previous investigators (3-5) have stated that because of their thermal instability and reactivity, sultones could not be easily analyzed by gas chromatography. If these problems can be overcome, gas chromatography offers a quick and simple means for sultone analysis.

EXPERIMENTAL PROCEDURES

Extraction

The neutral oil is extracted using a modification of the ASTM D 1568-63 method. A 25 g sample (38% sulfonate solution) is dissolved in 400 ml of 1:1 ethanol-water, extracted six times with 100 ml portions of redistilled 30-60 C petroleum ether, and the extract is evaporated to dryness in a tared flask. A 10% (w/v) solution of the neutral oil in hexane is then prepared for chromatographic analysis by dilution in a volumetric flask of appropriate size.

Apparatus

Column packing (6% OV-101 on 80/100 mesh Chromosorb W-HP): The procedure used to prepare the column packing is a modification of the one described by Liebrand and Dunham (6). The packing was found to be most reproducible and more conveniently prepared when made in 10-g batches. A solution of 3 g of OV-101 methyl silicone in 100 ml of $CHCl_3$ is added to a 250 ml suction flask and degassed under vacuum for 5 min. Nitrogen rather than laboratory air is allowed to flow through the flask as vacuum is being increased. The flask is brought to atmospheric pressure using nitrogen, and 10 g of 80/100 mesh Chromosorb W-HP is added. With gentle swirling the system is again degassed for a period of 5 min, then brought to atmospheric pressure using nitrogen. The contents of the flask are transferred to a sintered glass Buchner funnel, and vacuum is applied for ca. 5 min. The packing is then transferred to a glass column containing a sintered glass disc, and nitrogen is passed through it until dry (ca. 2 hr). The liquid phase concentration is determined by quantitative recovery of the OV-101 from the filtrate. The weights described generally result in a liquid phase concentration of ca. 6%. In our laboratory, packings prepared by this solution coating technique have produced the desired separations of the sultones under investigation. Commercially prepared packing, 6% OV-101 on 80/100 mesh Chromosorb W-HP, obtained from Supelco, Inc. (Bellefonte, PA) has also been used successfully to give the desired separations.

Chromatographic column: Two types of glass columns have been used in this work with equal success: (a) "Chromatoglass" columns (Analabs, Inc., North Haven, CT) 10 ft in length, 4 mm OD x 2 mm ID with 1/4 in. heated inlet and (b) a 10-ft 1/8 in. OD x 1.8 mm ID column (Supelco, Inc.) used in conjunction with a glass-lined injection port. Packed columns are conditioned by heating from 100 C to 250 C @1° per min and maintaining at 250 C overnight (ca. 15 hr). The columns are generally conditioned well enough for use the following day.

Silicone septums: Septum bleeding can be a problem at the conditions used for this analysis. The problem has been corrected by soaking septums in hexane for 2-3 hr, decanting, air drying, and then heating at 350 C for ca. 5 hr under a stream of nitrogen. One type of septum purchased from Supelco, Inc. (gray color) has been used without preconditioning with no trouble.

Chromatographic conditions: Analyses were performed on a Hewlett-Packard Model 5711 flame ionization gas chromatograph. The injection port temperature was maintained at 300 C (specific for C_{14} sultones) and the detector temperature at 250 C. The column temperature was programmed from 175 C to 240 C @2° per min with a 16-min post-injection interval. The flow rates were nitrogen (carrier)–25 ml/min, hydrogen 30 ml/min, and air 240 ml/min. Sensitivity settings were range 100, and attenuation x1, and the chart speed was 1/4 in. per min.

Analysis

Prepare a calibration solution in hexane containing C_{14} delta sultone and either C_{14} unsaturated gamma or C_{14} 2-chloro gamma sultone (at low concentrations the response of the two is similar). The concentration should closely approximate the expected levels of sultones in the samples. The solvent flush technique of injection is used in all work. A microliter plug of hexane is drawn into the syringe followed by 2 microliters of calibration solution. Chromatographic conditions have been previously described. The retention time for C_{14} delta sultone at these conditions should be ca. 35 min, but has been found to vary by as much as several minutes from column to column. C_{14} unsaturated gamma and 2-chloro gamma sultone have

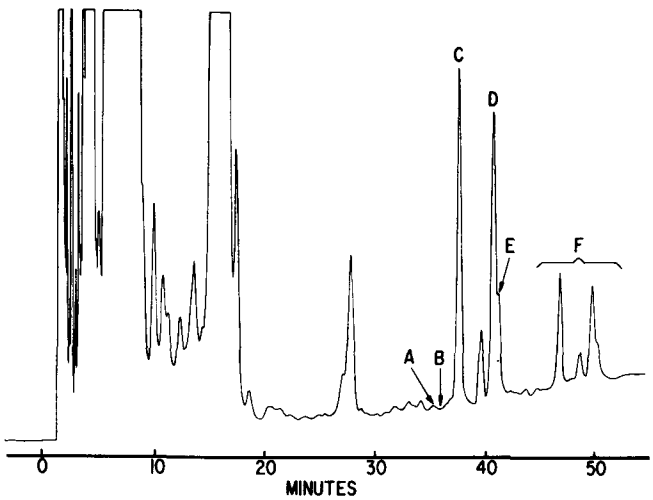

FIG. 1. Typical chromatogram of neutral oil from hypochlorite bleached alpha olefin sulfonate: A = C_{14} delta sultone; B = C_{14} unsaturated gamma and/or 2-chloro gamma sultone (not detected in sample); C = C_{14} 3-chloro delta sultone; D = C_{14} 5-chloro delta sultone (diastereomer); E = C_{14} 5-chloro delta sultone (diastereomer); F = C_{16} sultones.

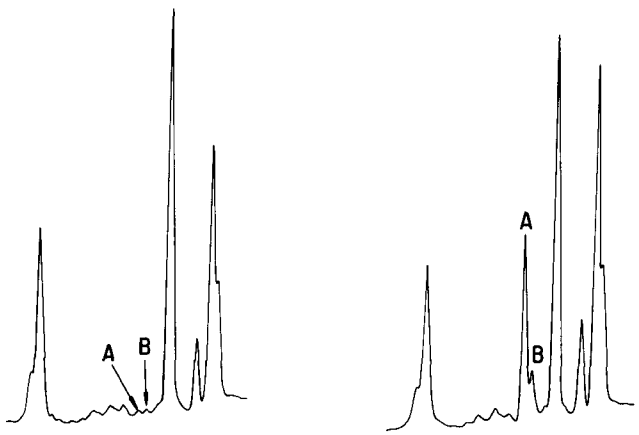

FIG. 2. Spiked samples of neutral oils showing different sultone levels. The first contains 2 ppm each of C_{14} delta sultone (A) and C_{14} unsaturated gamma sultone (B); the second contains 18 ppm of C_{14} delta sultone (A) and 5 ppm of C_{14} unsaturated gamma sultone (B).

retention times ca. 0.5 min later than the delta sultone. The initial injection on the column each day serves as a conditioner and is not used as an analysis. Daily calibration has been found to be a necessity.

The solution of previously extracted neutral oil is treated in the same manner as the calibration solution. A typical chromatogram of neutral oil from hypochlorite-bleached alpha olefin sulfonate is shown in Figure 1. Spiked samples of neutral oil containing various amounts of C_{14} delta sultone and unsaturated gamma sultone are shown in Figure 2.

Calculations

In our laboratories peak height measurements are used for calculations and results are reported as ppm of the original olefin sulfonate sample.

$$\text{ppm } C_{14} \text{ delta soltone in olefin sulfonate} = \frac{A/B \times C}{D \times 0.002 \text{ ml Sample injected}}$$

Where: A = Peak height C_{14} delta sultone in olefin sulfonate sample.

B = Peak height C_{14} delta sultone in calibration solution.

C = Micrograms of C_{14} delta sultone in 2 microliters of calibration solution.

D = Grams of original olefin sultonate sample used to obtain the oil, divided by the capacity of the flask (in ml) used to make the 10% solution of neutral oil.

Typical example:

$$\frac{\dfrac{21.2 \text{ mm}}{83.4 \text{ mm}} \times 0.428 \text{ micrograms}}{\dfrac{24.6 \text{ g}}{2 \text{ ml}} \times 0.002 \text{ ml}} = 5.4 \text{ ppm } C_{14} \text{ delta sultone}$$

For olefin sulfonate samples of multiple chain lengths, the total sultone content can be determined from the chain length distribution of the sample.

RESULTS AND DISCUSSION

The key to the successful chromatography of the delta and gamma sultones is the column, its preparation, and its conditioning. Numerous stationary phases were investigated, but only OV-101 separated C_{14} delta sultone from the C_{14} unsaturated gamma/2-chloro gamma sultone combination and also separated these from other components present in the sample. Apiezon L separated all three sultones of interest but other components in the neutral oil interfered with the C_{14} unsaturated gamma sultone. Additional stationary phases have been found which will separate these sultones, but again, interfering components preclude their use for neutral oil analysis.

Columns prepared with from 5-7.5% loadings of OV-101 performed equally well. At a concentration of 10% OV-101 a small increase in sultone response is observed, but the efficiency of the columns declines. Below 5% OV-101 concentrations the separation of the sultone components decreases significantly.

The procedure used for the preparation of column packings was found to be critical, and only the solution coating technique as previously described has resulted in successful and reproducible packings. Most commercially prepared packings made by similar procedures have produced good columns, but completely prepared purchased columns, while not extensively investigated, have not achieved the same degree of success.

As with most silicone liquid phases, the OV-101 columns used in this work have improved significantly with age. Columns have lasted through many months of almost continuous use, and when separation of the sultones deteriorated, repacking of the first 6 in. of the column usually restored column efficiency.

The all-glass system was a must for the analysis of the sultones in this method. The exposure of any bare metal surfaces in the system to the sample can result in absorption and/or decomposition of the sultones.

The investigations into the preparation of reproducible columns covered a period of many months. While none of the above-mentioned requirements for successful columns is unique to this method, it was not until the equal importance of all aspects was discovered that reproducible columns were consistently prepared.

Because of the fragile nature of glass columns, current investigation includes precoating of the walls of metal columns with stationary phase prior to packing, using techniques similar to those employed in capillary column preparation. Success in this operation has been limited due to the problems involved in obtaining a reproducible, thin film on the column walls and also because of the inherent problems involved in the efficient packing of such a

TABLE I

Cooperative Study for Sultones in Neutral Oil

Laboratory	Sample A		Sample B		Sample C		Sample C	
	Delta sultone (ppm)	2-Cl-Gamma sultone (ppm)	Delta sultone (ppm)	2-Cl-Gamma sultone (ppm)	Delta sultone (ppm)	2-Cl-Gamma sultone (ppm)	Delta sultone (ppm)	2-Cl-Gamma sultone (ppm)
1	19	7	13	ND[a]	33	8	29	ND
2a[b]	19	12	12	"	34	9	24	"
2b[b]	17	8	12	"	31	8	27	"
3	19	8	15[c]	"	34	9	28	"
4	19	7	20[c]	"	30	8	28	"
5	17	12	14	"	29	13[c]	25	"
6	20	11	11	"	27[c]	5[c]	33[c]	"
7	17	6	11	"	34	10	23	"
8	19	8	13	"	34	7	33[c]	"
9	17	7	11	"	32	9	25	"
Mean	18	9	13	—	32	9	28	—
Standard deviation	±1	±2	±1	—	±2	±1	±2	—
Amount added	17	6	14	0	34	8	28	0

[a]ND = none detected.

[b]Different analysts.

[c]Omitted from statistical calculations.

TABLE II

Precision of Sultone Analysis

Laboratory	Delta sultone (ppm)		2-Cl-Gamma sultone (ppm)	
	Mean	Standard deviation	Mean	Standard deviation
1	18.1	±0.4	7.0	±0.2
2a[a]	19.3	±0.6	11.7	±0.7
2b[a]	16.9	±0.5	7.7	±0.3
3	19.1	±0.4	8.0	±0.4
4	19.1	±0.2	6.6	±0.1
8	18.7	±0.5	7.7	±0.4
Amount added	17		6	

[a]Different analysts.

column. Several good columns were obtained which gave satisfactory separations of the sultones of interest; however, these columns did not have the efficiency of the glass columns.

Recovery studies, which have included the extraction of the neutral oil, and precision data have shown this method to be accurate and precise within acceptable limits. It has been given considerable testing through a cooperative study among nine laboratories (four intercompany and five suppliers). A set of four samples of neutral oils containing known amounts of C_{14} delta sultone and C_{14} 2-chloro gamma sultone was supplied to each laboratory. Outside labs used columns prepared by themselves, while the intercompany labs all used pretested columns prepared in our laboratory. Results are shown in Table I.

The standard deviation for all samples is ±2 ppm at the 10-30 ppm level of delta sultone. For control purposes the method was designed for rejection of samples with detectable amounts of C_{14} unsaturated gamma and/or C_{14} 2-chloro gamma sultones with no calculations required. As part of the cooperative study, however, laboratories were asked to calculate values for these sultones. Because they are incompletely resolved from delta sultone, the value for the gamma sultones is significantly affected by both the quality of separation achieved on the column and the amount of delta sultone present. The results show a wider range of values than for delta sultone but in most instances they are within several ppm of the true value. No one had difficulty in detecting the presence of the gamma sultones in the samples.

Six of the laboratories participated in a precision study on one of the samples. Results are shown in Table II. In each case the standard deviation was less than 1 ppm for all components.

The neutral oils from alpha olefin sulfonates are extremely complex mixtures, and as in any method of this type where extremely low levels of material are identified solely on the basis of retention time, it is desirable to have companion methods which can confirm the identifications. Thin layer chromatography has been shown to be effective for the separation and semiquantitative estimation of the same sultones as well as others. In the majority of our work TLC has been used in conjunction with gas chromatography, and correlation between the methods has been good. The combination of GC, TLC, and preparative TLC has been used extensively in the identification of the various sultones found in the samples analyzed.

Although this method is specific for C_{14} delta, unsaturated gamma and 2-chloro gamma sultones, other sultones, as shown in Figure 1, have been identified (G.E. Natarelli, in preparation). These sultones have also been determined quantitatively by GC, and the values agree with those obtained for total sultone content as determined by hydrolysis.

Silica Gel Chromatography

C_{14} unsaturated gamma sultones and C_{14} 2-chloro gamma sultone can be separated using silica gel column chromatography on a semi-micro basis. A 2 ml graduated, glass pipet is filled with 3.5 cm of 40-140 mesh silica gel, and 0.5 ml of the neutral oil solution is added to the column. The column is eluted with 2.5 ml of hexane, 3 ml of 10% ethyl ether in hexane, and finally 3 ml of 100% ethyl ether. Between each different elution the column is

dried with a gentle stream of air. All fractions are readjusted to a 0.5 ml volume prior to reexamination by GC. The hexane eluate will contain olefinic and paraffinic materials present in the neutral oil. The 10% ethyl ether fraction will contain the C_{14} 2-chloro gamma sultone, and the 100% ethyl ether fraction will contain C_{14} delta sultone and C_{14} unsaturated gamma sultone.

Besides separating the unsaturated gamma and 2-chloro gamma sultones, this procedure has been effective in removing nonsultone materials which may interfere with the analysis of sultones in the neutral oil. It has also been useful for concentrating samples prior to examination by thin layer chromatography.

Detection Limits

The method as presented has been able to consistently detect less than 1 ppm of sultone in a 38% olefin sulfonate solution. By concentrating the solution of the neutral oil and using silica gel column chromatography, 0.1 ppm of sultone can readily be detected. Further changes in GC conditions and sensitivity can give even lower limits of detection.

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