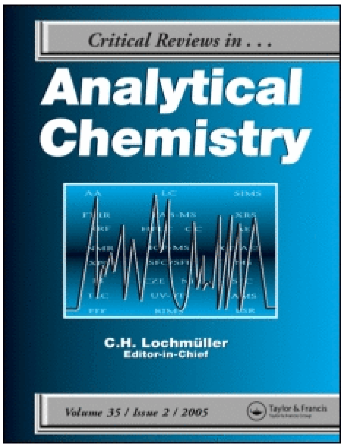

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A COMPARATIVE AND CRITICAL REVIEW OF ANALYTICAL METHODS FOR SEPARATION AND DETERMINATION OF ALIPHATIC AND AROMATIC SULFONATES

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I. INTRODUCTION

Sulfonates are extensively used in the petroleum industry[1] as flotation agents, emulsifiers, corrosion inhibitors, lubricants, etc. Sulfonates are also important because of their use in synthetic detergents which can lead to water pollution and become relevant to sewage treatment.[2] As such, a review of methods which have been used in the determination and separation of aliphatic and aromatic sulfonates is of interest.

In this review, seven methods of separation and twelve methods of determination for sulfonates, published during the past 20 years, are compared. Papers that are not included in this comparison are cited in the Appendix.

II. DETERMINATION METHODS

The methods reviewed involve titrimetry including two-phase titration, gravimetry, UV, visible, and IR absorption spectrometry, gas chromatography, nuclear magnetic resonance, mass spectrometry, atomic absorption, radiometry, and the use of ion-selective membrane electrodes.

A. Titrimetric Methods

One-phase titration methods are based on titration of the corresponding sulfonic acids with a standard base by using indicators, for example phenolphthalein or neutral red. A determination of aromatic sulfonation mixtures containing sulfuric and sulfonic acids was analyzed by Houff et al.[3] in 1957. After precipitating sulfates by adding barium hydroxide, the mixture was filtered. The filtrate was converted to the corresponding sulfonic acids by passing it through a cation exchanger in the (H^+) form and then titrating with 0.1 *N* NaOH using phenolphthalein indicator. Six commercial compounds containing aromatic sulfonates were determined in three replicates with accuracy and precision of ± 0.3 and ± 1%, respectively. In this review, accuracy is reported as relative % error, and precision is reported as relative % standard deviation from the mean. This method determines the total amount of sulfonate in a sample provided that the barium sulfonates are soluble in the presence of barium hydroxide solution.

Using neutral red and thymolphthalein indicators, Gribova[4] determined 1-naphthalenesulfonic acid in sulfuric acid by titrating with tetraethylammonium hydroxide in a benzene-ethanol (2:1) mixture. The first equivalent point, at which the color changes from red to yellow, indicates the complete neutralization of sulfonic acid and the sulfuric acid to hydrogen sulfate, HSO_4^-; the second equivalent point, at which the color changes from yellow to blue-green, indicates that the hydrogen sulfate is completely neutralized. The results of the 1-naphthalenesulfonic acid analysis were comparable with those obtained from the potentiometric titration with accuracy and precision of ± 0.074 and ± 0.46%, respectively. The titrimetric methods are simple and need only simple equipment, but they are usually slow.

B. Two-Phase Titration Methods

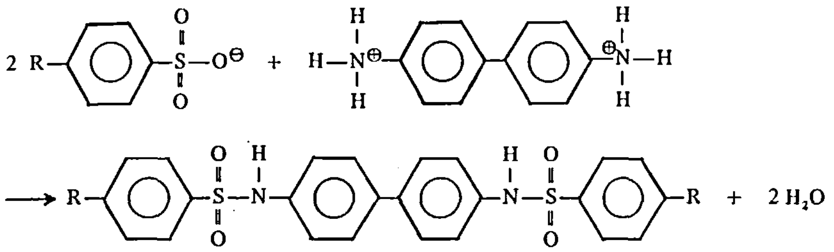
The determination of anionic surfactants by forming a complex with methylene blue, extracting into chloroform, and titrating with cationic surfactants until the color in the two phases is identical was introduced by Epton[5] in 1948. Using this technique, Fenwick[6] in 1971 determined the content of sulfonate in an oil-soluble petroleum sulfonate by titrating with Hyamine® 1622 [*p-tert*-octylphenoxyethoxyethyldimethylbenzylammonium chloride]. The complex of methylene blue-sulfonate in chloroform is substituted by that of Hyamine-sulfonate, and the methylene blue is liberated from the chloroform layer. The end-point is obtained when the colors of both phases are identical. The results of ten determinations (in samples of unknown concentration) were obtained with a mean of 67.6%, a standard deviation of 0.029%, and a coefficient of variation of 0.25.

Instead of methylene blue, a mixture of a cationic dye (dimidium-bromide: 2,7-diamino-10-methyl-9-phenylphenanthridinium bromide) and an anionic dye (disulfine blue, also known as Erioglaucine®) was used by Brewer[7] in 1972 to determine the sulfonate content of oil-soluble sulfonates. After the dimidium-sulfonate complex was formed in chloroform layer, the two-phase mixture was titrated with Hyamine®. The dimidium-sulfonate complex was replaced by Hyamine®-sulfonate until an excess amount of Hyamine® formed a chloroform soluble, blue complex with disulfine blue. The color in the chloroform layer then changed red through grey to blue. The grey color was taken as the end point. The amount of sulfonate was calculated from the amount of Hyamine® used. The results for sodium and calcium petroleum sulfonates obtained by two-phase titration were comparable with those obtained from ASTM D 855-56 and D 1216-56 methods, respectively.

Determinations of linear alkylbenzenesulfonates (LAS) in fresh and sea water by use of two-phase titration was reported in 1973 by Wang et al.[8] Wang et al. analyzed branched-chain alkybenzenesulfonates in commercial detergents.[9] The sulfonate sample in water was treated with a known excess of cetyldimethylbenzylammonium chloride to form a nondissociated complex of the quaternary ammonium sulfonate. After adding chloroform to the solution, the excess of quaternary ion was dissolved in chloroform, where it formed a yellow color. The two-phase mixture was then titrated with standardized sodium tetraphenylborate until the excess ammonium ion was removed from the chloroform layer and the yellow color disappeared. The accuracy for LAS was ± 10% in sea water and ± 5.2% in fresh water; the precision was ± 0.4%. This titration is simple, fast, and free from interference by inorganic salts in water samples, except for relatively high concentrations of potassium ion, which forms precipitates with tetraphenylborate anion. Another limitation is that the technique determines only the total content of anionic surfactant in water sample. The two-phase titration methods are reliable for determining the sulfonates in oil-soluble petroleum sulfonates.

C. Gravimetric Methods

An alkylarenesulfonate forms a precipitate with benzidine dihydrochloride as follows:



The amount of the alkylarenesulfonate is proportional to that of the corresponding precipitate and can be determined from a calibration curve. Maurmeyer and Rafalowitz[10] used this technique in 1964 to analyze sodium salts of dodecyl- and nonylbenzenesulfonates in commercial materials. The accuracy was within ± 3% for 15 mg of $C_{12}-SO_3^-$ and 22 mg of $C_{11}-SO_3^-$, and the precision was within ± 0.8% for both.

The composition of petroleum sulfonic acids in acid sludges, which were obtained by sulfonation of various petroleum hydrocarbon oils, was investigated by Chhibber et al.[11] in 1976. After neutralizing the sulfuric acid and petroleum sulfonic acids by titration with 0.5 *N* NaOH using thymol blue and phenolphthalein indicators, respectively, the oil part was removed by extraction with petroleum ether, and the aqueous part was evaporated to dryness for analysis for petroleum sulfonic acids. Six acid sludges (10 to 15 g) were analyzed in three replicates; the results were comparable to those obtained with the modified ASTM D-855 with an accuracy of ± 5.5%. In the same year, the determination of content of petroleum sulfonates by titrating the sample in a mixture of water and 2-propanol with a base using phenolphthalein indicator was reported by Parmar and Sahukar.[12] After removing the oil part by extraction with solvent naphtha, excess sodium carbonate was slowly added to the aqueous alcohol solution which resulted in two layers. The clear alcohol layer was evaporated to dryness for determination of the petroleum sulfonates. The results were also comparable with those obtained with the ASTM D-855 with an accuracy of ± 2.6%.

D. UV Absorption Methods

Since the UV spectrum of benzene having various alkyl substituents on the ring gives different maximum absorption peaks in the region of 210 to 290 nm, the concentration of an arenesulfonate in a solution can be determined by measuring the absorbance at a suitable wavelength and using Beer's Law. For a mixture of arenesulfonates, absorbances are measured at several wavelengths, and the concentration of each sulfonate is calculated by solving a set of linear equations.

Using this technique, the composition of alkylarenesulfonates in several commercial detergents was determined in the region of 210 to 230 nm by Kelley et al.[13] The maximum absorbance at 224 nm was used for studies of the alkylarenesulfonates. The accuracy and precision were within ± 1% for the three detergents tested.

Later, an improved automatic procedure for preparing liquid samples of detergents containing alkylarenesulfonate by using a Technicon® Preparative Sampler and instrumentally recording the peak height of absorbance at 224 nm was reported by Brandli and Kelley[14] in 1970. The peak height measured at 224 nm is proportional to the amount of alkylarenesulfonate. In the 12 random samples of detergents studied, the accuracy and precision were within ± 4.8 and ± 3.5%, respectively. The speed of analysis is about 10 min per sample. This can be used as a routine check for the composition of alkylarenesulfonate in detergent manufacturing.

A multicomponent analysis of mixtures of *ortho-*, *meta-*, and *para-* toluene-sulfonic acids in sulfuric acid solution was reported by Cerfontain et al.[15] From the spectrum of each component, represented in Figure 1, the absorbances of both standard and unknown mixtures were measured manually at 39 equidistant points between 243 and 281 nm with a Zeiss® PMQ II spectrophotometer. The concentration of each sulfonate in the unknown was computer calculated using a curve-fitting program to minimize the mean square residual,

$$r^2 = \frac{\sum_{i=1}^{k} (A_{i,calc} - A_{i,obs})^2}{k - n} \quad \ldots\ldots\ldots\ldots\ldots\ldots \quad (1)$$

where

$$A_{i,calc} = \sum_{j=1}^{n} \epsilon_{ij}(b)C_j$$

r = the mean square residual, ε_{ij} = the molar absorptivity of component j at wavelength i, C_j = the concentration of component j, b = the cell path length, $A_{i,obs}$ = the absorbance measured at wavelength i, k = the number of data points, and n = the number of constituents in the unknown mixture. It corresponds to the absorbance calculated at wavelength i.

Using the same technique[15] in the region of 240 to 300 nm, Cerfontain et al.[16] analyzed several more isomeric mixtures of arenesulfonic acids. The applicability of this method depends on the differences in shape of the absorption spectra of the components. Errors range from ± 0.8 to ± 20%.

E. Colorimetric Methods

Determination by colorimetric methods is based on the formation of a colored dye-sulfonate complex. The color intensity of this complex is proportional to the amounts of sulfonate and can be measured by a colorimeter or a spectrophotometer in the visible region.

1. Methylene Blue Method

A determination of anionic detergent, mainly sodium alkylbenzenesulfonates, in sewage effluents by use of a basic methylene blue solution in chloroform was reported by Longwell and Maniece.[17] The absorbance of methylene blue-sulfonate complex in chloroform was measured with a photoelectric absorptiometer at 650 nm. The results showed about 97% recovery of added detergent in effluent in the range of 10 to 20 ppm. The colorimetric method with methylene blue involving formation of the dye-sulfonate complex and extracting it into chloroform is time consuming. Since thiocyanates (at 30 ppm) largely interfere with the extraction, they should be removed by oxidation with hydrogen peroxide before extracting with chloroform.

Another determination of trace amounts (ppm) of alkylbenzenesulfonates in river waters by forming methylene blue-sulfonate complex and adsorbing on polyurethane foam was reported by Tanaka et al.[18] in 1973. The color intensity of the foam is proportional to the concentration of alkylbenzenesulfonate and may be estimated by visual comparison with a series of standards. The accuracy of determination of alkylbenzenesulfonate found in the Ikeda City River (Japan) was ± 12% at 11 ppm and ± 8% at 16 ppm; the limit of detection was 0.5 ppm.

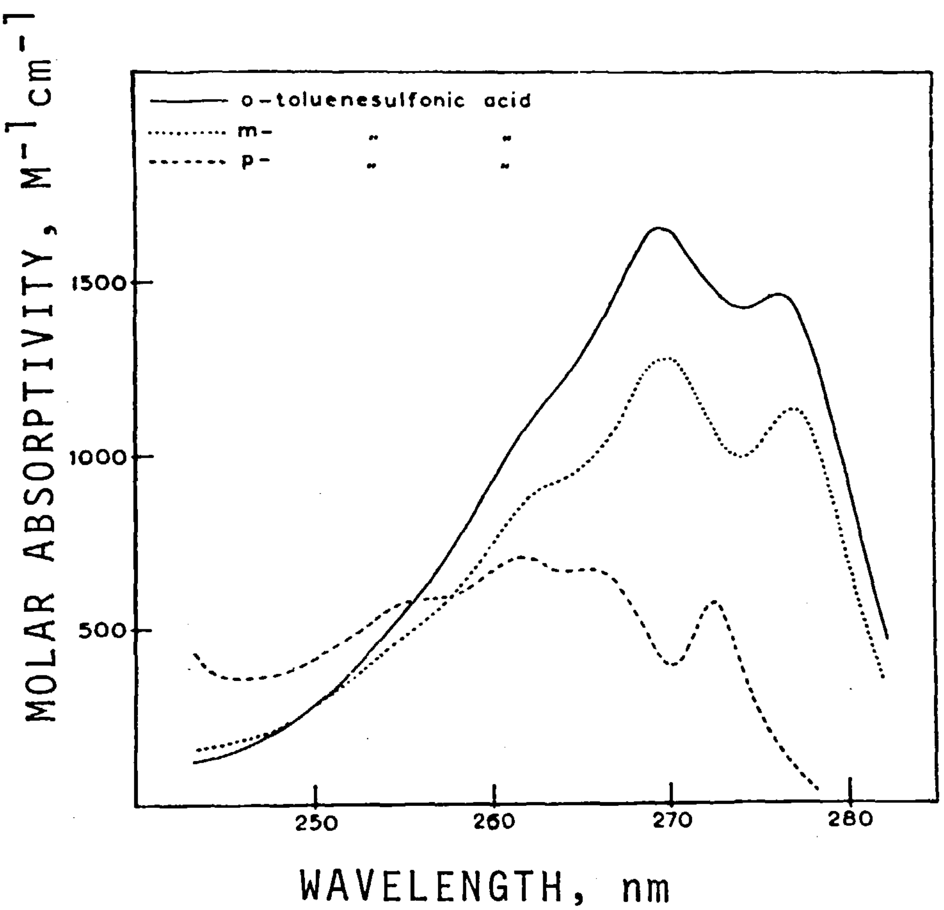


FIGURE 1. UV absorption spectra of three isomeric toluene sulfonic acids in 82.4 weight % sulfuric acid (From Cerfontain, H., *Anal. Chem.*, 35, 1005 (1963). Copyright by the American Chemical Society. With permission.)

2. Azure A (C.I. 52005) Method

In 1976, Wang[19] and Ross[20] used Azure A to determine trace amounts (0 to 10 ppm) of linear and branched-chain alkylbenzenesulfonates in water. The Azure A-sulfonate complex was soluble in chloroform, and the absorbance of that measured in a spectrophotometer at 623 nm. The concentration of alkylbenzenesulfonate is determined by comparing with a calibration curve of absorbance vs. concentration. The colorimetric method with Azure A has several advantages over that with methylene blue:[17]

1. The color of the complex is more intense.
2. The dye reagent is more stable under light exposure.
3. The chloroform extraction time is less.

3. Diazosulfanilic Acid Method

A determination of aromatic sulfonates by alkali fusion and subsequent formation of azo dyes by coupling with diazosulfanilic acid was studied by Whitlock et al.[21] in 1972. Fusion at 360°C gives quantitative conversion to sulfite and the corresponding phenols. Six sodium salts (3 to 10 mg) of benzenesulfonates and naphthalenesulfonates were analysed, and the azo dyes were measured at 461 nm by visible spectrophotometry with a precision of ± 2.2%. This is a complementary method for gas chromatography[28] in the determination of sulfonates which have low volatility after converting them to the corresponding phenols. The process, however, has the same limitations of gas chromatography[28] and is not suitable for the determination of sulfonates containing free halogen groups.

F. IR Spectrometric Methods

In general, if the position and intensity of a stretching band, arising from vibrations of a sulfonate group, are not affected significantly by changes in alkyl substitution on a benzene ring, a variety of homologs and isomers of alkylbenzenesulfonates can be determined by IR spectrometric methods by appropriate selection of wavelengths. As early as 1949, the IR spectrum of ammonium xylenesulfonates in a KBr pellet was studied by Schreiber[22] and by Barnard et al.[23] It is shown in Figure 2. The band, representing S-O asymmetric stretching vibration, centered at 1175 cm^{-1},[24] was used for the analysis of toluene- and xylenesulfonate solutions by Kullbom and Smith[25] in 1963. Thirteen samples of ammonium and sodium xylenesulfonates were analyzed and the results were comparable with those obtained with a gravimetric method with a relative error of ± 1%.

G. Gas Chromatographic Methods

Mixtures of alkanesulfonates, of arenesulfonates, and of alkane- and arenesulfonates can be analyzed by gas chromatography provided that sulfonates are converted to volatile, thermally stable derivatives. Kirkland[26] thus analyzed several systems of sodium sulfonates by converting them to the corresponding sulfonyl chlorides. A column (2 ft × 6 mm) packed with Chromosorb® (40/50 mesh) coated with 20% silicone grease and a helium carrier gas were used. The following mixtures were studied:

1. 1-Butanesulfonate and 3-methyl-1-butanesulfonate
2. Benzenesulfonate, *p*-toluenesulfonate, and 2,5-dimethylbenzenesulfonate
3. Benzenesulfonate, *p*-toluenesulfonate, and 2-naphthalenesulfonate
4. *p*-*n*-Butylbenzenesulfonate and 1-dodecanesulfonate

The accuracy in systems 1, 2, and 4 was within ± 2.8, ± 5.1, and ± 2% respectively, and ± 21% for system 3. Although the chromatographic time for each system is less than 12 min, it takes several minutes to 2 hr to prepare a sulfonyl chloride sample. This method is not applicable to sulfonates containing substituents that react with thionyl chloride, such as $-OH$ or $-NH_2$ groups.

Another analysis of long-chain α-alkenesulfonates (C_{14}-C_{18}) and hydroxyalkanesulfonates by hydrogenation with H_2/Pd and conversion to sulfonyl chlorides was reported by Nagai et al.[27] in 1970. A glass column (2.5 m × 4 mm) packed with 3% Silicone SE-30® on Chromosorb® W (60/80 mesh) was used. The qualitative and quantitative analyses of unknown mixtures were determined by comparing the retention times and peak areas with those of standards. Mixtures of C_{16}- and C_{18}-α-alkenesulfonates/hydroxyalkanesulfonates were analyzed with accuracy of ± 2.8and 2.2%, and precision of ± 7.0 and 5.9%, respectively.

A determination of arenesulfonates involving alkali fusion was reported by Siggia et al.[28] in 1969. The resultant phenol, which corresponds to the amount of arenesulfonate, is measured by gas chromatography. The accuracy obtained for five pure arenesulfonates was within ± 3% and for a mixture of three arenesulfonates, within ± 4%.

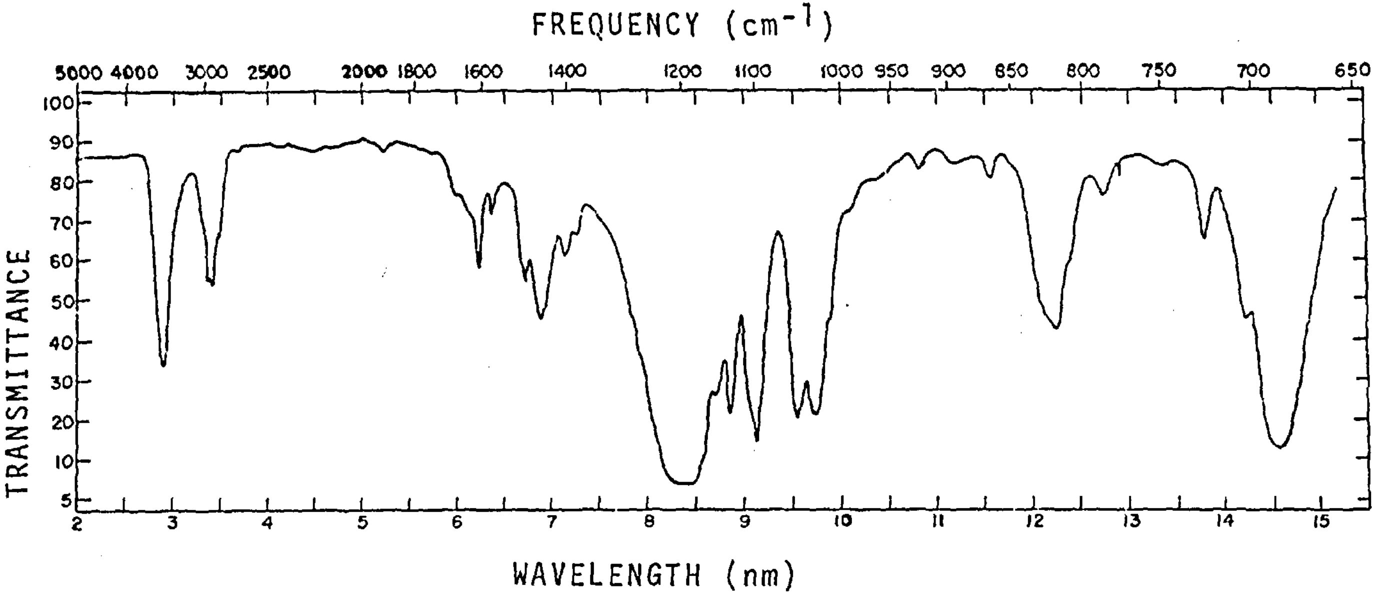


FIGURE 2. IR spectrum for ammonium xylenesulfonate in KBr pellet (From Kullbom, S. D. and Smith, H. F., *Anal. Chem.*, 35, 912 (1963). Copyright by the American Chemical Society. With permission.)

H. Nuclear Magnetic Resonance

From the nmr spectra of a mixutre of isomers, if the absorption regions are relatively separated and the areas are proportional to the number of nuclei involved, a quantitative analysis of the mixture is possible. In 1974, Cerfontain et al.[30] determined the composition of a mixture of isomeric toluenedisulfonates by obtaining areas under different absorption regions from a nmr spectrum and solving a set of linear equations as in Equation 2.

$${}_jA = ({}_jp_1x_1 + {}_jp_2x_2 + \cdots + {}_jp_ix_i)\, S \cdots\cdots\cdots \quad (2)$$

where ${}_jp_i$ = the number of magnetically equivalent nuclei of isomer i which absorbs in area j, x_i = the mole fraction of isomer component i, ${}_jA$ = the area of region j, i = 1, 2, . . . , m = components of isomer, j = 1, 2, . . . , n = the well separated regions in the spectrum, and S = a proportional constant. A mixture of toluene-2,5-, -3,4-, and -3,5-disulfonic acids in sulfuric acid was analyzed with accuracy and precision within ± 6%.

I. Mass Spectrometry

Since sulfonates and most sulfonic acids of commercial importance have low volatility, they may be converted to the corresponding volatile sulfonic esters by reaction with diazomethane or tetramethylammonium hydroxide and may be identified by mass spectrometry. In 1970, Heywood et al.[31] determined the identity of five unknowns containing benzene-, naphthalene-, and anthraquinone-sulfonates by comparing the molecular ions and fragmentation patterns of nine reference compounds with those of the sample. This method is used only for qualitative analysis of unknown sulfonates.

J. Atomic Absorption Methods

Sulfonates that are extractable into a suitable organic solvent and that can form an ion-association compound with a proper metal complex cation can be determined by atomic absorption methods.[32] In 1976, Crisp et al.[33] determined linear alkylate sulfonates (LAS) in water samples at a level below 50 ppb by use of atomic absorption. The LAS was extracted into chloroform and formed a compound with bis(ethylenediamine)copper(II). The copper compound in chloroform was measured at 324.7 nm with an atomic absorption spectrophotometer (Perkin-Elmer® 300 S). The accuracy of the recovery of LAS in sea water was 92%, the precision was within ± 5% in the range of 10 to 200 ppb, and the limit of detection was 2 ppb. Most anions (Cl^-, NO_3^-, SO_4^{2-} at 0.5 *M*; SCN^-, ClO_4^-, NO_2^-, CH_3COO^- at concentrations of 1 g/*l*) and metal cations (Cu^{2+}, Ni^{2+} at 100 mg/*l*; Al^{3+}, Cr^{3+}, Mn^{2+}, Zn^{2+}, Co^{2+} at 10 mg/*l*) do not seriously interfere with the determination of LAS, but sulfide (0.1 mg/*l*) and Fe^{3+} (1 mg/*l*) do. These interferences can be suppressed by treating the sample with 30% H_2O_2 and 2% EDTA, respectively, before adding bis(ethylenediamine) Cu(II). This method is reliable for determining trace amounts of sulfonates down to 10 ppb in fresh water or sea water.

K. Radiometric Methods

A determination of trace amounts of anionic surfactants by a radiometric method was reported by Taylor and Waters[34] in 1972. It is based on the fact that anionic surfactants form a complex with ^{59}Fe-labeled ferroin, $[^{59}Fe(II)(1, 10\text{-phen})_3]^{2+}$, and these complexes are soluble in chloroform. The amount of labeled ferroin extracted into chloroform is proportional to the concentration of anionic surfactants and can be measured by a proportional counter. Using this technique, Clementz[35] reported the determination of alkylarenesulfonates in crude oils. The detection limit of petroleum sulfonate was 0.5 μg in crude oils. The results were comparable with those of the two-phase titration method.[7] Although the radiometric method is slow, it has an advantage over the two-phase titration method in determining petroleum sulfonates in crude oils because the radiometric method is not limited by the dark color of crude oils and brines.

L. Use of Ion-Selective Membrane Electrodes

A liquid membrane, containing a suitable cation which has a larger ion-association constant or higher sensitivity response with sulfonates than with other anions, can be used as a sulfonate ion-selective electrode membrane. In 1968, Coetzee and Freiser[36] reported a membrane composed of methyltricaprylylammonium ion in 1-decanol that had a linear response to *p*-toluenesulfonate from 10^{-1} to 10^{-3} *M* with a response time within 1 min and a useful life of 1 month. The crystal violet cation and its analogs in nitrobenzene or in 1,2-dichloroethane as an effective ion-exchange site in the membrane electrode were studied by Ishibashi and Kohara in 1972[37] and 1973.[38] The assembled cell is represented in Figure 3,[39] where the salt bridge is saturated KCl in agar. The membrane potential of the cell was measured by use of an electrometer across the two saturated calomel electrodes. The results exhibited a linear response (56 mV/log[-sulfonate]) for benzenesulfonate from 10^{-1} to 10^{-5} *M* for *p*-toluenesulfonate from 10^{-1} to 10^{-5} *M*, and for 1-naphthalenesulfonate from 10^{-2} to 2×10^{-4} *M*.

The interferences of nitrate and 1-naphthalenesulfonate ions are large at a benzenesulfonate electrode, while those of nitrate and benzenesulfonate ions for a 1-naphthalenesulfonate electrode are small. The selectivity coefficients $K_{i,j}$ for benzenesulfonate and 1-naphthalenesulfonate electrodes calculated from Equation 3 are tabulated in Table 1. The membrane potentials are stable in the pH range between 2.5 and 12.

$$E = \text{constant} + \frac{2.303\,RT}{nF} \log \left(A_i + K_{i,j} A_j^{\frac{z_i}{z_j}} \right) \cdots\cdots \quad (3)$$

where E = the membrane potential, i = the primary sulfonate ion, j = the interfering ions in the sample solution, A_i, A_j = activities of ions i and j, respectively, and Z_i, Z_j = charges of ions i and j, respectively. The use of ion-selective membrane electrodes provides a rapid and convenient measurement of individual concentration of sulfonates in the range of 10^{-5} — 10^{-1} *M*.

M. Summary of Observations on Methods of Determination

1. Among the 12 methods of determination of sulfonates, the mass spectrometric method is used only for qualitative analysis. The other methods can be used for quantitative analysis.
2. The type of sulfonates determined, the accuracy, precision, amounts used, detection limit, and speed of the process are summarized in Table 2.
3. From Table 2, the most rapid methods are two-phase titration,[6-8] UV,[14] colorimetry with Azure A,[20] IR,[25] and use of an ion-selective membrane electrode.[38] Among these, the ion-selective membrane electrode not only has been used in individual determination of arenesulfonates, but also has potential for the individual determination of alkanesulfonates.
4. The applications, advantages, and limitations of the methods of determination are summarized and compared in Table 3.

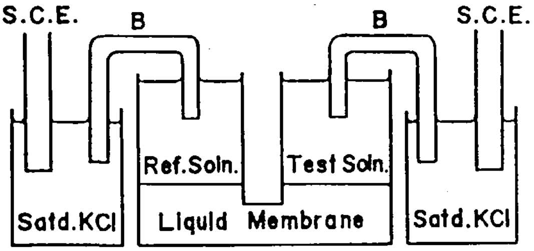


FIGURE 3. Assembled cell for ion-selective membrane electrode; B : salt bridge. (From Ishibashi, N. and Kohara, H., *Anal. Letters*, 4, 787 (1971) by courtesy of Marcel Dekker, Inc.)

5. From the viewpoint of accuracy, the methods of titrimetry[3,4] and two-phase titration with two dyes[7] give an accuracy within ± 0.3%. Of these two methods, the two-phase titration is faster than the one-phase (conventional) titration.

III. SEPARATION METHODS

Separation methods for sulfonates are needed in industrial and analytical fields to purify petroleum sulfonates for use in lubricating oils and greases, to purify water by removing trace amounts of alkylarenesulfonates, or analytically to investigate fast separation methods for aliphatic and aromatic sulfonates which are useful in industry or pharmacy. The following seven separation methods for analytical use are reviewed here: solvent extraction, continuous electrophoresis, and gas, ion-exchange, paper, thin-layer, and liquid chromatography.

A. Solvent Extraction

Separation of petroleum sulfonic acids from oil in a mixture of water and alcohol (1:1) at 40 to 45°C was reported by Myshkin et al.[40] in 1961. After the oil was separated and removed from a separatory funnel, the aqueous alcohol solution was treated with hydrochloric acid and then the sulfonic acids were extracted into an ether layer, which was dried to a constant weight and used for determining the content of petroleum sulfonic acids. Only qualitative analysis was reported.

A removal of anionic detergents (mainly alkylarenesulfonate) in water by extraction with kerosene containing a liquid amine anion exchanger was reported by Dunning et al.[2] in 1965. The extracted ammonium-sulfonate complex in the organic phase was washed with a basic solution and the sulfonate, which migrated to the aqueous phase, was determined while the organic solvent with the liquid amine was reused. This method depends mostly on the selectivity of the liquid amine anion exchanger which must be insoluble in water and form ion pairs with the sulfonates. The solvent extraction technique is usually time consuming.

B. Continuous Electrophoresis

A separation of 4-biphenylsulfonate and 4,4′-biphenyldisulfonate by use of continuous electrophoresis was studied by Skelly[41] in 1965. The mono- and di-sulfonates were separated on a Beckman/Spinco Model CP continuous-flow paper electrophoresis cell and were collected in separate volumetric flasks. Since these two sulfonates have the

Table 1
SELECTIVITY COEFFICIENTS ($K_{i,j}$) FOR BENZENESULFONATE AND 1-NAPHTHALENESULFONATE ELECTRODES

Benzenesulfonate electrode			α-Naphthalenesulfonate electrode		
Interferent (j)	$C_j(M)$	$K_{BS,j}$	Interferent (j)	$C_j(M)$	$K_{NS,j}$
Cl^-	0.5	0.003	Cl^-	0.5	0.0004
NO_3^-	0.005	0.76	NO_3^-	0.005	0.03
Phenol-4-sulfonate	0.005	0.016	Benzenesulfonate	0.005	0.07
Benzene-*m*-disulfonate	0.005	0.005	1,5-Naphthalene-disulfonate	0.005	0.0007
Benzoate	0.005	0.04			
α-Naphthalene-sulfonate	0.00025	16	1,3,6-Naphthalene-trisulfonate	0.1	0.00006
1,3,6-Naphthalene-trisulfonate	0.005	0.0008	4-Hydroxy-2-naphthalenesulfonate	0.005	0.025
			2,3-Dihydroxynaphthalene-6-sulfonate	0.005	0.00045

From Ishibashi, N., Kohara, H., and Horinouchi, K., *Talanta*, 20, 867, (1973). Copyright by Pergamon Press, Ltd. With permission.

same absorptivity at 266 nm (shown in Figure 4), the concentration ratio of mono-, di- and the total concentration of sulfonates can be obtained by UV spectrophotometry. The accuracy was within 1.4% for 24.85 mg of monosulfonate and within 5% for 5 mg of disulfonate. The precision was ± 0.7%. Although the accuracy and precision are reliable in the range of 5 to 25 mg, this procedure takes about 12 hr per analysis.

C. Gas Chromatography

1. Gas-Liquid Chromatography

Besides those methods previously mentioned,[26-29] a trace amount of linear alkylbenzenesulfonate (LAS) in waste water at ppm levels was estimated by Swisher[42] in 1966. After the water in a sample was evaporated, the residue was desulfonated, and the resultant phenyl-*n*-alkanes were detected by gas chromatography. Only semiquantitative results were reported.

In 1967, Parsons[43] qualitatively analyzed a mixture of naphthalene mono-, di-, and tri-sulfonic acids by converting the sulfonic acids to the corresponding sulfonyl fluorides. A chromatogram was obtained with good resolvable peaks in 3 min. and is represented in Figure 5. Since naphthalenetrisulfonyl fluoride is more volatile and thermally stable than the sulfonyl chloride, more reproducible peaks are obtained. However, it takes more time (1.5 hr) to prepare a fluoride sample.

2. Gas-Solid Chromatography

A separation of alkylbenzenesulfonic acids by converting to the corresponding sulfonyl fluorides and analyzing by gas adsorption chromatography was reported by Krylov[44] in 1976. A column of 3000 × 3 mm packed with silochrome-2 adsorbent, nitrogen carrier gas, and a hydrogen flame-ionization detector were used. The separation is based on the varying stability of hydrogen bonding between the hydroxyl-group protons of silochrome and the electron density of the aromatic sulfonyl fluorides. Ten aromatic sulfonic acids were separated and the chromatogram is represented in Figure 6. Chromatograms of aromatic sulfonyl fluorides obtained on silochrome-2: (1,2,3) *p*-, *m*-, and *o*-toluenesulfonyl fluorides, (4) benzenesulfonyl fluoride, (5,6,7) *p*-, *m*-, and *o*-cumenesulfonyl fluoride, (8) *m*-xylene-4-sulfonyl fluoride, (9) *m*-xylene-2-sulfonyl fluoride, and (10) *p*-xylenesulfonyl fluoride.

D. Ion-Exchange and Liquid-Solid Adsorption Chromatography

A separation of binary mixtures of both aliphatic and aromatic monosulfonic/disulfonic acids by using an Amberlite® XAD-2 resin was reported by Scoggins and Miller[45] in 1968. Separation on the XAD-2 macroreticular resin is based on adsorption controlled by van der Waal's forces. The disulfonates were eluted first with water or NaCl solution and then the monosulfonates were eluted with methanol, 10-mℓ fractions being collected. The alkanesulfonates were determined titrimetrically and the arenesulfonates by UV spectrometry. The accuracy was within ± 5%, but the process is relatively slow.

In 1970, a cross-linked polyalkyleneamine anion exchange resin, Bio-Rex® 5-Cl^- (270/325 mesh), was used by Stehl[46] to separate some homologs of arenesulfonates. A mobile phase of water : acetonitrile : methanol (1:1:1) and a salt gradient of 0 to 1.0 *M* LiCl as eluent were used. Mono- and di-sulfonates were separated within 30 to 45 min. There are two advantages of this method:

1. Some arenesulfonates containing an $-OH$ or $-NH_2$ group, which are not suitably handled by GC (26), can be easily separated by this technique.
2. The gradient elution improves the efficiency of separation by lowering the height equivalent to a theoretical plate (HETP).

Table 2
SUMMARY OF OBSERVATION ON METHODS OF DETERMINATION

Method	Type of sulfonates determined	Accuracy (±%)	Precision (±%)	Amount of sample used (g)	Detection limit (g)	Speed of process	Ref.
Titrimetric	Aromatic	0.3	1.0	0.5—0.6	—	Slow (~2 hr)	3
	Aromatic	0.074	0.46	0.2	—	Slow (~2 hr)	4
Two-phase titrimetric (methylene blue)	Aromatic	—	0.25	8×10^{-2}	—	Fast (~0.5 hr)	6
Two-phase titrimetric (two dyes)	Aromatic	0.3	0.9	$(2—10) \times 10^{-2}$	—	Fast (~0.5 hr)	7
Two-phase titrimetric (back titrimetric)	Aromatic	5.2—10	0.4	$(1—10) \times 10^{-4}$	—	Fast (~0.5 hr)	8
Gravimetric	Aromatic	3	0.8	2×10^{-2}	—	Slow (~1 hr)	10
	Aromatic	5.5	—	10—15	—	Slow (~1 hr)	11
	Aromatic	2.6	—	10	—	Slow (~3 hr)	12
UV	Aromatic	1	1	0.9—1.1	—	Relatively fast (~1 hr)	13
	Aromatic	4.8	3.5	$(1.8—2.3) \times 10^{-1}$	—	Fast (~20 min)	14
UV (multicomponent)	Aromatic	0.1—20	—	$(1—10) \times 10^{-4}$	—	Relatively fast (~1 hr)	15
Colorimetric (methylene blue)	Aromatic	1—3	—	$(2—25) \times 10^{-5}$	—	Slow (~4 hr)	17
Colorimetric (methylene blue + poly-urethane foam)	Aromatic	8—12	—	1×10^{-4}	[a]1×10^{-5}	Relatively fast (~1 hr)	18
Colorimetric (Azure A)	Aromatic	—	—	$(5—15) \times 10^{-2}$	—	Fast (~0.5 hr)	20
Colorimetric (diazosulfanilic acid)	Aromatic	—	2.2	$(3—10) \times 10^{-3}$	[b]3×10^{-7}	Relatively fast (~1 hr)	21
IR	Aromatic	1.0	—	0.6—0.9	—	Fast (~0.5 hr)	25
GC (sulfonyl chloride)	Aliphatic, aromatic, and mixtures of both	2—5	—	0.5	—	Slow (~3 hr)	26

GC (H_2 + sulfonylization)	Aliphatic	2.2—2.8	5.9—7.0	3×10^{-5}	—	Slow (~4 hr)	27
GC (alkali fusion)	Aromatic	3—4	—	$(1.7—8.6) \times 10^{-3}$	—	Relatively slow (~1.5 hr)	28
GC (pyrolysis)	Aromatic	2.8	—	$(8.6—43) \times 10^{-3}$	—	Relatively slow (~1.5 hr)	29
NMR	Aromatic	6	6	8×10^{-2}	—	Relatively slow	30
Atomic absorption	Aromatic	8	5	$(5—20) \times 10^{-10}$	[c]1.0×10^{-10}	Relatively slow (~1.5 hr)	33
Radiometric	Aromatic	comparable to (7)	—	$(5—100) \times 10^{-6}$	[d]5×10^{-7}	Slow (~3 hr)	35
Use of ion-selective membrane electrode	Aromatic	—	—	$(1.7—1700) \times 10^{-4}$	[e]1.7×10^{-5}	Fast (few minutes)	38

[a] The lowest detectable concentration of alkylbenzenesulfonate is 0.5 ppm using 20 m*ℓ* of water.

[b] The minimum detectable amount for phenol with absorbance = 0.05, molar absorptivity = 5×10^4 (cm $^{-1}M^{-1}$, cell length = 1 cm, and cell volume = 3 m*ℓ*.

[c] The concentration of LAS which gave an absorbance equal to twice the standard deviation of a set of 16 absorbance readings at or near blank level was 2×10^{-6} g/*ℓ* using 50×10^{-6} *ℓ*.

[d] The theoretical detection limit in crude oils is approximately 0.5 ppm petroleum sulfonate using 1 m*ℓ* of undiluted oil.

[e] In a series of diluting solutions of benzenesulfonate at a constant ionic strength, the concentration starts to deviate from the Nernst linear response at 10^{-5} *M* using 10 m*ℓ* solution.

TABLE 3
SUMMARY OF OBSERVATION ON METHODS OF DETERMINATION

Method	Applications	Advantages	Limitations	Ref.
Titrimetric	To determine the purity of sulfonate in a mixture	Simple equipment	Barium sulfonates must be soluble in the presence of $Ba(OH)_2$	3
	To determine the industrial sulfonated products	The end point is visual	Need to prevent access of CO_2 during the titration	4
Two-phase titrimetric (methylene blue or cationic/ anionic dyes)	To determine sulfonates in oil-soluble petroleum sulfonates	Simple equipment	—	6,7
Two-phase titrimetric (back titrimetric)	To determine trace amounts of LAS or ABS in fresh or sea water	Better than Ref. 17	Not applicable to determine sulfonates in the presence of relatively high potassium ion content	8
Gravimetric	To determine alkylarene-sulfonates by precipitating with benzidine	—	—	10
	To determine the content of petroleum sulfonic acids in acid sludges	Simple equipment	—	11
	To determine the content of sulfonate in oil-soluble petroleum sulfonates	Simple equipment	—	12
UV	To check the content of alkylarenesulfonate in detergents	—	Phenyl chromophores absorbing in 220—230 nm cause interference	13,14
UV (multicomponent)	To determine concentration of individual arenesulfonates in an isomeric mixture	—	Applicability depends on differences in shape of spectrum of each component	15,16
Colorimetric (methylene blue)	To determine alkylarene-sulfonates in detergents	—	SCN^- ions must be removed before extracting with chloroform	17
Colorimetric (methylene blue + polyurethane foam)	To determine trace amounts of alkylbenzensulfonate in river waters	The amount of methylene blue-sulfonate complex bonded on the foam is compared visually	—	18
Colorimetric (Azure A)	To determine ABS or LAS in water	Better than Ref. 17	Only applicable to determine the content of anionic sulfactants	20

Colorimetric (diazosulfanilic acid)	To determine sulfonates having low volatility after converting to the corresponding phenols	A complementary method for GC Ref. 28	Not suitable to determine sulfonates containing halogen groups	21
IR	To determine various isomers of alkylarenesulfonates	—	—	25
GC (sulfonyl chloride)	To separate and determine aliphatic, aromatic, or mixture of both	—	Not applicable to sulfonates not containing $-OH$ or $-NH_2$ groups	26
GC (hydrogenation and sulfonylization)	To determine the contents of α-alkenesulfonates and hydroxyalkanesulfonates (C_{14}-C_{18}) in synthetic detergents	—	Some side reactions may interfere the determination	27
GC (alkali fusion)	To determine homologs of arene sulfonates	—	Not applicable to sulfonates containing free halogen groups	28
GC (pyrolysis)	To determine mono- and disulfonates	Applicable to nonvolatile sulfonates	Affected by the presence of H_2SO_4	29
NMR	To determine isomeric arenesulfonates	—	A well-separated spectrum is needed	30
Mass spectrometric	For qualitative analysis of arenesulfonates	—	Need access to spectra of enough reference compounds	31
Atomic absorption	To determine ppb levels of anionic detergents in fresh or sea water	—	S^{2-} and Fe^{3+} give large interferences	33
Radiometric	To determine petroleum sulfonate in crude oils	Better than Ref. 7	Only a linear calibration curve is used	35
Use of ion-selective-membrane electrode	To determine individual arenesulfonates	Fast response	Some anions may interfere	38

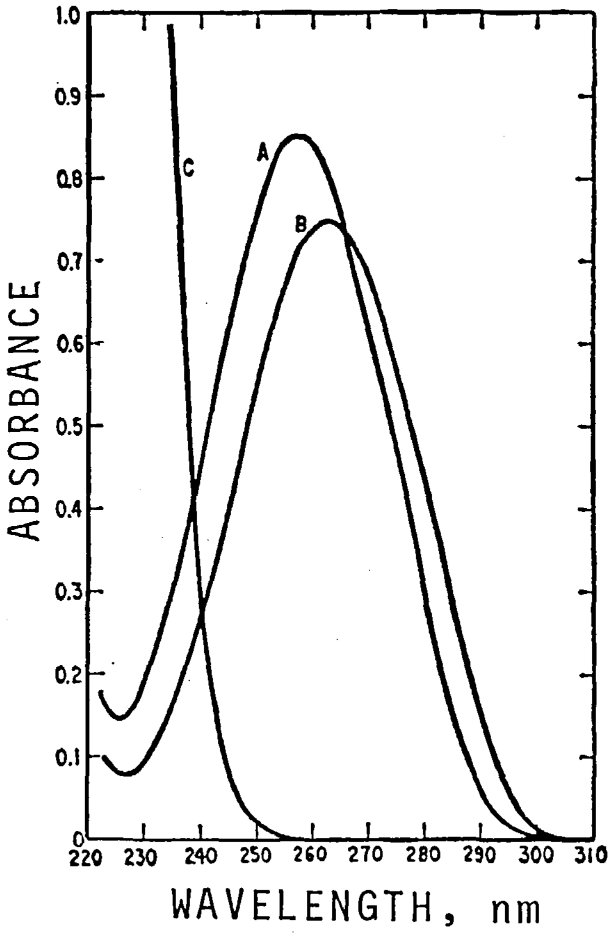


FIGURE 4. UV spectra for biphenyl mono- and disulfonates. (A) 1.00 mg sodium biphenylsulfonate/100 m*l* solution; (B) 1.00 mg disodium biphenyldisulfonate/100 m*l* solution; (C) 2% acetic acid as electrolyte. (From Skelly, N. E., *Anal. Chem.*, 37, 1526 (1965). Copyright by the American Chemical Society. With permission.)

The separation of linear (LAS) and branched (ABS) alkylbenzenesulfonates by use of a weakly acidic cation-exchange resin, Amberlite® CG-50 (100/200 mesh), was reported by Fudano and Konishi[47] in 1970. A column (500 × 26 mm) was slurry packed and washed with an eluent (0.5 *M* ammonium sulfate-43% methanol) for 1 hr before the sample was introduced. The bound sulfonates were eluted with the eluent in an order of LAS and then ABS, which were measured with the aid of an UV detector. The accuracy was ± 6.6% for LAS and ± 1.1% for ABS, and the precision was within ± 0.7%. It took about 15 hr to obtain the separated peaks in the chromatogram.

Using the same technique in 1971, Fudano et al.[48] separated 3-hydroxypentadecanesulfonate and 2-pentadecenesulfonate by eluting with 0.5 *M* NaCl-30% 2-propanol. The amount of sulfonates was determined by the colorimetric methylene blue method.[17] The accuracy was within ± 2.3% for 4 mg of each, but the time of analysis was about 24 hr.

Another separation of four isomeric monosulfonic acids (derived from sulfonation

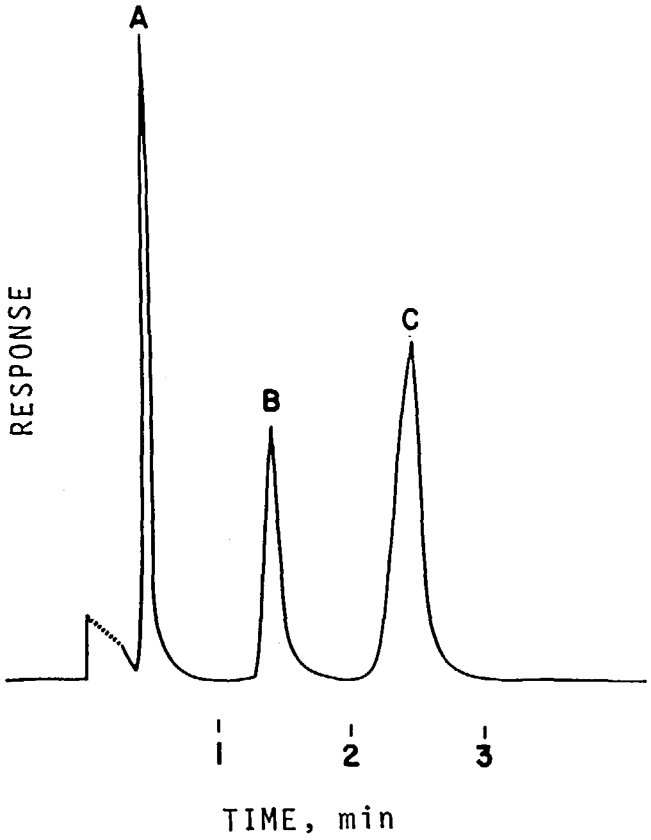


FIGURE 5. Chromatogram of naphthalene mono-, di-, and trisulfonyl fluorides. (A) 2-naphthalenesulfonyl fluoride; (B) 2,6-naphthalenedisulfonyl fluoride (C) 1,3,6-naphthalenetrisulfonyl fluoride. (From Parson, J. S., *J. Gas Chromatogr.*, 5, 254 (1967), by permission of Preston Publications, Inc.)

of phenanthrene) by using a weak acid SG-1 cation-exchange resin was reported by Kachurin and Vasilenko[49] in 1975. The procedure used a gradient elution of potassium chloride solution (0.5 to 0.02 *M*) and a column of 500 × 10 mm. The mixture of 2-, 3-, 9-, and 1-phenanthrenesulfonate was separated, and the compositions were determined by UV multicomponent analysis in the region of 250 to 306 nm. The accuracy was within ± 7% for a 0.3-g sample. Again, the process took more than 26 hr.

E. Paper Chromatography

In 1964, Coyne and Maw[50] studied the separation of several alkanesulfonic acids by their conversion to the corresponding ammonium sulfonates and using paper chromatography. Acetic-acid-washed Whatman® No. 1 papers and developing reagents of bromocresol green or silver fluoresceinate were used. The seven solvents systems investigated were as follows:

1. *t*-Butyl alcohol-formic acid-water (16:1:4)
2. Acetone-formic acid-water (16:1:3)
3. Mesityl oxide-formic acid-water (25:25:12)
4. Phenol-formic acid-water (75:1:25)

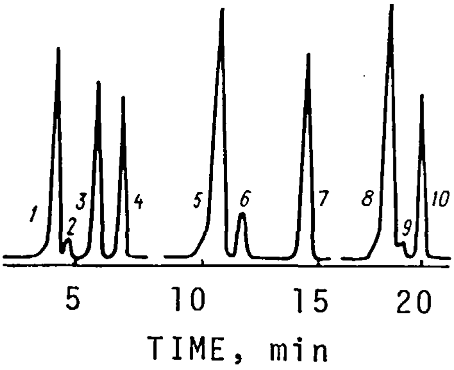


FIGURE 6. Chromatogram of ten aromatic sulfonyl fluorides. (1) *p*-toluenesulfonyl fluoride, (2) *m*-toluenesulfonyl fluoride, (3) *o*-toluenesulfonyl fluoride, (4) benzenesulfonyl fluoride, (5) *p*-cumenesulfonyl fluoride, (6) *m*-cumenesulfonyl fluoride, (7) *o*-cumenesulfonyl fluoride, (8) *m*-xylene-4-sulfonyl fluoride, (9) *m*-xylene-2-sulfonyl fluoride, (10) *p*-xylene sulfonyl fluoride. (From Krylov, E. N., *Ind. Lab.*, 42, 1023 (1976). Copyright by Plenum Publishing Corp. With permission.)

5. Ethanol-aqueous ammonium acetate (5:2)
6. Ethyl acetate-acetic acid-water (3:1:1)
7. Ethanol-ammonium hydroxide-water (20:1:4)

The R_f values of seven alkanesulfonates (10 μg each) measured are tabulated in Table 4. Among these, the solvent system 2 is the most suitable to separate methane- and ethanesulfonates.

F. Thin-Layer Chromatography

A separation of alkanesulfonates and alkylbenzenesulfonates using thin-layer chromatography was reported by Takeshita et al.[51] in 1976. A stationary phase of polyamide in cellulose and 2-propanol mixture and a developing solvent of 0.1 to 1.0 *N* aqueous ammonia-pyridine (15:1) were used. After developing, the layer was sprayed with pinacryptol yellow reagent and examined under UV light at 254 nm. R_f values were used for identifying constituents of sulfonates and the intensity of the yellow spots was used for quantitative measurement. The R_f values were higher for sulfonates with a shorter carbon chain than those with a longer carbon chain. The detection limit was 2 μg for C_4-C_{18} alkanesulfonates and C_1-C_{14} benzenesulfonates.

In the same year, Franc et al.[52] separated a mixture of 1- and 2-naphthalenesulfonic acid using Silufol® UV-254 as a stationary phase and *t*-butyl alcohol:ethanol (1:1) as a developing solvent. A stable brown-black color is developed after spraying with hydroxylamine solution and then cupric acetate solution. The chromatogram was evaluated on a densitometer at 480 nm. R_f values of 0.6 and 0.0 were obtained for 1-naphthalenesulfonic acid and 2-naphthalenesulfonic acid, respectively. A standard deviation of 3.5% and a detection limit of 10 μg were reported.

G. Liquid Chromatography

1. Conventional Liquid-Liquid Chromatography

Several binary mixtures of arenesulfonic acids were separated by Fritz and Gillette[53]

Table 4

R_f VALUES OF ALKANESULFONATES IN SEVEN SOLVENT SYSTEMS USING PAPER CHROMATOGRAPHY

	Solvent Systems (R_f × 100)						
Alkanesulfonate	1	2	3	4	5	6	7
Methanesulfonate	34	35	69	41	68	17	61
Bromomethanesulfonate	59	53	70	44	72	37	64
Iodomethanesulfonate	57	56	71	48	70	39	63
Ethanesulfonate	64	42	68	56	73	20	67
2-Bromoethanesulfonate	70	65	77	54	77	34	72
Methanedisulfonate	10	7	61	7	32	5	22
Ethane-1,2-disulfonate	14	14	66	7	45	5	39

in 1968 by use of liquid-liquid chromatography. A solution of 5% Alamine® 336 hydrochloride in toluene coated on Chromosorb® W as a stationary phase, a dilute aqueous acid ($HCl/HClO_4$) as a mobile phase, a glass column (110 × 13 mm), and a Bausch and Lomb Spectronic® 600 spectrophotometer were used. The binary systems studied were

1. 2-Aminobenzenesulfonate and 2-amino-5-nitrobenzenesulfonate
2. 2-Aminobenzenesulfonate and 6,7-dihydroxy-2-naphthalenesulfonate
3. Benzenesulfonate and *p*-toluenesulfonate

The first component in the mixture was eluted with 0.5 *M* HCl and the second component with 1.0 *M* HCl plus 1.0 *M* $HClO_4$. The accuracy was within ± 5% at 0.050 mmol for each species. It took about 1.5 hr to separate each binary mixture.

A separation of alkanemonosulfonates (C_{10}-C_{20}) from the alkane di- or polysulfonates was reported by Ali and Laurence[54] in 1973. They used a moist cellulose in petroleum ether as the packing material. The monosulfonic acid was eluted with 5% 1-butanol in petroleum ether and di- and polysulfonic acids with water, 25 m*l*-fractions being collected. The sulfonic acids were determined titrimetrically. The accuracy and precision were ± 1.8 and ± 0.8%, respectively, for 26-wt % dodecanesulfonate, but the process is time consuming.

2. *High-Pressure Liquid-Liquid Chromatography (HPLLC)*

A separation of eight arenesulfonates in 50 min and five arenesulfonates in 5 min using HPLLC (Siemens,® SP200) was reported by Kraak and Huber[55] in 1974. Flow rates of 0.30 m*l*/min and 0.64 m*l*/min were used. The chromatograms are shown in Figures 7 and 8, respectively. In these systems, an aliphatic amine (tri-*n*-octylamine) coated on Diatomite (5 to 10 μm) as a stationary phase, a dilute perchloric acid (pH = 1.5) solution as a mobile phase, a glass column (185 × 3.0 mm), and a stainless-steel precolumn (500 × 10 mm) were used. In 1977, Terweij-Groen and Kraak[56] used the same system to separate a mixture containing alkanesulfonic acids (C_6, C_7, and C_8) in 8 min. The chromatogram is represented in Figure 9. The separation of sulfonic acids depends on ion-pair formation ($R_3NH,O_3S\text{-}R$) on the stationary phase and can be adjusted by changing the pH, the anionic concentration of the mobile phase, and the temperature in order to obtain a good resolution.

Using reversed-phase high-pressure liquid-liquid chromatography in 1975, Wahlund[57] reported separating a mixture of benzenesulfonate and *p*-toluene-sulfonate in

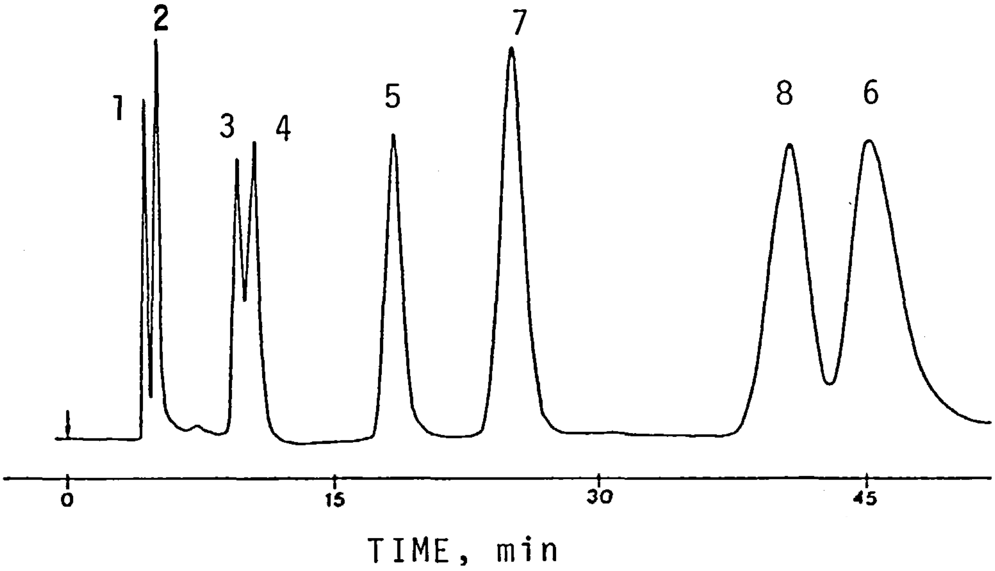


FIGURE 7. Separation of eight arenesulfonates by HPLLC. (1) 3-aminotoluenesulfonic acid, (2) 2-aminobenzenesulfonic acid, (3) benzenesulfonic acid, (4) 4,5-dihydroxy-2,7-naphthalenedisulfonic acid, (5) 4-nitrobenzenesulfonic acid, (6) 2-naphthol-3,6-disulfonic acid, (7) 2-naphtholsulfonic acid, (8) 1-naphthol-5-sulfonic acid. (From Kraak, J. C., *J. Chromatogr.*, 102, 333 (1974). With permission.)

22 min. A stationary phase of 1-pentanol coated on silica supports, a mobile phase of aqueous tetrabutylammonium (TBA) salt with a flow rate of 0.72 m*l*/min, a stainless-steel column (300 × 2.7 mm), and a precolumn (150 × 4.5 mm) were used. The chromatogram is shown in Figure 10. As before, the separation of sulfonates is based on the partition of ion-pairs ($R_4N^{\oplus}$, $^{\ominus}O_3SR$) between the stationary and the mobile phase. The concentration of $R_4N^{\oplus}$ in the mobile phase can be adjusted in order to obtain well-resolved peaks and relatively fast separation.

In liquid-liquid chromatography, the stationary phase is usually slightly soluble in the mobile liquid . Therefore, a precolumn is provided for presaturation of the mobile liquid and the liquid stationary phase in order to avoid stripping the stationary liquid in the column.

H. High-Pressure Liquid-Solid Chromatography (HPLSC)

The possibility of using high-speed liquid-solid chromatography for the separation of arenesulfonates was investigated by Kirkland[58] in 1971. Zipax SAX (a strong anion exchanger made up of dense, spherical, porous-layer beads) was used to bind sulfonates, and dilute aqueous perchloric acid was used as mobile phase with a volume flow rate of 0.54 m*l*/min at a column pressure of 370 psig. Five arenesulfonates were separated in 30 min. The chromatogram is shown in Figure 11. Although the mixture was not completely resolved, separation was reasonably fast.

In 1976, Knox and Laird [59] used SAS silica, a reversed-phase material made of short-chain hydrocarbon groups bonded to the surface of spherical silica gel, as a stationary phase and a water-propanol (5:2) mixture containing 1% of cetyltrimethylammonium bromide as a mobile phase to separate four isomeric naphthylaminesulfonic acids. The separation is based on the distribution of cetyltrimethylammonium-sulfonate ion pairs

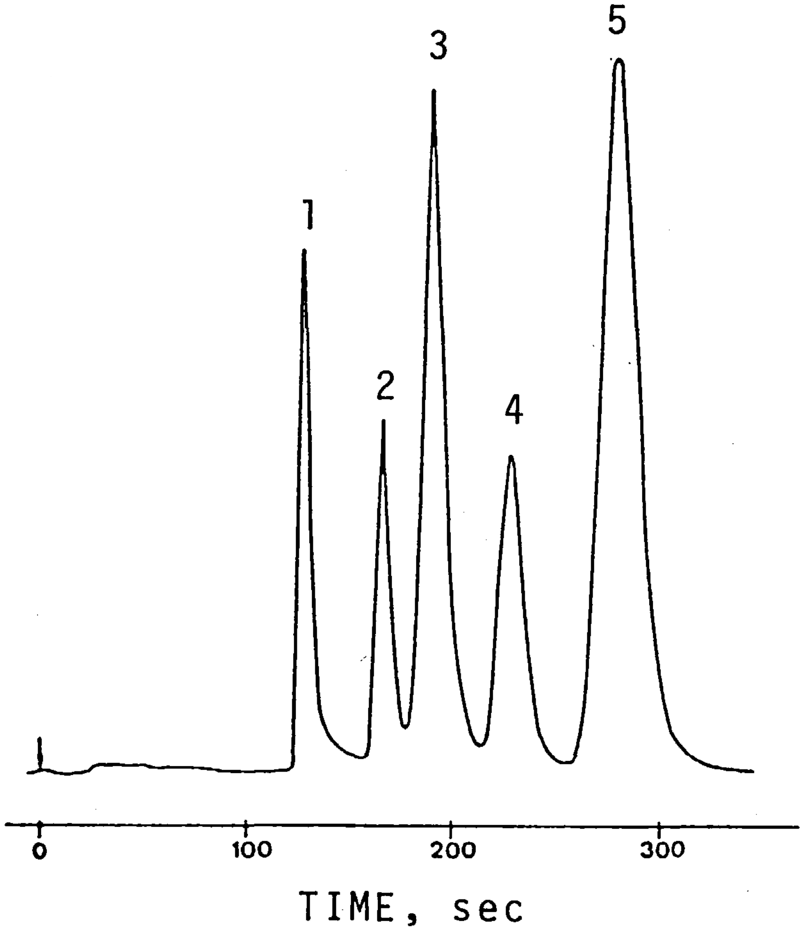


FIGURE 8. Separation of 5 arenesulfonates by HPLLC. (1) 3-aminotoluenesulfonic acid, (2) benzenesulfonic acid, (3) 4-nitrobenzenesulfonic acid, (4) 2-naphthol-3,6-disulfonic acid, (5) 2-naphthol-6-sulfonic acid. (From Kraak, J. C., *J. Chromatogr.*, 102, 333 (1974). With permission.)

between the water-rich eluent and adsorbed-layer rich in propanol. The chromatogram is presented in Figure 12.

From the characteristics obtained in batch experiments,[60] Pietrzyk and Chu[61] separated six benzenesulfonic acid derivatives by using reversed-phase HPLC in 1977. A stationary phase of nonpolar Amberlite® XAD-4, which is a polystyrenedivinylbenzene copolymer, a mobile phase of 0.1 *M* NaCl in 40% MeOH, a pressure of 300 to 700 psi, and a flow rate of 0.4 m*l*/min were used. The chromatogram is shown in Figure 13.

In liquid-solid chromatography, the packing materials,[58,60,61] usually tend to swell and therefore require maintenance of a constant level of water in the eluent (e.g., guard column) to ensure reproducible separations. In order to overcome this procedural disadvantage, stationary phases having short-chain hydrocarbon groups bonded on the surface of silica gel have been developed.[59] Since glass with controlled pore size may have larger available volume and capacity than on the surface of the silica gel, the results of separation by HPLSC may be improved by using such glass.

FIGURE 9. Separation of three alkanesulfonates by HPLLC; C_6, C_7, and C_8 alkanesulfonic acids (From Kraak, J. C., *J. Chromatogr.*, 138, 245 (1977). With permission.)

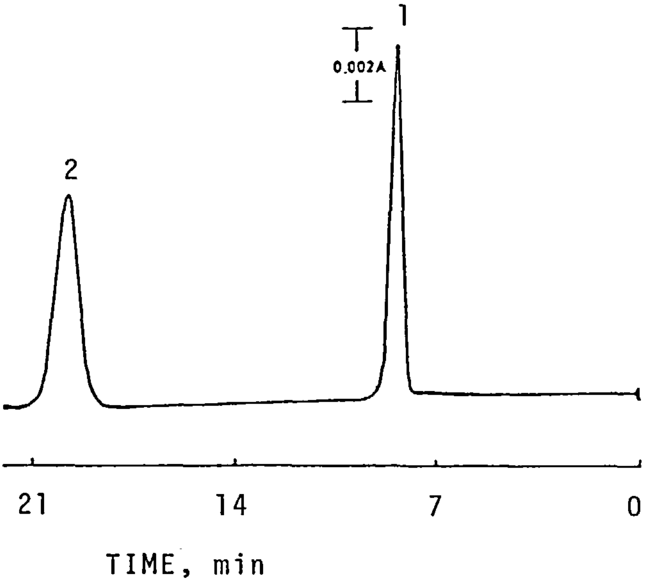


FIGURE 10. Separation of benzenesulfonate (1) and *p*-toluenesulfonate (2) by HPLLC. (From Wahlund, K. G., *J. Chromatogr.*, 115, 411 (1975). With permission.)

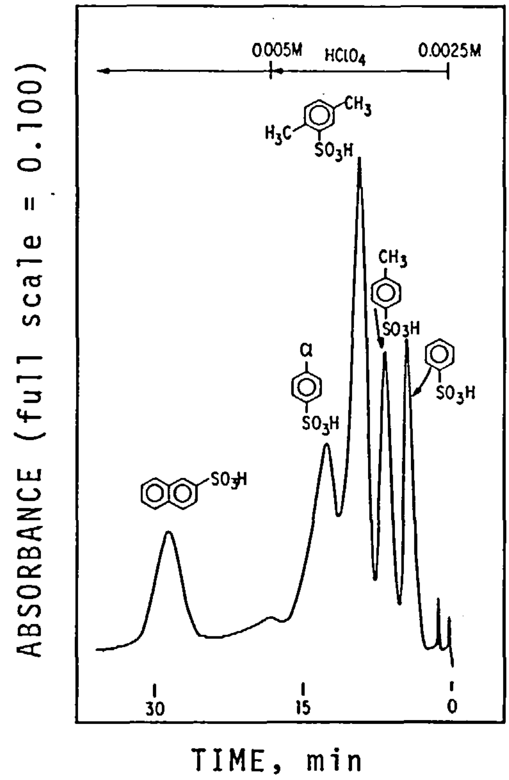


FIGURE 11. Separation of five arenesulfonates by HPLSC. (From Kirkland, J. J., *Anal. Chem.*, 43 (12), 37A (1971). Copyright by the American Chemical Society. With permission.)

I. Summary of Observations on Methods of Separation

A summary of methods, type of sulfonates separated, speed of the separation process, applications, advantages, amounts of sample used, and methods of determination is presented in Table 5.

IV. CONCLUSIONS

Among the 12 determination methods for sulfonates, titrimetric, two-phase titration, and gravimetric methods need only simple equipment. The two-phase titration method is particularly reliable for the determination of sulfonate contents in oil-soluble petroleum sulfonates. It is fast and provides good accuracy and precision. UV absorption, colorimetric, IR spectrometry, gas chromatographic, NMR, mass spectrometric, atomic absorption, and radiometric methods require more advanced instrumentation. Although the amount of sample used for each method is tabulated in Table 2, the suitable concentrations of samples are used[62] as follows: UV absorption, visible absorption, and atomic absorption methods are usually used for quantitative analysis at ppm, ppm, and ppb levels, respectively. IR spectrometric, nmr, and mass spectrometric methods are largely used for qualitative or structural identification at the moderate concentration level (20 to 50%). Gas chromatographic methods are widely used both for qualitative and quantitative analyses at the ppb level. The general time for analysis with instrumental techniques is short, but the time for preparing samples may be large.

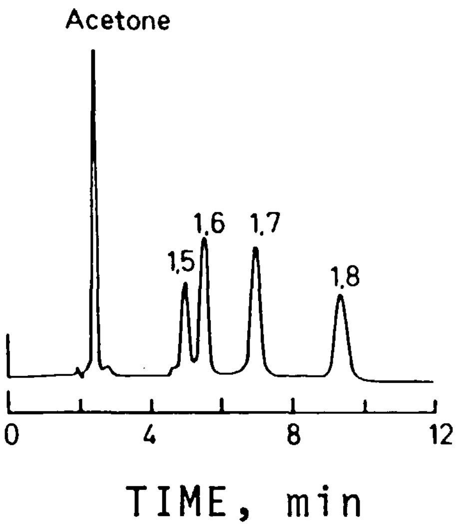


FIGURE 12. Separation of four naphthylaminesulfonic acids by HPLSC. Column: 120 × 5 mm stainless steel. (From Knox, J. H. and Laird, G. R., *J. Chromatogr.*, 122, 17 (1976). With permission.)

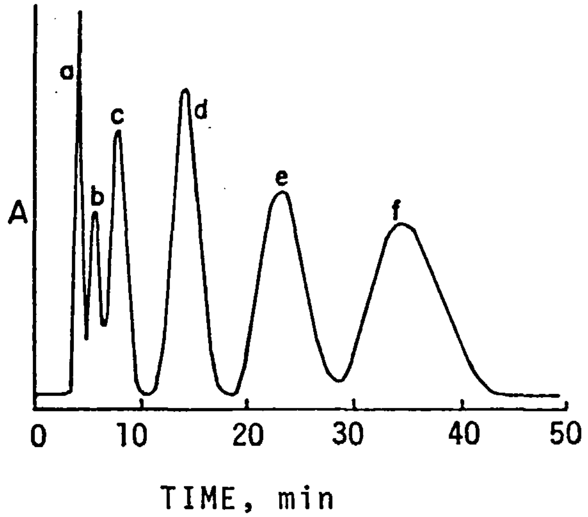


FIGURE 13. Separation of 6 benzenesulfonic acid derivatives by HPLSC. Column: 450 × 2.36 mm. (a) *p*-hydroxybenzenesulfonic acid, (b) benzenesulfonic acid, (c) *p*-methoxybenzenesulfonic acid, (d) *p*-nitrobenzenesulfonic acid, (e) 2,4-dinitrobenzenesulfonic acid, (f) 2,4,6-trinitrobenzenesulfonic acid. (From Pietrzyk, D. J., *Anal. Chem.*, 49, 860 (1977). Copyright by the American Chemical Society. With permission.)

Table 5
SUMMARY OF OBSERVATION ON METHODS OF SEPARATION

Type of sulfonates separated	Speed of the separation process	Applications	Advantages	Amounts of sample used	Method of determination	Method	Ref.
Aromatic	Slow	To purify water by removing trace amounts of alkylarenesulfonates in sewage	Simple equipment	2—20 ppm	—	Solvent extraction	2
	Slow	To separate and determine the content of sulfonate in oil-soluble petroleum sulfonic acids	—	—	Drying and weighing	Solvent extraction	40
	Very slow (~ 12 hr)	To separate arenemono- and disulfonates	—	$(2.5—5.0) \times 10^{-2}$ g	UV	Continuous electrophoresis	41
	Relatively slow	To separate arenesulfonates	Better than Ref. 26 for naphthalenetrisulfonate	0.5 g	Flame ionization detector	GC (sulfonyl fluoride)	43
	Relatively slow	To separate alkylbenzenesulfonic acids	—	—	Flame ionization detector	GC (sulfonyl fluoride)	44
Aromatic and aliphatic	Slow (1—8 hr)	To analyze alkane- and arene- mono- and disulfonates (until C_{14})	—	0.66—1.0 g aliphatic, 0.1 g aromatic	Titrimetry UV	Adsorption chromatography on XAD-2 macroreticular resin	45
Aromatic	Relatively fast (30—45 min)	To separate arenemono- and disulfonates	Better than GC[24] for sulfonates containing $-OH$ or $-NH_2$ groups	1×10^{-5} (each)	UV	Ion-exchange (polyalkylenamine)	46
Aromatic	Very slow (15 hr)	To separate linear and branched alkylbenzenesulfonates	—	9×10^{-3} g	UV	Ion-exchange (Amberlite® CG-50)	47
Aliphatic	Very slow (24 hr)	To separate α-olefinsulfonates and hydroxysulfonates (C_{14}-C_{16})	—	4×10^{-3} g (each)	Colorimetry[15] (methylene blue)	Ion-exchange (Amberlite® CG-50)	48

Table 5 (continued)
SUMMARY OF OBSERVATION ON METHODS OF SEPARATION

Type of sulfonates separated	Speed of the separation process	Applications	Advantages	*Amounts of* sample used	*Method of* determination	Method	Ref.
Aromatic	Very slow (26 hr)	To separate and determine isomeric monosulfonic acids	—	0.3 g	UV (multicomponent)	Ion-exchange (SG-1 resin)	49
Aliphatic	Slow	To separate and determine methane- and ethanesulfonates	Simple Whatman papers are used as absorbent of stationary phase	$(1—5) \times 10^{-6}$ g	Drying and spraying with bromocresol green or silverfluoresceinate	Paper chromatography	50
Mixtures of aliphatic and aromatic	Slow	To separate alkylalkane- (C_4-C_{18}) and alkylbenzenesulfonates (C_0-C_{14})	—	$(3—10) \times 10^{-6}$ g (each)	UV	Thin-layer chromatography	51
Aromatic	Slow	To separate 1- and 2-naphthalenesulfonic acid	Color developed is stable for several months	$(3—7) \times 10^{-5}$ g	Densitometry	Thin-layer chromatography	52
Aromatic	Relatively slow	To separate arenesulfonates	—	2×10^{-3} g (each)	UV	LLC	53
Aliphatic	Slow (4 hr)	To separate alkanemonosulfonates from alkane di- or polysulfonates (C_{10}-C_{20})	—	$(2.1—3.5) \times 10^{-2}$ g	Titrimetry	LLC	54
Aromatic	Fast (5—45 min)	To separate arenesulfonates	Fast separation	—	UV	HPLLC	55
Aliphatic	Very fast (8 min)	To separate C_6-C_8 alkanesulfonates	Fast separation	1×10^{-8} g	Tensammetry	HPLLC	56
Aromatic	Fast (22 min)	To separate benzenesulfonate and *p*-toluenesulfonate	Fast separation	$(3—4) \times 10^{-6}$ g (each)	UV	HPLLC (reversed phase)	57

Aromatic	Fast (30 min)	To separate arenesulfonates	Fast separation	$(5—150) \times 10^{-4}$ g	UV		HPLSC	58
Aromatic	Very fast (10 min)	To separate naphthylaminesulfonic acid isomers	Fast separation	$(1—50) \times 10^{-6}$ g	UV		HPLSC	59
Aromatic	Relatively fast	To separate benzenesulfonic acid derivatives	Inexpensive Amberlite® XAD-4 resin is used as a stationary phase	$(5—50) \times 10^{-6}$ g	UV		HPLSC	61

Mass spectrometry is usually combined with gas chromatography to quantitatively analyze mixtures. Although the radiometric methods are slow (30 min per each counting), they are not limited by the dark color of crude oils. The use of ion-selective membrane electrodes gives a fast response, generally within 1 min. They have been used in the determination of individual aromatic sulfonates in the range of 10^{-5} to $10^{-1}M$. The application of ion-selective membrane electrodes to measure the concentration of alkanesulfonates, however, has not been reported as yet.

Among the seven separation methods for sulfonates reviewed here, solvent extraction and paper and thin-layer chromatography need only simple equipment, while continuous electrophoresis, and gas, ion-exchange and liquid chromatography require a fair degree of instrumentation. The speed of analysis for gas, high-pressure liquid-liquid, and high-pressure liquid-solid chromatography is fast, but it may take several hours to prepare samples for gas chromatography. Solvent extraction, and paper and thin-layer chromatography are slow in nature. Continuous electrophoresis and ion-exchange chromatography (with cation-exchange resins) are very slow. From the papers reviewed, it can be concluded that high-pressure liquid-liquid chromatography and high-pressure liquid-solid chromatography are powerful techniques for the analysis of sulfonates. Since a precolumn is generally needed in liquid-liquid chromatography and a guard column is usually used in liquid-solid chromatography, an organic compound chemically bonded to an innert matrix, such as controlled-pore glass, used as stationary phase, should offer advantages over the reviewed liquid-liquid chromatography and liquid-solid chromatography methods, although the capacity of the chemically bonded resin should be relatively large for successful application.

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APPENDIX

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