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L. Ronald Whitlock[a]; Sidney Siggia[b]
[a] Research Laboratories, Eastman Kodak Company Kodak Park, Rochester, New York [b] Department of Chemistry, University of Massachusetts, Amherst, Massachusetts

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FUSION REACTION GAS CHROMATOGRAPHY

L. Ronald Whitlock
Research Laboratories, Eastman Kodak Company
Kodak Park, Rochester, New York 14650

Sidney Siggia
Department of Chemistry, University of Massachusetts
Amherst, Massachusetts 01002

I. INTRODUCTION

The conventional gas chromatograph is an efficient tool for separating mixtures of volatile compounds into their individual components for quantitative measurement and for preparative isolation of the components. Many compounds, however, are nonvolatile or lack sufficient volatility for gas chromatographic separation. These compounds may contain polar functional groups (i.e., -COOH, -OH, $-NO_2$, $-NH_2$, etc.), which cause low volatility or poor chromatographic behavior, or ionic groups (i.e., $-SO_3Na$, R_4NX, $-SO_4Na$, -N=NCl, etc.), which are either completely nonvolatile or thermally unstable. Other compounds have too large molecular weights for conventional gas chromatographic separation.

Derivatization of polar and some ionic compounds has been an extremely successful technique for certain highly reactive functional groups. These procedures commonly include silylation, acetylation, or esterification of carboxylic acid, amine, and hydroxyl-containing compounds.[1-3] Some compounds, however, are either slow to react or do not form volatile derivatives using these techniques. For such compounds, chemical reactions must be found to transform the nonvolatile material into new compounds that can be chromatographed.

The use of chemical conversions of compounds to be separated is often described by the term reaction gas chromatography.[4-6] This term, however, has been used to describe all types of chemical transformations which, literally, can occur anywhere within the gas chromatographic system and for a wide variety of purposes.

"Fusion reaction gas chromatography" is the name given to a recently developed procedure for the chemical transformation of certain nonvolatile compounds, including polymers, which are normally impossible to separate using gas chromatography. The principal purpose of the fusion reaction procedure is to allow quantitative measurements on these materials, although small-scale preparative fusion reaction gas chromatography could be the method of choice for the synthesis or isolation of certain compounds.

II. THE FUSION REACTION

In the analysis of organic materials, the chemist is often confronted with compounds that react very slowly or not at all when solution reaction methods are used. Solution reactions are often limited to dilute reagent concentrations owing to low reagent solubility or to reagent-sample-solvent incompatibility. In addition, the solution reaction temperature is limited by the reflux temperature of the solvent under normal conditions. To circumvent these problems, the use of fusion reactions for the chemical transformation is an obvious choice.

Fusion reactions use 100 percent reagent mixed with a small amount of sample, usually at mole ratios of 30 to 1 and sometimes as high as 50 to 1. The fusion reaction temperature must be above the fusion reagent melt temperature but held below the thermal decomposition temperature of the sample components. Hence, for many organic compounds fusion temperatures of 300-350°C are used. Few compounds will remain unreacted under these conditions.

Two factors control the resistance of a compound to chemical reaction: the inherent stability of the molecular bonds and the steric configuration of the molecule. For example, primary amides are hydrolyzed rather easily with alkali while tertiary amides are fairly resistant to hydrolysis. Polymeric esters, where the ester groups are pendant from a hydrocarbon polymer, are very difficult to

hydrolyze completely in solution.[7] Poly(methyl methacrylate), for example, saponifies to only 30 percent with 1 N potassium hydroxide in amyl alcohol (bp 137°C) after ninety hours at reflux.[8] Similarly, sodium sulfonates fail to react with 5 N sodium hydroxide in ethylene glycol at a reflux temperature of 200°C.[9] Alkali fusion with potassium hydroxide, however, proceeds rapidly and completely for both of these compounds.[9,10]

Historically, chemists have looked upon fusion reactions as being crude and similar to pyrolysis. Yet this is not the case. Fusion reactions can be clean, quantitative, and stoichiometric, provided two precautions are taken. The fusion temperature must be kept below the compound pyrolysis temperature and, for some compounds, oxygen and carbon dioxide must be excluded.[9] These precautions are met fairly easily by the use of a fusion reaction chamber connected directly to a gas chromatograph as described in this paper.

III. FUSION REAGENTS

Reagents used for fusion reaction gas chromatography fall into four categories at present: alkaline, acid, reductive, and oxidative. Alkaline[9-18] and, to a lesser extent, reductive fusions[19,20] are well established as useful analytical procedures. Acid and oxidative fusions have considerable potential use for the analysis of some materials and are just now being investigated.[21]

A. Alkali Fusion

For alkali fusion, sodium[16,18] and potassium hydroxides,[9-18] as well as other alkali-metal hydroxides,[15,16] have been used. However, potassium hydroxide is much preferred because of its lower melting point and the significantly higher solubility of organic compounds in a potassium hydroxide melt compared to a sodium hydroxide melt. The former dissolves even C_{16}-alkyl benzenesulfon-

ates. Commercially available potassium hydroxide contains about 15 wt percent water (present as the hemihydrate) and works well for fusion. The water is essential since it lowers the potassium hydroxide melting point to about 125°C (compared to 360°C for pure KOH) and contributes to the hydrolysis reaction. Experiments have shown that this water of hydration is driven off very slowly, causing a beneficial microstirring action during the fusion reaction. The water is released completely only at temperatures higher than 400°C. To improve the potassium hydroxide fusion character for some applications, experiments have shown that the addition of a flux agent (1 to 10 wt percent), such as sodium acetate, aids the achievement of a homogeneous melt during the fusion reaction.[9-13]

B. Acid Fusion

Two acid fusion reagents have been reported to date, sodium hydrogen sulfate[21] and crystalline orthophosphoric acid.[22] The anhydrous form of sodium hydrogen sulfate has a melting point of 315°C and the monohydrate melts at 58.5°C. The water associated with the hydrated form is needed for this application since the reaction of interest is usually hydrolysis. The amount of water, in addition to the melt temperature, can be regulated by mixing the monohydrate with the anhydrous form. Sodium hydrogen sulfate, however, has two properties that limit its usefulness. First, oxidation and dehydration of the organic matter can occur since the reagent is used in a hot, concentrated form. Second, the reagent undergoes a series of thermal degradations causing a continual change in its chemical composition during the normal temperature rise used for fusion.[23]

Crystalline orthophosphoric acid is a better reagent because it is stable and shows little tendency to oxidize materials. It has a melting point of 42°C and is the reagent of choice for acid fusion.

C. Reductive Fusion

Reductive fusion gas chromatography employs a highly concentrated organic reagent, solvent-free, which is either a strong

reducing agent by itself or slowly decomposes to release the reducing agent for reaction. Hydrazine could be used but is volatile and unstable in air. A number of hydrazides have been used, but carbohydrazide has found the greatest application.[19,20] The hydrazides were chosen since these compounds are solid, stable at room temperature, and readily available in pure form.

To elucidate the reactive species responsible for the reducing properties of carbohydrazide, its decomposition products have been determined at 225°C, the fusion temperature.[19] Carbohydrazide was found to decompose yielding H_2, O_2, N_2, CO, NH_3, and hydrazine. Moreover, these gases continue to evolve for over an hour during a reductive fusion reaction. The hydrogen evolved is probably the source of much of the carbohydrazide's reducing ability, although the hydrazine has been shown to be effective by itself for some reductions.

Inorganic hydrides have been studied but are, in general, too strongly reducing[21] and the reduction is difficult to control.

D. Oxidative Fusion

Reagents for oxidative fusion have only recently been investigated. Possible oxidative fusion reagents, with their melting points given in parentheses, include[21] potassium metaperiodate (582°C), sodium metaperiodate (300°C), lead tetraacetate (174°C), potassium dichromate (398°C), sodium dichromate (357°C), and chromium trioxide (196°C).

E. Flux Agents

Fluxes are incorporated in the fusion reaction for two reasons. The flux controls the melting point of the fusion reagent. For example, if a fusion-reagent melting point is sufficiently high to cause thermal decomposition of the sample before fusion occurs, a flux material can be added to depress the melting point to a lower, more acceptable temperature. A flux can also be used to increase the fusion temperature if the melting point of the flux is higher than that of the fusion reagent.

Fluxes are also very useful for promoting sample solubility in the melt in order to achieve a more homogeneous fusion mixture. This will facilitate reaction completeness in the shortest time and increase the precision of the analysis.

A number of fluxes have been used with alkali fusion;[9,10] however, sodium acetate was found to be the most useful. The properties of a good flux agent include proper melting point; nonreactivity towards the sample, reaction products, and fusion reagent; and solubility at melt temperature for the organic compounds of interest.

IV. FUSION REACTION APPARATUS

A. Reaction Unit

The fusion reaction and gas chromatographic separation are performed in a single apparatus. A detailed schematic diagram of the apparatus used for the alkali fusion of sulfonates and adaptable to most fusion applications is shown in Figure 1. The fusion reaction unit is a modified version of a pyrolysis unit first described by Ettre and Varadi[24] and now commercially available from the Perkin-Elmer Corp., Norwalk, Conn. (Pyrolysis Accessory 154-0825). The fusion unit consists of a borosilicate glass tube, a small section of which is made of quartz and surrounded by a variable-temperature furnace, section I, Figure 1. Section A of the tube is used to store sample boats awaiting fusion and section D is used to store the boats after the analysis is complete. Section B is a side-arm capped with a rubber septum used to add liquids to the fusion sample boats when required.

To convert the Perkin-Elmer pyrolysis accessory to a unit suitable for fusion reaction gas chromatography, several modifications must be made. The gas-sampling valve located between the fusion chamber and the gas chromatograph should be removed. The

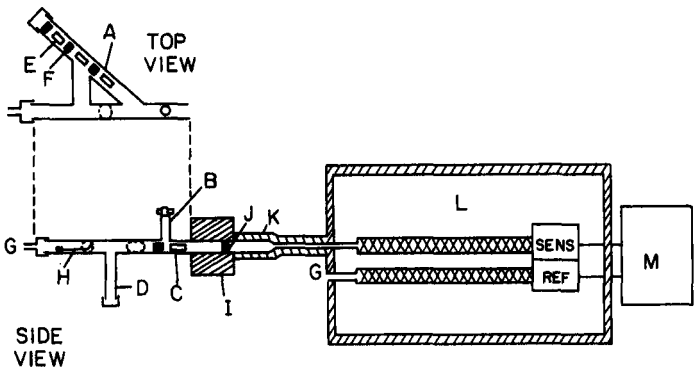


FIGURE 1

Apparatus for alkali fusion reaction gas chromatography. A-storage area for samples awaiting analysis; B-side-arm with rubber septum; C-furnace inlet; D-storage area for sample boats after analysis; E-platinum sample boat; F-pusher; G-carrier-gas inlet; H-retriever; I-variable-temperature furnace; J-boat stop; K-heated connector; L-gas chromatograph; M-recorder.

heated flexible connector tubing supplied with the unit is not suitable for conducting high-boiling reaction products to the gas chromatograph and should be removed. A short section of 1/8-inch stainless-steel tubing covered with asbestos insulation and a Nichrome wire heating element is a suitable replacement (K, Figure 1). The side-arm capped with a rubber septum is added to the fusion-tube assembly to allow syringe injection directly into the sample boat for acidification or for liquid reagent addition.

An additional modification must be made when the products of the fusion reaction are volatile ones, as is the case with the alcohols produced during the fusion of carboxylic esters. A cold trap must be inserted between section K and the gas chromatograph to collect the volatile reaction products. An 8- by 0.125-in. stainless-steel tube shaped in a loop and packed with silanized glass wool to reduce dead volume and inhibit aerosol formation has proven suitable.[10] The trap loop is immersed in liquid nitrogen during the fusion. Upon completion of the reaction the coolant is replaced with a heater and the contents are swept directly into the gas chromatograph.

B. Sample Handling

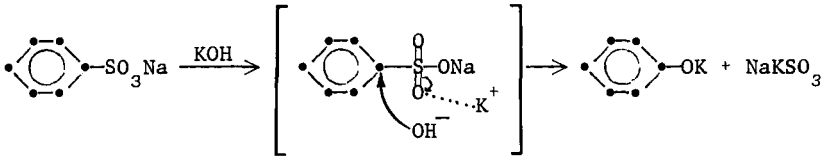
Samples for fusion (usually 1-10 mg) are weighed into 11- x 4-mm microsize platinum boats (Arthur H. Thomas Co., No. 3183-010). The sample boats are moved in and out of the furnace and within the fusion unit by small steel cylinders (F, Figure 1) manipulated externally with a magnet. Precautions should be taken to add the reagent for fusion to the samples in a dry atmosphere to reduce the amount of adsorbed water. The potassium hydroxide reagent should be added as a preground, fine powder in order to cover the sample and ensure good mixing. The reagent is prepared by adding 1-10 percent sodium acetate to the potassium hydroxide and heating in a stainless-steel crucible under inert atmosphere until a uniform melt is obtained. The cooled reagent is then crushed in a dry box to a fine powder.

V. MATERIALS ANALYZED USING FUSION REACTION GAS CHROMATOGRAPHY

A. Aryl Sulfonates

The alkali fusion of benzenesulfonic acid to produce phenol as a commercial process has been known for more than 100 years.[25] Recent work of Makolkin[26] and Oae, et al.,[27] has conclusively demonstrated that the fusion reaction mechanism is an S_N2 nucleophilic aromatic substitution. This has clarified several inconsistencies in some of the older literature concerning the reaction mechanism and products obtained.

Aryl Sulfonate Alkali Fusion
S_N2 Mechanism



With this mechanism, the phenol produced after acidification resembles the starting sulfonate and its identification and measurement also identify and measure the sulfonate. The fusion reaction, therefore, should be especially useful for sulfonate analysis since it is specific for sulfonate. The presence of either alkali metal sulfate (a common impurity) or nonsulfonated organic compounds will not interfere, making a preliminary separation unnecessary. By using gas chromatography to measure the phenols produced, the method is both specific for sulfonate and selective for mixtures.

When using a high-temperature reaction, such as fusion, the possibility of thermal decomposition or pyrolysis of either the sulfonate or the phenol salt must be considered. An examination of their thermal stabilities, in air and helium atmospheres, using thermogravimetric analysis has shown, however, that these compounds are stable well above the temperatures used for fusion.[9,11] Typical decomposition temperatures are shown in Table I. Thus, most sulfonates are stable to temperatures well above 400°C, some above 500°C. However, these results support the observation that for consistent and quantitative results, the reaction must be under an inert atmosphere because of partial decomposition of the phenol salts in air.

Typical analyses of several sulfonic acids and salts are given in Table II. A standard deviation of 1 to 3 percent was obtained using 1- to 5-mg samples. Some sulfonate samples were analyzed containing a threefold excess of sodium sulfate. No deleterious effect on the sulfonate analysis was observed.[9]

The versatility of the method is shown by the analysis of a mixture of three sulfónates, Table III. A chromatogram of the phenols produced after acidification of the fusion products is shown in Figure 2. The phenol, p-cresol, and 2,5-xylenol peak areas were used to determine the sodium benzenesulfonate, sodium p-toluenesulfonate, and sodium 2,5-dimethylbenzenesulfonate contents, respectively, of the mixtures.

TABLE I

Decomposition Temperature of Some Sulfonic Acids, Alkali Metal Sulfonates, and Alkali Metal Phenolates in Air and Helium Atmospheres[a]

Compound	Decomposition Temp, °C	
	Air	Helium
Potassium phenolate	215	420
Potassium 2-naphtholate	250	480
Sodium p-nitrophenolate	...	350**
Benzenesulfonic acid sodium salt	520	520
m-Benzenedisulfonic acid disodium salt	...	570
1,3,5-Benzenetrisulfonic acid trisodium salt	...	560
p-Sulfobenzoic acid monopotassium salt	390	405**
m-Sulfobenzoic acid monosodium salt	...	430**
p-Chlorobenzenesulfonic acid sodium salt	450	450
p-Aminobenzenesulfonic acid sodium salt	...	255
m-Nitrobenzenesulfonic acid sodium salt	...	400**
p-Acetylbenzenesulfonic acid sodium salt	...	350
Dodecylbenzenesulfonic acid sodium salt	400	400
p-Diphenylaminesulfonic acid sodium salt	420	420
1-Naphthalenesulfonic acid sodium salt	...	480
2-Naphthalenesulfonic acid sodium salt	...	510
2,7-Naphthalenedisulfonic acid disodium salt	...	520
4-Amino-1-naphthalenesulfonic acid sodium salt	285	...
1-Anthraquinonesulfonic acid sodium salt	...	450**
2-Anthraquinonesulfonic acid sodium salt	...	430**
m-Aminobenzenesulfonic acid	...	365*
p-Aminobenzenesulfonic acid	...	260*
p-Toluenesulfonic acid	...	270*

[a]No asterisk, determined by TGA; one asterisk, determined by DSC; two asterisks, determined by TGA, confirmed by DSC.

TABLE II

Analysis of Sulfonic Acids and Salts by Alkali Fusion Reaction Gas Chromatography

Compound	Analysis,wt%	Standard deviation
p-Toluenesulfonic acid	97.4 (10)	1.3
Benzenesulfonic acid sodium salt	96.7 (4)	1.4
2,5-Dimethylbenzenesulfonic acid sodium salt	98.1 (4)	1.2
p-Sulfobenzoic acid monopotassium salt	95.5 (5)	2.5
p-Phenolsulfonic acid sodium salt	97.3 (5)	2.8
Benzenesulfonamide	95.7 (3)	1.5
2-Naphthalenesulfonic acid sodium salt	97.6 (5)	2.1

[a]Figure in parentheses is number of trials.

The sulfonation of toluene with concentrated sulfuric acid yields a mixture of o-, m-, and p-toluenesulfonic acid along with varying amounts of the starting materials--toluene and sulfuric acid. Direct alkali fusion of the sulfonation mixture and measurement of the cresols by gas chromatography gives a rapid analysis of this difficult system.[28]

TABLE III

Analysis of Sulfonic Acid Sodium Salt Mixtures by Alkali Fusion Reaction Gas Chromatography

Blend	Benzenesulfonic acid sodium salt, wt %		p-Toluenesulfonic acid sodium salt H_2O, wt %		2,5-Dimethylbenzenesulfonic acid sodium salt, wt %	
	Actual	Found	Actual	Found	Actual	Found
A	28.6	27.8	20.4	20.5	51.0	48.7
B	69.0	67.8	10.8	10.5	20.2	19.3
C	25.7	26.3	35.2	34.0	39.1	38.0

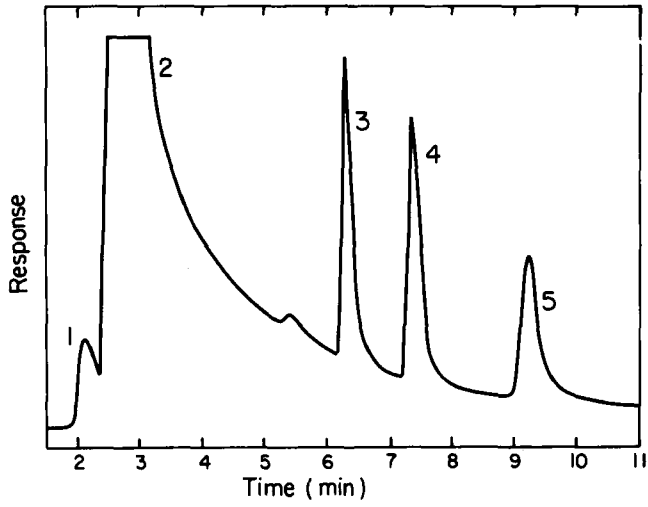


FIGURE 2

Gas chromatogram of sodium salts of benzenesulfonic acid, p-toluenesulfonic acid, and 2,5-dimethylbenzenesulfonic acid after alkali fusion and acidification. Separation on a 12-ft, SE-30 (12%) column.

Peak 1, gaseous decomposition product of maleic acid; 2, water; 3, phenol; 4, p-cresol; 5, 2,5-xylenol.

A chromatogram of the fusion reaction products is shown in Figure 3. The cresol isomer separation was obtained on a column of 10 percent tricresyl phosphate/5 percent phosphoric acid coated on Anakrom ABS. The analysis for each isomer was 19 percent ortho, 9 percent meta, and 72 percent para.

Alkylbenzenesulfonates (ABS) are widely used as detergents, and their physical properties as well as their detergent action will vary depending on the nature of the alkyl side-chain attached to the sulfonated aromatic ring. Analysis of these compounds has always been difficult owing to the large number of isomers and homologs present in any single sample.

Chromatograms of the alkali fusion products of two ABS samples are shown in Figure 4. One sample is a branched dodecylbenzenesulfonate. With both samples a whole series of components

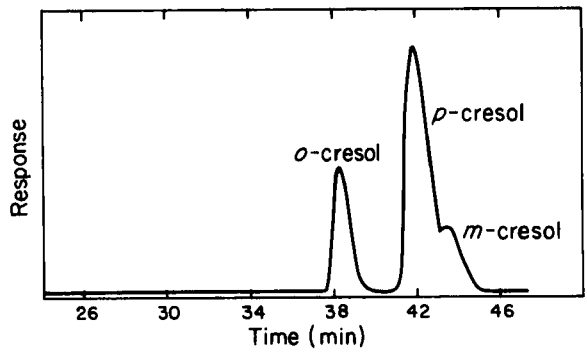


FIGURE 3

Chromatogram of the isomers of toluenesulfonic acid after alkali fusion and acidification. Separation on a 10 ft, 10% tricresyl phosphate, 5% phosphoric acid column.

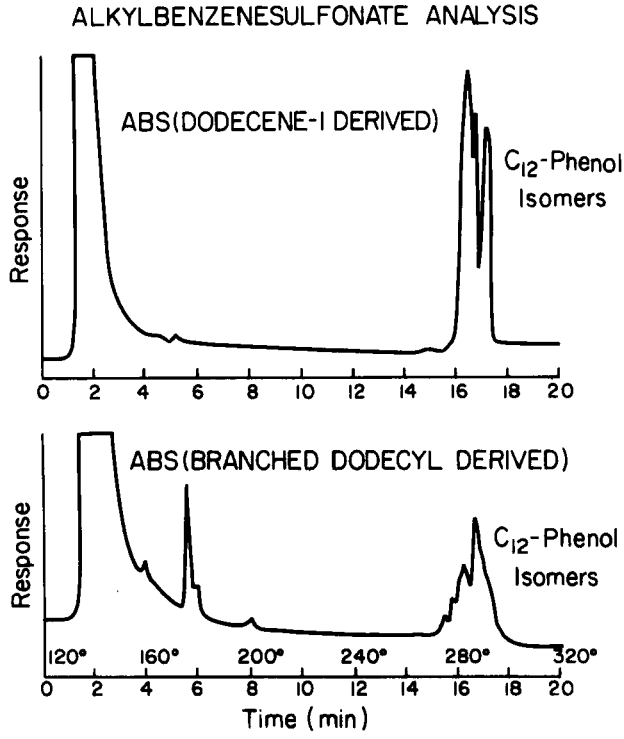


FIGURE 4

Chromatograms of alkylbenzenesulfonates after alkali fusion and acidification. Separation on an 8 ft, 12% SE-30 column.

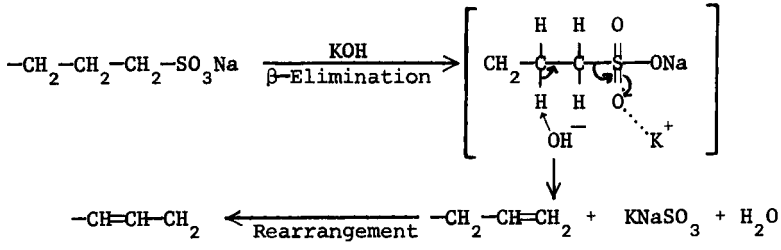
are evident. The major peaks in the chromatograms, appearing at retention times between 16 and 18 min, were identified as various isomers of dodecylphenol.[28] A positive identification of each component was not attempted, however, but could be obtained easily using combined gas chromatography and mass spectrometry.

It should be pointed out that alkali fusion of some sulfonates may give phenols of low volatility and these cannot be measured conveniently by gas chromatography. These include some highly polysulfonated compounds, those sulfonates containing other very polar functional groups, and certain high-molecular-weight sulfonates. To extend the alkali fusion method to include these materials, the phenol measurement can be accomplished by using the coupling reaction with a diazotized amine.[11] The azo dye produced by this reaction is measured by visible spectrophotometry. Alternatively, the sulfite produced by the fusion reaction (see reaction 1) can be measured titrimetrically.[9] Pyrolysis gas chromatography can be used where the sulfur dioxide pyrolysis product is measured quantitatively.[20]

B. Alkyl Sulfonates

The alkali fusion of linear alkyl sulfonates has been reported by Nakagawa, et al.[16] Using gas chromatography and infrared spectroscopy for the identification of the fusion products, they concluded that the reaction follows a β-elimination mechanism. This produces the 1-olefin initially followed by partial thermal rearrangement to give a cis-trans mixture of internal olefins plus 1-olefin.

Alkyl Sulfonate Alkali Fusion

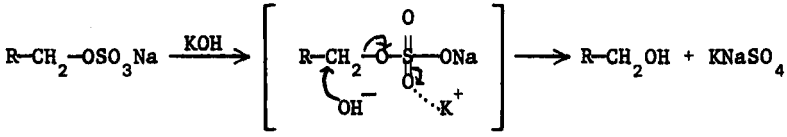


Because of the multiple reaction products, the fusion reaction gas chromatographic method for alkyl sulfonates is not satisfactory. For these sulfonates, titrimetric measurement of the sulfite produced by alkali fusion is suggested[9] or, alternatively, pyrolysis gas chromatography and measurement of the sulfur dioxide pyrolysis product.[20] Either procedure gives an analysis for total alkyl sulfonate.

C. Alkyl Sulfates

The alkali fusion of alkyl sulfates was briefly examined by Nakagawa, et al.[15] They reported that alkali fusion of alkyl sulfates produces the corresponding alcohol according to the reaction mechanism:

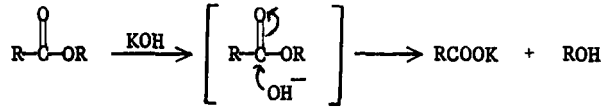
Alkyl Sulfate Alkali Fusion



From the gas chromatographic separation and identification of the alcohols produced, they were able to determine the alkyl carbon number distribution of commercial sodium alkyl sulfate mixtures. The authors also noted some nonalcohol hydrocarbon products. These may have resulted from sample pyrolysis since the fusion temperature used, 400°C, was unusually high.

D. Carboxylic Esters and Polyesters

Carboxylic esters have uses as solvents, plasticizers, paint additives, resins, fibers, plastics, coatings, films, and molding materials. Ester analysis is often accomplished using the saponification reaction. The esters hydrolyze to yield the acid salts and alcohols. The acyl-to-oxygen bond is cleaved and nucleophilic substitution occurs at the acyl carbon:



For saponification, a known amount of an alkali hydroxide solution is added to the sample; the solution is refluxed, and the excess hydroxide is measured by titration. Esters are known to vary widely in reactivity so that reaction conditions must be established accordingly. Some esters hydrolyze with great difficulty or incompletely. The analysis by saponification of samples containing acids, or alkali-labile groups, such as halogen, cannot be accomplished without interference from these groups.

Alkali fusion of carboxylic esters and gas chromatographic measurement of the alcohols eliminate many difficulties inherent with other methods. The fusion reaction is not limited to solution conditions of reaction temperature or alkali concentration. Thus, even for the most resistant esters, hydrolysis is virtually complete. The analysis is specific and provides for the determination of mixtures in a short time. The fusion products define the ester composition using only 1-5 mg of sample.

Several classes of esters have been analyzed by alkali fusion gas chromatography.[10] Methyl, ethyl, and butyl phthalates and terephthalates were fused at 240 to 320°C for 0.5 hr with 99 to 100 percent conversion. The analyses for these esters, based on measurement of the alcohols, are given in Table IV and show a standard deviation of 1-3 percent.

The analyses of several halogenated carboxylic esters are shown in Table V. The total reaction time (15 min) is rapid compared to solution saponification. A significant advantage for this method is the elimination of the interference from the alkali-labile group, chlorine, present in these types of esters. Solution saponification would give high values owing to the concurrent halogen hydrolysis reaction.

TABLE IV

Analysis of Phthalate and Terephthalate Esters

Compound	Fusion temp., °C	Time, hr	% converted	Standard deviation	Alcohol liberated
Dimethyl terephthalate	280	0.5	98.8	2.5	MeOH
Diethyl terephthalate	320	0.5	99.1	3.1	EtOH
Dibutyl terephthalate	300	0.5	100.4	0.8	BuOH
Diethyl phthalate	240	1.0	98.8	2.4	EtOH

Polymethacrylates are very stable towards hydrolysis, and, consequently, they are difficult to analyze by saponification techniques. Their stability is attributed principally to the steric effects of carboxyl shielding from neighboring ester groups and to higher bond strength compared to other acrylate compounds. Poly(methyl methacrylate) (Plexiglas) and the butyl and isobutyl polymethacrylates gave 98 to 100 percent conversion to the respective alcohols by alkali fusion as shown by gas chromatographic analysis of the alcohols given in Table VI.

TABLE V

Analysis of Chlorinated Esters By Fusion Gas Chromatography[a]

Compound	Analysis, mole %	Standard deviation	Alcohol liberated
Methyl m-chlorobenzoate	100.2	1.7	MeOH
Methyl 2,4-dichlorophenoxyacetate	98.4	0.6	MeOH
Methyl 2,4,5-trichlorophenoxyacetate	99.5	2.1	MeOH
Methyl 2-(2,4,5-trichlorophenoxy) propionate	99.0	2.6	MeOH

[a]Samples were fused 15 min at 260°C.

TABLE VI

Alkali Fusion Gas Chromatography of Polyesters

Polyester	Fusion temp., °C	Time, hr	% converted	Alcohol liberated
Poly(methyl methacrylate)	360	0.5	99	MeOH
Poly(butyl methacrylate)	320	1.0	98	BuOH
Poly(isobutyl methacrylate)	320	1.0	100	i-BuOH
Poly(methyl acrylate)	320	0.5	101	MeOH
Monobutyl ester of poly-(methyl vinyl ether/maleic acid)	320	0.75	96	BuOH

The ester contents of poly(methyl acrylate) and the monobutyl ester of poly(methyl vinyl ether-co-maleic acid) were determined using similar conditions, and the results are also shown in Table VI.

Polymethacrylates are known to depolymerize at high temperatures (220 to 450°C).[29] Experiments have shown, however, that thermal depolymerization before alkali fusion is slight. The chromatogram in Figure 5 shows methanol as the only fusion product with no depolymerization products or polymer fragments evident.

Poly(α-chloroacrylates) are generally limited to exotic uses, although they are stronger, harder, and more craze-resistant than polymethacrylates. Although resistance to solution saponification has been noted, alkali fusion gas chromatography provides a useful means of analysis for these polymers. The data shown in Table VII indicate conversions of the three poly(α-chloroacrylates) to within 4 percent of the predicted values.

Various mixtures of methyl, ethyl, and isopropyl poly(α-chloroacrylates) were analyzed. A typical chromatogram of the liberated alcohols is shown in Figure 6. This illustrates the versatility of the method for establishing quantitatively and qualitatively the composition of polymeric materials. The alcohol

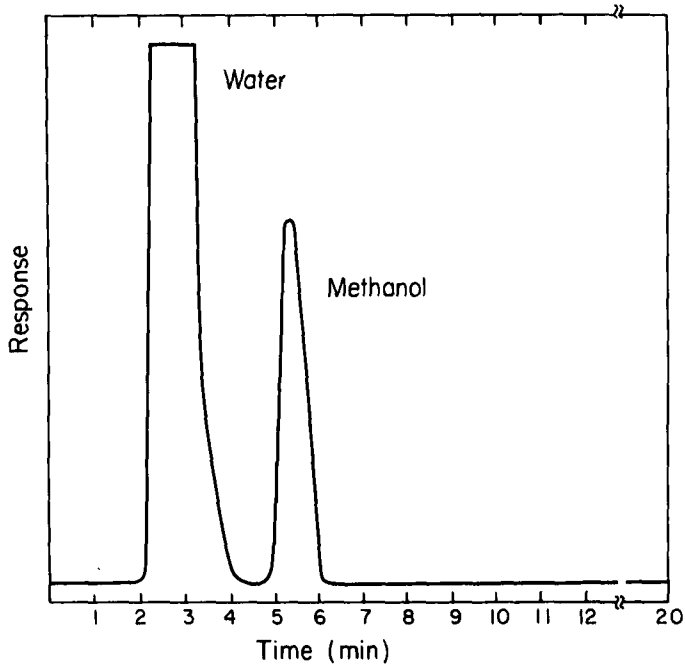


FIGURE 5
Gas chromatogram of poly(methyl methacrylate) after alkali fusion. Separation on a 7 ft, 80-100 mesh, Poropak Q column.

Peak 1, water; 2, methanol.

peaks are well resolved and easily quantitated. The results of the analysis of several polymer mixtures are given in Table VIII.

TABLE VII

Alkali Fusion Gas Chromatography of Polyesters

Polyester	Fusion temp., °C	Time, hr	% converted	Alcohol liberated
Poly(ethyl α-chloroacrylate)	320	0.5	98	EtOH
Poly(methyl α-chloroacrylate)	300	0.5	104	MeOH
Poly(isopropyl α-chloroacrylate)	300	0.5	99	i-PrOH

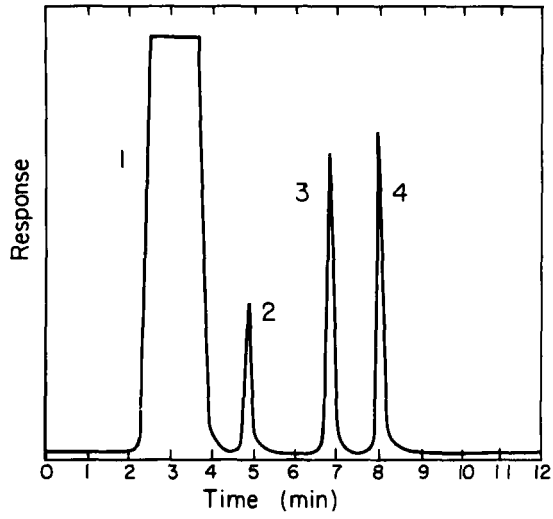


FIGURE 6

Gas chromatogram of poly(methyl α-chloroacrylate), poly(ethyl α-chloroacrylate) and poly(isopropyl α-chloroacrylate) after alkali fusion. Separation on a 7 ft, Poropak Q column.

Peak 1, water; 2, methanol; 3, ethanol; 4, isopropyl alcohol.

Acidic hydrolysis of esters in aqueous solution results in an equilibrium mixture of a carboxylic acid and an alcohol. In an acid fusion reaction, the volatile reaction products are liberated as they are produced, thus driving the reaction to completion.

TABLE VIII

Analysis of Poly(α-Chloroacrylate) Mixtures by Alkali Fusion Gas Chromatography

	Methyl		Ethyl		Isopropyl	
Blend	Actual	Found	Actual	Found	Actual	Found
A	24	27	34	35	42	42
B	24	26	38	39	39	40
C	28	27	26	28	46	49
D	16	17	26	26	58	60
E	37	40	42	38	21	20
G	0	0	31	30	68	65

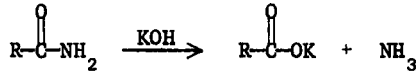
Although esters have been analyzed successfully by alkali fusion, acid fusion can be used as a valuable complementary technique for some applications. For example, a number of carboxylate esters can be hydrolyzed only by an acid fusion in order to liberate a volatile reaction product.

Cellulose esters can be attacked by either acid or alkali fusion, but only acid fusion will liberate a volatile product. Cellulose acetate was fused at 170°C for 0.75 hr using crystalline orthophosphoric acid to liberate acetic acid.[22] The analysis of cellulose acetate is given in Table IX.

The chromatogram in Figure 7 shows the acid fusion reaction products from cellulose acetate.

E. Carboxylic Amides and Polyamides

When treated with alkali, carboxylic amides hydrolyze to the acid salt and either ammonia (from primary amides) or amines (from secondary and tertiary amides) Nucleophilic attack occurs



on the acyl carbon. The complete hydrolysis of amides tends to be even more difficult than hydrolysis of the corresponding esters.[30] The major limitations of procedures using alkaline hydrolysis have been the dependence of the reaction on base concentration and reaction temperature. Hydrolysis of amide polymers has been found to be dependent on many of the polymer parameters, including chain conformation, polymer morphology and tacticity, and dielectric constant.[31] Therefore, as with polyesters, complete solution hy-

TABLE IX

Acid Fusion Gas Chromatography of Cellulose Acetate

Cellulose ester	Fusion temp., °C	Time, hr	% converted	Standard deviation
Cellulose acetate	170	0.75	99.2	0.7

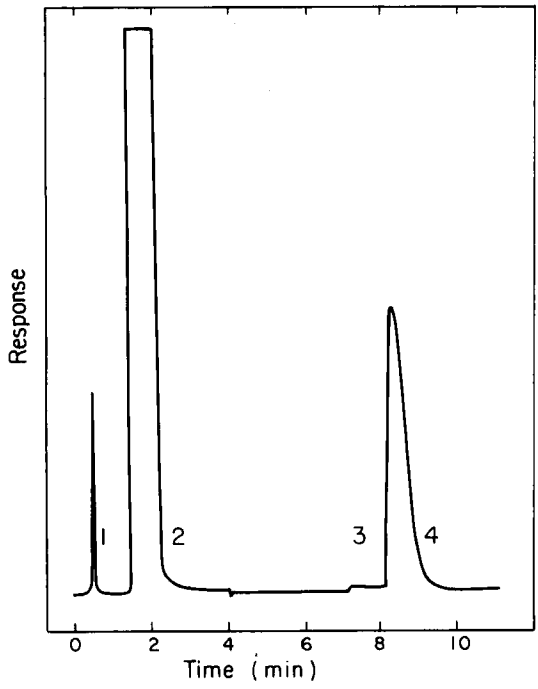


FIGURE 7
Gas chromatogram of cellulose acetate after acid fusion. Separation on a Chromosorb 101 column.
Peak 1 and 3 unidentified; 2, water; 4, acetic acid.

drolysis of polyamides requires carefully chosen conditions often accompanied by long reaction times.

Alkali fusion reaction gas chromatography was successfully applied to anilides and ureas.[12] Typical analyses and fusion conditions are given in Table X. The analyses were based on measurement of aniline or N-methylaniline.

Polyamides with pendant amide groups on the polymer backbone and polymeric nitriles have been analyzed by alkali fusion.[12] Polyacrylamide and polyacrylonitrile liberate ammonia quantitatively, as shown by the data in Table XI. The alkali fusion reagent provides the water to convert the nitrile to the amide, and upon further reaction, to ammonia and a carboxylic acid salt. Alkali

TABLE X

Determination of Amide Compounds by Alkali Fusion Gas Chromatography

Compound	Fusion temp., °C	Time, hr	% converted	Standard deviation[a]
Acetanilide	320	0.5	100.5	1.5
Benzanilide	320	0.5	97.9	1.8
Carbanilide	340	0.5	98.2	1.9
N,N'-Dimethyl-carbanilide	360	0.6	99.3	1.7

[a]Five or more determinations.

fusion of the monobutylamide of poly(methyl vinyl ether-co-maleic acid) gave the expected n-butylamine content, based on an independent analysis,[12] as shown in Table XI. Nylons composed of diacid-diamine linkages, hydrolyze by fusion quantitatively to the diamine and the diacid salt.[12] Alkali fusion analyses of Nylon 66 and Nylon 610 are given in Table XI. The liberated 1,6-hexanediamine was used to determine the amount of amide.

TABLE XI

Alkali Fusion Reaction Gas Chromatographic Analysis of Miscellaneous Polymers

Compound	Fusion temp., °C	Time, hr	% converted	Amine liberated
Polyacrylamide	300	0.3	99	NH_3
Polyacrylonitrile	300	0.5	99	NH_3
Monobutylamide of poly(methyl vinyl ether-co-maleic acid)	300	0.5	103	$BuNH_2$
Nylon 66	360	0.5	98	$C_6H_{12}(NH_2)_2$
Nylon 610	360	0.5	100	$C_6H_{12}(NH_2)_2$

A chromatogram of Nylon 66 after alkali fusion is shown in Figure 8.

F. Imides and Polyimides

Alkali fusion has been used successfully for the analysis of unsubstituted and substituted imides; the fusion products are ammonia and primary amines, respectively.[13] Fusion for 30 min at 250°C resulted in the complete reaction of several imides, as shown by the results given in Table XII. The volatile reaction products were trapped during fusion in a loop immersed in liquid nitrogen, attached to the reaction unit. For unsubstituted imides the gas chromatographic analysis time is shortened significantly since ammonia elutes before the residual water released from the

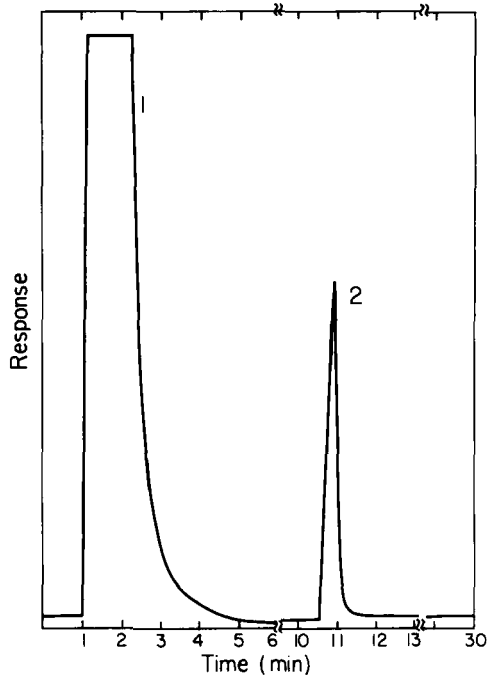


FIGURE 8
Gas chromatogram of Nylon 66 after alkali fusion. Separation on a 3-ft. Chromosorb 103 column.

Peak 1, water; 2, 1,6-hexanediamine.

TABLE XII

Analysis of Monomeric Imides
by Alkali Fusion Reaction Gas Chromatography[a]

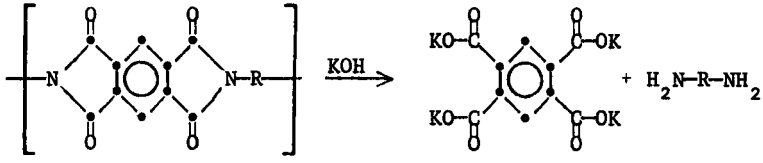
Compound	% converted[b]	Standard deviation	Amine liberated
Diacetimide	98.4	1.0	Ammonia
Succinimide	98.5	0.5	Ammonia
Saccharin	99.6	1.0	Ammonia
Sodium saccharin	99.3	1.0	Ammonia
Phthalimide	99.4	1.0	Ammonia
Pyromellitic diimide	98.1	0.9	Ammonia
N-Benzylsuccinimide	100.9	1.0	Benzylamine

[a] Fusion for 30 min at 250°C.

[b] Based on 5-7 determinations.

fusion reagent. An ammonia calibration curve can be prepared by injecting known volumes of ammonia through the rubber septum located on the fusion unit (B, Figure 1) and collected in the cold trap. Volatilization and gas chromatographic measurement of the ammonia standard is accomplished following the identical procedure used for fused samples.

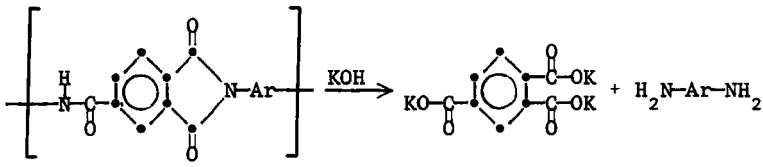
Polyimides are a class of thermally stable polymers used in the fabrication of parts, films, wire coatings, fabrics, and binders. The imide is the backbone structure. The alkali fusion products are a nonvolatile tetracarboxylic acid salt and a volatile diamine, as illustrated below.



Thermogravimetric studies have shown polyimides to be stable at 400°C in an inert atmosphere. Alkali fusion at 380°C for 5 min was used for the reaction of several imides listed in Table XIII. The principal product is the expected diamine, but a small amount of ammonia is also produced during fusion. The source of ammonia is currently under investigation.[22] The polyimide analyses are reported as weight percent nitrogen contributed by the diamine and ammonia. In this way, the total nitrogen calculated from the fusion reaction products can be compared to the elemental nitrogen values obtained either by the Kjeldahl or the Dumas combustion method. The nitrogen values from alkali fusion and elemental analysis are in close agreement. An advantage of the alkali fusion procedure is the identification and measurement of the diamine product and, for the case of terpolymers or tetrapolymers, of the diamine mixture. This is illustrated by Figure 9, which shows a chromatogram of the fusion products obtained from the imide terpolymer whose structure is shown in Table XIII.

G. Poly(amide-imides) and Aromatic Polyamides

Poly(amide-imide) polymers have both the amide and imide linkages. Like the polyimides, they have favorable thermal, mechanical, chemical, and electrical properties. They are used in laminating varnishes, high-temperature enamels, and adhesives. The alkali fusion products are the carboxylic acid salt and diamine. As was observed with the polyimides, a small amount of



ammonia is produced during fusion of these polymers. The poly (amide-imide) alkali fusion and elemental nitrogen analysis are given in Table XIV. The fusion conditions were 380°C for 5 min.

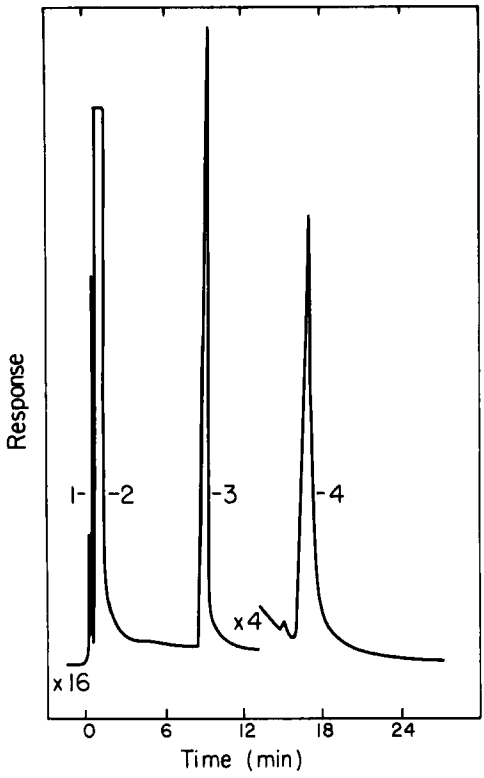


FIGURE 9
Gas chromatogram of polyimide terpolymer after alkali fusion. Separation on a 3-ft column packed with 10% FFAP on Anakrom ABS.

Peak 1, ammonia; 2, water; 3, 2,4-toluenediamine; 4, 4,4'-methylenediamine.

The results of both analyses for each compound are in close agreement.

Aromatic polyamides have important high-temperature properties. The alkali fusion analyses of two such polymers are also given in Table XIV.

H. Carbamates

Alkali fusion reaction gas chromatography has been described for the analysis of carbamates by Ladas and Ma.[32] Carbamates are

TABLE XIII

Alkali Fusion Gas Chromatographic Analysis of Polyimides

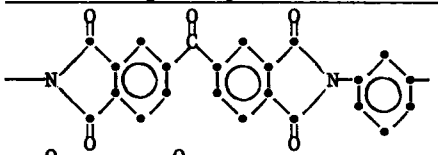
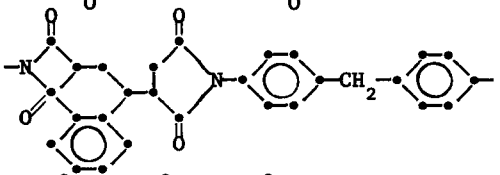
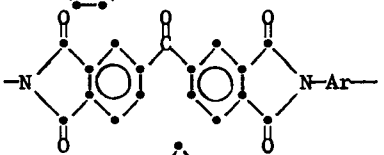
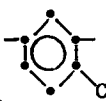
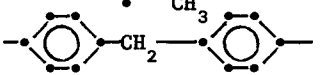
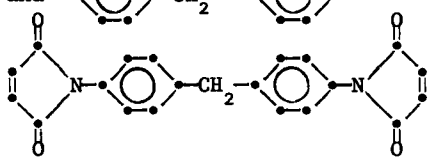
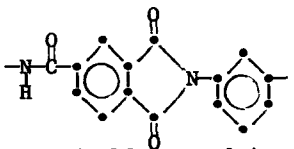
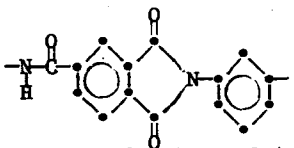
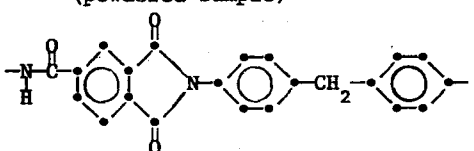
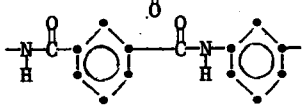
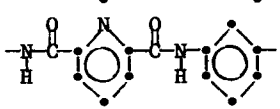
Polymer repeating unit	wt % Nitrogen in Polymer			
	Alkali Fusion			
	as Diamine	as Ammonia	Total	Elemental analysis
	6.51 ± .06	.99 ± .08	7.50 ± .12	7.28 ± .1
	5.96 ± .05	.16 ± .01	6.12 ± .06	5.95 ± .11
 where Ar=  and 	6.45 ± .03	.44 ± .07	6.89 ± .10	6.90 ± .04
	8.70 ± .13	.13 ± .02	8.83 ± .15	9.00 ± .06

TABLE XIV

Alkali Fusion Gas Chromatographic Analysis of Poly(amide-imides) and Aromatic Polyamides

Polymer repeating unit	wt % Nitrogen in Polymer			
	Alkali Fusion			
	as Diamine	as Ammonia	Total	Elemental analysis
 (molded sample)	9.91 ± .09	1.05 ± .08	10.96 ± .17	10.83 ± .06
 (powdered sample)	9.97 ± .08	0.60 ± .04	10.57 ± .12	10.71 ± .03
	7.75 ± .09	0.23 ± .04	7.98 ± .13	8.23 ± .03
	11.84 ± .07	0.75 ± .16	12.59 ± .23	12.63 ± .06
	11.23 ± .07	1.40 ± .04	12.63 ± .11	-----

used as herbicides, insecticides, and pharmaceuticals. The carbamate alkali fusion reaction products are an alcohol or a phenol and an acid salt.

$$R'HN-\overset{O}{\overset{\|}{C}}-OR \xrightarrow{KOH} R'HN-\overset{O}{\overset{\|}{C}}-OK + ROH$$

The fusion reaction takes places in a specially prepared reaction tube, packed with a 10 percent mixture of potassium hydroxide and glass beads. This tube is placed inside the injection port of the gas chromatograph. Alcoholic solutions of carbamates are injected directly into the reaction tube.

The complete saponification to the corresponding alcohols was reported by Ladas and Ma for methyl and ethyl carbamate and for propyl carbanilate. Carbamate samples from 0.01 to 0.1 moles gave standard deviations of 1-4 percent.

I. Siloxanes and Silicone Polymers

Sodium and potassium hydroxide have been used for the rapid alkali fusion of siloxane polymers to produce silicates for total silicone analysis employing either gravimetric or spectrophotometric methods.[17,18] The fusion reaction cleaves alkyl, aryl, and vinyl substituents to produce the corresponding hydrocarbon. Alkoxy groups are converted to alcohols. As a result, fusion methods are readily adapted to functional-group analysis of silicone materials. The alkyl content in polysiloxanes was quantitatively determined using alkali fusion and gasometric measurement of the hydrocarbon.[33] Hanson and Smith[14] have quantitatively determined trace alkoxy ($\equiv SiOR$) and vinyl ($\equiv SiCH=CH_2$) groups on silicone compounds using fusion with potassium hydroxide and gas chromatographic analysis of the alcohols and ethylene. This method is useful for silicone fluid, gum, and resin samples containing as low as 0.001 to 1 percent alkoxy or vinyl groups. Highly crosslinked polymeric siloxanes do not dissolve readily in solvents and are not easily decomposed by acid ashing. Thus, alkali fusion reactions provide the only practical dissolution method for these materials.

J. Azo and Nitro Compounds

Many azo and nitro compounds have low volatility or decompose upon heating making direct gas chromatography impossible. Reduction of these compounds to the respective amines would be a useful gas chromatographic procedure since the amine reaction products generally are volatile and thermally stable. Also, the amines would be characteristic of the starting azo or nitro compound, thus aiding sample identification.

For reductive fusion gas chromatography, the sample is fused with a solid reductant and the volatile reaction products are measured. This procedure makes unnecessary the use of the hydrogen carrier gas required when a hydrogenation catalyst is used for the reduction. Also, the sample does not have to be volatilized into a catalytic reactor as is normally required for other reduction gas chromatographic techniques.[6]

For the fusion reagent a number of organic compounds have been tested, but carbohydrazide has found the greatest application.

Carbohydrazide

This compound decomposes slowly at the fusion temperature (220°C) to hydrogen gas, hydrazine (H_2N-NH_2), and other low-molecular-weight gases. Carbohydrazide's reducing ability has been attributed to both H_2 and the hydrazine produced.[19] It is a better reductant for fusion than other compounds examined because (a) the samples can be coated, from solution, directly onto the reducing reagent providing maximum interaction; (b) the fusion reaction can be extended to longer times owing to the nonvolatility of the fusion reagent; and (c) there is no interference owing to saturation of aromatic rings.

For reductive fusions, platinum sample boats must be used. Experiments have shown that the platinum boat acts as an efficient reduction catalyst. Other platinum and palladium catalysts were

added to the fusion reaction, porcelain boats being used in place of the platinum boat. None gave conversions greater than the platinum boat alone.[19]

Some results using the reductive fusion method for azo compounds are given in Table XV.

The percent converted values are given for both of the primary amines produced from each azo compound, when possible. A typical reductive fusion chromatogram of p-phenylazoaniline showing the aniline and p-phenylenediamine reduction products is given in Figure 10.

The nonvolatile azo compounds gave essentially quantitative conversions to the corresponding volatile amines. However, several azo compounds gave 10 to 25 percent less than quantitative conversions. The low conversion values were attributed to partial volatilization of the azo compounds before reaction. Even for these compounds, however, the precision of the reaction was excellent. Therefore, by employing pure azo compounds as standards and constructing a working calibration curve for all the experi-

TABLE XV

Determination of Azo Compounds by Carbohydrazide Reduction Gas Chromatography[a]

Compound	Reduction product	% converted	Rel. std. deviation
p-Phenylazophenol	Aniline	90.8	1.8
	p-Hydroxyaniline	90.7	1.5
p-Phenylazophenetole	Aniline	75.6	1.9
	p-Ethoxyaniline	75.5	1.9
4,4'-Azodiphenetole	**p-Ethoxyaniline**	**86.6**	**1.5**
Sudan yellow	Aniline	97.7	2.2
p-Phenylazoaniline	**Aniline**	**83.0**	**0.8**
	p-Phenylenediamine	81.7	1.0
4,4'-Azodianiline	p-Phenylenediamine	97.0	2.1
Methyl Orange	N,N-Dimethyl-p-phenylenediamine	98.5	1.5

[a]Reductive fusion at 220°C for 10 min.

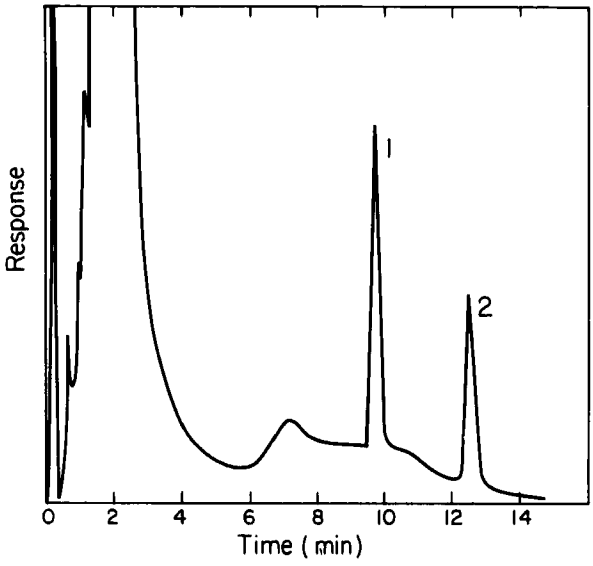


FIGURE 10
Gas chromatogram of p-phenylazoaniline after carbohydrazide reduction. Separation on a 2.5-ft column containing Chromosorb 103. Peak 1, aniline; 2, p-phenylenediamine.

mental conditions, the amine peak area can be related to the quantity of azo compound in the sample.

The reductive fusion method has been applied to nitro compounds and to azo compounds containing the nitro group. The results for the analysis of several of these compounds are shown in Table XVI. The nitro compounds react in 2-15 min with a 90-98 percent conversion. Even with both functional groups present, nearly quantitative conversion of both groups is obtained.

The carbohydrazide reduction of sulfonates to the parent hydrocarbon has been used for analysis of these completely nonvolatile compounds.[19,20] The results listed in Table XVII give the conversion of several sulfonated compounds, including some containing azo, amine, and other groups, to the corresponding reduced compounds. As with some azo and nitro compounds, the conversion is not quantitative but the precision of the reaction is excellent for these sulfonates.

TABLE XVI

Determination of Nitro and Nitro-Azo Compounds by Carbohydrazide Reduction Gas Chromatography[a]

Compound	Reaction Product	% converted	Rel. std. deviation
5-(p-Nitrophenyl)-azosalicylic acid sodium salt	p-Phenylenediamine	97.8	2.1
p-Nitroaniline	p-Phenylenediamine	91.7	1.5
Para Red	p-Phenylenediamine	97.7	1.8
5-(m-Nitrophenyl)-azosalicylic acid sodium salt	m-Phenylenediamine	97.7	1.4
p-Nitroazobenzene	p-Phenylenediamine	97.1	1.2
	Aniline	97.3	1.1

[a]Reductive fusion at 220°C for 2-15 min.

TABLE XVII

Determination of Sulfonated Compounds by Carbohydrazide Reduction Gas Chromatography[a]

Compound	Reduction product	% converted	Rel. std. deviation
Sulfanilic acid	Aniline	65.7	0.2
Methyl Orange	Aniline	65.7	1.5
	N,N-Dimethyl-phenylenediamine	98.5	1.6
Sulfanilanilide	Aniline	69.6	0.4
Sulfanilamide	Aniline	70.3	1.2
Benzenesulfonic acid sodium salt	Benzene	68.0	0.9
p-Toluenesulfonic acid sodium salt	Toluene	69.1	0.6

[a]Reductive fusion at 220°C for 2-4 min.

VI. SUMMARY

Fusion reactions have been combined with gas chromatography to obtain separation and measurement of several classes of organic compounds normally impossible to determine using conventional gas chromatography. The fusion reactions are necessary to transform into volatile derivatives those nonvolatile compounds that are slow to react or do not react at all under normal solution conditions. The work reported here shows that fusion reactions, though drastic, can be stoichiometric, quantitative, quite reproducible and, therefore, useful analytically.

The principal application has been alkali fusion to obtain complete hydrolysis of the component to products that are easily measured by gas chromatography. Examples discussed in this work include fusion of sulfonates to phenols, organic sulfates to alcohols, esters to alcohols, amides to ammonia or amines, imides to ammonia or amines, nitriles to ammonia, carbamates to alcohols, and siloxanes to the corresponding hydrocarbon. A particularly useful application has been the fusion gas chromatographic analysis of polymeric materials to establish their composition. Many polymers, in addition to those discussed here, have functional groups that can be hydrolyzed by alkali fusion to volatile compounds. This may permit polymer characterization with greater precision and speed that can be achieved with other techniques.

Other fusion reactions include reductive, oxidative, and acid fusions. Of these only reductive fusions have been explored in detail. Carbohydrazide reductions can be used to reduce azo and nitro compounds to amines, which are easily separated by gas chromatography. The nonvolatile sulfonates are converted to the corresponding hydrocarbon using the same procedure. The sulfonate reductions are generally reproducible but not quantitative.

Fusion reaction gas chromatography has several distinct advantages for chemical analysis. The method is very sensitive, permitting the analysis of milligram and microgram quantities.

Precision is high because sample manipulation is reduced to a minimum. The analysis time is often short compared to the hours or even days required to obtain the same information using other methods. When gas chromatography is used, the separation and measurement of isomers, homologs, polyfunctional compounds, and general mixtures becomes routine. Because of the nature of the fusion reaction, a standard set of conditions can be applied to a large number of compounds. This eliminates the necessity for many preliminary experiments to establish individual conditions for each compound.

Obviously some precautions must be taken and problems can occur with some applications. Most importantly, the sample and its reaction products must be stable at the fusion temperature. This can often be tested by thermal analysis techniques if doubt exists. Generally, if a thermal-stability problem exists, it can be overcome by (1) using a lower fusion temperature (down to about 200°C is possible) and longer fusion times, (2) using an inert atmosphere for the fusion reaction to eliminate oxidation and other possible competing reactions, and (3) using a flux agent to lower the melting point of the fusion reagent and to achieve a more homogeneous fusion mixture. A second type of problem can occur when the fusion reagent reacts with more than one functional group on the sample compound. This can make identification of the original sample difficult. For example, the fusion of sulfonates containing a halogen substituent would result with the hydroxyl substitution for both groups. Thus, additional information would be needed to characterize this type of sample.

Future developments in fusion reaction gas chromatography seem inevitable. These may include new fusion reagents, especially for reductive, oxidative, and acid fusions. The development of new fusion reagents could greatly broaden the application of fusion reactions to include many other organic compounds as well as meet for unexplored analytical needs. In addition, the application of fusion methods for the characterization of polymeric materials will continue to yield useful results for these normally slow-to-react compounds.

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