Separation of Aliphatic and Aromatic Acids, Aromatic Sulfonates, Quaternary Ammonium Compounds, and Chelating Agents on a Reversed-Phase Column Without Ion Pairing

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Abstract

Cleaning products contain a wide variety of components. These include inorganic materials, weak acids, anionic surfactants, cationic surfactants, amphoteric compounds, and nonionic materials. The separation of these generally requires the use of multichromatographic modes. A system is developed that would give the maximum information for a cleaning product in a single chromatographic run. With the use of a hydrophobic, high-carbon-loading, and a relatively hydrophobic surface reversed-phase packing, such compounds as aromatic sulfonates, quaternary ammonium compounds, weak acids, nitrilotriacetic acid, ethylenediaminetetraacetic acid, and nonionic materials may be separated in a single run. The mode of separation is considered to be a combination of reversed-phase, ion-suppression reversed-phase, and adsorption chromatography. The separation is made on a YMC-Packl ODS-AQl column (4.6 × 250 mm, 120 Å). The separation employs a gradient run starting with 0.01N H_2SO_4 for 10 min followed by a gradient for 15 min to 100% acetonitrile and continuing for an additional 5 min with 100% acetonitrile. The flow rate is 1 mL/min, and the separation is monitored at 210 nm.

Introduction

Cleaning agents are composed of complex mixtures containing anionic, cationic, and nonionic surfactants. Also included are complexing agents and inorganic materials. This study is not designed to give an overall approach for the analysis of these products, but to give the maximum amount of information that may be obtained in a single chromatographic run.

With the diverse classes of compounds present in these mixtures, it usually requires multichromatographic modes for separation. These would include ion-exchange, ion-pairing reversed-phase, regular reversed-phase, and adsorption chromatography. These different modes are presented in Snyder and Kirkland's book (1) on liquid chromatography (LC). A compilation of the complete analysis of surfactants is summarized in a book by Schmitt (2).

The separation of the long-chain alkyltrimethylammonium ion has been accomplished by reversed-phase ion-pair high-performance LC (HPLC) using ultraviolet-absorbing counter ions (3). Alkylbenzene sulfonate chain distribution has been determined by HPLC (4), and alkyl sulfonates have been measured by HPLC using indirect photometric detection (5). The HPLC determination has been made on the distribution of alkylphenoxy ethoxymers (6). The simultaneous determination of linear alkylbenzene sulfonates, alkylphenol polyethoxylates, and nonylphenol has been carried out by HPLC (7).

It has been found that the aforementioned materials can be separated in a single run. The mode of separation included regular reversed-phase and ion-suppression reversed-phase chromatography. It is also suspected that adsorption chromatography also occurred.

Experimental

Instrumentation

The HPLC system consisted of a Waters Corporation (Milford, PA) Model 600S controller, Waters Model 616 pumps, a Waters Model 486 UV–vis detector, and a ThermoQuest (San Jose, CA) SpectraSystem AS3000 autosampler.

Data handling was made with Polymer Laboratories (Amherst, MA) Calibre software V.2.0.

The column was a YMC-Pack ODS-AQ (4.6 × 250 mm) (Catalog Number AQ-2546WT, Waters Corporation).

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The injection volume was 20 µL, and separation was monitored at 210 nm. Elution was made with a gradient as follows: (*a*) 0.01N H2SO4 for reservoir A; (*b*) CH3CN for reservoir B; and (*c*) 100% A for 10 min, ramp to 100% B in 15 min, and then remain at 100% B for 5 min. A 5-min reequilibration was used.

Materials

The acetonitrile, acetic acid, and water were HPLC grade (Fisher Scientific, Fair Lawn, NJ). The dodecyl-, tetradecyl-, and hexadecyl-benzyldimethylammonium halides were obtained from Sigma (St. Louis, MO). Glycolic acid, citric acid, lactic acid, phthalic acids, ethylenediaminetetraacetic acid (EDTA), nitrilotriacetic acid (NTA), and uracil were obtained from Aldrich (Milwaukee, WI).

Preparation of standards

Compounds having an aromatic functionality were prepared at concentrations of 100 to 200 µg/mL, and those containing a carbonyl functionality were prepared at 1000 to 3000 µg/mL. All standards were prepared in deionized water. The dissolution of materials not soluble in water may be assisted with the use of acetonitrile. Materials such as NTA require the use of sodium hydroxide solution in order to obtain solubility; however, the amount should be kept to a minimum because peak splitting may result.

Preparation of samples

Because of the varying concentrations of components in cleaning products, it is recommended that the sample be injected "neat" and at a tenfold dilution. If the sample is at a pH greater than 12, it should be reduced to pH 10. This prevents peak splitting if 0.01N H_2SO_4 is not able to neutralize the sample at the moment of injection.

Results and Discussion

The HPLC chromatograms of a number of standard mixtures are given in Figures 1 through 5, and the retention times are recorded in Table I.

Because of the acid eluent, the ionization of the weak acids was suppressed and those components that were injected in salt form were immediately converted to the acid form. Their retention and separation were considered to be a combination of reversed-phase partition and adsorption chromatography. Even the very polar uracil, which is generally used to determine the void volume of reversed-phase columns, had a retention time of 8.71 min.

Benzene sulfonic and xylene sulfonic acids chromatographed very nicely; however, dodecylbenzene sulfonic acid did not. Possibly, the dodecylbenzene sulfonic acid was being irreversibly adsorbed.

The homologous series dodecyl-, tetradecyl-, and hexadecyl-benzyldimethylammonium chlorides were very likely separated by reversed-phase chromatography, with the alkyl moiety giving the difference in partition.

Examples of the separation of cleaning products are given in Figures 6 and 7. Although an extensive amount of information can be obtained by this separation, more definitive results are necessary for positive identification. This would require a combination of spiking with standards, the use of photodiode-array detection, or LC–mass spectrometry. For nonultraviolet-absorbing species, the use of evaporative light-scattering detection would be useful.

Because the components in cleaning products are generally made from technical-grade materials, they will give a family of peaks rather than one distinct peak.

In conclusion, a system has been developed that gives a separation of diverse compounds in a single chromatographic run.

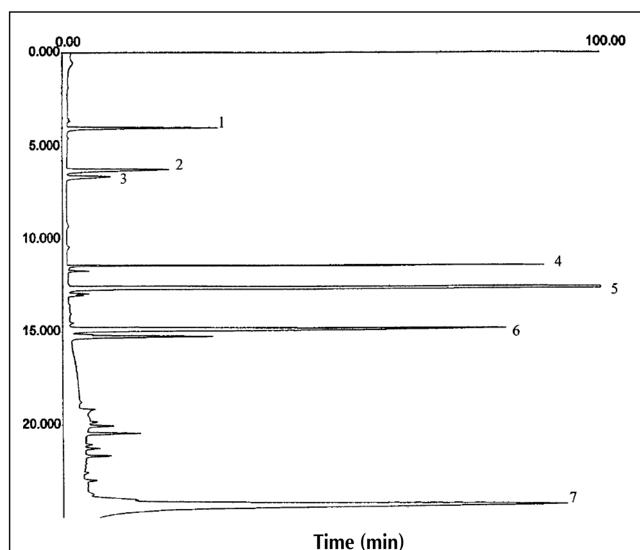

Figure 1. HPLC chromatogram of glycolic acid (1), lactic acid (2), acetic acid (3), citric acid (4), benzene sulfonic acid (5), xylene sulfonic acid (6), and 11-mol ethylene oxide of 4 nonylphenol (7).

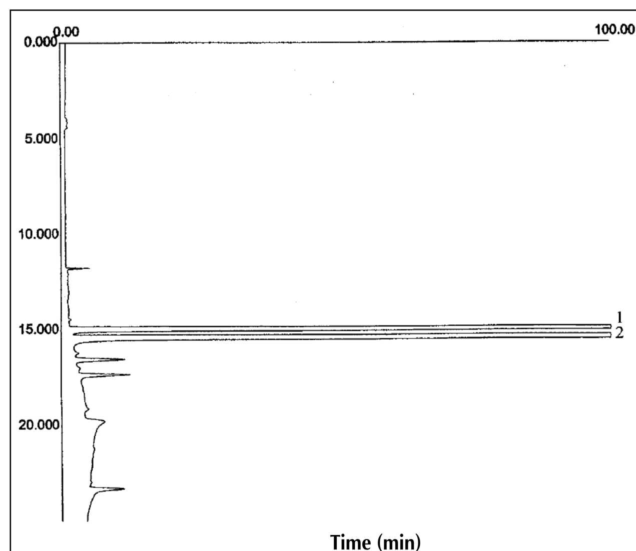

Figure 2. HPLC chromatogram of *o*-phthalic acid (1) and isophthalic acid (2).

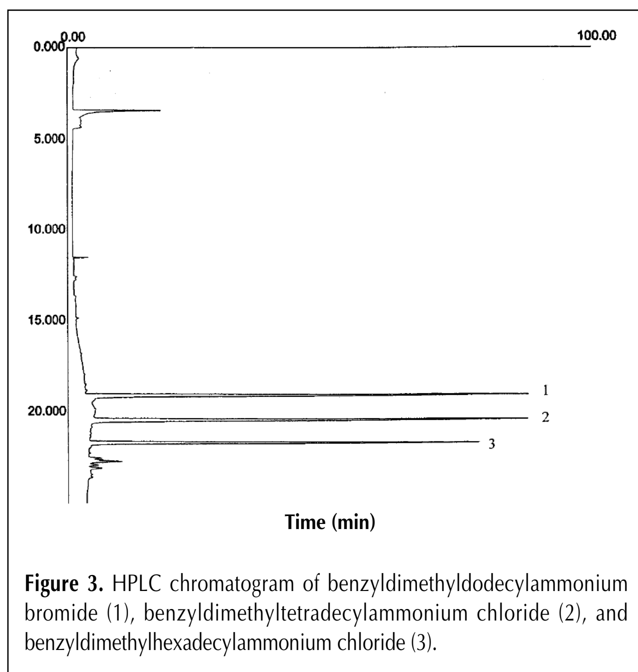

Figure 3. HPLC chromatogram of benzyldimethyldodecylammonium bromide (1), benzyldimethyltetradecylammonium chloride (2), and benzyldimethylhexadecylammonium chloride (3).

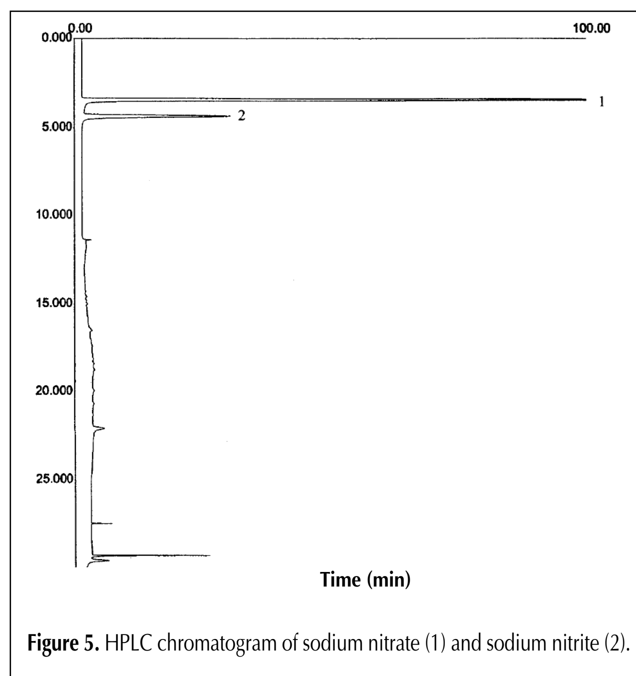

Figure 5. HPLC chromatogram of sodium nitrate (1) and sodium nitrite (2).

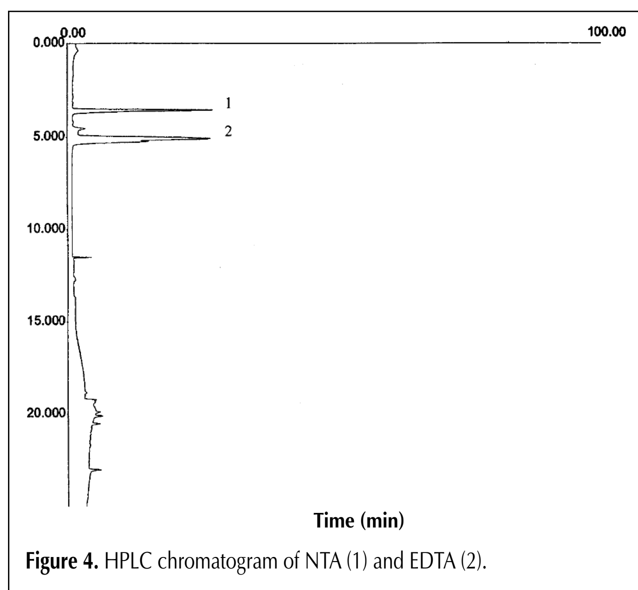

Figure 4. HPLC chromatogram of NTA (1) and EDTA (2).

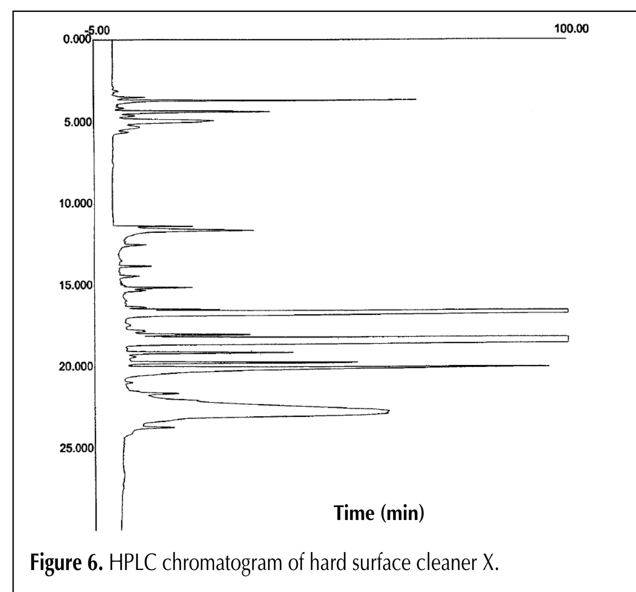

Figure 6. HPLC chromatogram of hard surface cleaner X.

Table I. HPLC Retention Times for Various Compounds

	Rt (min)		Rt (min)
Void volume	2.85	Uracil	8.71
Hydrobromic acid*	3.38	Citric acid	11.47
NTA	3.57	Benzenesulfonic acid†	11.20
Oxalic acid	3.59	Xylene sulfonic acid†	12.72
Nitric acid†	3.65	*o*-Phthalic acid	15.07
Hydriodic acid*	3.77	*p*-Phthalic acid	15.32
Glycolic acid	4.07	*m*-Phthalic acid	15.50
Formic acid	4.11	Benzyldimethyldodecyl NBr	19.09
Nitrous acid†	4.50	Benzyldimethylhexadecyl NCl	20.42
EDTA	5.45	Benzyldimethyltetradecyl NCl	21.69
Cyanuric acid	6.27	9-mol ethylene oxide adduct 4-nonylphenol	22.81
Lactic acid	6.65		
Acetic acid	7.08		

* Injected as potassium salts.
† Injected as sodium salts.

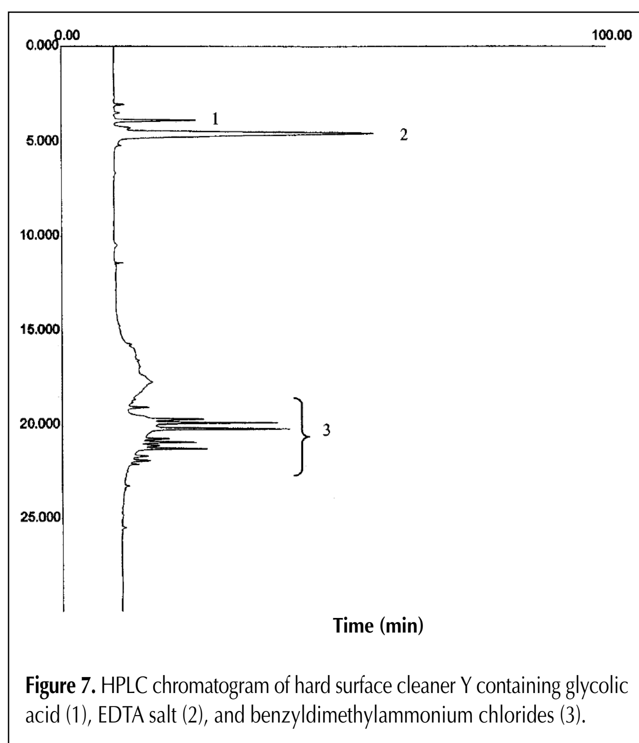

Figure 7. HPLC chromatogram of hard surface cleaner Y containing glycolic acid (1), EDTA salt (2), and benzyldimethylammonium chlorides (3).

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