

High Performance Liquid Chromatographic Determination of Sodium Sulfate in Anionic Surfactants

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ABSTRACT

Sodium sulfate is separated from anionic surfactants on a separation column packed with strong anion exchange resin, and is detected by a post column derivatization method based on a chemical reaction between sulfate and ferric ion. A calibration curve shows a linear relationship in the range of 10-300 mg/100 mL for sodium sulfate. The lower limit of determination is 2 mg/100 mL. Anionic surfactants such as sodium alkylbenzene sulfonate and sodium alkyl sulfate do not interfere with the determination. A personal computer was connected to the chromatographic system for data processing and control of an automatic sampler. This personal computer controlled liquid chromatographic system provides good recovery, reproducibility, agreement with conventional methods and full automatic determination.

INTRODUCTION

Anionic surfactants used as detergents or dispersing agents usually contain small amounts of sodium sulfate as a by-product of sulfation or sulfonation. Therefore, a simple and easy determination of sodium sulfate in anionic surfactants is of concern to industrial analysts. Although sodium sulfate has been determined by many methods, the determination of sodium sulfate in sulfate and sulfonate type anionic surfactants is not straightforward because of the interference of anionic surfactants. Typical methods applicable to the determination of sodium sulfate in anionic surfactants are: titrimetry using barium nitrate as a titrant (1), potentiometric titration with lead nitrate(2), conductometric titration with barium chloride(1), barium perchlorate(3), and gravimetry removing the surfactants by pretreatments (4). But these methods have some disadvantages, such as use of heavy metals, interference of anionic surfactants, and the fact that they are complicated procedures. To reduce these disadvantages, high performance liquid chromatographic (HPLC) methods have been reported (5,6) for the determination of sodium sulfate in detergents. However, there is no HPLC method applicable to the determination of sodium sulfate in sulfate and sulfonate type anionic surfactants.

This paper describes a personal computer controlled HPLC system for the determination of sodium sulfate in sulfate and sulfonate type anionic surfactants employing a post column derivatization method. The sulfate is separated from anionic surfactants and is detected using ultraviolet (UV) absorption at 340 nm (7,8). The proposed HPLC method reduced the interference of anionic surfactants such as sodium alkylbenzene sulfonate, sodium alkylsulfate, and others. The personal computerized data processing system provides a multipoint calibration curve, appropriate control of an automatic sampler, and fully automatic determination of sulfate, which is not available with commercial data processing instruments.

EXPERIMENTAL PROCEDURES

Reagents

All anionic surfactants used in this study were synthesized in our laboratories. Sodium nitrate, sodium sulfate, ferric nitrate, sodium chloride, sodium phosphate and nitric acid were analytical reagent grade.

HPLC Apparatus and Operating Conditions

The high performance liquid chromatograph used in this study consisted of a Milton Roy type high pressure pump (NSP-800-3, Nihonseimitsu, Japan), a peristaltic pump (NP-1, Nihonseimitsu, Japan) used for the delivery of the color-producing agent, and an ultraviolet (UV) spectrometer with a dual flow-through cell (NS-340, Nihonseimitsu, Japan). The separation column was a 150 mm × 4 mm id stainless steel column packed with strong anion exchange resin (LS-222, 6 μm, Toyo Soda, Japan). An automatic sampler (SJ-1700 ASI, ATTO, Japan) was modified for connection to the data processing system. TYGON[®] flexible plastic tubing (1/16 in. id, 1/8 in. od) was used for the peristaltic pump.

A 0.06 M aqueous solution of sodium nitrate was employed as the mobile phase at a flow rate of 1.0 mL/min. The color-producing agent used for the post column derivatization method was 0.01 M ferric nitrate (aqueous solution) in 0.26 M nitric acid. The flow rate was 0.5 mL/min. Fifty μL of sample solution was injected into the separation column with the aid of the automatic sampler.

Standard solutions were prepared by dissolving 10-300 mg of sodium sulfate in 100 mL of deionized water. All the anionic surfactants were prepared as 0.1-10.0% aqueous solution.

Data Processing System

The data processing system consisted entirely of Hewlett Packard instruments. The personal computer was an HP-85 with a 16k bytes memory module (82903A). A digital multimeter (5438A) and a relay actuator (59306A) were used for data acquisition and control of the automatic sampler, respectively. The system is illustrated in Figure 1. The HP-85 computer controls the digital multimeter, the relay actuator and the automatic sampler. It also performs chromatographic data processing and calculation of sulfate content. The digital multimeter acquires the analog signal from the UV detector. The signal is transferred to the personal computer through the built-in A/D converter. The personal computer, the digital multimeter and the relay

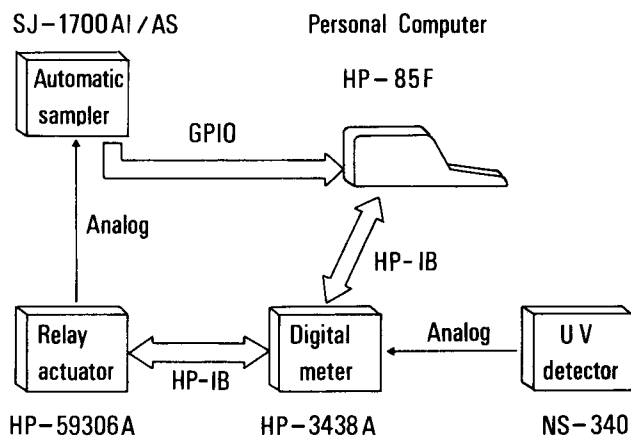


FIG. 1. Illustration of data processing system.

actuator are connected to each other using an HP-IB interface. The injection signal from the automatic sampler is transferred to the personal computer with the aid of a GPIO interface.

The values used for calculation of sulfate content in the anionic surfactants are entered manually by keyboard. The chromatographic determination of sulfate then is carried out automatically, controlled by the computer.

RESULTS AND DISCUSSION

Chromatography

As a result of preliminary examinations, a 0.06 M sodium nitrate aqueous solution was used as the mobile phase. At a higher concentration of sodium nitrate, the separation of sulfate from other components was incomplete. Long analysis time was required at lower concentrations. The sulfate and sulfonate type anionic surfactants did not interfere with the elution of sulfate being strongly held on the separation column.

Detection of sodium sulfate is performed by measuring UV absorption at 340 nm of the complex between sulfate and ferric ion (FeSO_4^+). The concentration of hydrogen ion in a mixture of the color-producing agent and a column eluant must be sufficiently high, because ferric ion precipitates above $\text{pH} = 2$. But in too high a concentration of hydrogen ion, sulfate is protonated to HSO_4^- , which does not complex with ferric ion and is therefore not detected. Considering these points, the concentration of nitric acid in the color-producing agent was set at 0.26 M. The peak area of sulfate increased proportionally to the concentration of ferric ion in the color-producing agent. At a ferric ion concentration of over 0.01 M, the peak area increase became small and baseline drift occurred. The optimum concentration of ferric ion in the color-producing agent was 0.01 M.

A calibration curve was calculated using the peak areas of standard sodium sulfate aqueous solutions. A linear calibration curve was observed in the range of 10-300 mg/100 mL. The lower limit of determination was 2 mg/100 mL.

Recovery of sodium sulfate in sodium alkylbenzene sulfonate was examined. The level of sodium sulfate in the anionic surfactant was determined before and after the addition of a known amount of sodium sulfate. The examinations were repeated five times and average of recoveries was 99.7%. This shows sodium sulfate in this anionic surfactant was recovered quantitatively.

Chloride is also contained in anionic surfactants as a byproduct of sulfation or sulfonation using chlorosulfonic acid. Additionally, phosphate is sometimes added to increase the stability of anionic surfactants. These inorganic ions also elute under these chromatographic conditions and form complexes which have UV adsorption. Figure 2 shows the chromatogram separating phosphate, chloride and sulfate. Sulfate was completely separated from these inorganic ions without interference.

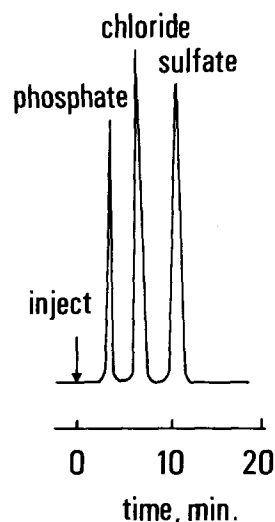


FIG. 2. Separation of inorganic ions.

Evaluation of Data Processing System

The proposed data processing system was evaluated using 0.1% of standard aqueous sodium sulfate solution. The signal from the UV detector was divided in two parts. One was connected to the proposed data processing system. Another was connected to a commercial data processing instrument (model 730, Waters Associates, Framingham, MA). The analysis was repeated 10 times. Calculated relative standard deviations (RSD) were 0.4% for the proposed data processing system and 0.5% for the commercial data processing instrument. There were no differences in relative standard deviations between the proposed data processing system and the commercial data processing instrument. Further, the additional functions of the proposed data processing system provide full automatic determination of sulfate in anionic surfactants.

Application

The application of this chromatographic method for the determination of sodium sulfate in actual sulfate and sulfonate type anionic surfactants was investigated. Table I shows the comparison of sodium sulfate contents in various kinds of anionic surfactants between the proposed HPLC method and the conventional method. The determination of sodium sulfate in anionic surfactants was done by potentiometric titration with lead nitrate. The levels of sodium sulfate reported for HPLC method were the average of five repeated measurements. The proposed HPLC method showed good reproducibility and agreement with the conventional method.

TABLE I

Comparison of Sodium Sulfate Levels Between the HPLC and Conventional Methods

Sample	HPLC method		Conventional method (%) ^a
	Content (%)	RSD (%)	
Sodium α -olefin sulfonate	4.80	0.8	4.86
Sodium alkylbenzene sulfonate	9.38	0.5	9.14
Sodium alkane sulfonate	2.14	1.1	2.18
Sodium polyoxyethylene alkyl sulfate	0.56	1.9	0.64
Sodium alkyl sulfate	0.10	2.0	0.11

^aPotentiometric titration with lead nitrate.

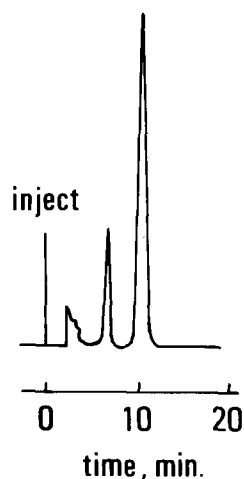


FIG. 3. Chromatogram of sodium alkylsulfate.

Figure 3 shows the chromatogram for sodium alkylsulfate. The sulfate eluted at ca. 10 min as a sharp peak. There was no interference from sodium alkylsulfate. A

peak eluting before sulfate seems to be chloride: the by-product of sulfation by chlorosulfonic acid.

To examine the lifetime of the separation column, ca. 10% aqueous solution of anionic surfactant was injected 50 times. Although the anionic surfactants which did not elute from the separation column were the major components, there was no decrease of column efficiency on repeated analysis. This personal computer controlled HPLC system can be used for routine analysis of sodium sulfate in various kinds of anionic surfactants.

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