Nonsolvent Quantitation of Anionic Surfactants and Inorganic Ingredients in Laundry Detergent Products

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ABSTRACT: This paper reports the development of a method for measuring alkylbenzene sulfonates and alkyl sulfates (AS) without requiring the use of chlorinated organic solvents, such as chloroform. Alkylbenzene sulfonates and AS are precipitated with calcium and then isolated by filtration. Through this filtration process, they are separated from inorganic sulfur compounds. After the precipitate is prepared, the level of sulfur is measured by inductively coupled plasma atomic emission spectrometry (ICP–AES) to determine the total anionic surfactant level. Separately, AS are hydrolyzed in an autoclave, and the level of alkylbenzene sulfonates is then measured in the same manner. By using the autoclave, a safe and rapid hydrolysis step has been achieved. In addition to alkylbenzene sulfonates and AS, phosphate, silicate, sulfate, and zeolite can be determined with this sample preparation. This sample preparation procedure was investigated by ICP–AES and was confirmed applicable for simultaneous measurements of alkylbenzene sulfonates, AS, phosphate, silicate, sulfate, and zeolite without using organic solvents. Relative standard deviation for the analysis is less than 1.7%, recovery is more than 99.0%, and the calibration curve gives a correlation coefficient of $R = 1.000$. The detection limit of this method for alkylbenzene sulfonates and AS is 0.6%, for zeolite, 0.04%, for phosphate, 0.4%, for silicate, 0.1%, and for sulfate, 0.2%, by weight in product. This method is applicable to various laundry detergent products that contain the materials mentioned above and is 10 times faster than the six wet chemical methods normally used to analyze these compounds.

JAOCS 74, 787–792 (1997).

KEY WORDS: Alkylbenzene sulfonate, alkyl sulfate, autoclave, inductively coupled plasma spectrometry, laundry detergent, phosphate, silicate, sulfate, zeolite.

Most methods for quantitating anionic surfactants require a quantitative reaction between anionic and cationic surfactants. Since a simple titration methodology was reported by Hartley and Runnicles (1,2) in 1938, many improved methods have been published. In 1945, Jones (3) found that complexes of anionic surfactants and methylene blue freely dissolved in chloroform, although methylene blue was water-soluble and was not extracted from an aqueous layer into chloroform. In 1947, Epton (4,5) used this phenomenon to develop a two-phase titration for anionic surfactant quantitation, and it has now become universally accepted methodology for anionic surfactant determinations. Many variations on the original Epton method have been tested; different indicators, titrants of standardization, and so on have been investigated (6–10). In most variations, methylene blue has been used as an indicator, and chloroform is used as an extraction solvent. In the method, anionic surfactants are titrated with a cationic surfactant. As more cationic surfactant is added, the methylene blue is liberated from the anionic surfactant methylene blue complex. The liberated methylene blue transfers from the chloroform layer to the aqueous layer. At the titration endpoint, the chloroform and the aqueous layers become even in color. The main advantage of applying this method to detergent products is that the widely varied matrices in detergent products do not interfere with the titration (11). Because of that advantage and simplicity of the method, it is still widely used for anionic surfactants quantitation.

Chloroform is potentially hazardous, and its use in the working environment is now restricted by law (12). It is reported that chloroform may cause liver, heart, and kidney disease by inhalation (13). This means that the analytical methods need to be revised to avoid using harmful solvents, such as chloroform. Some approaches have been published to determine surfactants by means of a precipitation technique (14–18). In these communications, organic ion pairs are used, and the complex of surfactants and counter ion is extracted with chloroform or benzene. In the method described in this paper, anionic surfactants are precipitated from an aqueous solution by combining with calcium. The precipitate is separated by filtration from analytical interferences, and sulfur in the surfactants is determined by inductively coupled plasma atomic emission spectrometry (ICP–AES) without using any organic solvents.

For inorganic ingredients in detergent products, several approaches have been reported to replace current wet chemical methods with ICP–AES methods for improved productivity (19,20). In the wet chemical methods and the improved ICP–AES methods, the assumption of Zeolite A ($Na_{12}Al_{12}Si_{12}O_{48}{\cdot}27H_2O$) being blended in detergent products is used for the conversion calculation. Silicate is calcu-

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lated from the difference between total silicon and the silicon calculated to be contained in the zeolite, based on the aluminum measurement. If another type of zeolite is used in a detergent product, the conversion formula must be changed to reflect the difference in molecular formula. With the procedure described in this paper, silicate is separated from zeolite in the sample preparation, and the molecular formula difference does not result in a larger variation in the silicate measurement. With the procedure described in this paper, phosphate, silicate, sulfate, and zeolite in detergent products, in addition to anionic surfactants, can be determined by using one sequential procedure.

EXPERIMENTAL PROCEDURES

Reagents and materials. The following reagents were purchased from Wake Pure Chemical (Osaka, Japan): aluminum, silicon, and phosphorus traceable standard solutions (1000 mg/L), zeolite (A-4) powder, sodium tripolyphosphate (anhydrous), and sodium silicate. Sodium sulfate (anhydrous), nitric acid, and sulfate traceable standard solution (1000 mg/L, equivalent to 333.3 mg/L as sulfur) were purchased from Kanto Chemical (Tokyo, Japan). Sodium carbonate and calcium chloride (dihydrate) were purchased from Nacalai Tesque (Kyoto, Japan). Sodium salt of linear alkylbenzene sulfonate (LAS) and alkyl sulfate (AS) were prepared in-house. Deionized water was prepared with a Milli-Q SP reagent water system of Nippon Millipore Ltd. (Tokyo, Japan).

Apparatus. Sulfur, aluminum, silicon, and phosphorus measurements were accomplished with an Inductively Coupled Plasma Atomic Emission Spectrometer (Model SPS-4000; Seiko Instruments, Tokyo, Japan) and a computer (PC-9801FA; NEC; Tokyo, Japan) for data collection. The carbon chainlength distribution of LAS and AS was measured with an API-III from PE-Sciex (Toronto, Canada), coupled to a Macintosh IIfx computer (Palo Alto, CA) for system control and a Macintosh Quadra 800 computer for data handling. Alkyl sulfate hydrolysis was accomplished with an autoclave (Model SS-325; Tomy Seiko Co., Ltd., Tokyo, Japan) and a 100-mL pressure-stable glass vessel (S1516BT-RED 100; Iwaki Glass Corp., Chiba, Japan). Stainless-steel beakers (100-mL and 500-mL) were purchased from Iuchi-Seieido (Osaka, Japan). Filter papers from Advantec (Tokyo, Japan) with 0.1-µm pore size (A010A047A), 0.2-µm pore size (A020B047A), and 0.45-µm pore size (A045A047A) were used. Analytical conditions for ICP–AES were as follows: wavelength used for measurements, S (182.036 µm), Al (396.152 µm), Si (212.412 µm), and P (213.618 µm); measurement height, 10 mm; carrier gas (1.0 L/min), plasma gas (16 L/min), support gas (0.5 L/min); slit, 20 µm; integral time (2 s × three times).

Preparing linearity test solutions. Ten milliliters each of commercial traceable standard solutions of aluminum, silicon, and phosphorus, and 30 mL sulfate commercial traceable standard solution were pipetted into a 100-mL volumetric flask, along with three drops of nitric acid. The flask was made to volume with deionized water and labeled as standard solution A. This solution contained 100.0 mg/L of Al, Si, P, and S.

Standard solution B was prepared by accurately diluting standard solution A 10-fold with deionized water. Three drops of nitric acid were also added. This solution contained 10.00 mg/L of Al, Si, P, and S.

Aliquots of solution A (5, 10, and 50 mL) and of standard solution B (1.0, 5.0, and 10 mL) were pipetted into six 100-mL volumetric flasks along with 8 mL of nitric acid. The flasks were made to volume with deionized water. These solutions contained 0.10, 0.50, 1.00, 5.00, 10.0, and 50.0 mg/L of Al, Si, P, and S.

Preparing calcium solution. Calcium solution was prepared by mixing 10.0 g calcium chloride (dihydrate) with 100 mL deionized water.

Preparing test solutions for investigating surfactants, phosphate, and zeolite recovery vs. filter pore size. A test surfactant mixture was prepared by mixing 25 g LAS, 25 g AS, 10 g tripolyphosphate, 10 g zeolite, and 10 g sodium carbonate. Twenty grams of this test detergent mixture was weighed and transferred to a 500-mL stainless-steel beaker, along with about 250 mL deionized water (50°C), then mixed well. The solution was cooled to room temperature and then quantitatively transferred to a 1000-mL volumetric flask. The flask was made to volume with deionized water and labeled as solution A. Solution A (10 mL) was pipetted into a 50-mL beaker, and 10 mL of calcium solution was added. The solution was mixed with a magnetic stirrer for 5 min and filtered through a 0.1-µm pore size filter paper by suction. The filter was washed five times with 10-mL aliquots of deionized water. In the same manner, the solution was filtered through 0.2- and 0.45-µm pore size filter papers. The filtrates were transferred to 100-mL pressure-stable glass vessels, and 8 mL nitric acid was added to them. The vessels were sealed and heated at 121°C for 60 min in an autoclave. The solutions were cooled and made to 100 mL with deionized water. These solutions were used for investigating surfactants, phosphate, and zeolite recovery vs. filter pore size.

Preparing test solutions for investigating silicate and sulfate recovery vs. filter pore size. A silicate and sulfate mixture was prepared by mixing 25 g sodium silicate, 25 g sodium sulfate, and 10 g sodium carbonate. Two grams of this mixture was weighed and transferred to a 100-mL stainless steel beaker, along with about 50 mL deionized water (50°C), then mixed well. The solution was cooled to room temperature, then quantitatively transferred to a 100-mL volumetric flask. The flask was made to volume with deionized water and labeled as solution B. This solution (10 mL) was pipetted onto a filter, while being vigorously stirred, then filtered through a 0.1-µm filter paper by suction. The filter was washed five times with 10-mL aliquots of deionized water. In the same manner, the solution was filtered through 0.2- and 0.45-µm filter papers. The filtrates were transferred to 100-mL pressure-stable glass vessels, and 8 mL nitric acid was added to them. The vessels were sealed and heated at 121°C for 60 min in an autoclave. The solutions were cooled and made to 1000 mL with deionized water. These solutions were used for investigating silicate and sulfate recovery vs. filter pore size.

Preparing test solutions for investigating AS hydrolysis. Sodium alkyl sulfate (1.20 g) was weighed in a 200-mL beaker, and about 50 mL deionized water (50°C) was added. The solution was mixed well, cooled, and transferred into a 250-mL volumetric flask. The flask was made to volume with deionized water and labeled as AS solution. In the same manner, sodium alkylbenzene sulfonate (1.40 g) was prepared and labeled as LAS solution. AS solution (25 mL) was pipetted into a series of 100-mL pressure-stable glass vessels, and 25 mL of sulfuric acid (0.1 N, 0.5 N, 1.0 N, and 5.0 N) was added to them. Five vessels were prepared for each sulfuric acid normality; 20 vessels were prepared in total. In the same manner, LAS solutions were prepared. The vessels were sealed and heated at 121°C in an autoclave for 0, 10, 30, 60, and 180 min. After cooling, the solutions were quantitatively transferred to 100-mL volumetric flasks and made to volume with deionized water. These solutions were analyzed by Japan Industrial Standard (JIS) K3362 for evaluating AS hydrolysis (21).

Sample preparation for commercial product analysis. Commercial product sample (3 g) was accurately weighed and transferred to a 100-mL stainless-steel beaker, along with about 50 mL deionized water (50°C), and the solution was mixed to dissolve the solid material. The solution was transferred to a 100-mL volumetric flask and made to volume with deionized water. Calcium solution (10 mL) was added to 10 mL of this solution and mixed. The solution was then filtered through a 0.1-µm pore size filter paper by suction. The filter paper was washed five times with 10-mL aliquots of deionized water.

The washed filter paper was placed in a 100-mL pressure-stable glass vessel, along with 8 mL nitric acid and 22 mL deionized water. The vessel was sealed and heated at 121°C for 60 min in an autoclave. The vessel was cooled, and the content was quantitatively transferred to a 100-mL volumetric flask. The flask was made to volume with deionized water. This solution was used for total anionic surfactant, phosphate, and zeolite measurements.

The filtrate was transferred to a 100-mL pressure-stable glass vessel, along with 8 mL nitric acid. The vessel was sealed and heated at 121°C for 60 min in an autoclave. The vessel was cooled, and the content was quantitatively transferred to a 100-mL volumetric flask. The flask was made to volume with deionized water. This solution was used for silicate and sulfate measurements.

Sample preparation for alkylbenzene sulfonate analysis. Commercial product solution (25 mL) was pipetted into a 100-mL pressure-stable glass vessel, along with 25 mL sulfuric acid (1 N). The vessel was sealed and heated at 121°C for 60 min in an autoclave. The vessel was then cooled, and the solution was neutralized with sodium hydroxide solution (2 N) to the phenolphthalein endpoint. The solution was quantitatively transferred to a 100-mL volumetric flask and made to volume with deionized water.

Calcium solution (10 mL) was added to 10 mL of the autoclaved solution and mixed well. The solution was then filtered through a 0.1-µm pore size filter paper by suction. The filter paper was washed five times with 10-mL aliquots of deionized water. The washed filter paper was then placed in a 100-mL pressure-stable glass vessel, along with 8 mL nitric acid and 22 mL deionized water. The vessel was sealed and heated at 121°C for 60 min in an autoclave. The vessel was cooled, and the content was quantitatively transferred to a 100-mL volumetric flask. The flask was made to volume with deionized water. This solution was used for alkylbenzene sulfonate measurements.

RESULTS AND DISCUSSION

Anionic surfactants, phosphate, and zeolite recovery vs. filter pore size. Alkylbenzene sulfonates and AS easily complex with alkaline-earth metals and precipitate (9,10). Based on the assumption that the calcium–surfactant complex, calcium phosphate, and zeolite could be trapped with a certain pore size filter paper, the filtration process of the materials was investigated with three different pore-size filters. Sulfur (derived from sulfate and sulfonate surfactants), phosphorus, and aluminum levels of the filtrates were measured by ICP–AES to evaluate the penetration of the materials through the filters. The results are shown in Table 1. No surfactant complex, phosphate, or zeolite penetrated through the 0.1- and 0.2-µm pore size filters.

Silicate and sulfate recovery vs. filter pore size. The recoveries of silicate and sulfate were investigated. Silicate and sulfate are water soluble and do not precipitate upon addition of calcium. The levels of silicon and sulfur in the filtrate were

TABLE 1
Surfactants, Aluminum, and Phosphorus Analyses of Filtrates by ICP–AES[a]

	Initial solution	Filtrate with 0.1-µm pore filter	Filtrate with 0.2-µm pore filter	Filtrate with 0.45-µm pore filter
Sulfur (cps)′	4.4×10^4	4.0×10^1	6.8×10^1	9.9×10^1
Aluminum (cps)	5.2×10^5	5.8×10^1	5.7×10^1	9.6×10^2
Phosphorus	7.2×10^4	4.2×10^1	5.1×10^1	8.9×10^1

[a] Abbreviations: ICP–AES, inductively coupled plasma atomic emission spectrometry; cps, counts per second (ICP–AES signal intensity).

TABLE 2
Silicate and Sulfate Analyses of Filtrates by ICP–AES[a]

	Initial solution	Filtrate with 0.1-µm pore filter	Filtrate with 0.2-µm pore filter	Filtrate with 0.45-µm pore filter
Silicate (cps)	1.1×10^6	1.1×10^6	1.1×10^6	1.1×10^6
Sulfate (cps)	1.9×10^4	1.9×10^4	1.9×10^4	1.9×10^4

[a] For abbreviations, see Table 1.

TABLE 3
Chainlength Distributions of C_{10}–C_{15} LAS and C_{12}–C_{18} AS[a]

	C_{10}	C_{11}	C_{12}	C_{13}	C_{14}	C_{15}	C_{16}	C_{17}	C_{18}
LAS (%)	12.7	36.0	30.1	19.1	1.5	0.6	—	—	—
AS (%)	—	—	43.6	—	28.2	—	14.1	—	14.1

[a] As measured by ion spray mass spectrometry. Abbreviations: LAS, linear alkylbenzene sulfonate; AS, alkyl sulfate.

measured by ICP–AES. Table 2 shows that no silicate and sulfate were lost in the process of the sample preparation described in the Experimental Procedures section.

In general, sulfate is blended or present as an impurity in laundry detergents. As mentioned, it has been confirmed that sulfate and sulfonate surfactants can be separated from inorganic sulfate through the filtration sample preparation step. Therefore, surfactants and sulfate can be separately determined by measuring sulfur of precipitate and filtrate, respectively, by ICP–AES.

LAS and AS recovery vs. carbon chainlength. The carbon chainlength distribution of LAS and AS used for this investigation was measured by an ion-spray mass-spectrometry method reported by Ogura *et al.* (22). The results are shown in Table 3. From these results and the results of the investigation of anionic surfactants recovery vs. filter pore size, it was concluded that C_{10}–C_{15} LAS and C_{12}–C_{18} AS can be completely recovered with the sample preparation described in this paper.

AS hydrolysis. AS are hydrolyzed into alcohols and sulfate under acidic conditions with a mineral acid, whereas alkylbenzene sulfonates are not. In International Standard (ISO) 2870 (23) or Japan Industrial Standard (JIS) K3362 (21), detergents are heated in sulfuric acid on a hot plate or a sand bath for 3 h to hydrolyze AS, and then the alkylbenzene sulfonates, which are not hydrolyzed under these conditions, are titrated by using a two-phase titration method (21,23). Alkylbenzene sulfonates and AS are separately quantitated, based on the results of total anionic surfactant and of alkylbenzene sulfonate measurement.

Alkyl sulfate hydrolysis was investigated based on differences of acid concentration and hydrolysis time in an autoclave. The results are shown in Figure 1. Higher hydrolysis temperature accelerated the hydrolysis, and lower acidic conditions can be applied to make the method comparable to the ISO and JIS methods. With the procedure described in this paper, more samples can be handled safely and rapidly than with the ISO and JIS methods.

Physical interferences. Solution viscosity, based on the type and concentration of acid, affects the particle size of the aerosol in an ICP nebulizer. This particle size is directly related to ICP signal intensity. Kawauchi and Ishida (20) investigated this phenomenon for aluminum, phosphorus and silicon and reported that ICP–AES intensity reached a plateau at 6% or higher hydrochloric and nitric acid concentrations. This physical interference for sulfur was investigated. The result is shown in Figure 2. Sulfur had the same tendency as aluminum, phosphorus, and silicon for hydrochloric and nitric acids. Nitric acid was used for this investigation.

Linearity and precision. The calibration data obtained from the linearity test solution for aluminum, silicon, phosphorus, and sulfur gave straight lines; aluminum, $Y = 14{,}000\ X + 14$ ($R = 1.000$); silicon, $Y = 2500\ X - 460$ ($R = 1.000$); phosphorus, $Y = 1400\ X - 385$ ($R = 1.000$); and sulfur, $Y = 470\ X - 13$ ($R = 1.000$). The relative standard deviation of the measurements at each level is less than 1.7%. Based on the pre-

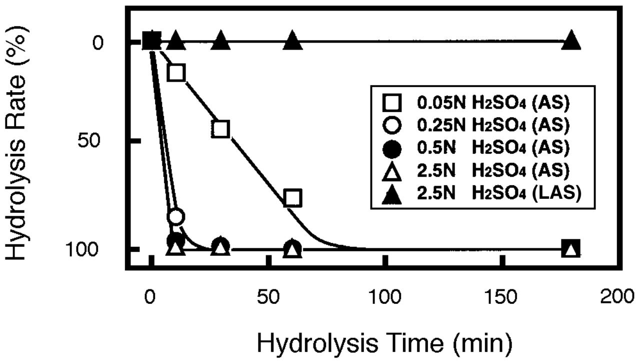

FIG. 1. Plot of linear alkylbenzene sulfonate (LAS) and alkyl sulfate (AS) hydrolysis rate vs. hydrolysis time in various acid concentrations.

TABLE 4
Five Commercially Available Products, Analyzed by Wet Chemical Methods and the Method Described in This Paper[a]

Sample	Method used	LAS (%)	AS (%)	Zeolite (%)	Silicate (%)	Phosphate (%)	Sulfate (%)
A	Wet chemical[b]	7.0			2.3	20.5	26.2
	ICP	6.9			2.1	20.0	25.5
B	Wet chemical	6.1	2.4		4.2	20.1	17.3
	ICP	6.0	2.5		4.2	20.0	17.1
C	Wet chemical	4.0	2.9	20.3	8.3		5.4
	ICP	3.9	3.1	20.1	8.2		5.3
D	Wet chemical	5.4	2.3	17.7	6.2		6.2
	ICP	5.6	2.3	17.9	6.3		6.0
E	Wet chemical	7.2	1.2	7.8	8.0	5.7	1.2
	ICP	6.9	1.3	8.0	7.9	5.9	1.1

[a] LAS (%) and AS (%) are calculated as SO3 (MW = 80.06). Abbreviation: ICP, inductively coupled plasma; for others, see Table 3.

[b] Wet chemical methods used: titration methodology for LAS and AS (JIS K3362 5.3), titration methodology for zeolite (JIS K 3362 5.15), gravimetry for silicate (JIS K3362 5.11), colorimetry for phosphate (JIS K3362 5.10), gravimetry for sulfate (JIS K3362 5.12); methods as in Reference 21.

cision of those measurements, the limits of detection (LOD) were calculated as 0.1% for aluminum, 0.1% for silicon, 0.2% for phosphorus, and 0.5% for sulfate in the product (w/w).

The LOD was calculated from the following equation, where y_i is the number obtained empirically, and $\hat{y}_i$ is the number derived from the following calibration equation (24):

$$\mathrm{LOD} = 3 \times \left(\frac{\Sigma(y_i - \hat{y}_i)^2}{n-2} \right)^{1/2} \qquad [1]$$

Commercial product analysis. Five commercial products were analyzed by three wet chemical methods and by the method described in this paper. The results are shown in Table 4. Results obtained from the method in this paper are in good agreement with those from the wet chemical methods. Total required time for the analysis of the five products was 6 h, including sample preparation, instrumental measurement, and preparation of the calibration curve. This was 10 times faster than the time required to prepare and measure the same samples by the six wet chemical methods.

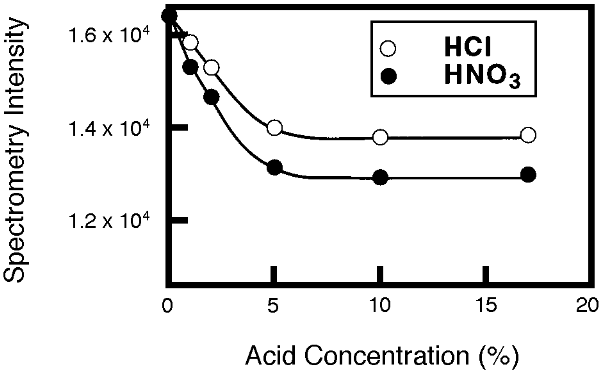

FIG. 2. Plot of acid concentration vs. inductively coupled plasma atomic emission spectrometry intensity of sulfur.

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[Received January 2, 1997; accepted March 26, 1997]