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The Determination of Anionic Surfactants in Water by an Azure A Method

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KEY WORDS: Pollutant, Detergent, Anionic Surfactant, LAS, ABS, Analytical Techniques, Water Analysis, Spectrophotometric Method, Colorimetric Method, Azure A Method.

Various methods for the analysis of anionic surfactants (such as LAS and ABS) in aqueous solution were reviewed, evaluated, and/or assessed. Emphasis was placed on the development of field test kits based on a modified colorimetric method involving the use of Azure A.

The simplified and improved Azure A Method requires only 6 ml of aqueous reagent and 25 ml of chloroform for analyzing one sample. The principles, analytical procedures and limitations of the method are described in detail.

A field test kit based on the use of a portable spectrophotometer (or photometer), is proposed for use by the personnel with limited training in chemistry.

INTRODUCTION AND LITERATURE REVIEW

There are many diverse types of pollutants which produce problems today. One of these is the surfactant-type pollutants from laundries, showers and kitchens. Surfactants as a whole are strong poisons for aquatic organisms; they seem to modify the environment in a way which is unfavorable for aquatic organisms useful to man (Ref. 1). Several new processes are being

developed for more efficient removal of such surfactant-type pollutants from wastewater (Refs. 2 and 3). Monitoring and analysis of the initial and residual surfactant concentrations in the waste streams is an important task of environmental engineers and chemists. The objective of this paper is to review, evaluate, and assess various methods for analyzing the anionic surfactants, such as linear alkylate sulfonate (LAS), in water or wastewater. LAS is an alkylbenzene sulfonate and since 1965 it has been the only alkylbenzene sulfonate used by the U.S. detergent industry. Before 1965 the alkylbenzene sulfonate in major use was derived from tetrapropylene (preferred nomenclature TBS) and before that, from kerosene (preferred nomenclature KBS). In addition to LAS, the U.S. detergent industry uses significant amounts of other anionic surfactants in some of its products: alkyl sulfates, alcohol ethoxylate sulfates, α -olefin sulfonates, for example.

Generally there are four major types of analytical methods for determining anionic surfactants: infrared method; gas chromatographic and paper chromatographic methods; two-phases titration method; and colorimetric methods.

The infrared method (Refs. 4 and 5) for surfactant analysis was developed by an analytical subcommittee of the Soap and Detergent Association as a specific, quantitative procedure that provides an unequivocal identification and measure of alkylbenzene sulfonate in water. This method involves the collection and isolation of a few milligrams of alkyl benzene sulfonate or linear alkylate sulfonate and its quantitative determination based on infrared absorption of an amine complex of the anionic surfactant. This method is complicated and time-consuming. It requires a large sample size (e.g., at least 10-liter sample would be required if 1 mg/l of LAS is present in the water sample) and infrared equipment. Besides, it is suggested by American Water Works Association (Ref. 4) that the infrared method be applicable to raw water samples only, not to sewage or industrial wastes.

Gas chromatographic analysis of anionic surfactants has been researched by Swisher (Ref. 6) and Knight (Ref. 7). Since the method requires sophisticated instrumentation, it cannot be considered as a field analytical method, and thus will not be discussed further. Examination of surfactants by paper chromatography has been conducted by Drewry (Ref. 8). Based on Drewry's technique, development of a field test kit for surfactant analysis is possible. However, use of the paper chromatographic technique or the test kit would require a well-trained chemical technician.

Analysis of LAS and other ionic surfactants by a two-phase titration method has been suggested by Calspan Corporation (Refs. 9 and 10). The method is termed "two-phase titration method" because water-insoluble chloroform is employed as an extractant for reagent separation from the water sample. This water-chloroform two-phase mixture is then titrated with a standard

sodium tetraphenylboron reagent with intermittent shaking to insure equilibrium between the chloroform and the aqueous phases. This titration method is superior to the standard Methylene Blue Method (Ref. 5) in that it is applicable to analyzing either *cationic* or *anionic* surfactants in both *fresh* and *saline* waters. However, the field military wastewater generated from showers, laundries and kitchens is known to be generally anionic in nature and to have low salinity. An even simpler field test kit based on a colorimetric method was suggested for evaluation or development under this research program.

The most commonly used colorimetric procedures for branched-chain alkylbenzene sulfonate (ABS) or LAS are the methylene blue technique (Refs. 4, 5, 11, 12, 13), methyl green technique (Refs. 14, 15), crystal violet method (Ref. 16), and azure A method (Refs. 17 and 18). All these methods depend on the formation of colored salt when the added dye reacts with ABS or LAS. The dye-surfactant complex is soluble in a solvent extractant but not in water, whereas the dye and the surfactant are soluble in water but not in the solvent extractant (such as chloroform). The color intensity of the dye-surfactant complex in the solvent is proportional to the surfactant concentration. This intensity can be measured in a spectrophotometer (or a filter photometer) and compared with standard solutions for apparent surfactant content in terms of mg/l ABS or LAS.

The commercial field test kits manufactured by Lovibond of American, Inc. (Albertson, L. I., N.Y., U.S.A.) and Delta Scientific Corp. (Lindenhurst, N.Y., U.S.A.) are operated on the basis of methylene blue method (Refs. 5, 11 and 12). Lovibond test kit requires a lengthy time (about 30 min.) to perform a test. The Delta method is faster (about 20 min.) but is subject to interference from the chloroform-extractable pollutants present in the wastewater. Hellige Inc. (Long Island City, N.Y., U.S.A.) also manufactures a field test kit using methylene blue method. The Hellige method is, however, similar to the Delta method.

Hach Chemical Co. (Ames, Iowa, U.S.A.) manufactures two field test kits for the analysis of anionic surfactant in aqueous solution. One kit uses crystal violet method; while another kit uses methyl green method. Both test procedures are simple enough for a people with limited chemistry training to perform. Unfortunately, both are extremely time-consuming (about 60 min. per test is required).

Using azure A for the determination of long-chain alkyl sulfates was first suggested by Steveninck and Riemersma (Ref. 17) in 1966. A Japanese scientist later evaluated its applicability to the measurement of ABS in water sample (Ref. 18) in 1972. The current azure A method is not applicable to the analysis of surfactant in the wastewater containing chloroform-extractable pollutants (such as oil).

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the authors modified the current azure A method (Ref. 18) for field use. The amount of reagents and apparatus required for each test, the time required for the separation of chloroform from a shaken chloroform-water mixture, and the interference caused by the chloroform-extractable pollutants are all reduced. The following sections describe the principles, required reagents, required apparatus, and the analytical procedures for the Calspan improved colorimetric method. A Calspan Corporation developed field test kit based on the modified method is also introduced.

MODIFIED AZURE A METHOD

A. Principle

The water sample to be analyzed is treated with chloroform and an excess amount of azure A reagent. In the presence of the chloroform, the Azure A reacts with anionic surfactant and forms a chloroform-soluble blue-colored complex (see Figure 1). Such complexes can be designated as azure A active

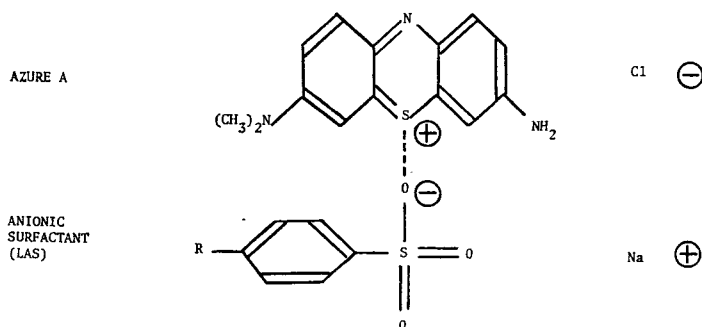


FIGURE 1 The chloroform soluble blue-coloured complex of anionic surfactant with Azure A.

substances (AAAS). The intensity of blue color in the vigorously rocked and subsequently settled chloroform layer is proportional to the concentration of the azure A-surfactant complex.

The blue color of the azure A-surfactant complex can be measured colorimetrically by making spectrophotometric readings in the chloroform. A typical percent transmittance curve in Figure 2 covers a wide wavelength range from 195 to 667 nm. The figure, corresponding to a treated 150 μg -LAS sample, shows that the optimum wavelength for the azure A-detergent complex is 623 nm. The measurement was made with a Bausch & Lomb Model Spectronic 600 Spectrophotometer.

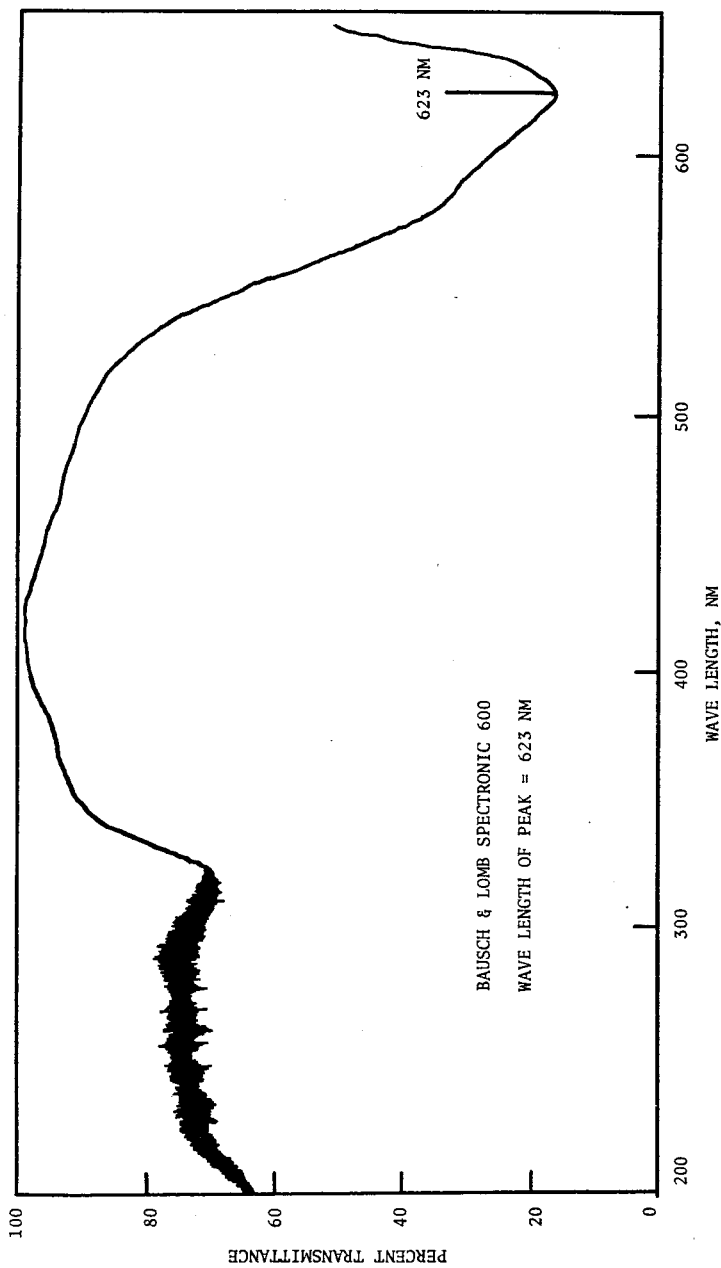


FIGURE 2 Transmittance curve of Azure A-LAS complex at full visible wavelength range.

B. Reagents

a) Stock linear alkylate sulfonate (LAS) solution (not required for the field test kit): Weigh an amount of the reference material equal to 1.000 g LAS on a 100% active basis. Dissolve in distilled water and dilute to one liter; 1.00 ml = 1.00 mg LAS. Store in refrigerator to minimize biodegradation.

b) Standard linear alkylate sulfonate (LAS) solution (not required for the field test kit): Dilute 50.00 ml of stock LAS solution to one liter with distilled water; 1.00 ml = 50.0 μ g LAS.

c) Azure A reagent: Dissolve 100 mg azure A (Fisher No. A-970 or equivalent), 24.8 grams $\text{Na}_2\text{HPO}_4 \cdot 7\text{H}_2\text{O}$, and 52.5 grams citric acid in 400 ml distilled water. Add 4 ml concentrated sulfuric acid to the 400 ml mixture, and shake until dissolution is complete. Dilute the solution to 500 ml.

d) Buffer solution: Add 4 ml concentrated sulfuric acid, 24.8 grams $\text{Na}_2\text{HPO}_4 \cdot 7\text{H}_2\text{O}$ and 52.5 grams citric acid in 400 ml distilled water. Shake until dissolution is complete. Then, dilute the solution to 500 ml.

e) Chloroform, anhydrous.

f) Glass wool (optional).

C. Apparatus (also see Recommended Field Test Kit)

a) Graduated cylinder: 50 ml.

b) Separatory funnel: 250 ml, preferably with inert teflon stopcock.

c) Filtering funnel (optional): 65 mm.

d) Spectrophotometer or filter photometer providing a light path of 1 cm or longer, and exhibiting maximum transmittance at or near 623 nm.

D. Analytical Procedures

a) Fill a test cell with pure chloroform for use as a blank when the interference due to chloroform-extractable foreign substances is negligible. (Note A). Insert the cell containing the blank into a spectrophotometer or a photometer. Adjust the instrument to 100% transmittance or zero absorbance at 623 nm or equivalent. (Note B).

b) Place an aliquot amount of water or wastewater sample into a separatory funnel, and dilute to 50 ml with distilled water if necessary. Add 5 ml of azure A reagent and 25 ml of chloroform to the separatory funnel. Stopper the separatory funnel, and shake it vigorously for at least 30 seconds.

c) Allow to stand undisturbed for 5 minutes after shaking. The chloroform will separate from the water and settle. If anionic surfactants are present, the chloroform layer will be blue in color.

d) Wedge a small plug of glass wool in the stem of the filtering funnel, and place the funnel in a clean dry test cell. Filter the chloroform layer through the glass wool. (Note C).

e) Place the prepared chloroform sample in the cell holder of the instrument, and read the % transmittance or the absorbance at 623 nm or equivalent (Note B). Convert the % transmittance (or the absorbance) to mg/l linear alkylate sulfonate (LAS) with a calibration curve shown in Figure 3 or equivalent.

Note A

When the method is applied to the examination of the anionic surfactant in a polluted water containing significant amount of chloroform-extractable foreign compounds (such as oil), the blank chloroform for instrument calibration should be prepared according to the following procedures: Place an aliquot amount of water sample into a separatory funnel and dilute to 50 ml with distilled water (the dilutions for the blank and for the azure A treated sample in the procedure D. b. should be the same). Add 5 ml buffer solution and 25 ml of chloroform to the separatory funnel. Stopper the separatory funnel and shake it vigorously for 30 seconds. Then, follow the procedure D. d. to get the blank chloroform sample.

The above modified method is generally applicable to a water or wastewater sample containing no more than 45 ppm chloroform-extractable compounds (or oil and grease). If the concentration of chloroform-extractable foreign compounds in the sample is close to or higher than 45 ppm, a special remedy has been developed by Calspan and is presented in the section on Limitations, Interferences and Remedies.

Note B

When a Delta Model 260 Photometer (Ref. 11) is used, its filter selector should be adjusted to 570 or 520. When a Hach DC-DR (or AC-DR) Colorimetric (Ref. 19) is used, its filter selector should be adjusted to 4445 or 9798.

Note C

The use of glass wool for removing the water drops in the chloroform layer is optional. If the glass wool is not available or not desirable to be used, the separated chloroform layer in a separatory funnel can simply be drained into a glass flask and swirled. The water drops in the chloroform, if any, will attach

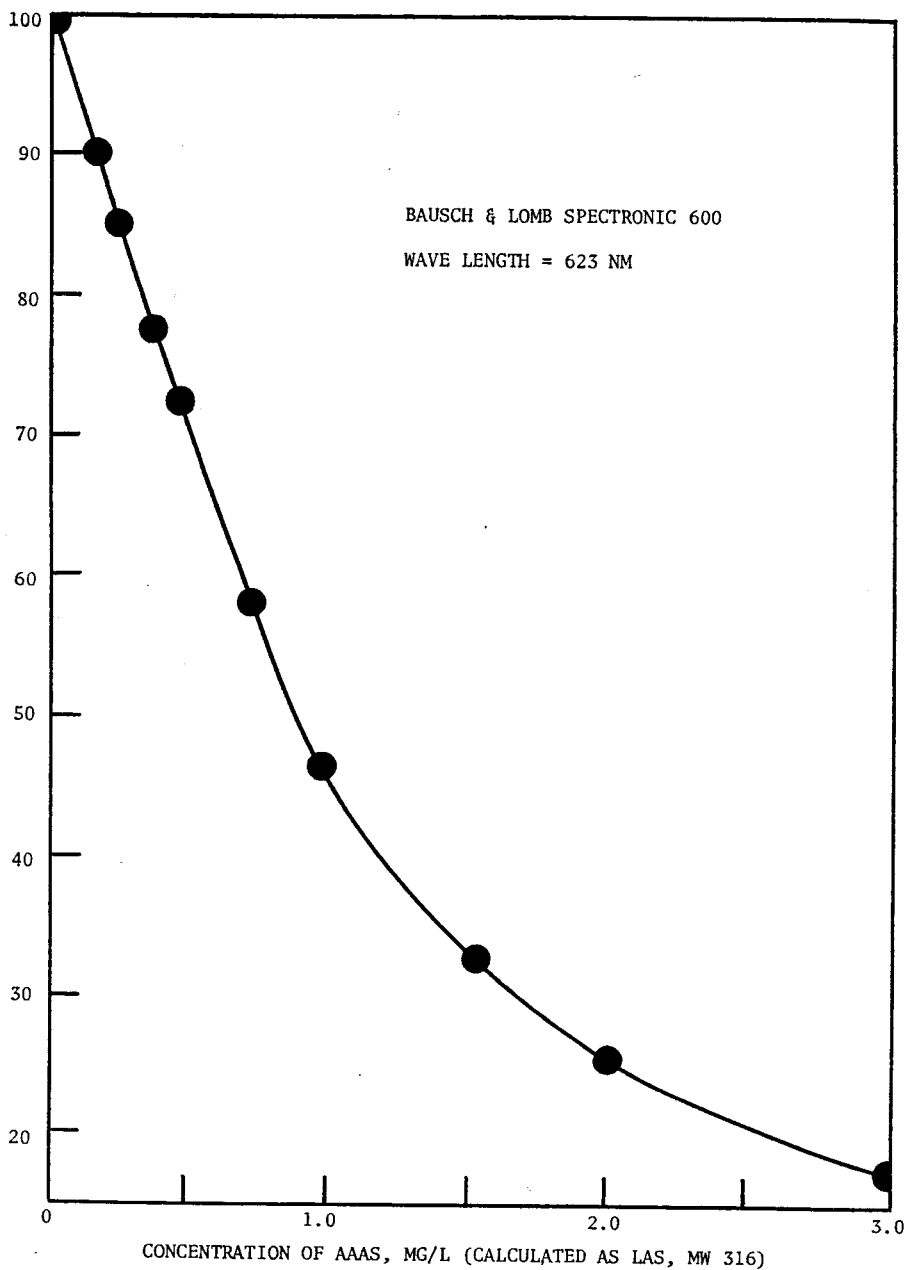


FIGURE 3 Calibration curve of LAS analyzed by Azure A Method (623 nm).

on the glass wall and be removed. The dewatered chloroform will then be placed in a clean dry test cell.

RECOMMENDED FIELD TEST KITS

A field test kit for performing the analytical tests involves the use of a portable spectrophotometer or a filter photometer. The apparatus and chemical reagents to be packed in these kits are fully described below.

- a) Graduated cylinder: 50 ml.
- b) Separatory funnel: 250 ml, preferably with inert teflon stopcocks.
- c) Filtering funnel (optional): 65 mm.
- d) Glass wool (optional): 100 ml.
- e) One or two bottles of chloroform: 250 ml each, stored in the glass or metal bottles.
- f) One bottle of azure A reagent: 100 ml, stored in a plastic bottle.
- g) One glass hypodermic syringe (optional): 25 ml capacity; for measuring chloroform.
- h) Two plastic hypodermic syringes: 5 ml capacity; for measuring azure A reagent and buffer solution.
- i) One bottle of buffer solution: 100 ml solution stored in a plastic bottle.
- j) One glass Erlenmeyer flask (optional): 125 ml capacity, wide mouth, heavy duty rim, graduated.
- k) Spectrophotometer or filter photometer (calibration curves included), any one of the following is recommended:
 - Delta Model 260 Photometer (Ref. 11).
 - Hach DR/2 Spectrophotometer (Ref. 16).
 - Hach DC-DR (or AC-DR) Colorimeter (Ref. 19).

Figures 4-a and 4-b are two calibration curves furnished by Calspan for the Delta Model 260 Photometer.

EXPERIMENTAL EVALUATION AND DISCUSSION

A. General Evaluation and Discussion

The Azure A Method, in common with other Methylene Blue Method or cationic dye methods, can give an accurate measure of the molar amount of anionic surfactant present: however, the amount by weight cannot be calculated unless the molecular weight of the material in that particular sample is known or determined. This is difficult in any specific case, because the anionic surfactant present may be natural or synthetic; the synthetic may be alkyl sulfate, ethoxylate sulfate, olefin sulfonate or LAS; the LAS

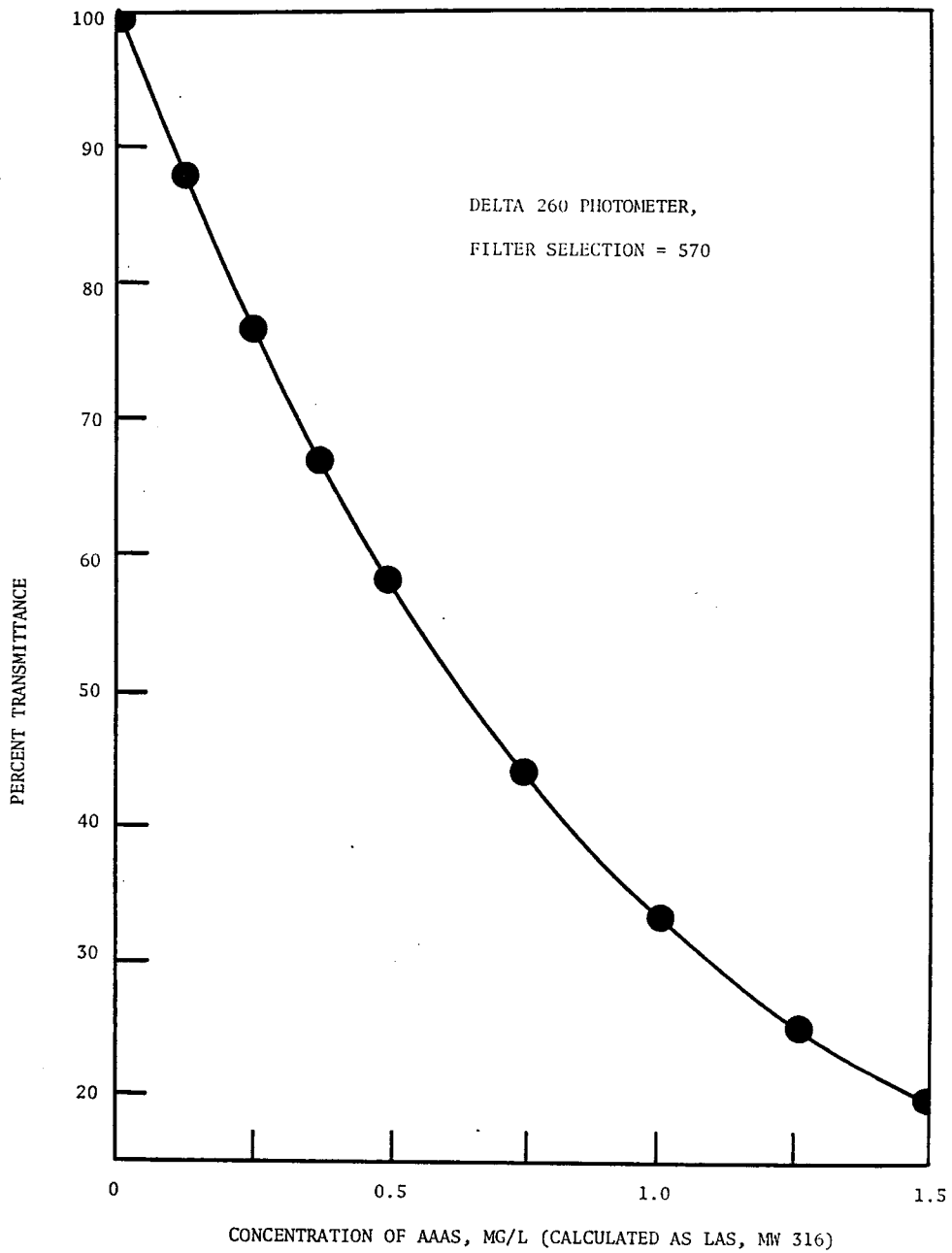


FIGURE 4a Calibration curve of LAS analyzed by Azure A method (Delta 260 photometer).

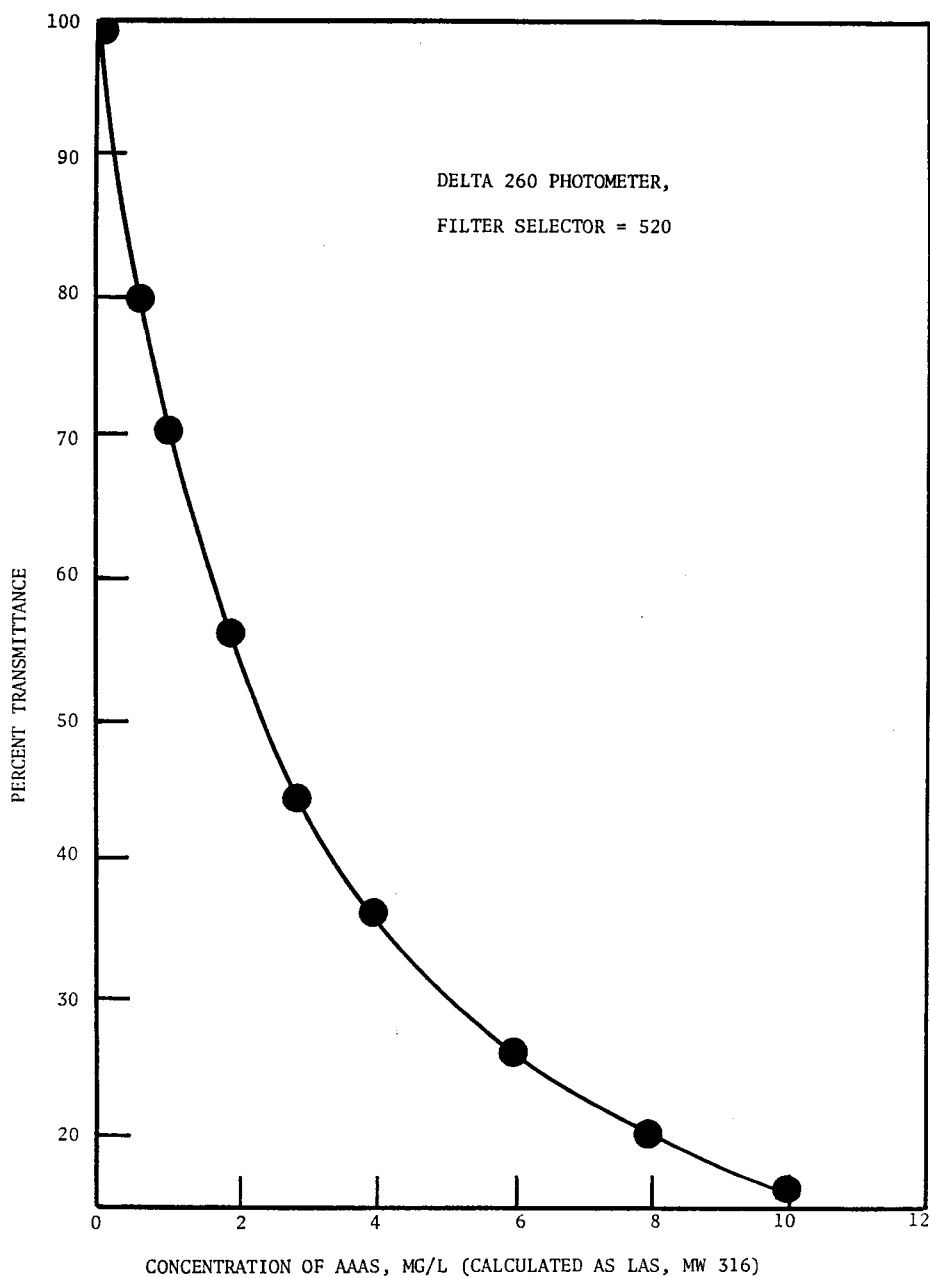


FIGURE 4b Calibration curve of LAS analyzed by Azure A method (Delta 260 photometer).

may have any distribution of homologs from C_{10} to C_{14} alkyl groups, with the distribution changing throughout the course of its biodegradation. Thus it is important that the nature and molecular weight of the calibration standard be specified. The standard anionic surfactant selected for evaluation and calibration was linear alkylate sulfonate (LAS) supplied in liquid form by the Analytical Quality Control Laboratory, Environmental Protection Agency, 1014 Broadway, Cincinnati, Ohio, U.S.A. The standard LAS was not the sodium salt (which is the form used in the detergent industry) but was instead the free sulfonic acid having an average molecular weight of 316. As the sodium salt its molecular weight would be 22 units higher, or 338.

A series of standard LAS samples with concentrations of 0, 0.1, 0.5, 1.0, 1.5, 2.0, and 3.0 mg/l was initially analyzed by the modified Azure A Method with a Bausch & Lomb Spectrophotometer, Model Spectronic 600. The light path of the instrument cell and the wavelength used were 1 cm and 623 nm, respectively. The plots of the peak transmittance values versus the standard LAS concentrations gave the LAS calibration curve shown in Figure 3. The applicabilities of the Azure A Method was thus demonstrated.

It should be noted that the horizontal axis of Figure 3 is labeled "Concentration of AAAS, mg/l (Calculated as LAS, mw 316)". This is due to the fact that a solution of 3.16 mg/l of the standard LAS acid corresponds to 3.38 mg/l of its equivalent sodium salt. This seven percent (7%) difference is not of great consequence in environmental and biological work, but nevertheless it should be well understood by a chemist who conducts the surfactant analysis. This special labeling would make it less easy for a thoughtless user to assume blindly that whatever he or she measures is necessarily LAS.

The colorimetric method can also be applied to the analysis of LAS with a filter photometer, such as the Delta Model 260 Photometer or the Hach AC-DR (or DC-DR) Colorimeter. The former was selected for evaluation. It was found that the filter selector 570 was particularly applicable to detecting anionic surfactant at 0–1.5 mg/l LAS range (Figure 4-a) and the filter selector 520 was applicable to detecting the surfactant at 0–10 mg/l LAS range (Figure 4b). From these studies the applicabilities of commercial filter photometer to the Azure A Method were demonstrated. A bonus finding is the use of two different filter selectors (or two different wavelengths) for the field surfactant analysis. An appropriate filter selector for high LAS range can be used for the analysis of a raw wastewater sample; while another filter selector for low LAS range can be used for the analysis of a treated waste effluent or a water sample with low LAS content.

Azure A Method can also be used to analyze anionic surfactant content other than LAS, such as branched-chain alkylbenzene sulfonate (supplied in powdered form by the Soap and Detergent Association, New York, NY, U.S.A.). Cold Power laundry detergent (supplied in powder form by Colgate-

Palmolive Company, New York, N.Y.), Ahoy dishwashing detergent (supplied in liquid form by the Great Atlantic & Pacific Tea Co., Inc., New York, N.Y.), Chiffon Lemon Dishwashing Lotion (supplied in liquid form by the Armour-Dial, Inc., Phoenix, Arizona), can all be analyzed for their apparent anionic surfactant content in terms of mg/l AAAS. However, the method cannot be used for measuring the surfactant content of nonionic Cascade dishwashing detergent (supplied in powdered form by Procter & Gamble, Cincinnati, Ohio), Ivory Soap (a product of Procter and Gamble, Cincinnati, Ohio), and cationic Lysol Deodorizing Cleaner II (manufactured by Lehn & Fink Products Division of Sterling Drug Inc., Montvale, N.J.). Laboratory test performed by the authors have demonstrated these facts. It is then concluded that the Azure A Method is capable of analyzing only anionic nonsoapy surfactants.

During the evaluation period, it was also found that the modified Azure A Method is superior to the standard Methylene Blue Method (Ref. 5) in the following aspects: sharper color contrast of the treated chloroform compared to a blank, more rapid chloroform/water separation rate, much less water drops in the treated and separated chloroform layer, and more stable dye reagent. Therefore, the modified Azure A Method is highly recommended for field use for monitoring the wastewater's anionic surfactant concentration and controlling the waste treatment process.

B. Limitations, Interferences and Remedies

A chemist or a wastewater treatment operator must understand the limitations of the Azure A Method when he interprets the surfactant data.

The possible interferences of the Azure A Method are not completely known so far. Since the molecular structure of Azure A (shown in Figure 1) is similar to that of methylene blue, it is expected that organically bound sulfates, sulfonates carboxylates, and some inorganic ions such as nitrates and chlorides will cause positive interferences; while organic amines will cause negative interferences. The degree of interference has not been quantified.

It has been demonstrated that the Azure A Method cannot be used for quantitative analysis of soaps, nonionic surfactants and cationic surfactants. So far there is no convenient analytical method which can quantitatively measure soap or nonionic surfactants in the field. The cationic surfactants, however, can be measured in the field by the Calspan developed two-phase titration method (Refs. 10 and 20).

The presence of chloroform-extractable foreign compounds in a water sample will cause positive interference for the Azure A Method. If the concentration of chloroform-extractable foreign compounds, such as oil and

grease, is lower than 45 mg/l, using a buffer solution treated chloroform (prepared according to Note A in Analytical Procedures) as blank for instrument calibration will solve the problem.

If the concentration of chloroform-extractable foreign compounds in a water sample is higher than 45 mg/l the remedy for the surfactant analysis by the Azure A Method will be the pre-extraction of those chloroform soluble compounds from the sample. It was observed during this research that azure A, LAS and ABS individually are all water soluble, but not chloroform soluble. Only when the dye (i.e. azure A) complexes with the surfactant (either LAS or ABS), thus the dye-surfactant complex becomes chloroform soluble. In other words, a *plain chloroform extraction* (without adding any dye or buffer for the surfactant complexation) prior to the colorimetric detergent analysis will remove the chloroform-extractable pollutants, such as oil and grease, from the water sample. Such chloroform-oil mixture should be initially collected at the bottom of an extraction separatory funnel, then completely drained and discarded. The pretreatment procedures of plain chloroform extraction are briefly described below:

a) Place an aliquot amount of water or wastewater sample into a separatory funnel, and dilute to 50 ml with distilled water if necessary.

b) Add 25 ml of chloroform to the separatory funnel. Stopper the separatory funnel, and shake it vigorously for at least 30 seconds.

c) Allow to stand undisturbed for a few minutes after shaking. The chloroform will separate from the water and settle. If chloroform-extractable compounds are present, the chloroform layer will be colored or turbid.

d) Completely drain the spent and settled chloroform. Add another 25 ml fresh chloroform to the separatory funnel containing the water sample, and repeat steps b and c until the spent and settled chloroform becomes crystal clear (i.e., nearly 100% transmittance at an appropriate wavelength against a pure chloroform as blank).

e) The pretreated 50 ml water sample can then be analyzed for its surfactant content by the modified colorimetric method. The pure chloroform can serve as the blank for instrument calibration, if necessary.

SUMMARY, CONCLUSIONS AND RECOMMENDATIONS

Various methods for the analysis of anionic surfactants in aqueous solution were reviewed, evaluated, and/or assessed. None of the surveyed methods can be easily and rapidly used in the field by the personnel with limited chemistry training.

The Azure A Method, initially developed by Steveninck and Riemersma in 1966 (Ref. 17), was modified and simplified for the field use. Its principle,

required reagents, required apparatus, and analytical procedures are introduced in this paper in detail. The surfactants measured by Azure A Method can be reported to be either mg/l AAAS (i.e., azure A active substance). Based on the Azure A Method, a field test kit for analyzing anionic nonsoap surfactants was developed under this program.

The applicabilities of the Azure A Method and the related field test kits to the measurement of AAAS content of detergent solutions were evaluated. The method and the test kit can be used by the waste treatment personnel with limited training in analytical chemistry for measuring *anionic* nonsoap synthetic surfactants.

If a filter photometer (such as Delta Model 260 Photometer) is to be used for anionic surfactant analysis by the modified Azure A Method, an appropriate filter selector for high AAAS range (such as Figure 4b) can be useful for the analysis of a raw wastewater sample; while another filter selector for low AAAS range (such as Figure 4a) can be used for the analysis of a treated waste effluent or a water sample with low AAAS content.

The limitations of Azure A Method were also investigated. It was found that the method cannot be used for quantitative analysis of *soap*, *nonionic surfactant* and *cationic surfactant*.

The Azure A Method was found to be superior to the standard Methylene Blue Method (Ref. 5) for the following reasons: (1) the Azure A Method provides sharper color contrast due to its dye-surfactant complex compared to a blank; (2) the separation rate of chloroform from water is faster; (3) much less water drops present in the treated and separated chloroform layer; (4) the effective AAAS detecting range is broader; (5) there is a smaller deviation in analytical data; (6) the dye reagent is more stable under light exposure; and (7) the interferences caused by the chloroform-extractable pollutants can be greatly reduced.

If it is allowable to report the surfactant content of an aqueous sample as mg/l AAAS (i.e., azure A active substances), the Azure A Method is highly recommended to be used for anionic surfactant analysis in the field.

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