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Calspan Report No. ND-5296-M-4

IMPROVED COLORIMETRIC METHODS AND FIELD TEST KITS FOR ANALYZING ANIONIC SURFACTANTS IN WATER AND WASTEWATER

LEVEL II

Fourth Interim Report
for the Period 16 April - 15 August 1973

By

Lawrence K. Wang
Project Engineer

August 1973

Prepared for

Department of the Army
U. S. Army Mobility Equipment
Research and Development Center
Fort Belvoir, Virginia

Contract NO. DAAK02-73-C-0206

Prepared for

Calspan Corporation
Environmental Systems Department
P. O. Box 235
Buffalo, New York 14221

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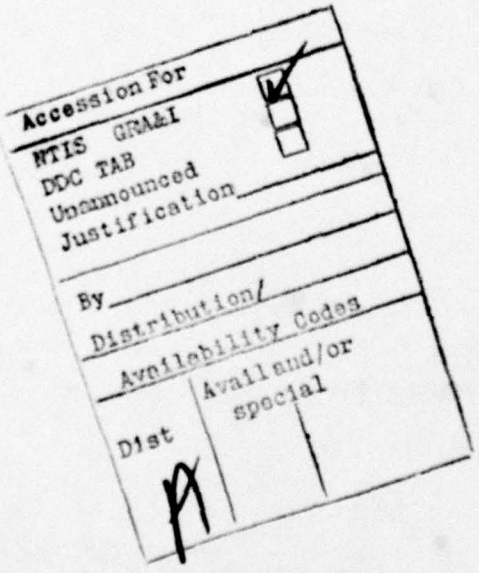
ABSTRACT

Various methods for the analysis of surfactants in aqueous solution were reviewed, evaluated, and/or assessed. Emphasis was placed on the development of field test kits based on two improved colorimetric methods involving the use of methylene blue and Azure A.

The simplified and improved Methylene Blue Method and Azure A Method require only 5 or 6 ml of aqueous reagent and 25 ml of chloroform for analyzing one sample. The principles, analytical procedures and limitations of the two methods are described in detail.

A field test kit based on the use of a portable spectrophotometer (or photometer), and a field test kit based on the use of color comparison device(s) are proposed for use by military personnel with limited training in chemistry.



IMPROVED COLORIMETRIC METHODS AND FIELD TEST KITS FOR ANALYZING ANIONIC SURFACTANTS IN WATER AND WASTEWATER.

Lawrence K. Wang
Calspan Report No. ND-5296-M-4

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1.0 INTRODUCTION

Under Contract No. DAAK02-73-C-0206, Calspan Corporation was authorized by the U. S. Army Mobility Equipment Research and Development Center (USAMERDC) to develop test methods, techniques, and devices for determining the optimum operational parameters of a physicochemical system designed for the treatment of wastewaters generated at field laundries, showers, and kitchens. The existing Army Standard water purification units (described in Ref. 1) are being considered as basic components of the physicochemical treatment system involving powdered carbon adsorption, polyelectrolyte coagulation, and diatomaceous earth filtration (Ref. 2).

One of the primary objectives of this on-going research is to establish the methods for determining the optimum dosages of powdered activated carbon and polyelectrolyte. It is known (Ref. 2) that the powdered carbons are mainly responsible for the removal of dissolved organics from wastewater. The spent carbons as well as the suspended pollutants in the wastewater are expected to be removed by the subsequent polyelectrolyte coagulation and filtration. A logical approach to defining the chemical dosage requirements is to determine first the powdered carbon dosage based on the dissolved organic content and the initial pH of the wastewater to be treated and then determine the polyelectrolyte dosage based on the carbon dosage and the suspended solids in the wastewater.

The first step of determining required carbon dosage is not an easy task under field conditions because a rather rapid means for analyzing dissolved organics is required due to the variations in this parameter with time.

The dissolved organics content is generally measured in terms of biochemical oxygen demand (BOD), chemical oxygen demand (COD) and total organic carbon (TOC). BOD and COD determinations are extremely time consuming and it becomes impractical to measure these parameters before starting each field waste treatment operation. Although TOC analysis is a rapid method for characterizing wastewater and monitoring the treatment

system, its field application is totally limited by the nonportability and sophistication of TOC analyzers. Therefore, the development of field analytical method(s) to replace BOD, COD and TOC is necessary.

It has been known (Ref. 3) that the dissolved organic pollutants in the kitchen, laundry, and shower wastewaters of field military operations are mainly contributed by the dishwashing detergents, laundry detergents, soaps, food constituents, oil and dirts. It is hypothesized that the ratios of TOC/detergent, COD/detergent, and BOD/detergent for a specific waste stream would be fairly constant. If these ratios for the target wastewaters can be predetermined and documented, a simple measurement of detergent level in the wastewater would give the approximate TOC, COD, and/or BOD values. Accordingly, the chemical dosages for treating such wastewater can be computed.

This report first reviews and assesses various methods for the analysis of detergents (i.e., surfactants) in aqueous solution. Since none of these available methods were considered to be satisfactory for the rapid field application, the emphasis of this research was placed on the development of field test kits based on two improved colorimetric methods involving the use of methylene blue and azure A. The analytical techniques and devices developed under this program are summarized and concluded in Section 7.0, SUMMARY, CONCLUSIONS AND RECOMMENDATIONS.

2.0 LITERATURE REVIEW

Generally there are four types of analytical methods for analyzing detergents (or surfactants): infrared method; gas chromatographic and paper chromatographic methods; two-phase titration method; and colorimetric methods.

The infrared method (Refs. 4 and 5) for surfactant analysis was developed by an analytical subcommittee of the Soap & Detergent Association as a specific, quantative procedure that provides an unequivocal identification and measure of surfactant in water. This method involves the collection and isolation of a few milligrams of alkyl benzene sulfonate (i.e., ABS) or linear alkylate sulfonate (i.e., LAS), and its quantitative determination based on infrared absorption of an amine complex of the surfactant (i.e., ABS, LAS, or equivalent). 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 ppm of ABS or LAS is present in the water sample) and infrared equipment. Besides, it is suggested by AWWA (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 detergents by paper chromatography has been conducted by Drewry (Ref. 8). Based on Drewry's technique, development of a field test kit for detergent 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 was first 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 both cationic and anionic surfactants in both fresh and saline waters (Ref. 7). However, the field military wastewater generated from showers, laundries and kitchens is known to be generally anionic in nature and to have low salinity (Ref. 3). An even simpler field test kit based on a colorimetric method is suggested for evaluation or development under this research program.

The most commonly used colorimetric procedures for 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-detergent complex is soluble in a solvent extractant but not in water, whereas the dye and the detergent are soluble in water but not in the solvent extractant (such as chloroform) The color intensity of the dye-detergent complex in the solvent is proportional to the detergent concentration. This intensity can be measured in a spectrophotometer (or a filter photometer) and compared with standard solutions for apparent detergent 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. 11507) and Delta Scientific Corp. (Lindenhurst, N. Y. 11757) 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.

Hach Chemical Co. (Ames, Iowa, 50010) manufactures two field test kits for the analysis of anionic detergent in aqueous solution. The first kit uses crystal violet method, which is introduced in Appendix I; while the second kit uses methyl green method, which is introduced in Appendix II.

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 detergent in the wastewater containing chloroform-extractable pollutants (such as oil), and is subject to the interference caused by the presence of inorganic salts in a water sample.

Under Contract No. DAAK02-73-C-0206, sponsored by the USAMERDC, Calspan Corporation significantly simplified and improved the standard methylene blue method (Ref. 5) and 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 shaked chloroform-water mixture, the interference caused by the chloroform-extractable pollutants, and the interference caused by the inorganic salts, are all greatly reduced. Sections 3.0 and 4.0 describe the principles, required reagents, required apparatus, and analytical procedures for the two Calspan improved colorimetric methods. Section 5.0 introduces the Calspan developed field test kits based on the two improved methods.

3.0 MODIFIED METHYLENE BLUE METHOD

3.1 Principle

The water sample to be analyzed is treated with 25 ml of chloroform and an excess amount of methylene blue reagent under an appropriate pH condition. When methylene blue reacts with anionic detergent such as, linear alkylate sulfonate (LAS) or the like, a blue-colored salt forms. Such methylene blue-detergent complexs are often designated as methylene blue-active substances (MBAS), which are soluble in chloroform. The intensity of blue color in the vigorously rocked and subsequently separated chloroform layer is proportional to the concentration of the methylene blue-detergent complex.

Figure 1 shows the chemical reaction between the methylene blue and the detergent.

The intensity of the methylene blue-detergent complex can be measured by making spectrophotometric readings in the chloroform. Figure 2 shows the % transmittance curve of the treated 25 ml chloroform sample (resulting from the addition of 150 g of LAS) at a wavelength range of 195-667 mμ. The optimum wavelength which gives the minimum % transmittance or the maximum absorbance is 652 mμ. The measurement was made with a Bausch & Lomb Model Spectronic 600 Spectrophotometer.

3.2 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 = 1.00mg LAS. Store in a refrigerator to minimize biodegration.

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 = 50.0μg LAS.

c. Methylene blue reagent: Dissolve 625 mg methylene blue (Eastman No. P573 or equivalent), in 400 ml distilled water. Then gradually add

DETERGENT

METHYLENE
BLUE

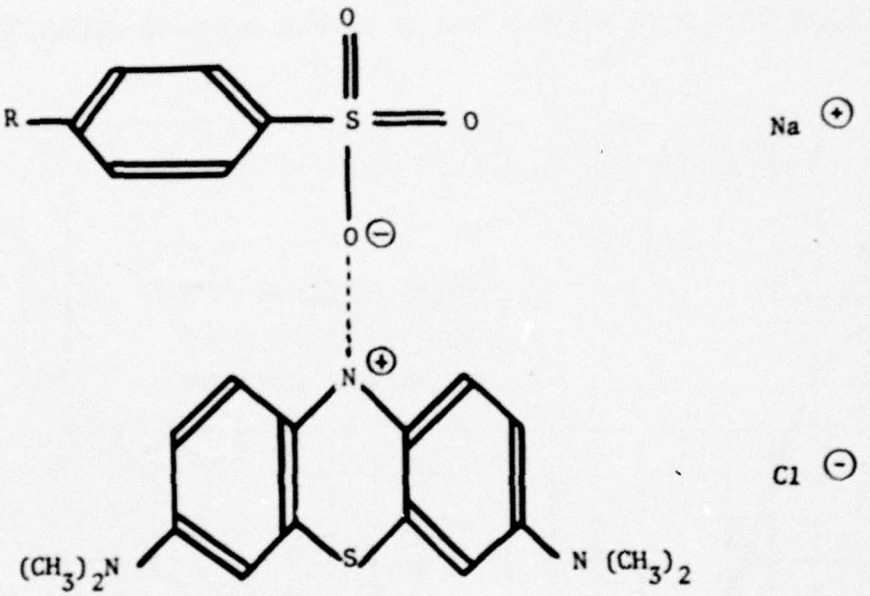


FIGURE 1. THE CHLOROFORM SOLUBLE BLUE-COLOURED COMPLEX OF ANIONIC DETERGENT WITH METHYLENE BLUE

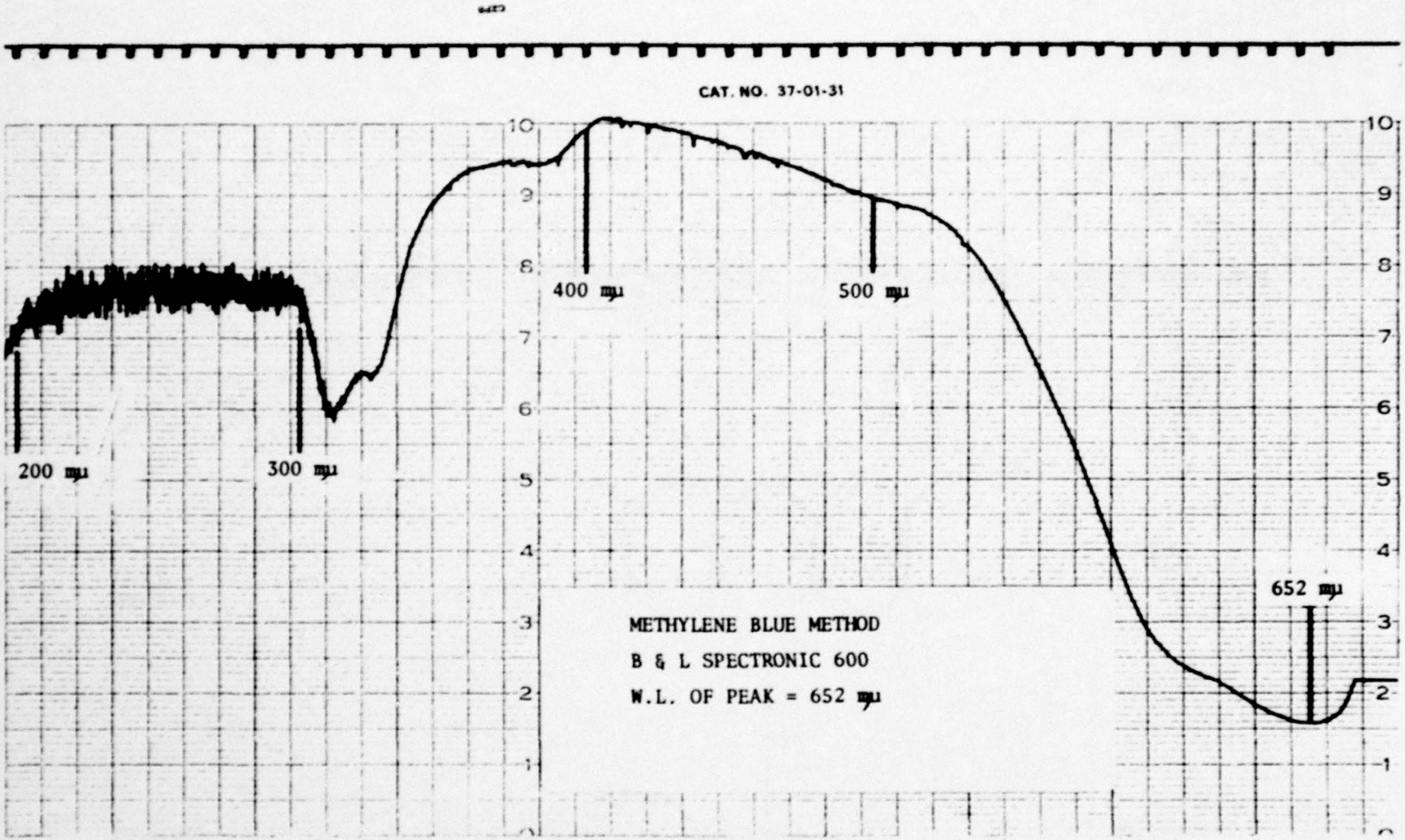


FIGURE 2. TRANSMITTANCE CURVE OF METHYLENE BLUE-LAS COMPLEX AT FULL VISIBLE WAVELENGTH RANGE

10.0 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 20.0 ml concentrated sulfuric acid to 400 ml distilled water in a 500-ml flask. Then add 150.0 grams $NaH_2PO_4 \cdot H_2O$, 24.8 grams $Na_2HPO_4 \cdot 7H_2O$, and 52.5 grams citric acid, and shake until dissolution is complete. Dilute to the 500-ml mark.

e. Chloroform, anhydrous

f. Glass wool (optional)

3.3 Apparatus (also see Section 5.0, Recommended Field Test Kits):

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 absorbance near 652 mμ.

e. Color comparison disc, chart, or bottles (optional, See Section 5.2): to be used only when a spectrophotometer or photometer is not available.

3.4 Analytical Procedures of Methylene Blue Method Using Portable Spectrophotometer or Photometer:

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 652 mμ 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 1 ml of methylene blue reagent, 5 ml of buffer solution, 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 652 mμ 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 to be used 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 methylene blue treated sample in the procedure 3.4.b should be same). Add 5 ml buffer solution and 25 ml of chloroform to the separatory funnel. Stopper the separatory funnel and shake it vigrrously for 30 seconds. Then, follow the procedure 3.4.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 Section 6.3, Limitations, Interferences and Remedies.

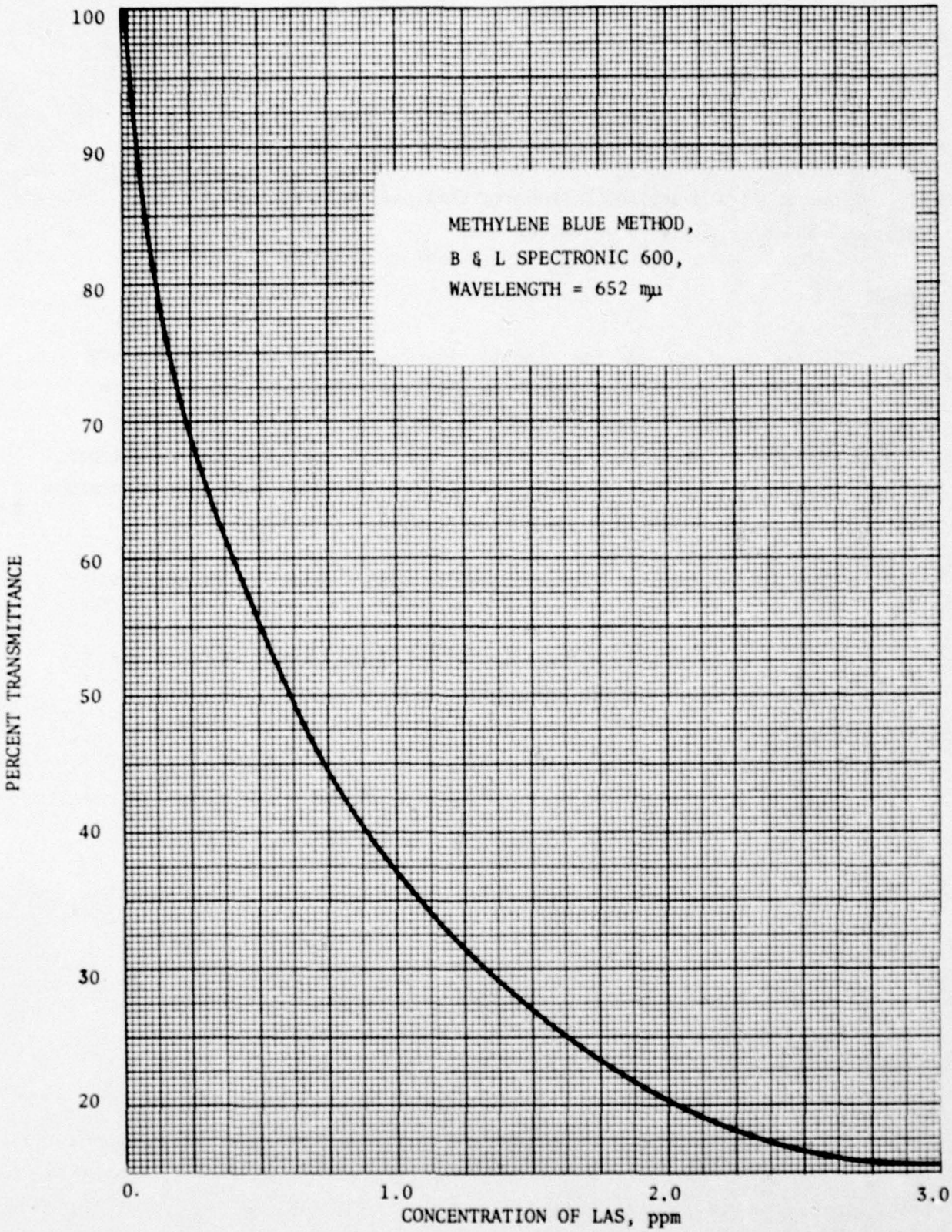


FIGURE 3. CALIBRATION CURVE OF LAS ANALYZED BY METHYLENE BLUE METHOD (652 mμ)

NOTE B

When a Delta Model 260 Photometer (Ref. 11) is used, its filter selector should be adjusted to 660 or 570.

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

3.5 Analytical Procedures of Methylene Blue Method Using Color Comparison Device or Chart

Follow the procedures 3.4.b through 3.4.d inclusive. Then compare the blue color developed in the separated chloroform layer with a color bottle set, a color chart or a color comparison disc (see Section 5.2). Read the mg/l LAS from either of these color comparison devices or chart.

4.0 MODIFIED AZURE A METHOD

4.1 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 detergent and forms a chloroform-soluble blue-colored complex (see Figure 4). Such complexes can be designated as azure A active 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-detergent complex.

The blue color of the azure A-detergent complex can be measured colorimetrically by making spectrophotometric readings in the chloroform. A typical percent transmittance curve in Figure 5 covers a wide wavelength range from 195 to 667 mμ. The figure, corresponding to a treated 150 μg-LAS sample, shows that the optimum wavelength for the azure A-detergent complex is 623 mμ. The measurement was made with a Bausch & Lomb Model Spectronic 600 Spectrophotometer.

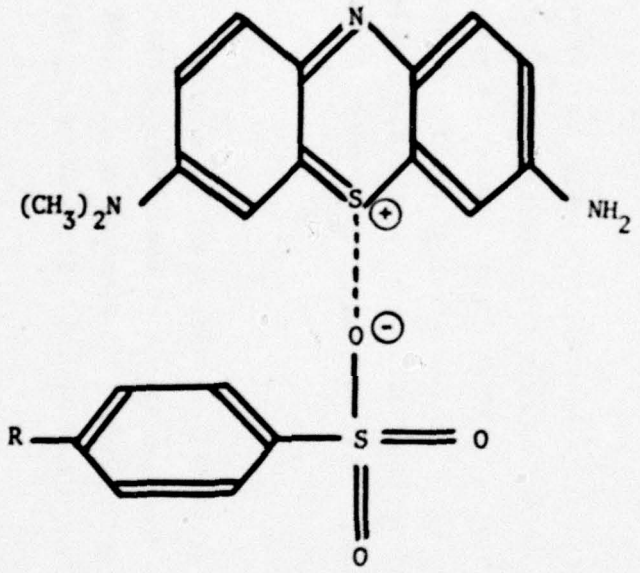
4.2 Reagents

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 μg LAS.

c. Azure A reagent: Dissolve 100 mg azure A (Fisher No. A-970 or equivalent), 24.8 grams $Na_2HPO_4 \cdot 7H_2O$, 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.

AZURE A



Cl ⊖

DETERGENT

Na ⊕

FIGURE 4. THE CHLOROFORM SOLUBLE BLUE-COLOURED COMPLEX OF ANIONIC DETERGENT WITH AZURE A

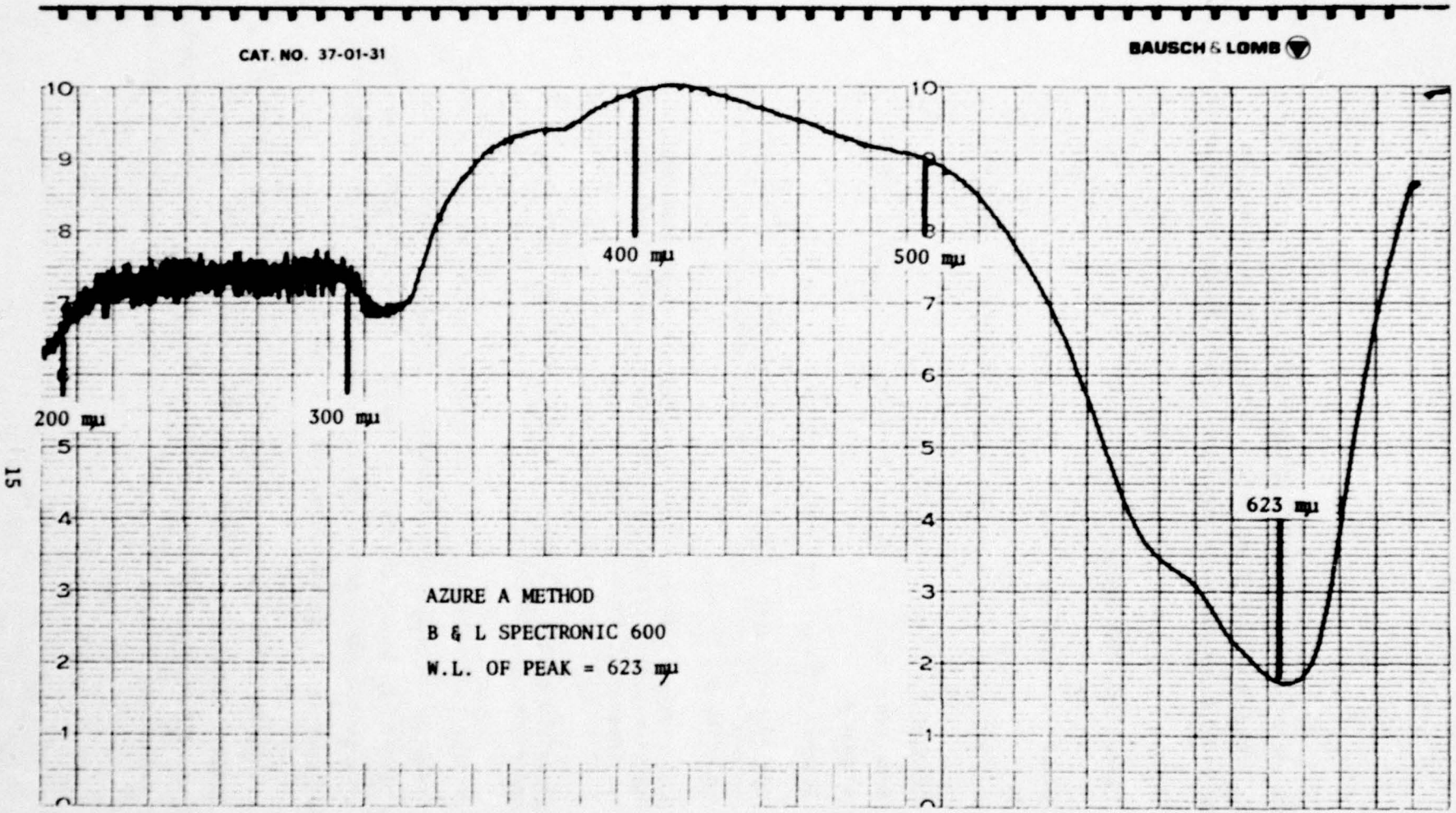


FIGURE 5. TRANSMITTANCE CURVE OF AZURE A-LAS COMPLEX AT FULL VISIBLE WAVELENGTH RANGE

d. Buffer solution: Add 4 ml concentrated sulfuric acid, 24.8 grams $Na_2HPO_4 \cdot 7H_2O$ 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).

4.3 Apparatus (also see Section 5.0, Recommended Field Test Kits):

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 mμ.

e. Color comparison disc, chart, or bottles (optional, See Section 5.2): To be used only when a spectrophotometer or photometer is not available.

4.4 Analytical Procedures of Azure A Method Using Portable Spectrophotometer or Photometer:

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 mμ 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 mμ or equivalent (Note B). Convert the % transmittance (or the absorbance) to mg/l linear alkylate sulfonate (LAS) with a calibration curve shown in Figure 6 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 4.4.b should be 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 4.4.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 Section 6.3, 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)

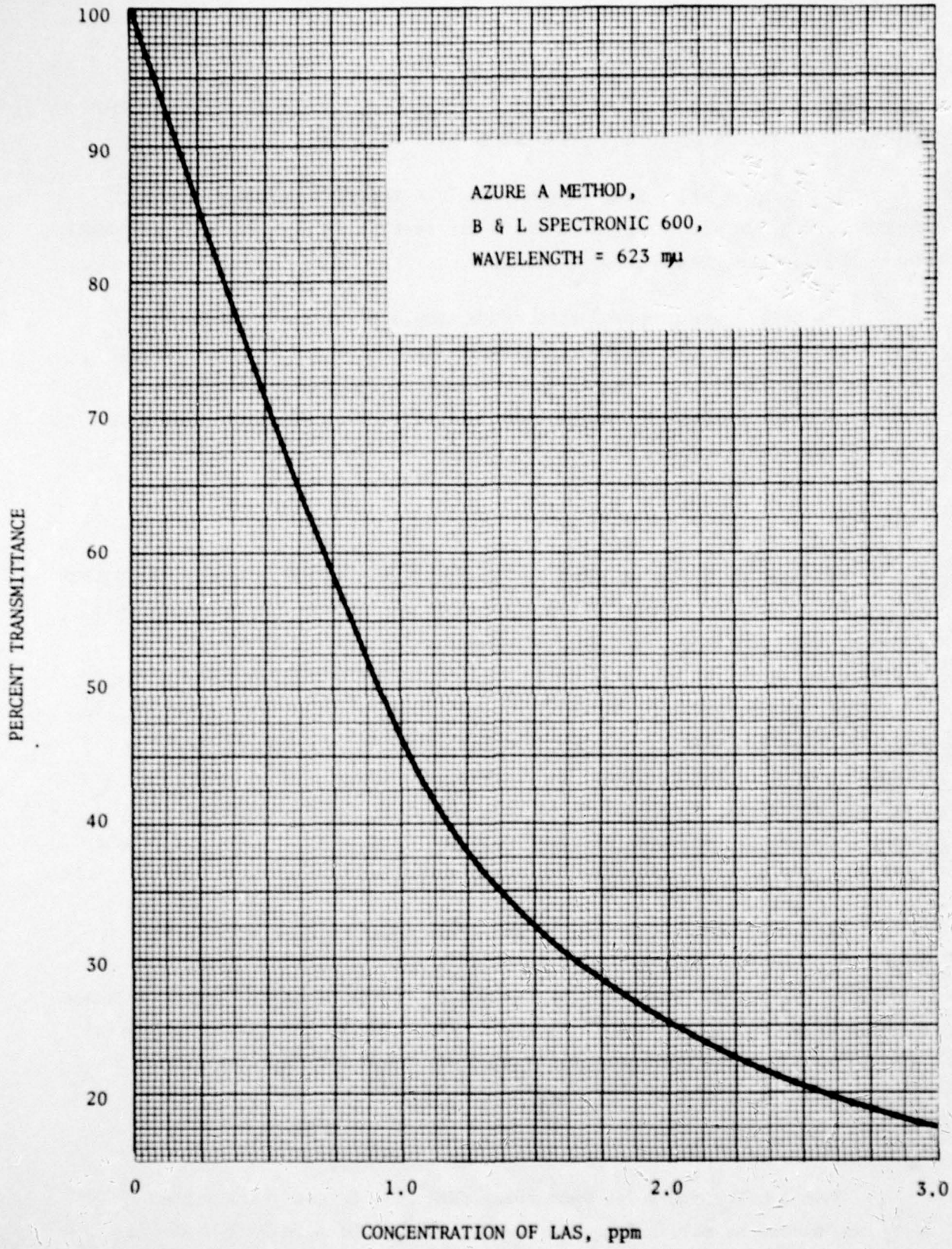


FIGURE 6. CALIBRATION CURVE OF LAS ANALYZED BY AZURE A METHOD (623 mμ)

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

4.5 Analytical Procedures of Azure A Method Using Color Comparison Device or Chart

Follow the procedures 4.4.b through 4.4.d inclusive. Then compare the blue color developed in the separated chloroform layer with a color bottle set, a color chart or a color comparison disc (see Section 5.2). Read the mg/l LAS from either of these color comparison devices or chart.

5.0 RECOMMENDED FIELD TEST KITS:

Two types of field test kits for performing the analytical tests described in Sections 3 and 4 were developed under this program. The first type (Section 5.1) involves the use of a portable spectrophotometer or a filter photometer. The second type (Section 5.2) involves the use of a color comparison device or chart for determining the anionic surfactant concentration. The apparatus and chemical reagents to be packed in these kits are fully described below.

5.1 Field Test Kits Using Portable Spectrophotometer or Photometer

Methylene Blue Method

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): 4 cu. in.
e. One or two bottles of chloroform: 250 ml each, stored in the glass or metal bottles
f. One bottle of methylene blue 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 methylene blue reagent and buffer solution.
i. One bottle of butter 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 7-a and 7-b are two calibration curves furnished by Calspan for the Delta Model 260 Photometer.

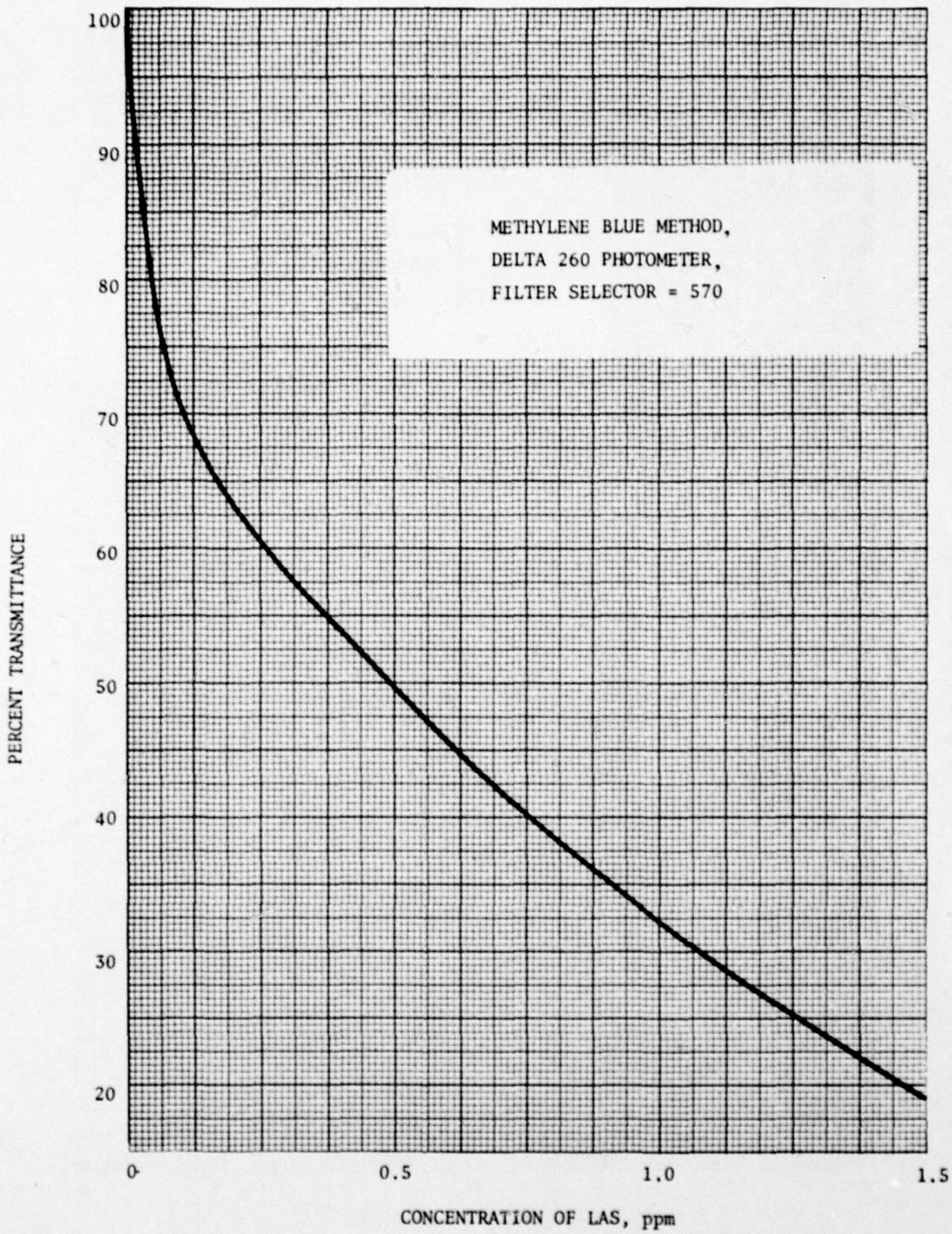


FIGURE 7-a. CALIBRATION CURVE OF LAS ANALYZED BY METHYLENE BLUE METHOD (DELTA 260 PHOTOMETER)

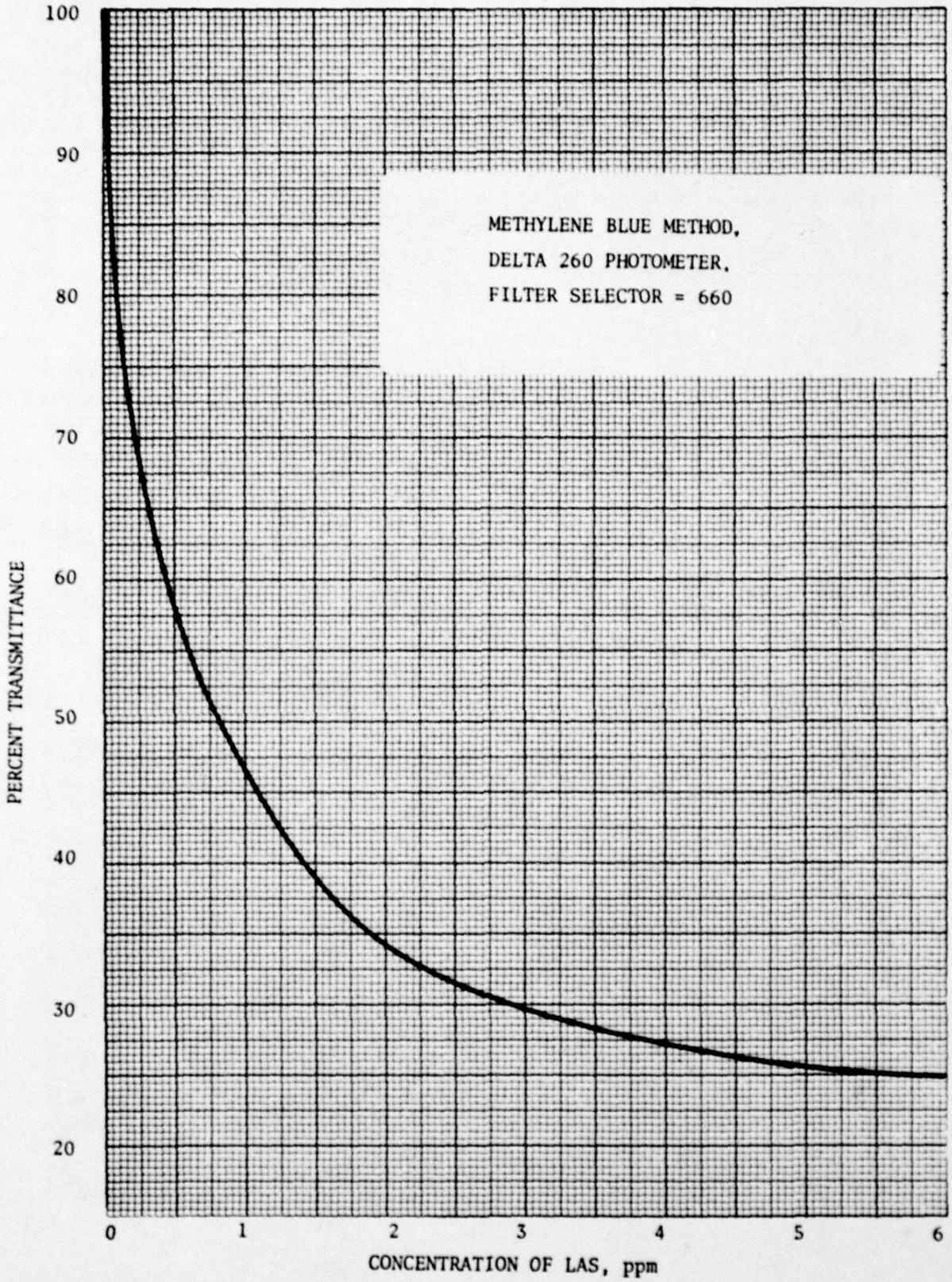


FIGURE 7-b. CALIBRATION CURVE OF LAS ANALYZED BY METHYLENE BLUE METHOD (DELTA 260 PHOTOMETER)

Azure A Method

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): 4 cu. in.

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 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 8-a and 8-b are two calibration curves furnished by Calspan for the Delta Model 260 Photometer.

5.2 Field Test Kits Using Color Comparison Device or Chart

Methylene Blue Method

A color comparison device or chart is used in the field to replace a spectrophotometer or a filter photometer. Ten other items are exactly same as the Items a through j, inclusive, for the field test kit described in Section 5.1, Methylene Blue Method.

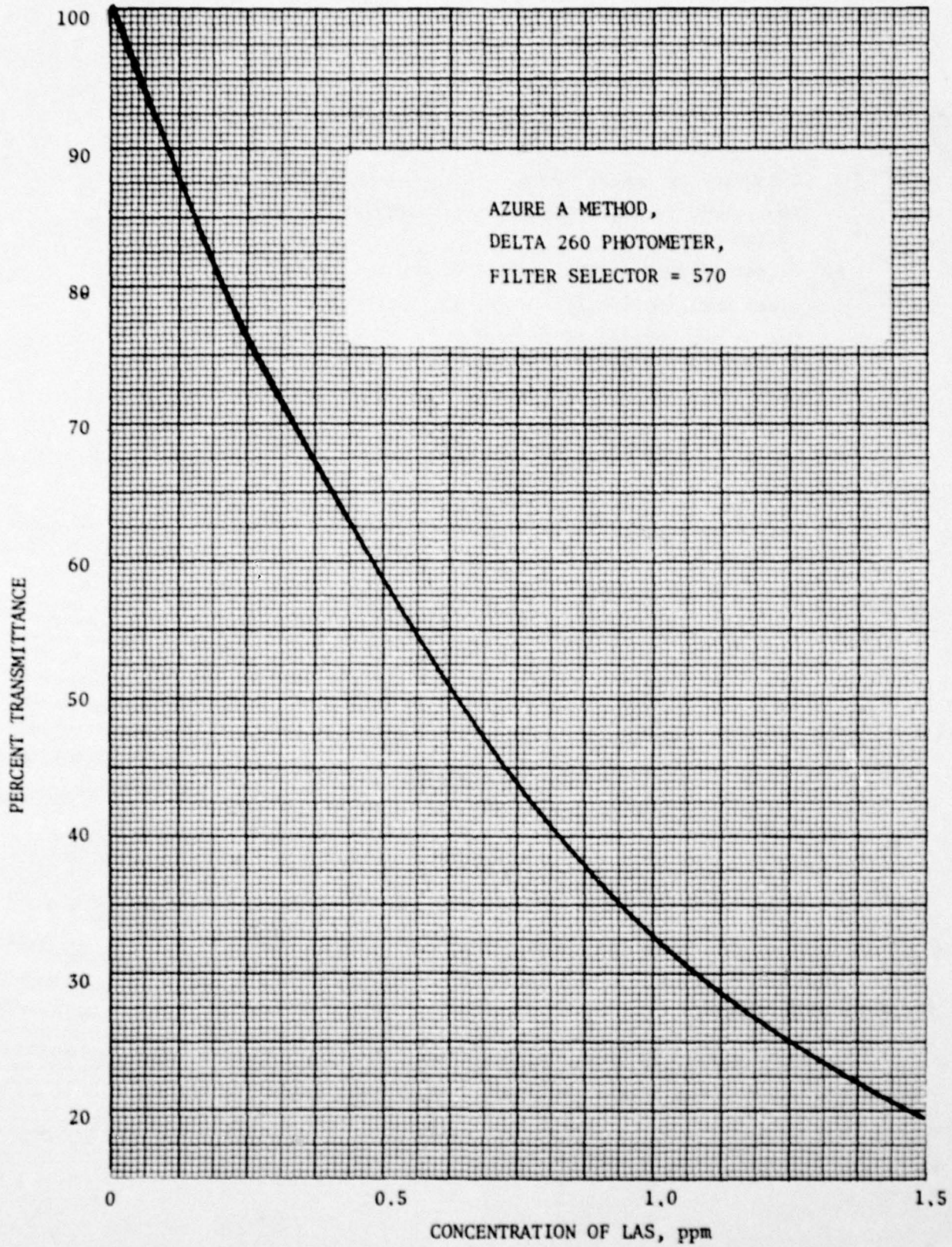


FIGURE 8-a. CALIBRATION CURVE OF LAS ANALYZED BY AZURE A METHOD (DELTA 260 PHOTOMETER)

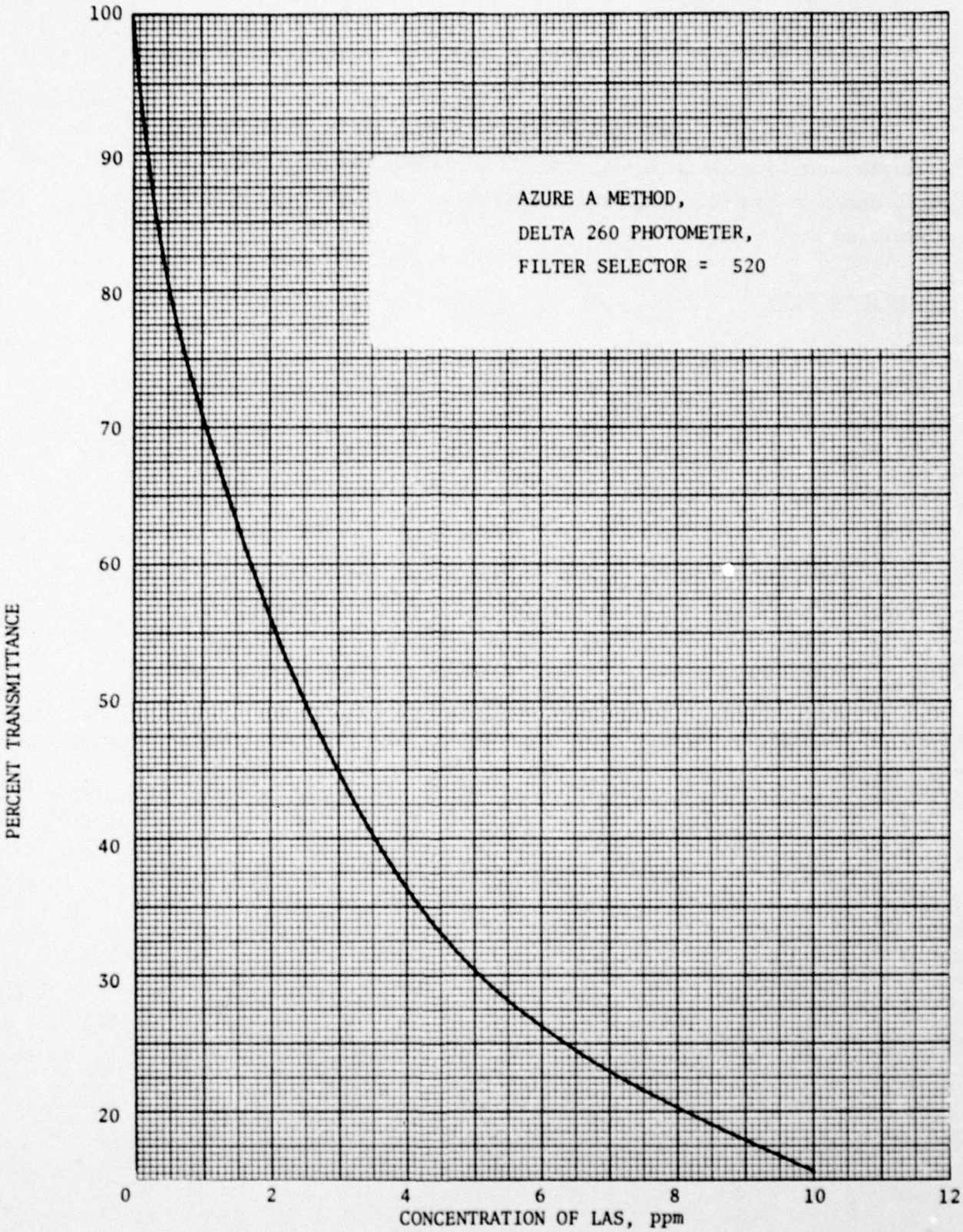


FIGURE 8-b. CALIBRATION CURVE OF LAS ANALYZED BY AZURE A METHOD (DELTA 260 PHOTOMETER)

A set of color bottle standards (not shown) can be used for detergent analysis based on Methylene Blue Method. A color comparison disc, shown in Figure 9, or a color comparison chart can also be used instead of the bottle standards.

Azure A Method

When Azure A Method is selected for use, similarly a color comparison device or a chart can be used in the field to replace a spectrophotometer or a filter photometer. In addition to a color comparison device or a chart, ten other necessary items are required and are exactly same as the Items a through j, inclusive, for the field test kit described in Section 5.1, Azure A Method.

A set of color bottle standards (not shown) was specifically prepared for the field analysis of anionic detergent with Azure A Method.

Standard samples can be kept in a set of glass ampules instead of a set of glass bottles for better preservation.

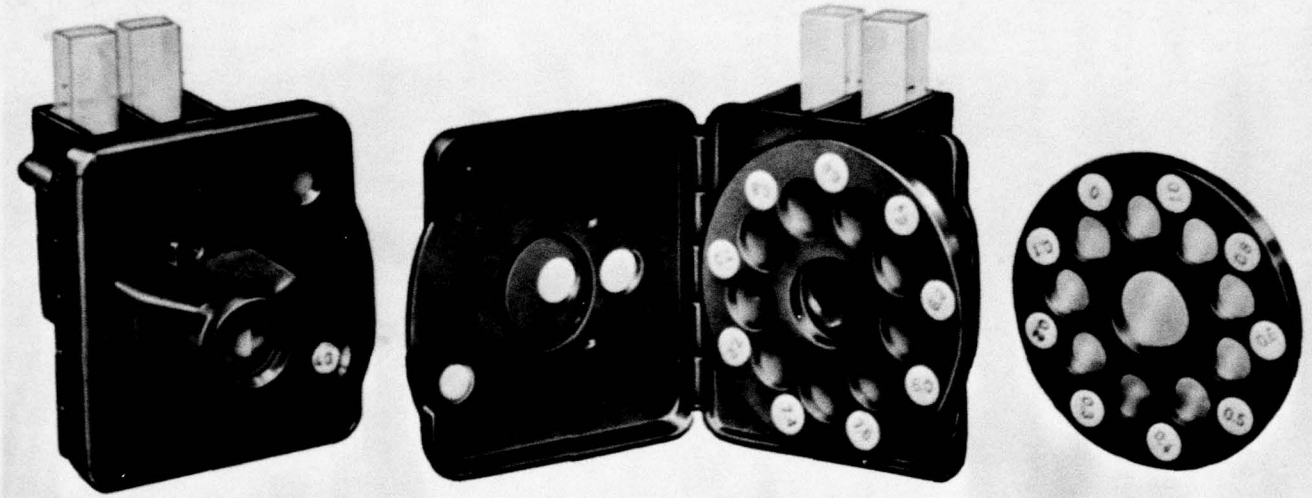


FIGURE 9 COLOR COMPARISON DISC FOR A FIELD TEST KIT

6.0 EVALUATION

6.1 Materials

The following surface-active agents or products were selected for evaluation:

a. Linear alkylate sulfonate (LAS): It is supplied in liquid-form by the Analytical Quality Control Laboratory, Environmental Protection Agency, 1014 Broadway, Cincinnati, Ohio 45202, and has an average molecular weight of 316.

b. Alkyl benzene sulfonate (ABS): It is supplied in powder form by the Soap and Detergent Association, 475 Park Ave., New York, New York 10016. Its formulation is listed below:

- Alkyl benzene sulfonate 48.7%
- Sodium Sulfate 47.0%
- Free Oil 0.4%
- Water 3.9%
- *pH (1% Solution)* 6.0
- Equiv. M. Wt. 365

c. Laundry detergent, Cold Power: It is supplied in powder form by Colgate-Palmolive Company, New York, New York. It is biodegradable, and contains sodium sulfate, sodium silicate, alkylbenzene sulfonate, soap, ethoxylated alcohol, moisture, carboxymethyl cellulose, cold water brighteners, aluminum silicates, colorant and perfume.

d. Dishwashing detergent, Ahoy Detergent: It is supplied in liquid form by the Great Atlantic & Pacific Tea Co., Inc., New York, New York 10017. The detergent can be used for washing dishes, glassware, pots and pans, fabrics, and automobiles. It contains the following materials:

- Water 68.5%
- Sodium dodecylbenzene sulfonate 16.0%
- Sodium xylene 4.0%
- Sodium sulfate 2.5%

- Carbamide 1.7%
- Alcohol ether sulfate 1.7%
- Alcohol ethoxylate 1.0%
- Coconut diethanolamide 1.0%
- Sodium citrate 0.3%
- Opacifier, preservative and perfume 3.3%

e. Chiffon Lemon Dishwashing Lotion: The lotion is a product of Armour-Dial, Inc., Phoenix, Ariz. 85077. The ingredients of the lotion are:

- Linear alkylbenzene sulfonate 23.0%
- Ethoxylated alkyl sulfate 5.0%
- Ammonium xylene sulfonate 5.0%
- Alkyl diethanolamide 3.0%
- Opacifier, ethyl alcohol, perfume and dye 1.9%
- Water 62.1%

f. Cascade dishwashing detergent: The detergent is supplied in powder form by Procter & Gamble, Cincinnati, Ohio. It contains nonionic surfactant, complex sodium phosphates, chlorinated trisdoium phosphate, sodium silicate, sodium sulfate, colorant and perfume.

g. U. S. military bar soap, "Floating Soap", received from the U. S. Army Mobility Equipment Research and Development Center, Fort Belvoir, Virginia.

h. Ivory Soap, a product of Procter and Gamble, Cincinnati, Ohio. The soap is the purest one available in the market. The manufacturer claims that Ivory contains 94 to 100% soap.

i. Cetyldimethylbenzylammonium chloride, a cationic detergent.

j. Synthetic wastewater, prepared with tap water, biodegradable laundry detergent, automatic dishwasher detergent, ground bar soap, clay, lubricating oil, and canned dog food. The formulation of synthetic wastewater is reported in Table 1.

TABLE 1

FORMULATION OF SYNTHETIC WASTEWATER

MATERIALS USED	QUANTITY
LABORATORY TAP WATER: (CALSPAN CORPORATION)	1000.0 GAL.
BIODEGRADABLE LAUNDRY DETERGENT: COLD POWER (COLGATE-PALMOLIVE CO.)	2.0 LB.
DISHWASHER DETERGENT: CASCADE DETERGENT (PROCTER & GAMBLE)	2.0 LB.
GROUND BAR SOAP: MILITARY SOAP (USAMERDC)	0.3 LB.
CLAY: BENTONITE SPV (AMERICAN COLLOID CO.)	0.4 LB.
SAE-10 LUBRICATING OIL: HEAVY DUTY (HD) OIL (PENN. CORP.)	0.1 LB.
CANNED DOG FOOD: BLUE RIBBON RECIPE (RIVAL PET FOODS)	3.7 LB.

The laundry detergent (Cold Power), the dishwashing detergent (Cascade), and the soap (military "Floating Soap") are described in Sections 6.1.c, 6.1.f, and 6.1.g, respectively. Three other materials used for the synthetic wastewater preparation are described in detail below:

- Powdered Volclay Bentonite SPV -- it is supplied by American Colloid Company, Skokie, Illinois, and contains silica, aluminum, iron, magnesium, sodium, potassium, calcium, and others.

- Heavy Duty (HD) oil, grade SAE-10-- It is supplied by Penn Corporation, Butler, Pa.

- Canned dog food -- Having a brand name Blue Ribbon Recipe, it is packed by Rival Pet Foods, A Division of Associated Products, Inc., Bridgeview, Ill., and contains protein, fat, fiber, moisture, vitamins, minerals, and ash.

6.2 Analysis of Surfactants by Improved Colorimetric Methods

Two identical series of standard LAS (Section 6.1.a) samples with concentrations of 0, 0.1, 0.5, 1.0, 1.5, 2.0, and 3.0 ppm were analyzed by the improved methylene blue method (Section 3.4) and azure A method (Section 4.4) with a Bausch & Lomb Spectrophotometer, Model Spectronic 600. The light path of the instrument cell was 1 cm. Analytical data were recorded as shown in Figures 10 and 11 by a Bausch & Lomb Recorder, Model VOM5, at a recording speed of 1 inch/min. Figure 10 shows that the methylene blue treated samples have transmittance spectra similar to Figure 2 with absorption peaks at 652 mμ wavelength. Similarly Figure 11 shows that the azure A treated samples yield transmittance spectra similar to Figure 5, and have absorption peaks at 623 mμ. The plots of the peak transmittance values versus the standard LAS concentrations gave two calibration curves, Figure 3 for methylene blue method and Figure 6 for azure A method. The applicabilities of the two improved colorimetric methods are thus demonstrated.

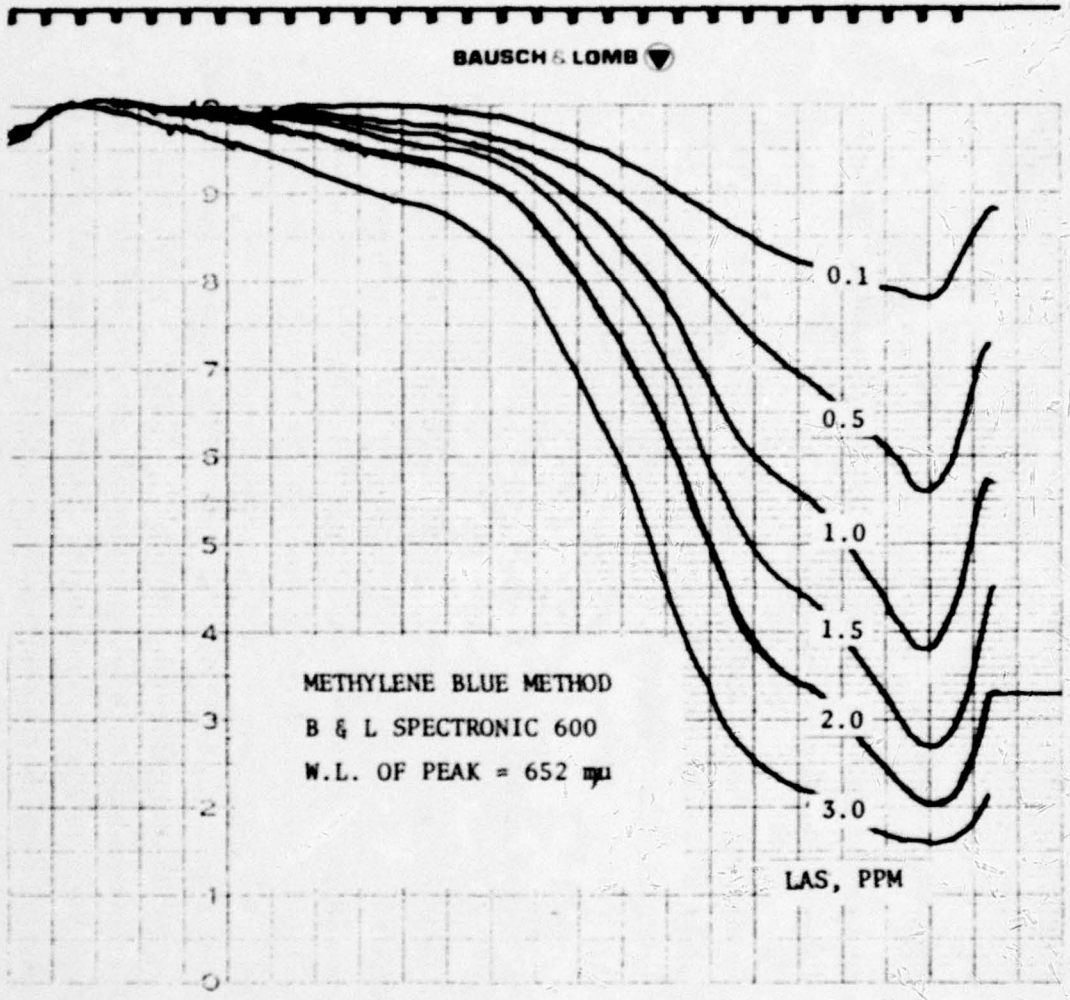


FIGURE 10 TRANSMITTANCE CURVES OF LAS STANDARDS TREATED BY METHYLENE BLUE AND RELATED REAGENTS.

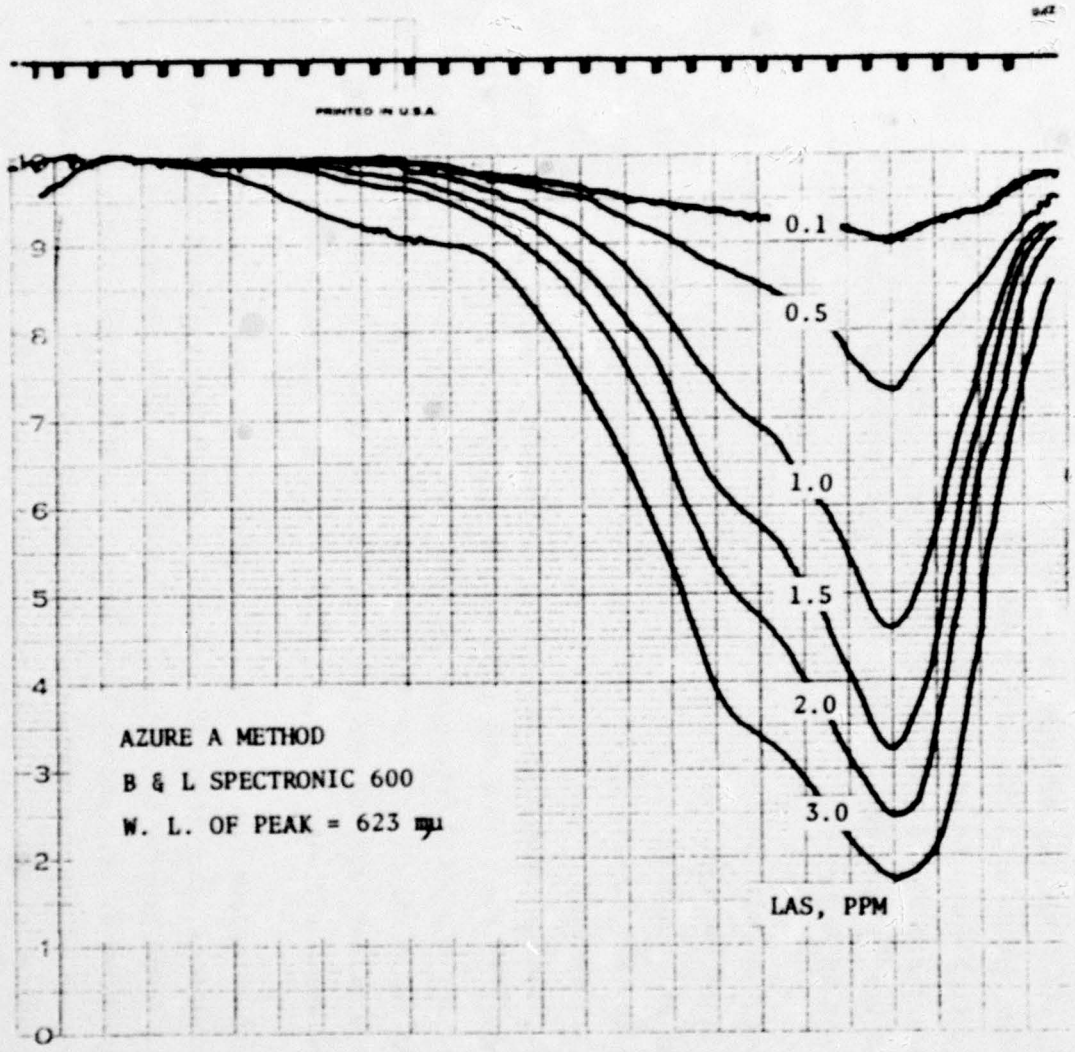


FIGURE 11 TRANSMITTANCE CURVES OF LAS STANDARDS TREATED BY AZURE A AND RELATED REAGENTS

The two colorimetric methods 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. The analytical procedures outlined in Sections 3.4 and 4.4 were adapted for LAS analyses with methylene blue method and azure A method, respectively. Both were found to be easy and convenient. Figures 7-a and 7-b, which are calibration curves of LAS standards analyzed by methylene blue method with the Delta Model 260 Photometer, show that the filter selector 570 can be used for analyzing anionic detergents at a low concentration range (0-1.5 ppm LAS; shown in Figure 7-a); while the filter selector 660 can be used for a higher detergent concentration range (0-4 ppm LAS; shown in Figure 7-b).

When the Delta photometer was used for analyzing LAS with azure A method, it was found that the filter selector 570 was particularly applicable to detecting anionic detergent at 0-1.5 ppm LAS range (Figure 8-a) and the filter selector 520 was applicable to detecting the detergent at 0-10 ppm LAS range (Figure 8-b). From these studies, of course, the applicabilities of commercial filter photometer to the two improved methods were demonstrated. A bonus finding is the use of two different filter selectors (or two different wavelengths) for the field detergent 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.

Both methylene blue and azure A methods can be used to analyze anionic surfactants other than LAS, such as, alkylbenzene sulfonate (Section 6.1.b), Cold Power laundry detergent (Section 6.1.c), Ahoy dishwashing detergent (Section 6.1.d), and Chiffon Lemon Dishwashing Lotion (Section 7.1.e). However, neither of the two methods can analyze the nonionic Cascade dishwashing detergent (Section 6.1.f), U. S. military "floating soap" (Section 6.1.g), Ivory soap (Section 6.1.h), and a cationic surfactant, cetyldimethylbenzyl-ammonium chloride (Section 6.1.i).

A synthetic wastewater prepared with tap water, biodegradable laundry detergent, automatic dishwasher detergent, ground bar soap, clay,

lubricating oil, and dog food (Section 6.1.j) was analyzed by both methylene blue and azure A methods, with a spectrophotometer (B & L Spectronic 600), a filter photometer (Delta Model 260 Photometer), and a color comparison device (Color bottle standards). Figures 12 and 13 show the Spectronic 600 spectral transmittance curves for the analysis of the synthetic wastewater by the methylene blue method (Section 3.4) and the azure A method (Section 4.4), respectively. Based on the peak transmittance values in Figures 12 and 13, and the calibration curves in Figures 3 and 6, the anionic detergent contents of the synthetic wastewater samples were calculated and reported in Table 2. The measured LAS content of synthetic wastewater, as indicated in Table 2, should be 43 $\pm$ 5.5 ppm according to methylene blue method, and 43.75 $\pm$ 1.25 ppm according to azure A method.

When the synthetic wastewater was analyzed with Delta Model 260 Photometer, its LAS content was measured to be 42 $\pm$ 7 ppm by methylene blue method, and 42.5 $\pm$ 2.5 ppm by azure A method. It is then tentatively concluded that of the colorimetric methods evaluated, azure A method gave lower deviation in its LAS data, and thus could be better. It should be further noted that if the Delta Model 260 Photometer is considered for use as a field instrument, the optimum LAS detecting ranges of methylene blue method are 0-1.5 ppm for filter selector 570 (Figure 7-a) and 0.25-3.0 ppm for filter selector 660 (Figure 7-b); while the optimum LAS detecting ranges of azure A method are 0-1.5 ppm for filter selector 570 (Figure 8-a) and 0.25-10.0 ppm for filter selector 520 (Figure 8-b). It is conceivable that azure A method has a wider LAS detecting range and, therefore, could be more applicable to the field use.

Besides, during the evaluation period, it was also found that the improved azure A method is superior to the improved methylene blue method 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.

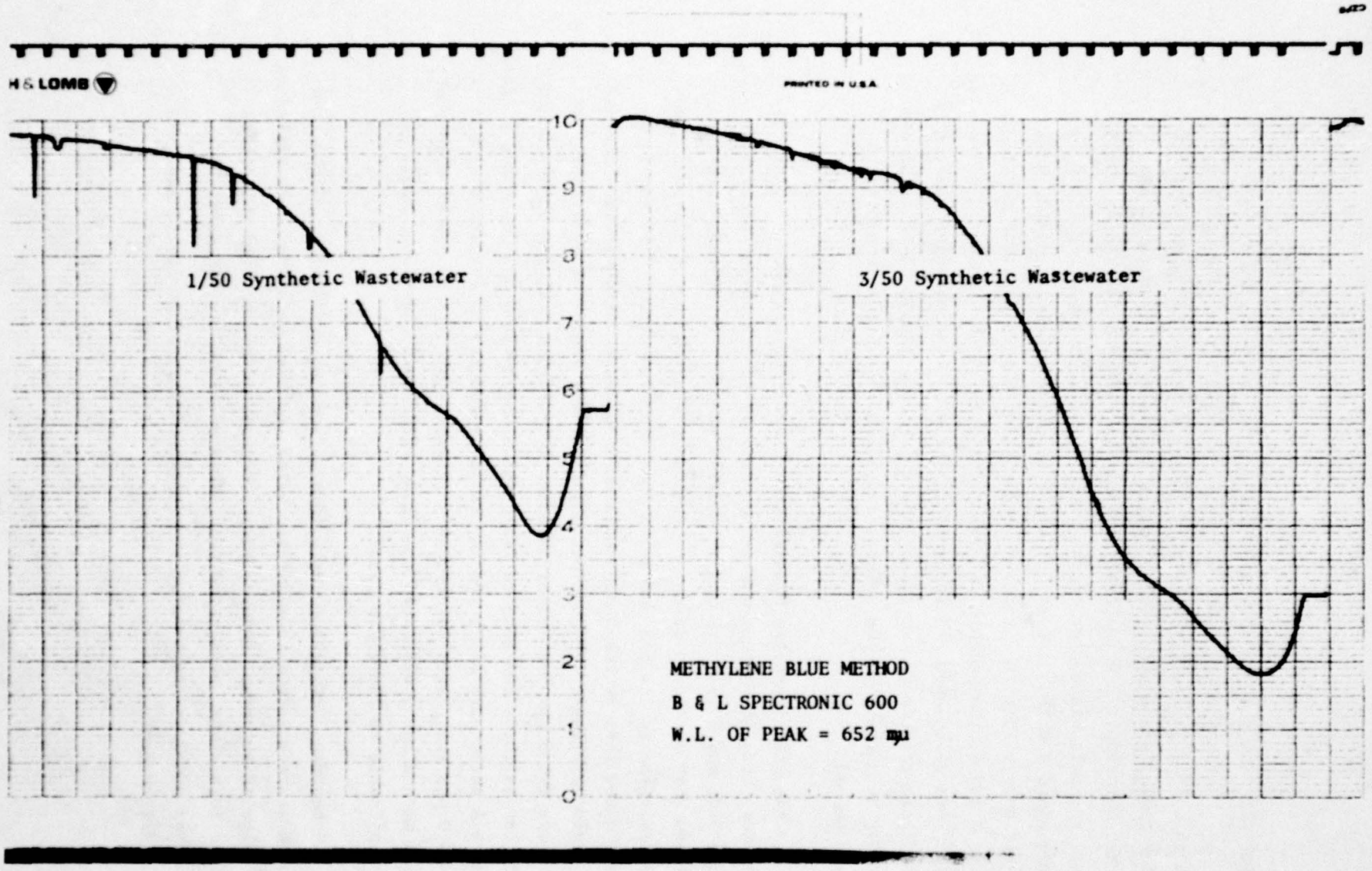


FIGURE 12 ANALYZING DETERGENT CONTENT OF SYNTHETIC WASTEWATER WITH METHYLENE BLUE METHOD

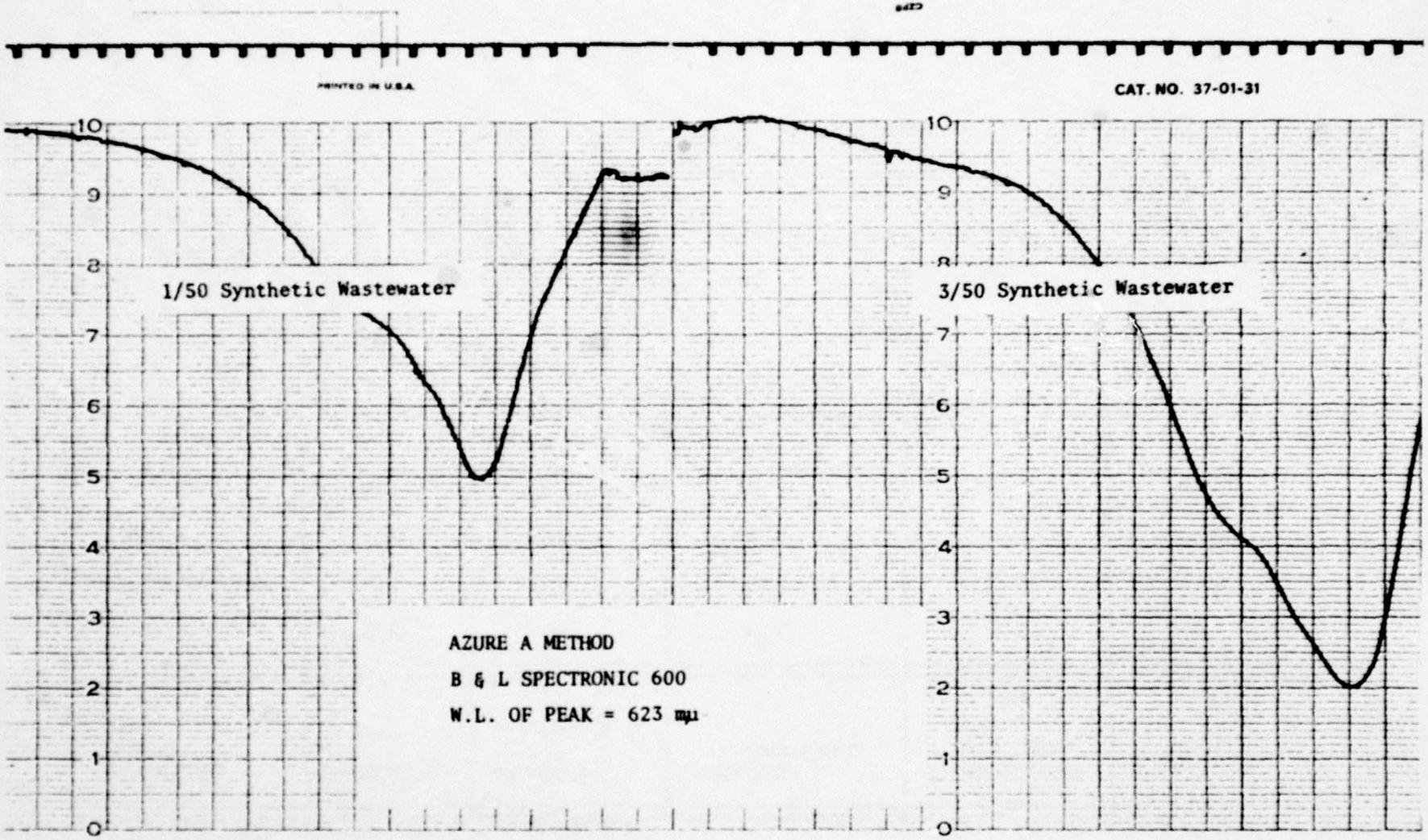


FIGURE 13 ANALYZING DETERGENT CONTENT OF SYNTHETIC WASTEWATER WITH AZURE A METHOD

TABLE 2

ANALYZING LAS CONTENT OF SYNTHETIC WASTEWATER
WITH BAUSCH & LOMB SPECTORNIC 600

ANALYTICAL METHOD USED	WAVELENGTH mμ	DILUTION OF WASTEWATER	PERCENT TRANSMITTANCE	LAS CONTENT OF DILUTED SAMPLE ppm	LAS CONTENT OF WASTEWATER ppm
Methylene Blue	652	1/50	37.5	0.97	48.5
Methylene Blue	652	3/50	18.0	2.25	37.5
Azure A	623	1/50	50.0	0.90	45.0
Azure A	623	3/50	20.0	2.55	42.5

The same synthetic wastewater was also analyzed for its LAS content following the procedures outlined in Sections 3.5 and 4.5, and its samples were compared with the preprepared bottle standards (Figures not shown) having eight LAS concentrations: 0, 0.1, 0.5, 1.0, 1.5, 2.0, 3.0, and 6.0 ppm. An 1:50 diluted wastewater sample, treated by either methylene blue method or azure A method, was observed to be close to but slightly lighter than the 1-ppm bottle standard. Assuming the 1:50 diluted wastewater sample contains 0.9 ppm LAS, the detergent content of synthetic wastewater sample is 45 ppm (Note: 50 X 0.9 = 45), which is very close to the LAS values measured by a spectrophotometer and a filter photometer.

In summation, the applicability of two improved colorimetric methods, as well as the recommended field test kits, to the analysis of anionic nonsoapy detergents in aqueous solution was demonstrated to be positive and promising. Either the improved methylene blue method or the improved azure A method is highly recommended for field use for monitoring the wastewater's LAS concentration and controlling the waste treatment process. However, the improved azure A method is better than the improved methylene blue method.

6.3 Limitations, Interferences and Remedies

The basic problem with the colorimetric methods is that many naturally occurring substances also form extractable salts with dyes such as methylene blue or azure A. The colorimetric methods, although convenient, may show erroneous results. A chemist or a wastewater treatment operator must understand the limitations of the improved methylene blue method (Section 3.0) and the improved azure A method (Section 4.0) when he interprets the detergent data.

When the improved methylene blue method (Section 3.0) is used, possible interferences will be similar to those of the standard methylene blue method (Ref. 5). Both organic and inorganic compounds interfere with the measurement of LAS or ABS. Organic sulfates, sulfonates, carboxylates, phosphates, and phenols, which complex methylene blue, and inorganic cyanates,

chlorides, nitrates, and thiocyanates, which form ion pairs with methylene blue, are among the positive interferences. Organic materials, especially amines which compete with the methylene blue in the reaction, cause low results. Generally positive errors are much more common than negative errors when determining anionics in water.

The possible interferences of the improved azure A method (Section 4.0) are not completely known so far. Since the molecular structure of azure A (shown in Figure 4) is similar to that of methylene blue (shown in Figure 1), 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 in Section 6.2 that neither of the two improved methods (Sections 3.0 and 4.0) can be used for quantitative analysis of soaps, nonionic detergents and cationic detergents. So far there is no convenient analytical method which can quantitatively measure soap or nonionic detergents in the field. The cationic detergents, however, can be measured in the field by the Calspan developed two-phase titration method (Refs. 9 and 10).

The presence of chloroform-extractable foreign compounds in a water sample will cause positive interference for both improved colorimetric methods. If the concentration of chloroform-extractable foreign compounds, such as oil and grease, is lower than 45 ppm, using a buffer solution treated chloroform (prepared according to Note A in Section 3.4 or Note A in Section 4.4) 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 ppm, the remedy for the detergent analysis by one of the improved methods will be the pre-extraction of those chloroform soluble compounds from the sample. It was observed during this research that methylene blue, azure A, LAS and ABS individually are all water

soluble, but not chloroform soluble. Only when the dye (either methylene blue or azure A) complexes with the detergent (either LAS or ABS), does the dye-detergent complex become chloroform soluble. In other words, a plain chloroform extraction (without adding any dye or buffer for the detergent 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 detergent content by one of the improved colorimetric methods (Sections 3.0 and 4.0). The pure chloroform can serve as the blank for instrument calibration, if necessary.

7.0 SUMMARY, CONCLUSIONS AND RECOMMENDATIONS

a. Various methods for the analysis of anionic surfactants in aqueous solution were reviewed, evaluated, and/or assessed in Section 2.0. None of the surveyed methods can be easily and rapidly used in the field by military personnel with limited chemistry training.

b. The standard methylene blue method described in the Standard Methods for the Examination of Water and Wastewater, 13th Edition, by APHA, AWWA, and WOCF (Ref. 5), was greatly simplified and improved for the field use by military personnel. Its principle, required reagents, required apparatus, and analytical procedures are described fully in Section 3.0. The measured surfactant(s) in water or wastewater can be reported to be mg/l LAS (i.e., linear alkylate sulfonate) or mg/l MBAS (i.e., methylene blue active surfactant).

c. The Azure A method, initially developed by Steveninck and Riemersma in 1966 (Ref. 17), was also significantly improved and simplified for the field use. Its principle, required reagents, required apparatus, and analytical procedures are introduced in Section 4.0 in detail. The surfactants measured by azure A method can be reported to be either mg/l LAS or mg/l AAAS (i.e., azure A active surfactant).

d. Two types of field test kits for analyzing anionic nonsoapy detergents were developed under this program. Section 5.1 describes the field test kits which are based on the use of a portable photometer or spectrophotometer. Section 5.2 describes the kits involving the use of a color comparison device or chart.

e. The applicabilities of the improved methylene blue method, the improved azure A method and the related field test kits to the measurement of detergent(s) in aqueous solutions were evaluated. Both improved methods (Sections 3.0 and 4.0), as well as the test kits (Section 5.0), can be used by military personnel with limited training in analytical chemistry for measuring anionic nonsoapy snythetic detergents. Evaluation data are presented in Section 6.0.

f. Compared to the standard methylene blue method (Ref. 5), analyzing anionic surfactant by either the improved methylene blue method (Section 3.0) or the improved azure A method (Section 4.0) will require less time and less amount of reagents and apparatus for each test. With the improved methods, the interferences caused by the chloroform-extractable pollutants and inorganic salts can also be greatly reduced.

g. If a filter photometer (such as Delta Model 260 Photometer) is to be used for anionic surfactant analysis by one of improved colorimetric methods, an appropriate filter selector for high LAS range (such as Figure 8-b) can be useful for the analysis of a raw wastewater sample; while another filter selector for low LAS range (such as Figure 8-a) can be particularly useful for the analysis of a treated waste effluent or a water sample with low LAS content.

h. The limitations of methylene blue method and azure A method were also investigated. It was found that neither of the two methods can be used for quantitative analysis of soap, nonionic detergent and cationic detergent. Other limitations and possible remedies are described in Section 6.3.

i. The improved methylene blue method is much simpler than the standard methylene blue method (Ref. 5) and thus is recommended for use analyzing the surfactant content of raw and treated wastewater if the detergent (or surfactant) data have to be reported as mg/l MBAS (i.e., methylene blue active surfactant).

j. The improved azure A method was found to be superior to the improved methylene blue method for the following reasons: (1) the azure A method provides sharper color contrast due to its dye-detergent 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 LAS detecting range is broader; (5) there is a smaller deviation in analytical data; and (6) the dye reagent is more stable under light exposure.

k. If it is allowable to report the detergent content of an aqueous sample as mg/l LAS or mg/l AAAS (i.e., azure A active surfactant), the improved azure A method is highly recommended to be used for detergent analysis in the field.

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Mr. John G. Fisher, Engineering Assistant
Mr. Raymond N. King, Chemical Technician
Mr. Kurt W. Simmons, Laboratory Technician

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APPENDIX I

ANALYSIS OF ANIONIC SURFACTANT BY CRYSTAL VIOLET METHOD

(Ref. 16)

I.1. Reagent

a. Sulfate buffer solution: Hach Cat. No. 452-11

b. Toluene, ACS: Hach Cat. No. 684-11

c. Detergents test powder pillows: Hach Cat. No. 1008-99

I.2. Apparatus

a. Graduated cylinder: 50 ml

b. Graduated cylinder: 500 ml

c. Pipet: 10 ml

d. Separatory funnel: 500 ml

e. Support stand: 5" X 8"

f. Support ring: 4 inch

g. Spectrophotometer: Hach DR/2

Spectrophotometer (either Carrying Case Model or Laboratory Model).

I.3. Analytical Procedures of Crystal Violet Method

The following procedures are outlined in conjunction with the use of Hach DR/2 Spectrophotometer (Ref.16).

a. Take a water sample by filling a clean 500-ml graduated cylinder to the 300-ml mark. Pour the sample into a clean 500-ml separatory funnel.

b. Add 10 ml of Sulfate Buffer Solution. Stopper the separatory funnel and shake for five minutes.

c. Add the contents of one Detergents Test Powder Pillow. Stopper the separatory funnel and shake for five minutes.

d. Add 30 ml of Toluene to the separatory funnel. Stopper the funnel and shake vigorously for 1 minute.

e. Allow the separatory funnel to stand undisturbed for 15 minutes. The Toluene will separate from the water and float. The Toluene layer will be blue in color if detergents are present. After 15 minutes, remove the stopper, drain off the water and discard. See Note A.

f. Drain the Toluene into a clean dry sample cell. Allow at least 20 minutes but not more than 30 minutes from the addition of the Toluene for the color to fully develop and proceed with Step g.

g. Fill a clean sample cell with 25 ml of Toluene and place it in the cell holder. Insert the Detergents (Crystal Vilet Method) Meter Scale in the meter and adjust the Wavelength Dial to 605 mμ. Adjust the LIGHT CONTROL for a meter reading of zero mg/l.

h. Place the prepared sample in the cell holder and read the mg/l detergents (as LAS). See Notes B and C.

NOTES

A. Excessive agitation may cause an emulsion to form, requiring a longer time for phase separation. For these samples, remove most of the water layer and gently agitate the separatory funnel with a clean inert object in the funnel such as a Teflon coated magnetic stirring bar. Drain the water layer off, then drain the Toluene layer through a filtering thumble containing dry absorbent cotton and into a clean, dry sample cell. Proceed with Step g.

B. Perchlorate and periodate ions will interfere. High concentrations of chloride, such as those levels found in seawater and brines, will cause low results.

C. Acetone is a suitable cleaning agent for removing Toluene from glassware.

APPENDIX II

ANALYSIS OF ANIONIC SURFACTANT BY METHYL GREEN METHOD

(Ref. 15)

II.1 Reagent

a. Sulfate buffer solution: Hach Cat. No. 452

b. Methyl green powder pillows: Hach Cat. No. 1008

c. Toluene, reagent grade: Hach Cat. No. 684

II.2 Apparatus

a. Separatory funnel: 500 ml

b. Clippers for opening pillows

c. Graduated cylinder: 500 ml

d. Graduated cylinder: 50 ml

e. Serological pipette: 10 ml

f. Support stand: 5" X 8"

g. Support ring: 4 inch

h. Colorimeter: Hach AC-DR (or DC-DR), Cat. No. 1104

i. Detergent Color Disc: Hach Cat. No. 2221-00

II.3 Analytical Procedures of Methyl Green Method

The following procedures are outlined for use with the Hach AC-DR (or DC-DR) Colorimeter (Ref. 15).

a. Take a water sample by filling a 500 ml graduated cylinder to the 300 ml mark. Pour the water sample into a clean 500 ml separatory funnel.

b. Add 10 ml of Sulfate Buffer Solution. Stopper the separatory funnel and shake for 5 seconds.

c. Add the contents of one Methyl Green Powder Pillow. Stopper the separatory funnel and shake to dissolve.

d. Add 30 ml of Toluene to the separatory funnel and shake to dissolve. Toluene will not mix with the water but will float. Stopper the funnel and shake vigorously for 1 minute.

e. Allow to stand undisturbed for 15 minutes after shaking. The Toluene will separate from the water and float. If detergents are present, the Toluene layer will be blue in color. After 15 minutes, remove the stopper, drain off the water and discard.

f. Drain the Toluene into a clean and dry colorimeter bottle and allow to stand for 20 minutes.

g. Fill a colorimeter bottle with clear water and place it in the light cell. Insert the Detergents Meter Scale in the meter and use the 4015 Color Filter. Adjust the light control for a meter reading of zero ppm.

h. Place the sample of Toluene in the light cell and read as ppm anionic detergents.

NOTE

A suitable agent for removing Toluene from glassware is acetone.

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13. ABSTRACT

Various methods for the analysis of surfactants in aqueous solution were reviewed, evaluated, and/or assessed. Emphasis was placed on the development of field test kits based on two improved colorimetric methods involving the use of methylene blue and Azure A.

The simplified and improved Methylene Blue Method and Azure A Method require only 5 or 6 ml of aqueous reagent and 25 ml of chloroform for analyzing one sample. The principles, analytical procedures and limitations of the two methods are described in detail.

A field test kit based on the use of a portable spectrophotometer (or photometer), and a field test kit based on the use of color comparison device(s) are proposed for use by military personnel with limited training in chemistry.

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