METHODS OF ANALYSIS BY THE U.S. GEOLOGICAL SURVEY NATIONAL WATER QUALITY LABORATORY-- DETERMINATION OF METHYLENE BLUE ACTIVE SUBSTANCES BY SPECTROPHOTOMETRY

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CONVERSION FACTORS, ABBREVIATED WATER-QUALITY UNITS, AND ADDITIONAL ABBREVIATIONS AND SYMBOLS

Multiply	*By*	*To obtain*
centimeter (cm)	3.94×10^{-1}	inch
gram (g)	3.53×10^{-2}	ounce
liter (L)	2.64×10^{-1}	gallon
milligram (mg)	3.53×10^{-5}	ounce
milliliter (mL)	2.64×10^{-4}	gallon
nanometer (nm)	3.94×10^{-8}	inch

Degree Celsius (^{o}C) may be converted to degree Fahrenheit (^{o}F) by using the following equation:

$$^{o}F = 9/5(^{o}C) + 32.$$

Abbreviated water-quality units used in this report:

mg/L	milligram per Liter
M	molarity
N	normality (equivalents per liter)

Other abbreviations used in this report:

ASTM	American Society for Testing and Materials
CCV	continuing calibration verification
HPLC	high-performance liquid chromatography
LAS	linear alkylbenzene sulfonate
MBAS	methylene blue active substances
MDL	method detection limit
NWQL	National Water Quality Laboratory
USGS	U.S. Geological Survey

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By MARK R. BURKHARDT, PETE J. CINOTTO, GALEN W. FRAHM, MARK T. WOODWORTH AND JEFFREY W. PRITT

ABSTRACT

A method for the determination of methylene blue active substances in whole-water samples by liquid-liquid extraction and spectrophotometric detection is described. Sulfate and sulfonate-based surfactants are reacted with methylene blue to form a blue-colored complex. The complex is extracted into chloroform, back-washed with an acidified phosphate-based buffer solution, and measured against external standards with a probe spectrophotometer. The method detection limit for routine analysis is 0.02 milligram per liter. The precision is ±10 percent relative standard deviation. The positive bias from nitrate and chloride in U.S. Geological Survey method O-3111-83 for methylene blue active substances is minimized by adding a back-washing step.

INTRODUCTION

The National Water Quality Laboratory (NWQL) averages about 1,000 methylene blue active substance (MBAS) determinations a year in surface- and ground-water samples. Since the early 1970's, MBAS was determined by using the method reported by Wershaw and others (1987, p. 57). After a review in 1993, it was determined that this method was susceptible to artificially high results from the interfering anions nitrate and chloride. The MBAS method in Wershaw and others (1987, p. 57) differs from the MBAS method published by the American Public Health Association (1992, p. 5-36 to 5-38) in that it does not contain a back-wash step that removes interfering quantities of nitrate and chloride from the chloroform extraction solvent. The method described herein uses a back-wash step and so avoids the positive interferences caused by nitrate and chloride.

This report describes a method for determining MBAS in surface-, ground-, and drinking-water samples. It includes sampling and preservation requirements as well as the reporting of final results. Precision and accuracy data also are presented. This method supplements other methods of the U.S. Geological Survey (USGS) for determining organic substances in water and fluvial sediments (Wershaw and others, 1987; Fishman, 1993). The method was implemented in the NWQL on August 30, 1993.

In addition to the precision and accuracy data, detection limit calculation, and method procedure, this report includes information that will allow MBAS data produced at the NWQL from 1970 to August 29, 1993, to be back-corrected. The corrections can only be made if nitrate and chloride data are available from the same sampling event that produced the MBAS data.

ANALYTICAL METHOD
Organic Compounds and Parameter Codes: Methylene blue active substances, whole water recoverable, spectrophotometry
O-3128-95 (mg/L as MBAS): 38260

1. Application

This method is used to determine MBAS in drinking-, surface-, and ground-water samples. The analytical range is from 0.02 to 0.50 mg/L of MBAS. Samples containing concentrations of MBAS greater than 0.50 mg/L need to be diluted prior to analysis.

2. Summary of method

Sulfate and sulfonate-based anionic surfactants are reacted with methylene blue to form a blue-colored complex. The complex is extracted into chloroform, back-washed with an acidified phosphate-based buffer solution, and measured against external standards with a probe spectrophotometer. The method detection limit for routine analysis is 0.02 mg/L. The average precision is $\pm$10 percent relative standard deviation. This method is similar in substance to the MBAS method published by the American Public Health Association (1992).

3. Interferences

This method was implemented following a customer-requested audit of the MBAS method reported by Wershaw and others (1987, p. 57). The NWQL used the customer-provided data, experimental data, and information from the American Public Health Association (1992, p. 5-36 to 5-38) to conclude that nitrate and chloride interfere with the MBAS determination described by Wershaw and others (1987, p. 57). Other compounds interfere with the determination of MBAS (American Public Health Association, 1992) but are assumed to interfere to a lesser degree on the basis of their reactivity and low environmental concentration (American Public Health Association, 1992).

4. Instrumentation

4.1 *Spectrophotometer, probe-based* (Brinkmann PC 900 Colorimeter or equivalent) to measure the absorbance of the chloroform extract. Modules in this system include a 650-nm interference filter, fiber-optic probe and cables, and the main body housing the appropriate electronics.

4.2 Operating characteristics for the spectrophotometer are as follows:

Analytical wavelength----------	650 nm
Flow cell path length----------	2 cm
Function setting----------	ABS
Decimal point setting----------	3

5. Reagents

5.1 *Phenolphthalein indicator solution*: Add 5.0 g of phenolthalein to 500 mL of reagent-grade ethyl alcohol. Dropwise, add 1.0 *N* sodium hydroxide solution until a faint pink color is observed.

5.2 *Sodium hydroxide solution, 1 N*: Dissolve 40.0 g of sodium hydroxide in approximately 750 mL of deionized water in a 1,000-mL volumetric flask. After the sodium hydroxide has dissolved and cooled, dilute to 1,000 mL with deionized water.

5.3 *Sulfuric acid solution, 5 N*: Add 138 mL of concentrated sulfuric acid (18 *M*) to approximately 500 mL deionized water in a 1,000-mL volumetric flask. Swirl to mix, and dilute to 1,000 mL with deionized water.

CAUTION: Heat is generated when concentrated sulfuric acid is mixed with water. Wear protective eyeglasses, gloves, and clothing.

5.4 *Chloroform*: Use reagent-grade chloroform for all of the MBAS extractions.

CAUTION: Chloroform is a suspected carcinogen and is toxic. Take appropriate precautions to minimize inhalation and skin exposure. Work in a well-ventilated fume hood.

5.5 *Methylene blue reagent*: Dissolve 350 mg methylene blue in 500 mL of deionized water in a 1,000-mL volumetric flask. Add 20 mL of concentrated sulfuric acid and 50 g sodium phosphate dibasic. Shake well until sodium phosphate is dissolved. Dilute to 1,000 mL with deionized water.

CAUTION: Heat is generated when concentrated sulfuric acid is mixed with water. Wear protective eyeglasses, gloves, and clothing.

5.6 *Back-wash solution*: Add 20 mL concentrated sulfuric acid to 500 mL of deionized water in a 1,000-mL volumetric flask. Add 50 g sodium phosphate dibasic, and shake until sodium phosphate is dissolved. Dilute to 1,000 mL with deionized water.

CAUTION: Heat is generated when concentrated sulfuric acid is mixed with water. Wear protective eyeglasses, gloves, and clothing.

5.7 *Deionized water:* Use MBAS-free deionized water (ASTM Type II) to make all reagents.

6. Standards

6.1 *MBAS stock solution (1,000 mg/L)*: Obtain a linear alkylbenzene sulfonate (LAS) reference standard from the U.S. Environmental Protection Agency, Environmental Monitoring Systems Laboratory, Cincinnati, Ohio 45268. Weigh a quantity of the reference material equal to 1.0 g LAS on a 100-percent active basis. To obtain the needed amount, divide 1.0 g by the percent active stated on the ampule. For example, if the LAS solution stated 7.0 percent active, then

$$\frac{1.0 \times 100}{7.0} = 14.3 \text{ g of active LAS solution to be weighed and diluted to 1 L with deionized water.}$$

6.2 *MBAS intermediate standard solution (5.0 mg/L)*: Pipet 0.5 mL of MBAS stock solution into a 100-mL volumetric flask. Dilute to the mark with MBAS-free deionized water. Prepare the MBAS intermediate standard solution each day environmental samples are to be analyzed for MBAS.

6.3 *MBAS working standard solutions*: Add 40.0, 20.0, 10.0, 2.0, 1.0, and 0 mL of the MBAS intermediate standard solution to 400-mL volumetric flasks and dilute to the mark with deionized water. Mix the solutions gently to minimize bubbles in the volumetric flasks. These standards are equivalent to 0.5, 0.25, 0.05, 0.025, 0.0125, and 0 mg/L MBAS.

6.4 *Continuing calibration verification (CCV) solution*: Obtain a second LAS ampule from the U.S. Environmental Protection Agency with a lot number that does not match the lot number from the stock MBAS solution ampule (paragraph 6.1). Prepare the CCV by repeating the procedure in paragraph 6.1 and then prepare a 0.050-mg/L standard following the directions in paragraphs 6.2 and 6.3. The CCV is used as a third-party check on the MBAS working standard solutions as well as on the analyst's technique. Analyze the CCV solution every 10 samples to verify that the method is in control.

7. Sample preparation

Raw, unfiltered ground- and surface-water samples are collected in 500-mL polyethylene containers. MBAS samples are stored at 2 to 4°C after sampling until analysis.

8. Instrument performance

Evaluate the spectrophotometer each day throughout the analytical sequence by using the MBAS working standard solutions and by using blanks, matrix spikes, duplicates, and CCVs. The performance criteria for the calibration curve is discussed in section 9, and the performance checks are discussed in the quality assurance section.

9. Calibration

Use a first-order polynomial ($y = mx + b$, where y = absorbance and x = MBAS concentration, in milligrams per liter) least-squares curve-fitting algorithm to evaluate the calibration points. The correlation coefficient of the calibration curve must be greater than or equal to 0.995. A typical calibration curve for MBAS working standard solutions, in the concentration range from 0 to 0.50 mg/L, is shown in figure 1.

10. Procedure and data evaluation

10.1 Allow the spectrophotometer to warm up for at least 30 minutes. Place the fiber-optic probe into reagent chloroform, and, periodically throughout the 30 minutes, reset the autozero function until there is no drift in the equipment zero reading. The spectrophotometer must be equipped with a 650-nm interference filter.

10.2 Set up in a rack 12 500-mL clean glass separatory funnels with Teflon stopcocks and stoppers. Transfer 400 mL of a deionized water blank and 400 mL of each working standard solution into individual separatory funnels.

10.3 Add two to three drops of phenolphthalein solution into each separatory funnel. Add 1 *N* sodium hydroxide solution to change the working standard solution to a light pink color. Usually this process requires two to four drops of the sodium hydroxide solution.

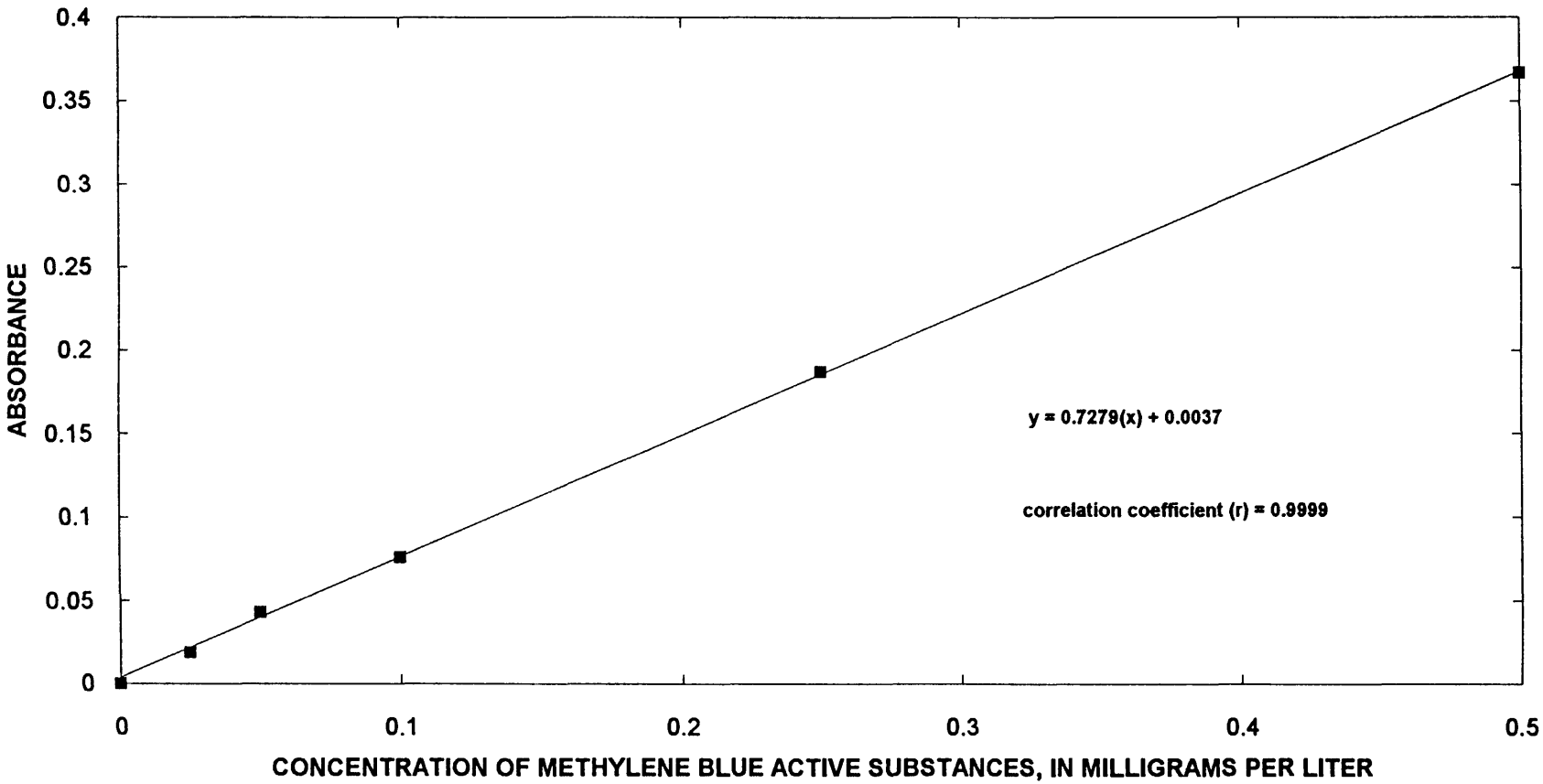

Figure 1.--Typical calibration curve for the determination of methylene blue active substances in whole-water samples using spectrophotometric method.

10.4 Add 5 *N* sulfuric acid solution dropwise to remove the pink color of the working standard solutions. The use of phenolphthalein and the acid-base pair will bring the pH of the working standard solutions to approximately 7.

10.5 Add 5 mL of methylene blue solution to each separatory funnel, cap the separatory funnel, and shake the mixture.

10.6 Add 15 mL of chloroform to each separatory funnel. Place the stopper on each separatory funnel and shake each funnel vigorously for 30 seconds. Allow the phases to separate. Drain the chloroform layer into a stoppered 250-mL flask. Repeat this step one additional time. There should be about 30 mL of chloroform in the stoppered 250-mL flask.

10.7 Dispose of the extracted water sample by placing it into an appropriate container and transporting it to the Safety Program holding area. A licensed waste disposal contractor disposes of the extracted water in an environmentally correct way. Transfer the chloroform from the stoppered flask to the drained separatory funnel. Add 25 mL of the back-wash solution. Shake the separatory funnel vigorously for 30 seconds. Allow the phases to separate.

10.8 Transfer 1.0 mL of the back-washed chloroform into a clean test tube. Add 4.0 mL of clean chloroform, place the probe into the chloroform mixture, and record the absorbance reading from the spectrophotometer.

10.9 Plot the absorbance readings of the working standard solution as a function of the known working standard solution concentrations. Use a first-order polynomial least-squares curve-fitting algorithm to evaluate the calibration curve. The correlation coefficient of the calibration curve must be greater than or equal to 0.995 for the analysis to continue. If the correlation coefficient is greater than or equal to 0.995, then perform steps 10.3 to 10.8 on 400 mL of each sample requiring MBAS determination.

11. Calculations

Determine MBAS in milligrams per liter by matching the corresponding absorbance reading to the appropriate concentration using the equation of the linear least-squares correlation line. Apply appropriate dilution factors to every sample that has been diluted.

12. Reporting of results

Report MBAS concentrations as follows: 0.02 mg/L and greater, two significant figures; less than 0.02 mg/L as < 0.02 mg/L.

13. Precision and bias

13.1 The precision was calculated using HPLC-grade reagent water as the sample matrix. Within-run precision ranged from 8 to 14 percent (see tables 2-5 later in this report). Between-day precision ranged from 11 to 13 percent (see tables 1 and 6 later in this report).

13.2 Between-day means are 92 and 97 percent for two concentrations. These means are based on two concentrations and 18 replicates of each (36 samples). The common matrix for these data was the HPLC-grade reagent water.

DISCUSSION OF RESULTS

A method detection limit (MDL) of 0.02 mg/L was produced using the protocol set forth by the U.S. Environmental Protection Agency (1992); the MDL is listed in table 1. The MDL data are based on the determination of MBAS in 18 replicates of HPLC-grade reagent water spiked at 0.05 mg/L of MBAS. The data were generated on two nonconsecutive days. Statistical details are listed in table 1. Notice that the calculated value for the MDL is 0.015 mg/L but has been rounded to 0.02 mg/L for use by NWQL.

Nine replicates of a ground-water sample taken from Arvada Well 14 were spiked with MBAS concentrations of 0.05 and 0.50 mg/L. The samples then were chilled for three days at 2°C. The MBAS concentration then was measured in each sample. The MBAS concentration in the native sample was measured to be <0.02 mg/L. The percent recovery, standard deviation, and relative standard deviation for these spiked samples are listed in tables 2 and 3.

Nine replicates of a surface-water sample taken from the South Platte River near Denver, Colorado, were spiked with MBAS concentrations of 0.055 and 0.50 mg/L. The samples then were chilled for two days at 2°C. The MBAS concentration then was measured in each sample. The MBAS concentration in the native sample was measured to be <0.02 mg/L. The percent recovery, standard deviation, and relative standard deviation for these spiked samples are listed in tables 4 and 5. HPLC-grade reagent-water samples were spiked with 0.05 and 0.50 mg/L of MBAS on two nonconsecutive days. The samples then were chilled for two days at 2°C. The MBAS concentration then was measured in each sample. The percent recovery, standard deviation, and relative standard deviation for these spiked samples are listed in tables 1 and 6.

The data from the surface-water, ground-water, and reagent-grade-water experiments show that the average percent recovery for MBAS using the method described is 98 percent with an average relative standard deviation of 11 percent. For 36 samples, about 4 hours is required to set up the glassware, extract with chloroform, perform the back-wash step, and read the absorbance. This time requirement can be influenced by glassware, waiting for emulsions to break, and dealing with potentially hazardous samples. Approximately 72 samples a day can be analyzed during an 8-hour shift, with sufficient clean glassware and two dedicated analysts.

Table 1.--*Calculated method detection limit (MDL) for methylene blue active substances by spectrophotometry*

[Measured concentrations pertain to 18 replicates of a 0.05-mg/L (milligram per liter) linear alkylbenzene sulfonate calibrant which was prepared in high-performance liquid chromatography grade reagent-water samples]

Replicate number	Measured concentration (mg/L)
1	0.053
2	.052
3	.053
4	.047
5	.049
6	.052
7	.038
8	.055
9	.041
10	.041
11	.045
12	.030
13	.047
14	.045
15	.041
16	.049
17	.047
18	.046

Average (mg/L)	= 0.046	Degrees of freedom	= 17
Standard deviation (mg/L)	= 0.006	*t* -value (99% confidence)	= 2.567
Number of points	= 18	MDL (mg/L)	= 0.015
Average percent recovery	= 92	Relative standard deviation (percent)	= 13

Table 2.--*Percent recovery, standard deviation, and relative standard deviation for ground-water samples from Arvada Well 14 spiked with methylene blue active substances for nine replicates of a 0.050-milligram-per-liter calibrant*

[Measured concentrations pertain to nine replicates of a 0.05-mg/L (milligram per liter) linear alkylbenzene sulfonate calibrant which was prepared in ground-water samples from Arvada Well 14]

Replicate number	Measured concentration (mg/L)
1	0.058
2	.055
3	.048
4	.042
5	.057
6	.053
7	.053
8	.041
9	.042

Average (mg/L)	=	0.050
Average percent recovery	=	100
Standard deviation (mg/L)	=	0.007
Relative standard deviation (percent)	=	14

Table 3.-- *Percent recovery, standard deviation, and relative standard deviation for ground-water samples from Arvada Well 14 spiked with methylene blue active substances for nine replicates of a 0.5-milligram-per-liter calibrant*

[Measured concentrations pertain to nine replicates of a 0.5-mg/L (milligram per liter) linear alkylbenzene sulfonate calibrant which was prepared in ground-water samples from Arvada Well 14]

Replicate number	Measured concentration (mg/L)
1	0.438
2	.486
3	.506
4	.555
5	.535
6	.498
7	.555
8	.576
9	.557

Average (mg/L)	=	0.523
Average percent recovery	=	105
Standard deviation (mg/L)	=	0.044
Relative standard deviation (percent)	=	8

Table 4.--*Percent recovery, standard deviation, and relative standard deviation for surface-water samples from the South Platte River near Denver, Colorado, spiked with methylene blue active substances for nine replicates of a 0.055-milligram-per-liter calibrant*

[Measured concentrations pertain to nine replicates of a 0.055-mg/L (milligram per liter) linear alkylbenzene sulfonate calibrant which was prepared in surface-water samples from South Platte River near Denver, Colorado]

Replicate number	Measured concentration (mg/L)
1	0.056
2	.051
3	.046
4	.053
5	.054
6	.061
7	.062
8	.058
9	.061

Average (mg/L)	=	0.056
Average percent recovery	=	98
Standard deviation (mg/L)	=	0.005
Relative standard deviation (percent)	=	9

Table 5.--*Percent recovery, standard deviation, and relative standard deviation for surface-water samples from the South Platte River near Denver, Colorado, spiked with methylene blue active substances for nine replicates of a 0.5-milligram-per-liter calibrant*

[Measured concentrations pertain to nine replicates of a 0.5-mg/L (milligram per liter) linear alkylbenzene sulfonate calibrant which was prepared in surface-water samples from South Platte River near Denver, Colorado]

Replicate number	Measured concentration (mg/L)
1	0.428
2	.414
3	.499
4	.533
5	.496
6	.521
7	.504
8	.516
9	.515

Average (mg/L)	=	0.492
Average percent recovery	=	98
Standard deviation (mg/L)	=	0.042
Relative standard deviation (percent)	=	8

Table 6.-- *Percent recovery, standard deviation, and relative standard deviation for reagent-water samples spiked with methylene blue active substances for 18 replicates of a 0.5-milligram-per-liter calibrant*

[Measured concentrations pertain to 18 replicates of a 0.5-mg/L (milligram per liter) linear alkylbenzene sulfonate calibrant which was prepared in high-performance liquid chromatography grade reagent-water samples]

Replicate number	Measured concentration (mg/L)
1	0.474
2	.472
3	.386
4	.434
5	.431
6	.445
7	.423
8	.459
9	.466
10	.560
11	.556
12	.466
13	.489
14	.549
15	.516
16	.569
17	.542
18	.517

Average (mg/L)	=	0.486
Average percent recovery	=	97
Standard deviation (mg/L)	=	0.054
Relative standard deviation (percent)	=	11

The correction equations for MBAS data produced from 1970 to August 29, 1993, at NWQL follow. The ability to correct this MBAS data is based on several factors, including:

(1) The nitrate-nitrite total concentration must be available for the sample to correct for nitrate-nitrite interference.

(2) Chloride concentrations must be available for the sample to correct for chloride interference.

(3) The correction factors were produced for nitrate concentrations ranging from 0 to 27 mg/L. This concentration range covers approximately 99 percent of the nitrate-nitrite data produced at the NWQL during 1989. The year 1989 was used to estimate the concentration range that would allow the largest percentage of MBAS data to be corrected using the minimal number of experiments.

(4) The correction factors were produced for chloride concentrations ranging from 0 to 340 mg/L. The concentration range covers 93 percent of the total chloride data produced at the NWQL during 1991.

(5) Both correction factors need to be applied to the data to minimize the error associated with the previous MBAS method.

(6) The new method detection limit is 0.02 mg/L. The old method detection limit was 0.01 mg/L. Correct the data from 1970 to August 29, 1993, for nitrate-nitrite and chloride and then apply the detection limit of 0.02 mg/L to the corrected data.

The correction equations were produced by analyzing 12 HPLC-grade water samples spiked with nitrate and chloride in May 1993 and 24 HPLC-grade water samples spiked with nitrate and chloride in September 1993, and by combining all of the data into two data sets (one for nitrate and one for chloride). The nitrate data in relation to MBAS data and the linear regression line used to determine the correction equation are shown in figure 2. The chloride data in relation to MBAS data and the linear regression line used to determine the correction equation are shown in figure 3.

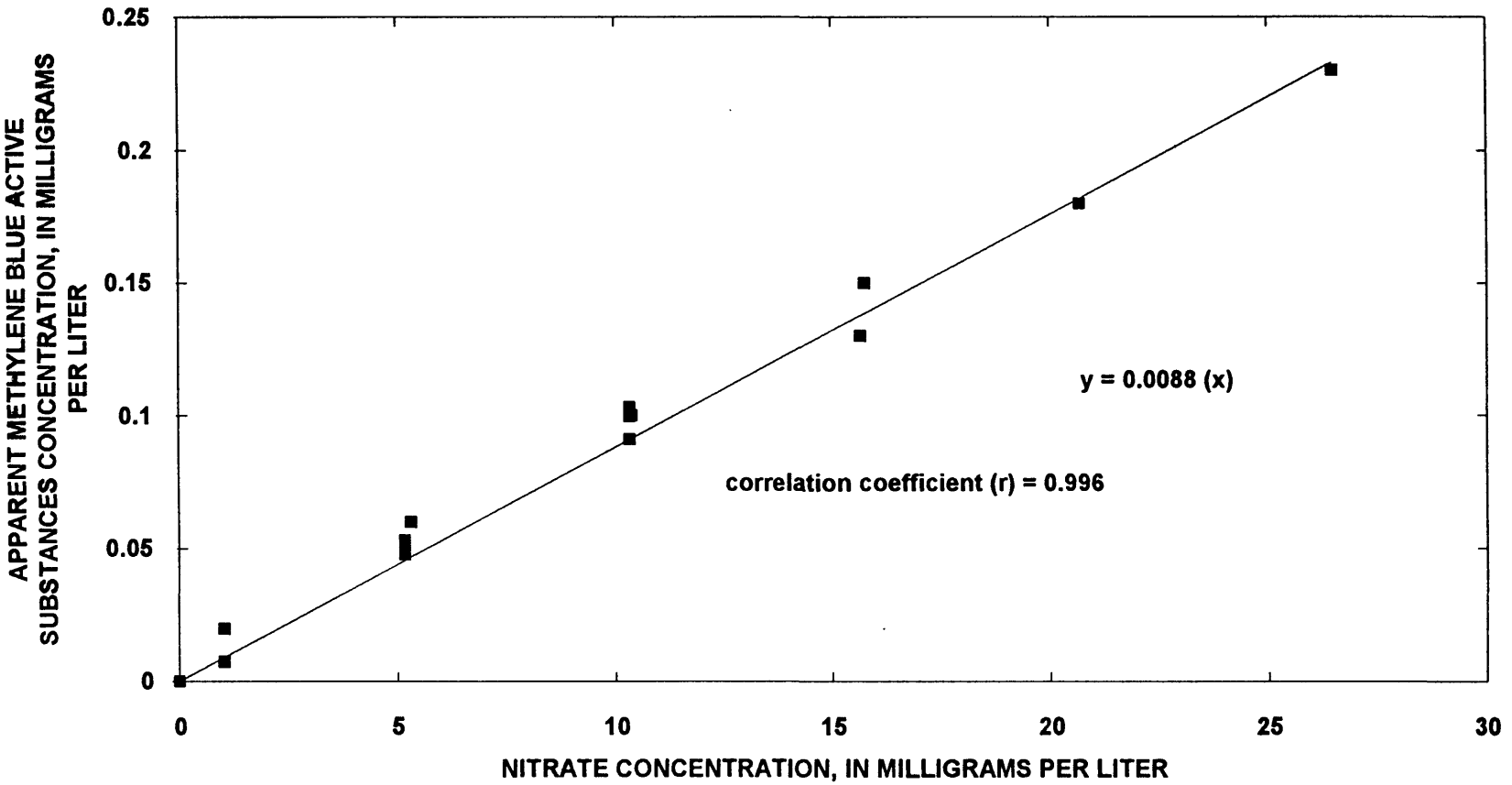

Figure 2.--Relations between concentrations of nitrate and apparent methylene blue active substances using method O-3111-83 (Wershaw and others, 1987, p. 57).

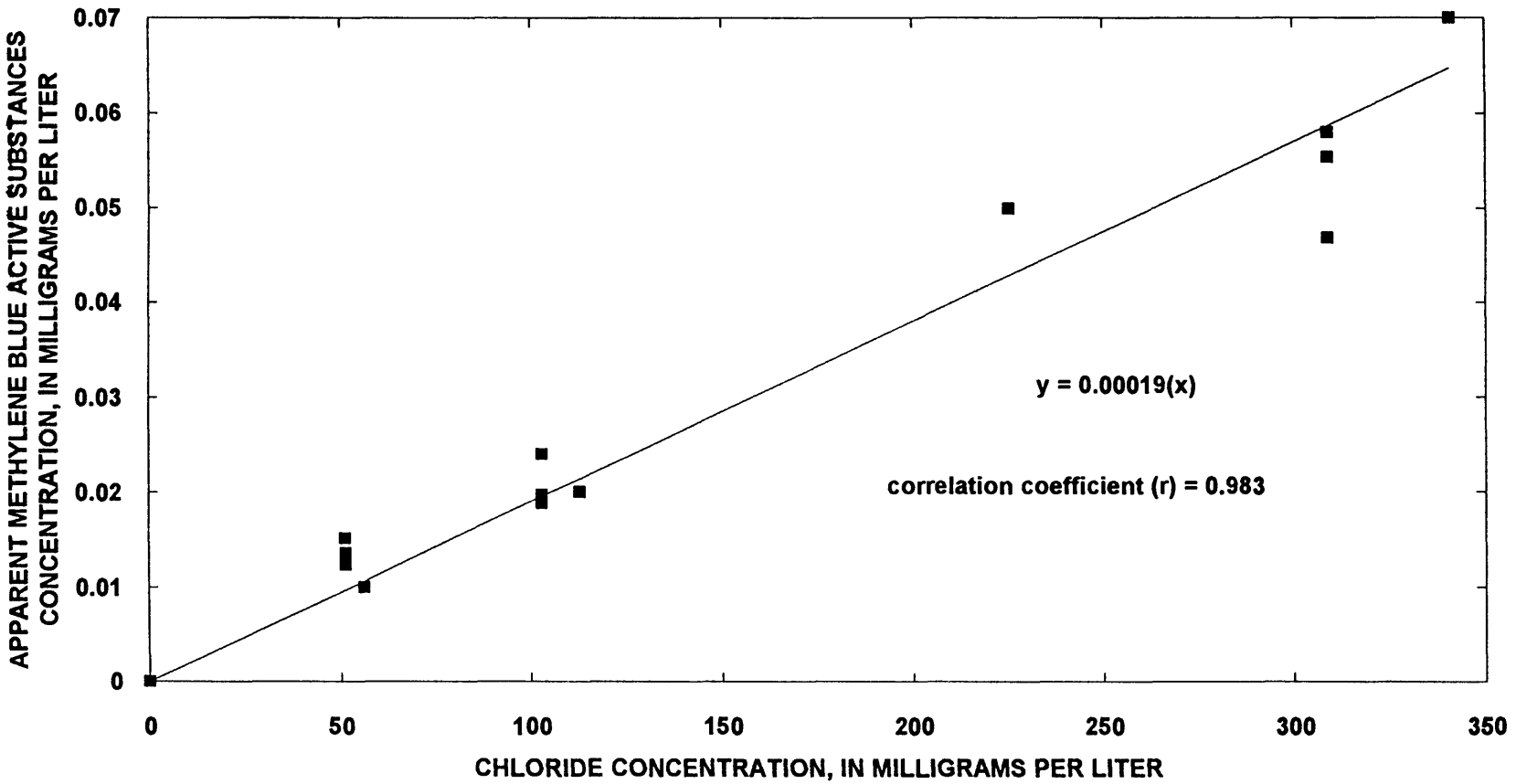

Figure 3.--Relations between concentrations of chloride and apparent methylene blue active substances using method O-3111-83 (Wershaw and others, 1987, p. 57).

Regression analyses were applied to the data using both the experimentally determined *y*-intercept (nitrate *y*-intercept = 0.0033, chloride *y*-intercept = 0.00015) and forcing the *y*-intercept to zero for various concentrations of nitrate and chloride. The regression analyses showed there was no significant difference between the data-correction equations using the experimentally determined *y*-intercept and the data-correction equations using the *y*-intercept forced through zero. In addition, the calculated intercepts are much smaller than the sensitivity of the method to detect and measure a small value different than zero. Therefore, the intercept coefficients are negligible for correcting the MBAS data and will not be used in the correction equations.

The nitrate-nitrite correction equation is

$$C = M - (0.0088)n$$

where C = corrected MBAS concentration, in milligrams per liter;
M = reported MBAS concentration, in milligrams per liter; and
n = total concentration of nitrate-nitrite, in milligrams per liter.

The chloride correction equation is

$$C = M - (0.00019)n$$

where C = corrected MBAS concentration, in milligrams per liter;
M = reported MBAS concentration, in milligrams per liter; and
n = total concentration of chloride, in milligrams per liter.

The correlation coefficients for the MBAS correction equations are
Nitrate-nitrite = 0.992
and Chloride = 0.967.

Examples of how to correct MBAS data from 1970 to August 29, 1993, are included.

Example 1. The data for a ground-water sample for MBAS are as follows:

MBAS	0.079 mg/L
Nitrate-nitrite	10 mg/L
Chloride	10 mg/L.

Applying the correction factor for nitrate-nitrite yields
$C = 0.079 - [(0.0088)10]$
$C = -0.009$ mg/L or <0.02 mg/L.

No chloride correction required.

Example 2. The data for a ground-water sample for MBAS are as follows:

MBAS	0.079 mg/L
Nitrate-nitrite	1 mg/L
Chloride	50 mg/L.

Applying the correction factor for nitrate-nitrite yields
$C = 0.079 - [(0.0088)1]$
$C = 0.079 - (0.0088)$
$C = 0.070$ mg/L.

Applying the chloride correction factor yields

$C = 0.070 - [(0.00019)50]$

$C = 0.070 - (0.0095)$

$C = 0.0607$ or 0.061 mg/L is the corrected value for MBAS.

QUALITY ASSURANCE

Every quality-control sample allows the monitoring of a specific part of the method to minimize error and ensure accuracy. The function of CCVs, blanks, duplicates, and matrix spikes, and how they are used to monitor the accuracy of the MBAS method, are explained as follows.

The use of a continuing calibration verification (CCV, paragraph 6.4) directly following the working standard solutions verifies the concentration and preparation of the calibration curve. The use of the CCVs every 10 samples verifies that the method is performing within the expected recovery and accuracy ranges throughout the analytical sequence. The percent recovery from the analysis of the first CCV needs to be maintained in a control chart to monitor long-term trends. The acceptance criteria for a CCV is $\pm$15 percent from the known MBAS concentration.

Use blanks every 10 samples to verify that the method is not contaminated. Contamination can come from the glassware, reagents, and poor technique. Blanks are MBAS-free deionized-water samples. The acceptance criteria for a blank is <0.02 mg/L MBAS.

Analyze duplicate samples every 10 samples to monitor the precision from sample to sample. Arbitrarily pick samples within the 10 and analyze a duplicate. If there is not enough sample volume, analyze two CCVs sequentially. The acceptance criterion for duplicates is $\pm$15 percent from the average of the two responses. Take care to apply the acceptance criterion when using samples containing low levels of MBAS. Matrix spikes are environmental samples that have a known concentration of MBAS added to the sample. Use matrix spikes to monitor the influence that the sample matrix may or may not have for the method to detect MBAS. Determine the concentration of MBAS in the environmental sample so that this concentration can be subtracted from the result of the matrix spike. If the concentration of MBAS is not known, the perceived spike recovery will be artificially large. Analyze matrix-spike samples every 20 samples (if samples are sufficient) or upon client request. The acceptance criterion for a matrix spike is $\pm$15 percent of the spiked quantity. If the matrix interferes with the analysis and if all of the other quality-check samples are acceptable, dilute and analyze the sample again. Convey these results to the customer, as well as the results of the original matrix spike, with an explanation of what was done and how to interpret the information.

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