

**Federal Water Pollution Control Administration**  
**Division of Research**  
**Analytical Quality Control Branch**

**FWPCA OFFICIAL INTERIM METHODS**  
**For Chemical Analysis of Surface Waters**  
**September 1968**

Federal Water Pollution Control Administration

Analytical Quality Control Branch

OFFICIAL INTERIM METHODS

for

Analyses of Surface Water Samples

Storet Parameter No. 00435

Parameter : Acidity, Total (mg/l as  $\text{CaCO}_3$ )

Method : Volumetric, with electrometric endpoint.

Reference : 1. Standard Methods for the Examination of Water and  
Wastewater, 12th ed., APHA, Inc., N.Y., 1965,  
46-47.  
2. ASTM 1968 preprint, D1067, pp. 38-41.

Modifications: None

Date: September 1968

Federal Water Pollution Control Administration

Analytical Quality Control Branch

OFFICIAL INTERIM METHODS

for

Analyses of Surface Water Samples

Storet Parameter No. 00410

Parameter : Alkalinity, Total (mg/l as  $\text{CaCO}_3$ )

Method : Volumetric, with electrometric endpoint.

Reference : 1. Standard Methods for the Examination of Water and  
Wastewater, 12th ed., APHA, Inc., N.Y., 1965,  
48-52.

2. ASTM 1968 preprint, D1067, pp. 38-41.

Modifications: None

Date: September 1968

Federal Water Pollution Control Administration

Analytical Quality Control Branch

OFFICIAL INTERIM METHODS

for

Analyses of Surface Water Samples

Storet Parameter No. to be assigned

Parameter : Aluminum, Dissolved ( $\mu\text{g/l}$ )

Method : Filtration through 0.45  $\mu$  membrane filter.  
Measurement by atomic absorption.

Reference : Method is specific to the particular instrument.  
General procedure is being selected.

Modifications: Use of 0.45  $\mu$  membrane filter only.

Date: September 1968

Federal Water Pollution Control Administration

Analytical Quality Control Branch

OFFICIAL INTERIM METHODS

for

Analyses of Surface Water Samples

Storet Parameter No. 01105

Parameter : Aluminum, Total ( $\mu\text{g/l}$ )

Method : Atomic absorption.

Reference : Method is specific to the particular instrument.  
General procedure is being selected.

Modifications: None

Date: September 1968

Federal Water Pollution Control Administration

Analytical Quality Control Branch

OFFICIAL INTERIM METHODS

for

Analyses of Surface Water Samples

Storet Parameter No. to be assigned

Parameter : Arsenic, Dissolved ( $\mu\text{g/l}$ )

Method : Filtration through 0.45  $\mu$  membrane filter.  
Measurement by silver diethyldithiocarbamate  
colorimetric method.

Reference : Standard Methods for the Examination of Water and  
Wastewater, 12th ed., APHA, Inc., N.Y., 1965,  
56-57.

Modifications: Filtration through 0.45  $\mu$  membrane filter only.

Date: September 1968

Federal Water Pollution Control Administration

Analytical Quality Control Branch

OFFICIAL INTERIM METHODS

for

Analyses of Surface Water Samples

Storet Parameter No. 01000

Parameter : Arsenic, Total, ( $\mu\text{g/l}$ )

Method : Measurement by silver diethyldithiocarbamate  
colorimetric method.

Reference : Standard Methods for the Examination of Water and  
Wastewater, 12th ed., APHA, Inc., N.Y., 1965,  
56-57.

Modifications: None

Date: September 1968

Federal Water Pollution Control Administration

Analytical Quality Control Branch

OFFICIAL INTERIM METHODS

for

Analyses of Surface Water Samples

Storet Parameter No. 00525

Parameter : Ash, Solids Dissolved (mg/l)

Method : Gravimetric, ignition at 600 C, modified.

Reference : Standard Methods for the Examination of Water and  
Wastewater, 12th ed., APHA, Inc., N.Y., 1965,  
247-248.

Modifications: Use of 0.45  $\mu$  membrane filter only, for solids  
separation.

Date: September 1968



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for

Analyses of Surface Water Samples

Storet Parameter No. 00540

Parameter : Ash, Solids, Suspended (mg/l)

Method : Gravimetric, ignition at 600 C, modified.

Reference : Standard Methods for the Examination of Water and  
Wastewater, 12th ed., APHA, Inc., N.Y., 1965,  
247-248.

Modifications: Use of 0.45  $\mu$  membrane filter only for solids  
separation.

Date: September 1968

Federal Water Pollution Control Administration

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OFFICIAL INTERIM METHODS

for

Analyses of Surface Water Samples

Storet Parameter No. 00510

Parameter : Ash, Solids, Total (mg/l)

Method : Gravimetric, ignition at 600 C.

Reference : Standard Methods for the Examination of Water and  
Wastewater, 12th ed., APHA, Inc., N.Y., 1965,  
247-248.

Modifications: None

Date: September 1968

Federal Water Pollution Control Administration

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for

Analyses of Surface Water Samples

Storet Parameter No. 00310

Parameter : Biochemical Oxygen Demand, 5 day (mg/l)

Method : Non-official method - modified Winkler - azide method.

Reference : Standard Methods for the Examination of Water and Wastewater, 12th ed., APHA, Inc., N.Y., 1965, 406-410; 415-421.

Modifications: 1. Full Bottle Technique

2. Scope and Application: For the BOD test to be most meaningful the laboratory procedure should duplicate environmental conditions -- temperature, mineral substrate, water movement, biological population, etc. If determination of the BOD in this manner was carried out the procedure would be considered "standard"; however, since it would be extremely difficult to reproduce these conditions from one laboratory to another the test must be recognized as a non-standard procedure, and therefore classified as "Non-Official".

3. Apparatus: Incubation bottles, 300 ml  $\pm$  3 ml capacity, with ground-glass stoppers.

4. Data Validity: The most valid BOD results are obtained when samples have at least 2 mg/l of depletion

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and at least 1 mg/l of oxygen remaining. Values that do not meet these criteria should be reported with the Subscript L - meaning that either the depletion or residual, were below the accepted limits.

The minimum number of dilutions that should be run on any sample is two - the preferable number is three. In all cases the only figures that should be used or averaged are those falling within the desired or minimum ranges. If all resulting values are below the minimum, then these data will be averaged and reported with the proper connotation.

Example: 3 dilutions - 2 within limits,  
1 below

Average only those two falling within limits.

3 dilutions - 1 within, 2 below  
Report only the value falling within the limits.

3 dilutions - 3 below  
Average all three, report value as BOD<sub>L</sub>

2 dilutions - 1 within, 1 below  
Report only the value falling within the limits.

2 dilutions - 2 within  
Average both values.

5. Precision and Accuracy: The expected standard deviation of the "Standard Methods" BOD procedure is approximately  $\pm 20$  percent of the mean value<sup>1</sup>. At present, data are not available to substantiate whether or not the full bottle technique will alter this reported deviation. However, it is felt that since the FWPCA procedure does not significantly alter the mechanics or chemistry of the Standard Methods procedure, the precision and accuracy will not be seriously affected.

<sup>1</sup>Ballinger, D.G., Lishka, R.J., Reliability and Precision of BOD and COD Determinations; Journal WPCF, May 1962, pp 470-474.

Federal Water Pollution Control Administration

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OFFICIAL INTERIM METHODS

for

Analyses of Surface Water Samples

Storet Parameter No. to be assigned

Parameter : Cadmium, Dissolved ( $\mu\text{g/l}$ )

Method : Filtration through 0.45  $\mu$  membrane filter.  
Measurement by atomic absorption.

Reference : Method is specific to the particular instrument.  
General procedure is being selected.

Modifications: Use of 0.45  $\mu$  membrane filter only.

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Federal Water Pollution Control Administration

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Analyses of Surface Water Samples

Storet Parameter No. 01025

Parameter : Cadmium, Total ( $\mu\text{g/l}$ )

Method : Atomic absorption.

Reference : Method is specific to the particular instrument.  
General procedure is being selected.

Modifications: None

Date: September 1968

Federal Water Pollution Control Administration

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for

Analyses of Surface Water Samples

Storet Parameter No. to be assigned

Parameter : Calcium, Dissolved, as Ca, (mg/l)

Method : Filtration through 0.45  $\mu$  membrane filter.  
Measurement by atomic absorption.

Reference : Method is specific to the particular instrument.  
General procedure is being selected.

Modifications: Use of 0.45  $\mu$  membrane filter only.

Date: September 1968

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for

Analyses of Surface Water Samples

Storet Parameter No. 00915

Parameter : Calcium, Total, as Ca, (mg/l)

Method : Atomic absorption.

Reference : Method is specific to the particular instrument.  
General procedure is being selected.

Modifications: None

Date: September 1968



Federal Water Pollution Control Administration

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OFFICIAL INTERIM METHODS

for

Analyses of Surface Water Samples

Storet Parameter No. 00340

Parameter : Chemical Oxygen Demand, High Level (mg/l)  
Official Interim Procedure #1

Method : Volumetric, dichromate reflux.

Reference : 1. Standard Methods for the Examination of Water and  
Wastewater, 12th ed., APHA, Inc., N.Y., 1965,  
510-514.  
2. ASTM Book of Standards, Part 23, 1967  
D1252-67, pp. 244-247.

Modifications: None

Date: September 1968

Federal Water Pollution Control Administration

Analytical Quality Control Branch

OFFICIAL INTERIM METHODS

for

Analyses of Surface Water Samples

Storet Parameter No. 00335

Parameter : Chemical Oxygen Demand, Low Level (mg/l)  
Official Interim Procedure #2

Method : Volumetric, dichromate reflux, modified.

Reference : 1. Standard Methods for the Examination of Water and  
Wastewater, 12th ed., APHA, Inc., N.Y., 1965,  
510-514.  
2. ASTM Book of Standards, Part 23, 1967  
D1252-67, pp. 244-247.

Modifications: See new method write-up.

Date: September 1968

Federal Water Pollution Control Administration

Analytical Quality Control Branch

OFFICIAL INTERIM METHOD

for

Chemical Oxygen Demand - Low Level

Interim Official Procedure #2

1. Scope and Application:

This method is applicable when the chloride level is less than 100 mg/l and the COD is in the range of 10-90 mg/l. Otherwise the scope and application is exactly as the Interim Official Chemical Oxygen Demand Procedure. Extreme care must be taken with this procedure because a trace of organic matter from the glassware or atmospheric contamination may cause a gross error. All glassware used in the test should be "aged" in that previous low level blank determinations must have been run to eliminate traces of organic material.

2. Apparatus:

2.1) Reflux apparatus: 125 ml Erlenmeyer flasks with standard ground glass 24/40 neck and 300 mm jacket Liebig, West, or equivalent condensers with 24/40 ground glass joint, and a hot plate or mantle with sufficient power to produce at least 9 watts/sq. in. of heating surface, or equivalent, to insure an adequate boiling of contents of the refluxing flask.

3. Sampling: As per Official Interim Procedure #1.

4. Preservation: As per Official Interim Procedure #1.

5. Reagents:

5.1) Standard potassium dichromate solution: 0.025N. Dissolve 12.259 g  $K_2Cr_2O_7$ , primary standard grade, previously dried at 103°C for 2 hours, in distilled water and dilute to 1000 ml. Mix this solution

thoroughly then dilute 100 ml to one liter with distilled water. See referee procedure for elimination of nitrite interference.

5.2) Sulfuric acid reagent: Conc.  $\text{H}_2\text{SO}_4$  containing 23.5 g silver sulfate,  $\text{Ag}_2\text{SO}_4$ , per 9 lb. bottle (1 to 2 days required for dissolution.)

5.3) Standard ferrous ammonium sulfate titrant: 0.025N

5.3.1) Dissolve 98 g of  $\text{Fe}(\text{NH}_4)_2 \cdot 6\text{H}_2\text{O}$  in distilled water.

Add 20 ml of conc.  $\text{H}_2\text{SO}_4$ , cool, and dilute to 1000 ml. Dilute 100 ml of this solution to 1 liter with distilled water. This solution must be standardized daily against  $\text{K}_2\text{Cr}_2\text{O}_7$  solution.

5.3.2) Standardization: To 15 ml of distilled water add 10 ml of 0.025N  $\text{K}_2\text{Cr}_2\text{O}_7$  solution. Add 20 ml of  $\text{H}_2\text{SO}_4$  and cool.

Titrate with ferrous ammonium sulfate using 1 drop of ferroin indicator. The color change is sharp, going from blue-green to reddish-brown.

$$\text{Normality} = \frac{(\text{ml } \text{K}_2\text{Cr}_2\text{O}_7) (0.025)}{\text{ml Fe } (\text{NH}_4)_2 (\text{SO}_4)_2}$$

5.4) Ferroin indicator solution: As per Official Procedure #1.

5.5) Silver Sulfate, reagent powder: As per Official Procedure #1.

5.6) Mercuric Sulfate: As per Official Procedure #1.

5.7) Sulfuric Acid: 36N, Reagent grade.

## 6. Procedure:

6.1) Determine chloride content of sample. Pipet 10 ml of sample into the reflux flask. Add 10 ml of 0.025N  $\text{K}_2\text{Cr}_2\text{O}_7$  solution then 2 ml of conc.  $\text{H}_2\text{SO}_4$  and mix. Add  $\text{HgSO}_4$  in the ratio of 10 mg  $\text{HgSO}_4$  to 1 mg chloride, and swirl until all mercuric sulfate has dissolved. Add 2 glass beads which have previously been ignited at  $600^\circ\text{C}$  for 1 hour.

Then add 18 ml of sulfuric acid-silver sulfate solution and gently swirl until the solution is thoroughly mixed.

6.2) Attach the flask to the condenser and reflux for 2 hours. Cool and wash down the condenser with 3 ml of distilled water. Disconnect the condenser and wash the flask with 2 ml of water. Cool to room temperature.

6.3) Titrate with standard ferrous ammonium sulfate using 1 drop of ferroin indicator.

6.4) Run a blank using 10 ml of COD-free distilled water through the entire procedure.

6.5) Concentration of dilute samples. If an increase in sensitivity is required, it may be obtained by reducing a 20 ml sample volume by boiling in the refluxing flask on a hot plate in the presence of all reagents. A blank should be carried through the same procedure. This technique has the advantage of concentrating without significant loss of easily digested volatile materials. Hard to digest volatile materials, such as volatile acids, are lost, but an improvement is gained over ordinary evaporative concentration methods.

#### 7. Calculation:

$$\text{mg/l COD} = \frac{(a - b) c \times 8000}{\text{ml sample}}$$

Where: a = ml  $\text{Fe}(\text{NH}_4)_2 (\text{SO}_4)_2$  used for blank;

b = ml  $\text{Fe}(\text{NH}_4)_2 (\text{SO}_4)_2$  used for sample;

c = normality of  $\text{Fe}(\text{NH}_4)_2 (\text{SO}_4)_2$ .

#### 8. Precision and Accuracy:

Data are unavailable on the precision and accuracy of this method at the present time.

Federal Water Pollution Control Administration

Analytical Quality Control Branch

OFFICIAL INTERIM METHODS

for

Analyses of Surface Water Samples

Storet Parameter No. to be assigned

Parameter : Chemical Oxygen Demand, Saline Waters (mg/l)  
Official Interim Procedure #3

Method : Volumetric, dichromate reflux, modified.

Reference : 1. Standard Methods for the Examination of Water and  
Wastewater, 12th ed., APHA, Inc., N.Y., 1965,  
510-514.  
2. ASTM Book of Standards, Part 23, 1967  
D1252-67, pp. 244-247.

Modifications: See new method write-up.

Date: September 1968

Federal Water Pollution Control Administration

Analytical Quality Control Branch

OFFICIAL INTERIM METHOD

for

Chemical Oxygen Demand, Saline Waters (mg/l)

Official Interim Procedure #3.

1. Scope and Application:

When the chloride level exceeds 1000 mg/l the minimum accepted value for the COD will be 250 mg/l. COD levels which fall below this value are highly questionable because of the high chloride correction which must be made. Otherwise the scope and application is exactly as the Interim Official Chemical Oxygen Demand Procedure #1.

2. Apparatus: As per Official Interim Procedure #1.

3. Sampling: As per Official Interim Procedure #1.

4. Preservation: As per Official Interim Procedure #1.

5. Reagents:

5.1) Standard potassium dichromate solution: As per Interim Official Procedure #1.

5.2) Sulfuric acid reagent: Conc.  $\text{H}_2\text{SO}_4$  containing 23.5 g silver sulfate,  $\text{Ag}_2\text{SO}_4$ , per 9 lb bottle (1 to 2 days required for dissolution).

5.3) Standard ferrous ammonium sulfate titrant, 0.25N:

5.3.1) Dissolve 98 g of  $\text{Fe}(\text{NH}_4)_2(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$  in distilled water. Add 20 ml of conc.  $\text{H}_2\text{SO}_4$ , cool, and dilute to 1000 ml. This solution must be standardized against the standard potassium dichromate solution daily.

- 5.3.2) Standardization: Dilute 25.0 ml of standard dichromate solution to about 250 ml with distilled water. Add 75 ml conc. sulfuric acid. Cool then titrate with ferrous ammonium sulfate titrant, using 10 drops of ferroin indicator.

$$\text{Normality} = \frac{(\text{ml } K_2Cr_2O_7)(0.25)}{\text{ml } Fe(NH_4)_2(SO_4)_2}$$

- 5.4) Ferroin indicator solution: As per Official Interim Procedure #1.

- 5.5) Silver Sulfate, reagent powder: As per Official Interim Procedure #1.

- 5.6) Mercuric Sulfate: As per Official Interim Procedure #1.

- 5.7) Sulfamic Acid: As per Official Interim Procedure #1.

- 5.8) Sulfuric Acid: 36N, reagent grade.

6. Procedure:

6.1) Pipet a 50 ml aliquot of sample not to exceed 800 mg/l of COD into a 500 ml, flat bottom, g.s. erlenmeyer. Add 25 ml of 0.25N  $K_2Cr_2O_7$  then 5.0 ml of conc.  $H_2SO_4$  (containing no silver sulfate). Add  $HgSO_4$  in the ratio of 10 mg to 1 mg chloride, based upon the mg of chloride in the sample aliquot. Swirl until all the mercuric sulfate has dissolved. Carefully add 70 ml of sulfuric acid-silver sulfate solution and gently swirl until the solution is thoroughly mixed. Glass beads should be added to the reflux mixture to prevent bumping, which can be severe and dangerous. (CAUTION: The reflux mixture must be thoroughly mixed before heat is applied. If this is not done, local heating occurs in the bottom of the flask, and the mixture may be blown out of the condenser).



6.2) Attach the flask to the condenser and reflux the mixture for two hours.

6.3) Cool, and wash down the interior of the condenser with 25 ml of distilled water. Break the joint of the condenser and wash the flask and condenser joint with 25 ml of distilled water. Remove the condenser and carefully add to the flask 175 ml of distilled water so that the total volume is 350 ml. Cool to room temperature.

6.4) Titrate with standard ferrous ammonium sulfate using 10 drops of ferroin indicator. (This amount must not vary from blank, sample and standardization). The color change is sharp, going from blue-green to reddish brown and should be taken as the end point although the blue-green color may reappear within minutes.

6.5) Run a blank, using 50 ml of distilled water in place of the sample together with all reagents and subsequent treatment.

6.6) For COD values greater than 800 mg/l a smaller aliquot of sample should be taken, however, the volume should be readjusted to 50 ml with distilled water having a chloride concentration equal to the sample.

6.7) Chloride correction\*- Prepare a standard curve of COD versus mg/l of chloride, using sodium chloride solutions of varying concentrations following exactly the procedure outlined. The chloride interval, as a minimum should be 4000 mg/l up to 20,000 mg/l chloride. Lesser intervals or greater concentrations must be run as per the requirements of the data, but in no case must extrapolation be allowed.

\*Burns, E. R., Craig, M., Journal WPCF, Vol. 37, pp 1716-1721, 1967

7. Calculation:

$$\text{mg/l COD} = \frac{(a - b) c \times 8000}{\text{ml sample}} - d \times 1.20$$

where

COD = chemical oxygen demand from dichromate

a = ml  $\text{Fe}(\text{NH}_4)_2 (\text{SO}_4)_2$  for blank;

b = ml  $\text{Fe}(\text{NH}_4)_2 (\text{SO}_4)_2$  for sample;

c = normality of  $\text{Fe}(\text{NH}_4)_2 (\text{SO}_4)_2$ ;

d = chloride correction from curve (step 6.7)

1.20 = Compensation factor to account for the extent  
of chloride oxidation which is dissimilar in  
systems containing organic and nonorganic  
material.

8. Precision and Accuracy:

Data are unavailable on the precision and accuracy of this method  
at the present time.

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OFFICIAL INTERIM METHODS

for

Analyses of Surface Water Samples

Storet Parameter No. 00940

Parameter : Chloride (mg/l)

Method : Volumetric, mercuric nitrate.

Reference : 1. Standard Methods for the Examination of Water and  
Wastewater, 12th ed., APHA, Inc., N.Y., 1965,  
87-90.  
2. ASTM Book of Standards, Part 23, 1967  
D512-67, pp. 25-27.

Modifications: None

Date: September 1968

Federal Water Pollution Control Administration

Analytical Quality Control Branch

OFFICIAL INTERIM METHODS

for

Analyses of Surface Water Samples

Storet Parameter No. 00365

Parameter : Chlorine Demand, 15 minutes (mg/l)

Method : No official method selected. Unofficial method  
is for control of disinfection.

Reference : Standard Methods for the Examination of Water and  
Wastewater, 12th ed., APHA, Inc., N.Y., 1965,  
381-383.

Modifications: None

Date: September 1968

Federal Water Pollution Control Administration

Analytical Quality Control Branch

OFFICIAL INTERIM METHODS

for

Analyses of Surface Water Samples

Storet Parameter No. 00370

Parameter : Chlorine Demand, 1 hour (mg/l)

Method : No official method selected. Unofficial method  
is for control of disinfection.

Reference : Standard Methods for the Examination of Water and  
Wastewater, 12th ed., APHA, Inc., N.Y., 1965,  
381-383.

Modifications: None

Date: September 1968

Federal Water Pollution Control Administration

Analytical Quality Control Branch

OFFICIAL INTERIM METHODS

for

Analyses of Surface Water Samples

Storet Parameter No. 00375

Parameter : Chlorine Demand, 2 hour (mg/l)

Method : No official method selected. Unofficial method  
is for control of disinfection.

Reference : Standard Methods for the Examination of Water and  
Wastewater, 12th ed., APHA, Inc., N.Y., 1965,  
381-383.

Modifications: None

Date: September 1968

Federal Water Pollution Control Administration

Analytical Quality Control Branch

OFFICIAL INTERIM METHODS

for

Analyses of Surface Water Samples

Storet Parameter No. 00380

Parameter : Chlorine Demand, 24 hour (mg/l)

Method : No official method selected. Unofficial method  
is for control of disinfection.

Reference : Standard Methods for the Examination of Water and  
Wastewater, 12th ed., APHA, Inc., N.Y., 1965,  
381-383.

Modifications: None

Date: September 1968

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OFFICIAL INTERIM METHODS

for

Analyses of Surface Water Samples

Storet Parameter No. 50060

Parameter : Chlorine, Residual (mg/l)

Method : Volumetric, (iodometric)

Reference : Standard Methods for the Examination of Water and  
Wastewater, 12th ed., APHA, Inc., N.Y., 1965,  
376-378.

ASTM Book of Standards, Part 23 (1967), 249-252.

Modifications: None

Date: September 1968



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OFFICIAL INTERIM METHODS

for

Analyses of Surface Water Samples

Storet Parameter No. to be assigned

Parameter : Chromium, Dissolved ( $\mu\text{g/l}$ )

Method : Filtration through 0.45  $\mu$  membrane filter.  
Measurement by atomic absorption.

Reference : Method is specific to the particular instrument.  
General procedure is being selected.

Modifications: Use of 0.45  $\mu$  membrane filter only.

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for

Analyses of Surface Water Samples

Storet Parameter No. 01030

Parameter : Chromium, Total ( $\mu\text{g/l}$ )

Method : Atomic absorption.

Reference : Method is specific to the particular instrument.  
General procedure is being selected.

Modifications: None

Date: September 1968

Federal Water Pollution Control Administration

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OFFICIAL INTERIM METHODS

for

Analyses of Surface Water Samples

Storet Parameter No. 00080

Parameter : Color (Pt - Co units)

Method : Platinum-cobalt.

Reference : Standard Methods for the Examination of Water and  
Wastewater, 12th ed., APHA, Inc., N.Y., 1965,  
127-129.

Modifications: Permanent color standards are acceptable if these are  
individually and periodically recalibrated against  
platinum cobalt standards.

See method comments attached.

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Federal Water Pollution Control Administration  
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OFFICIAL INTERIM METHOD  
for  
Color

Method Selection

The Platinum-Cobalt Method is selected as the Interim Official FWPCA Method. It is the simplest, most rapid, and is the most useful under all conditions. The Tristimulus and Spectrophotometric Methods are useful in detecting specific color problems.

Definitions

2. The term "color" in these methods is considered to be the color of the light transmitted by the water or waste water after removing the suspended material including the pseudocolloidal particles ("true color").

It is recognized that the color characteristics of water are affected by reflectance ("apparent color"). However, until a suitable method is available for making solution reflectance determinations, the color measurement will be limited to the characteristics of light transmitted by clarified samples.

The color of the filtered water is expressed in terms which describe the sensation realized when viewing the clarified water. The hue (red, yellow, green, etc.) of the color is designated by the term dominant wave length, the degree of brightness by luminance, and the saturation (pastel, pale, etc.) by purity.

The light transmission data are converted to the color classification terms by using standards adopted by the International Commission on Illumination ("CIE"), and the selected-ordinate method.

#### Purity of Reagents

3. Reagent grade chemicals shall be used in all tests.

#### Sampling

4. Samples for the color determination should be representative and must be taken in clean glassware. The color determination should be made within a reasonable period, as biologic changes occurring in storage may affect the color.

## Platinum-Cobalt Method

### Application

5. This method is applicable to the determination of color of water and waste water for routine control purposes.

### Principle of Method

6. Color is measured by visual comparison of the sample to platinum-cobalt standards where one unit of color being that produced by 1 mg/l platinum, in the form of the chloroplatinate ion.

### Interference

7. Even a slight turbidity interferes with the test. The recommended method for the removal of turbidity is by centrifugation.

The color is extremely pH dependent and invariably increases as the pH of the sample is raised. The pH must be measured and recorded along with the color.

### Reagents

8. Same as given under "Preparation of Standards", pages 128 and 129, Standard Methods for the Examination of Water and Wastewater, Twelfth Edition, 1965.

### Procedure

9. Same as given on page 129, Standard Methods for the Examination of Water and Wastewater, Twelfth Edition, 1965.

### Calculation

10. Same as given on page 129, Standard Methods for the Examination of Water and Wastewater, Twelfth Edition, 1965.

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OFFICIAL INTERIM METHODS

for

Analyses of Surface Water Samples

Storet Parameter No. 00095

Parameter : Conductivity, Specific (micromhos/cm at 25 C)

Method : Instrumental, wheatstone bridge modified.

Reference : 1. Standard Methods for the Examination of Water and  
Wastewater, 12th ed., APHA, Inc., N.Y., 1965,  
280-284.  
2. ASTM Book of Standard, Part 23, 1967  
D1125-64, pp. 179-184.

Modifications: Test conducted at standard temperature of 25 C only.

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OFFICIAL INTERIM METHODS

for

Analyses of Surface Water Samples

Storet Parameter No. to be assigned

Parameter : Copper, Dissolved

Method : Filtration through 0.45  $\mu$  membrane filter.  
Measurement by atomic absorption.

Reference : Method is specific to the particular instrument.  
General procedure is being selected.

Modifications: Use of 0.45  $\mu$  membrane filter only.

Date: September 1968



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OFFICIAL INTERIM METHODS

for

Analyses of Surface Water Samples

Storet Parameter No. 01040

Parameter : Copper, Total

Method : Atomic absorption.

Reference : Method is specific to the particular instrument.  
General procedure is being selected.

Modifications: None

Date: September 1968

Federal Water Pollution Control Administration

Analytical Quality Control Branch

OFFICIAL INTERIM METHODS

for

Analyses of Surface Water Samples

Storet Parameter No. 00720

Parameter : Cyanide (mg/l)

Method : Colorimetric or volumetric; distillation followed by benzidine pyridine color development or silver nitrate titration.

Reference : Standard Methods, 12th edition, 1965, 450-454.  
Aldridge, W. N. 1944. Analyst (69) 262-265.  
Nusbaum, I and P. Skupeko, 1951, Sewage and Ind. Wastes, 23 (7), 875.

Modifications: Standard Methods, Page 450, Delete Section 1.1, para. 2.

Cyanogen bromide forms an addition product with pyridine which in turn reacts with an aromatic amine with rupture of the pyridine ring to form an intensely colored dianilide of glutamic dialdehyde.

Benzidine is used as the aromatic amine producing an orange to red colored compound with maximum absorption at 480 mμ.

See Benzidine Pyridine method write-up attached.

Date: September 1968

Federal Water Pollution Control Administration  
Analytical Quality Control Branch  
OFFICIAL INTERIM METHOD  
for  
Benzidine Pyridine Method      Cyanide

Reagents

Purity of Reagents

Reagents shall be reagent grade and should conform to all specifications of the Committee on Analytical Reagents, ACS. Other grades of chemicals may be used if it has been determined that the reagent is of sufficient quality to allow its use without reducing the precision or accuracy of the method.

Purity of Water - Unless otherwise indicated, references to water shall be understood to mean reagent water conforming to specifications of reagent water (ASTM D1193).

- (a) Phosphoric Acid (85%) Concentrated phosphoric acid.
- (b) Phosphoric Acid Solution (1:9) Mix 1 volume of  $H_3PO_4$  (85%) with 9 volumes of water.
- (c) Methyl orange indicator (0.5g/liter). Dissolved 0.05 grams of methyl orange in water and dilute to 100 ml.
- (d) Bromine water (Saturated). To 250 ml of water add slightly more liquid bromine than will dissolve on shaking. Store in a glass stoppered actinic glass bottle.

(e) Sodium Arsenite Solution - Dissolve 2 grams of Sodium Arsenite  $\text{Na}_2\text{AsO}_3$  in 100 ml of water.

(f) N-butyl alcohol reagent grade.

(g) Pyridine Solution - Combine 25 ml of pure pyridine with 2 ml of conc. hydrochloric acid, dilute to 100 ml with water.

(h) Benzidine Hydrochloride Solution - Dissolve 2 grams of benzidine dihydrochloride in 100 ml of water and filter through filter paper.

(i) Benzidine Pyridine mixture - Add 0.3 ml of benzidine solution (h) to 5 ml of pyridine solution (g), mix and add immediately to sample.

#### Colorimetric Procedure

Take an aliquot or 20 ml of the absorption liquid obtained from the distillation procedure. The aliquot should contain less than 0.5 micrograms of cyanide.

Place the aliquot in a test tube 25 x 150 or larger preferably a screw cap culture tube; bring volume up to 20 ml with distilled. Add 2 drops of a methyl orange solution; shake and add dropwise a 10% phosphoric acid solution until a red color develops. Add saturated bromine water until definite bromine light yellow bromine color develops. Discharge bromine color with dropwise addition of sodium arsenite solution and add one drop in excess.

Add 10 ml of N-butyl alcohol.

Mix 0.3 ml of the benzidine reagent with 5 ml of pyridine solution; add to sample and mix by vigorous shaking.

Allow 15 minutes for color to develop, decant carefully the butyl alcohol phase and measure absorbance of the developed color with photometer at 480mμ. Determine the concentration of the cyanide in the sample by comparing with standards run simultaneously or when appropriate number of points are plotted on calibration curve to permit calculation of slope which will not differ by one part in a hundred. In all cases at least three standards are to be run each day samples are analyzed.

Colorimetric Procedure (for CN<sup>-</sup> Concentration lower than 1mg per liter).

Calculate the cyanide concentration as follows:

$$\text{CN}^{-}\text{milligrams per liter} = \frac{C \times 250}{\text{ml original sample} \times \text{ml of aliquot used}}$$

C = micrograms of cyanide determined.

References:

Aldridge, W. N. "A New Method for Estimation of Micro Quantities of Cyanide and the Cyanate, Analyst 69,262 (1944)

Nusbaum I and Skupeko P. "Determination Cyanides in Sewage and Polluted Waters "Sewage and Industrial Wastes 23, 7, 875 (July 1951)

American Society of Testing Materials, ASTM, Designation: D1193

Dissolved Oxygen  
INTERIM OFFICIAL PROCEDURE  
Azide Modification of Iodometric Method  
Full Bottle Technique

1. Scope and Application:

This method is applicable for use with most wastewaters and streams that contain nitrite nitrogen and more than 1 mg/l of ferrous iron. Other reducing or oxidizing materials should be absent. If 1 ml fluoride solution is added before acidifying the sample and there is no delay in titration, the method is also applicable in the presence of 100-200 mg/l ferric iron.

The azide modification is not applicable under the following conditions:

(a) samples containing sulfite, thiosulfate, polythionate, appreciable quantities of free chlorine or hypochlorite (b) samples high in suspended solids (c) samples containing organic substances which are readily oxidized in a highly alkaline solution, or which are oxidized by free iodine in an acid solution (d) domestic sewage (e) biological flocs (f) where sample color interferes with endpoint detection.

In instances where the azide modification is not applicable a DO probe will be used.

2. Apparatus:

2.1) Sample Bottles - 300 ml  $\pm$  3 ml capacity BOD incubation bottles with tapered ground glass pointed stoppers and flared mouths.

2.2) Pipets - with elongated tips capable of delivering 2.0 ml  $\pm$  0.1 ml of reagent.

SEP 1968

### 3. Sampling:

3.1) Where possible, collect the sample in a 300 ml BOD incubation bottle. Special cautions are required to avoid entrainment or solution of atmospheric oxygen or dissolution of dissolved oxygen.

3.2) Where samples are collected from shallow depths (less than 5 feet) use of an APHA-type sampler is recommended. Use of a Kemmerer-type sampler is recommended for samples collected from depths of greater than 5 feet.

3.3) When a Kemmerer is used, the BOD sample bottle should be filled to overflowing. (Overflow for approximately 10 seconds). Outlet tube of Kemmerer should be inserted to bottom of BOD bottle. Care must be taken to prevent turbulence and the formation of bubbles when filling bottle.

3.4) The sample temperature should be recorded at time of sampling as precisely as required.

### 4. Preservation of Samples:

4.1) Do not delay the determination of dissolved oxygen in samples having an appreciable iodine demand or containing ferrous iron. If samples must be preserved either 4.1.1 or 4.1.2 below may be employed.

4.1.1) Add 2 ml of manganous sulfate reagent and then 2 ml of alkali azide reagent to the sample contained in the BOD bottle. Both reagents must be added well below the surface of the liquid. Stopper the bottle immediately and mix the contents thoroughly. The sample should be stored at the temperature of the collection water; or water sealed and kept at a temperature of 10 - 20°C, in the dark.

4.1.2) Add 0.7 ml of concentrated  $H_2SO_4$  and 1 ml sodium azide solution

(2gNaN<sub>3</sub> in 100 ml distilled water) to the sample in the DO bottle. Store in sample as in method A. Complete the procedure using 2 ml of manganous sulfate solution, 3 ml alkali iodide solution, and 2 ml of concentrated H<sub>2</sub>SO<sub>4</sub>.

4.2) If either preservation technique A or B is employed, complete the analysis within 4-8 hours after sampling.

## 5. Reagents

5.1) Manganese sulfate reagent: As in Standard Methods.....

5.2) Alkaline-iodide-azide reagent: As in Standard Methods.....

5.3) Sulfuric acid, concentrated: As in Standard Methods.....

5.4) Starch solution: Prepare an emulsion of 10 g soluble starch in a mortar or beaker with a small quantity of distilled water. Pour this emulsion into 1 liter of boiling water, allow to boil a few minutes, and let settle overnight. Use the clear supernate. This solution may be preserved by the addition of 5 ml per liter of chloroform and storage in a 10°C refrigerator. Dry, powdered starch indicators such as "thyodene" may be used in place of starch solution.

5.5) Potassium Fluoride solution: Dissolve 40 g KF · 2H<sub>2</sub>O in distilled water and dilute to 100 ml.

5.6) Sodium thiosulfate stock solution, 0.75N: Dissolve 186.15 g Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub> 5H<sub>2</sub>O in boiled and cooled distilled water and dilute to 1 liter. Preserve by adding 5 ml chloroform.

5.7) Standard sodium thiosulfate titrant, 0.0375N: Prepare by diluting 50.0 ml of stock solution to 1 liter. Preserve by adding 5 ml of chloroform. Standard sodium thiosulfate, exactly 0.0375N is equivalent to 0.300 mg of DO per 100 ml. Standardize with 0.0375N potassium dichromate.



5.8) Standard potassium dichromate, 0.0375N: Dissolve 1.839 potassium dichromate, previously dried 2 hours at 103°C, in 1 liter of distilled water. The solution must be prepared in a volumetric flask.

5.9) Standardization of 0.0375N sodium thiosulfate: Dissolve 2 g  $\pm$  0.1 g KI in 100 to 150 ml distilled water; add 10 ml of 10% H<sub>2</sub>SO<sub>4</sub> followed by 20 ml standard potassium dichromate.<sup>1</sup> Place in dark for 5 minutes, dilute to 400 ml and titrate with the standard sodium thiosulfate titrant to a pale straw color. Add 1-2 ml starch solution and continue the titration drop by drop until the blue color disappears. Run in duplicate. Duplicate determination should agree within 0.05 ml.

## 6. Procedure:

6.1) To the sample collected in the BOD incubation bottle add 2 ml of the manganous sulfate solution followed by 2 ml of the alkali-iodide-azide reagent, well below the surface of the liquid; stopper with care to exclude air bubbles and mix well by inverting the bottle several times. When the precipitate settles, leaving a clear supernatant above the manganese hydroxide floc, shake again. With estuarine-type waters, a minimum 2 minute period of contact with the precipitate rather than settling is sufficient. When settling has produced at least 100 ml of clear supernate, carefully remove the stopper and immediately add 2.0 ml of conc. H<sub>2</sub>SO<sub>4</sub> (sulfamic acid packets, 3 gm, may be substituted for H<sub>2</sub>SO<sub>4</sub><sup>2</sup>) by allowing the acid to run down the

<sup>1</sup>The volume of standard dichromate to be employed in the standardization procedure may be reduced to 9 ml to accomodate the use of a 10 ml burette.

<sup>2</sup>Kroner, R.C., Longbottom, J.E., Gorman, R., A Comparison of Various Reagents Proposed for Use in the Winkler Procedure for Dissolved Oxygen, PHS Water Pollution Surveillance System Applications and Development Report #12, Water Quality Section, Basic Data Branch, July, 1964.

neck of the bottle, re-stopper, and mix by gentle inversion until the iodine is uniformly distributed throughout the bottle. Complete the analysis within 45 minutes.

6.2) Transfer the entire bottle contents by inversion into a 500 ml wide mouth erlenmeyer and titrate with 0.0375N thiosulfate solution (where problems of stability arise, 0.0375N PAO may be substituted as titrant<sup>2</sup>) to a pale straw color. Add 1-2 ml of starch solution or 0.1 g of powdered indicator and continue to titrate to the first disappearance of the blue color.

6.3) If ferric iron is present (100 to 200 ppm), add 1.0 ml of KF solution before acidification.

6.4) Occasionally a dark brown or black precipitate persists in the bottle after acidification. This precipitate will dissolve if the solution is kept for a few minutes longer than usual or, if particularly persistent, a few more drops of  $H_2SO_4$  will effect dissolution.

## 7. Calculation:

7.1) Each ml of 0.0375 sodium thiosulfate titrant is equivalent to 1 mg/l DO when the entire bottle contents are titrated.

7.2) If the results are desired in milliliters of oxygen gas per liter at 0°C and 760 mm pressure, multiply mg/l DO by 0.698.

7.3) To express the results as percent saturation at 760 mm atmospheric pressure, the solubility data in Table 25 (Whipple & Whipple Table, Page 409 Standard Methods, 12th Edition) may be used. Equations for correcting the solubilities to barometric pressures other than mean sea level are given below the Table.

<sup>2</sup>Kroner, R.C., Longbottom, J.E., Gorman R., A Comparison of Various Reagents Proposed for Use in the Winkler Procedure for Dissolved Oxygen, PHS Water Pollution Surveillance System Applications and Development Report #12, Water Quality Section, Basic Data Branch, July 1964.

7.4) The solubility of DO in distilled water at any barometric pressure, P (mm Hg), temperature, T°C, and saturated vapor pressure, u (mm Hg), for the given T, may be calculated between the temperature of 0° and 30°C by:

$$\text{ml/l DO} = \frac{(P - U) \times 0.678}{35 + T}$$

and between 30° and 50°C by:

$$\text{ml/l DO} = \frac{(P - U) \times 0.827}{49 + T}$$

8. Precision and Accuracy:

Exact data are unavailable on the precision and accuracy of this technique however, reproducibility is approximately 0.2 ppm of DO at the 7.5 ppm level due to equipment tolerances and uncompensated displacement errors.

Federal Water Pollution Control Administration

Analytical Quality Control Branch

OFFICIAL INTERIM METHODS

for

Analyses of Surface Water Samples

Storet Parameter No. 00950

Parameter : Fluoride (mg/l)

Method : Colorimetric, SPADNS, with distillation.

Reference : 1. Standard Methods for the Examination of Water  
and Wastewater, 12th ed., APHA, Inc., N.Y., 1965,  
144-146.  
2. ASTM Book of Standards, Part 23, 1967  
1968 preprint, D1179.

Modifications: None

Date: September 1968

Federal Water Pollution Control Administration

Analytical Quality Control Branch

OFFICIAL INTERIM METHODS

for

Analyses of Surface Water Samples

Storet Parameter No. 00950

Parameter : Fluoride (mg/l)

Method : Colorimetric, SPADNS, with distillation.

Reference : 1. Standard Methods for the Examination of Water  
and Wastewater, 12th ed., APHA, Inc., N.Y., 1965,  
144-146.  
2. ASTM Book of Standards, Part 23, 1967  
1968 preprint, D1179.

Modifications: None

Date: September 1968

Federal Water Pollution Control Administration

Analytical Quality Control Branch

OFFICIAL INTERIM METHODS

for

Analyses of Surface Water Samples

Storet Parameter No. 00910

Parameter : Hardness, Calcium (mg/l  $\text{CaCO}_3$ )

Method : Volumetric, with EDTA

Reference : ASTM Book of Standards, Part 23, 1967  
D1126-67, pp. 188-191.

Modifications: None

Date: September 1968

Federal Water Pollution Control Administration

Analytical Quality Control Branch

OFFICIAL INTERIM METHODS

for

Analyses of Surface Water Samples

Storet Parameter No. 00920

Parameter : Hardness, Magnesium (mg/l  $\text{CaCO}_3$ )

Method : Volumetric, with EDTA, by difference.

Reference : ASTM Book of Standards, Part 23, 1967  
D1126-67, pp. 188-191.

Modifications: None

Date: September 1968

Federal Water Pollution Control Administration

Analytical Quality Control Branch

OFFICIAL INTERIM METHODS

for

Analyses of Surface Water Samples

Storet Parameter No. 00900

Parameter : Hardness, Total (mg/l  $\text{CaCO}_3$ )

Method : Volumetric, with EDTA.

Reference : ASTM Book of Standards, Part 23, 1967  
D1126-67, pp. 188-191.

Modifications: None

Date: September 1968



Federal Water Pollution Control Administration

Analytical Quality Control Branch

OFFICIAL INTERIM METHODS

for

Analyses of Surface Water Samples

Storet Parameter No. to be assigned

Parameter : Iron, Dissolved

Method : Filtration through 0.45  $\mu$  membrane filter.  
Measurement by atomic absorption.

Reference : Method is specific to the particular instrument.  
General procedure is being selected.

Modifications: Use of 0.45  $\mu$  membrane filter only.

Date: September 1968

Federal Water Pollution Control Administration

Analytical Quality Control Branch

OFFICIAL INTERIM METHODS

for

Analyses of Surface Water Samples

Storet Parameter No. 01045

Parameter : Iron, Total

Method : Atomic Absorption

Reference : Method is specific to the particular instrument.  
General procedure is being selected.

Modifications: None

Date: September 1968

Federal Water Pollution Control Administration

Analytical Quality Control Branch

OFFICIAL INTERIM METHODS

for

Analyses of Surface Water Samples

Storet Parameter No. to be assigned

Parameter : Lead, Dissolved

Method : Filtration through 0.45  $\mu$  membrane filter.  
Measurement by atomic absorption.

Reference : Method is specific to the particular instrument.  
General procedure is being selected.

Modifications: Use of 0.45  $\mu$  membrane filter only.

Date: September 1968

Federal Water Pollution Control Administration

Analytical Quality Control Branch

OFFICIAL INTERIM METHODS

for

Analyses of Surface Water Samples

Storet Parameter No. 01049

Parameter : Lead, Total

Method : Atomic absorption.

Reference : Method is specific to the particular instrument.  
General procedure is being selected.

Modifications: None

Date: September 1968

Federal Water Pollution Control Administration

Analytical Quality Control Branch

OFFICIAL INTERIM METHODS

for

Analyses of Surface Water Samples

Storet Parameter No. to be assigned

Parameter : Magnesium, Dissolved

Method : Filtration through 0.45  $\mu$  membrane filter.  
Measurement by atomic absorption.

Reference : Method is specific to the particular instrument.  
General procedure is being selected.

Modifications: Use of 0.45  $\mu$  membrane filter only.

Date: September 1968

Federal Water Pollution Control Administration

Analytical Quality Control Branch

OFFICIAL INTERIM METHODS

for

Analyses of Surface Water Samples

Storet Parameter No. 00925

Parameter : Magnesium, Total

Method : Atomic absorption.

Reference : Method is specific to the particular instrument.  
General procedure is being selected.

Modifications: None

Date: September 1968

Federal Water Pollution Control Administration

Analytical Quality Control Branch

OFFICIAL INTERIM METHODS

for

Analyses of Surface Water Samples

Storet Parameter No. to be assigned

Parameter : Manganese, Dissolved

Method : Filtration through 0.45  $\mu$  membrane filter.  
Measurement by atomic absorption.

Reference : Method is specific to the particular instrument.  
General procedure is being selected.

Modifications: Use of 0.45  $\mu$  membrane filter only.

Date: September 1968

Federal Water Pollution Control Administration

Analytical Quality Control Branch

OFFICIAL INTERIM METHODS

for

Analyses of Surface Water Samples

Storet Parameter No. 01055

Parameter : Manganese, Total

Method : Atomic absorption.

Reference : Method is specific to the particular instrument.  
General procedure is being selected.

Modifications: None

Date: September 1968



Federal Water Pollution Control Administration

Analytical Quality Control Branch

OFFICIAL INTERIM METHODS

for

Analyses of Surface Water Samples

Storet Parameter No. 38260

Parameter : MBAS (Methylene Blue Active Substance) (mg/l)

Method : Methylene Blue Method.

Reference : Standard Methods for the Examination of Water and  
Wastewater, 12th ed., APHA, Inc., N.Y., 1965,  
297-299.

Modifications: None

Date: September 1968

Federal Water Pollution Control Administration

Analytical Quality Control Branch

OFFICIAL INTERIM METHODS

for

Analyses of Surface Water Samples

Storet Parameter No. 00610

Parameter : Nitrogen, Ammonia (mg/l)

Method : Manual - Distillation.  
Automated - In preparation.

Reference : 1. Standard Methods for the Examination of Water and  
Wastewater, 12th ed., APHA, Inc., N.Y., 1965,  
187-193.  
2. ASTM Book of Standards, Part 23, 1967  
D1426-58, pp. 336-338.

Modifications: New method write-ups. See attached.

Date: September 1968

Federal Water Pollution Control Administration

Analytical Quality Control Branch

OFFICIAL INTERIM METHOD

for

Nitrogen-Ammonia by Distillation

1. Scope

1.1 This distillation method covers the determination of ammonia-nitrogen exclusive of total Kjeldahl nitrogen in surface waters (both fresh and saline) and industrial waste water.

2. Purity of Reagents

2.1 Reagent grade chemicals shall be used in all tests. Unless otherwise indicated, it is intended that all reagents shall conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society, where such specifications are available. Other grades of reagents may be used, provided it is first ascertained that the reagent is of sufficiently high purity to permit its use without reducing the accuracy of the determination.

2.2 All reagents and standards are to be prepared with ammonia-free water. Such water is best prepared by the passage of distilled water through an ion-exchange column containing a strongly acidic cation-exchange resin mixed with a strongly basic anion-exchange resin. These resins should also be selected so that organic compounds which might subsequently interfere with the ammonia determination will be removed.

### 3. Sample Preservation

3.1 Until more conclusive data are obtained samples may be preserved by the addition of 1.0 ml concentrated  $\text{H}_2\text{SO}_4$  or 40 mg  $\text{Hg}^{++}$  per liter. If possible, the samples should be kept in a frozen state until analyzed.

## DISTILLATION METHOD

### 4. Application

4.1 This method is applicable to all types of water and is the method of choice where economics and sample load do not warrant the use of automated equipment.

### 5. Summary of Method

5.1 The sample is buffered at a pH of 9.5 with a borate buffer in order to decrease hydrolysis of cyanates and organic nitrogen compounds, and is then distilled into a solution of boric acid. The ammonia in the distillate can be determined either colorimetrically by nesslerization or titrimetrically with standard sulfuric acid with the use of a mixed indicator, the choice between these two procedures depending on the concentration of the ammonia. In the analysis of sea water the calcium and magnesium salts remain in solution as their soluble borates.

### 6. Interferences

6.1 A number of aromatic and aliphatic amines, as well as other compounds, both organic and inorganic, will cause turbidity upon the addition of Nessler reagent, so direct nesslerization has been discarded

as an official method. Cyanate, which may be encountered in certain industrial effluents, will hydrolyze to some extent even at the pH of 9.5 at which distillation is carried out. Volatile alkaline compounds such as hydrazine will influence the titrimetric results. Some volatile compounds, such as certain ketones, aldehydes, and alcohols, may cause an off-color upon nesslerization in the distillation method. Some of these, such as formaldehyde, may be eliminated by boiling off at a low pH prior to distillation and nesslerization. Residual chlorine must also be removed by pretreatment of the sample with sodium thiosulfate before distillation.

## 7. Apparatus

7.1 An all-glass distilling apparatus with an 800-1000 ml flask.

7.2 Spectrophotometer or filter photometer for use at 425 mμ and providing a light path of 1 cm or more.

7.3 Nessler tubes: Matched Nessler tubes (APHA Standard) about 300 mm long, 17 mm inside diameter, and marked at 225 mm ± 1.5 mm inside measurement from bottom.

7.4 Erlenmeyer flasks: The distillate is collected in 500 ml glass-stoppered flasks. These flasks should be marked at the 350 and the 500 ml volumes. With such marking, it is not necessary to transfer the distillate to volumetric flasks.

## 8. Reagents

8.1 Ammonium chloride, standard solution. - (1 ml = 0.01 mg  $\text{NH}_3\text{-N}$ ). - Dissolve 3.819 g  $\text{NH}_4\text{Cl}$  in water and bring to volume in a 1 liter volumetric flask for use as a stock solution. Dilute 10 ml of this stock solution to 1 liter in a volumetric flask for use as the standard ammonium chloride solution.

8.2 Boric acid solution (20 g/l). - Dissolve 20 g  $\text{H}_3\text{BO}_3$  in water and dilute to 1 liter.

8.3 Mixed indicator. - Mix 2 volumes of 0.2 percent methyl red in 95 percent ethyl alcohol with 1 volume of 0.2 percent methylene blue in 95 percent ethyl alcohol. This solution should be prepared fresh every 30 days.

Note 1. -- Specially denatured ethyl alcohol conforming to Formula 3A or 30 of the U.S. Bureau of Internal Revenue may be substituted for 95 percent ethanol.

8.4 Nessler reagent. - Dissolve 100 g of mercuric iodide and 70 g of potassium iodide in a small amount of water. Add this mixture slowly, with stirring, to a cooled solution of 160 g of NaOH in 500 ml of water. Dilute the mixture to 1 liter. If this reagent is stored in a Pyrex bottle out of direct sunlight, it will remain stable for a period of up to 1 year.

Note 2. -- This reagent should give the characteristic color with ammonia within 10 minutes after addition, and should not produce a precipitate with small amounts of ammonia (0.04 mg in a 50 ml volume).

8.5 Borate buffer. - Add 88 ml. of 0.1 N NaOH solution to 500 ml of 0.025 M sodium tetraborate solution (5.0 g  $\text{Na}_2\text{B}_4\text{O}_7$  per liter) and dilute to 1 liter.

8.6 Sulfuric acid, standard solution (0.02 N, 1 ml = 0.28 mg  $\text{NH}_3\text{-N}$ ). - Prepare a stock solution of approximately 0.1 N acid by diluting 3 ml of concentrated  $\text{H}_2\text{SO}_4$  (sp gr 1.84) to 1 liter with  $\text{CO}_2$ -free distilled water. Dilute 200 ml of this solution to 1 liter with  $\text{CO}_2$ -free distilled water. Standardize the approximately 0.02 N acid so prepared against 0.0200 N  $\text{Na}_2\text{CO}_3$  solution. This last solution is prepared by dissolving 1.060 g anhydrous  $\text{Na}_2\text{CO}_3$ , oven-dried at  $140^\circ \text{C}$ , and diluting to 1 liter with  $\text{CO}_2$ -free distilled water.

Note 3. -- An alternate and perhaps preferable method is to standardize the approximately 0.1 N  $\text{H}_2\text{SO}_4$  solution against a 0.100 N  $\text{Na}_2\text{CO}_3$  solution. By proper dilution the 0.0200 N acid can then be prepared.

8.7 Sodium hydroxide (1 N). - Dissolve 40 g NaOH in ammonia-free water and dilute to 1 liter.

8.8 Dechlorinating reagents. - A number of dechlorinating reagents may be used to remove residual chlorine prior to distillation. These include:

(a) Sodium thiosulfate (1/70 N): Dissolve 3.5 g  $\text{Na}_2\text{S}_2\text{O}_3$  in ammonia-free water and dilute to 1 liter. One ml of this solution will remove 1 mg/l of residual chlorine in 500 ml of sample.

(b) Sodium arsenite (1/70 N): Dissolve 1.0 g  $\text{NaAsO}_2$  in ammonia-free water and dilute to 1 liter.

## 9. Procedure

9.1 Preparation of equipment. -- Add 500 ml of ammonia-free water to an 800 ml Kjeldahl flask. The addition of boiling chips which have been previously treated with dilute NaOH will prevent bumping. Steam out the distillation apparatus until the distillate shows no trace of ammonia with Nessler reagent.

9.2 Sample preparation. - To 400 ml of sample add 1.0 N NaOH until the pH is 9.5, checking the pH during addition with a pH meter.

9.3 Distillation. - Transfer the sample, the pH of which has been adjusted to 9.5, to an 800 ml Kjeldahl flask and add 25 ml of the borate buffer. Distill 300 ml at the rate of 6-10 ml/min. into 50 ml of 2% boric acid contained in a 500 ml glass stoppered Erlenmeyer flask. Dilute the distillate to 500 ml in the flask and nesslerize an aliquot to obtain an approximate value of the ammonia-nitrogen concentration. For concentrations above 1.0 mg/l the ammonia should be determined titrimetrically. For concentrations below this value it is determined colorimetrically.

9.4 Determination of ammonia in distillate. - Determine the ammonia content of the distillate either titrimetrically or colorimetrically as described below. (See 9.4.1 and 9.4.2).

9.4.1 Titrimetric determination. - Add 3 drops of the mixed indicator to the distillate and titrate the ammonia with the 0.02 N  $\text{H}_2\text{SO}_4$ , matching the end point against a blank containing the same volume of ammonia-free water and  $\text{H}_3\text{BO}_3$  solution.

9.4.2 Colorimetric determination. — Prepare a series of 14 Nessler tubes containing the following volumes of the standard solution: 0.0, 0.2, 0.4, 0.6, 0.8, 1.0, 1.2, 1.4, 1.7, 2.0, 2.5, 3.0, 3.5, and 4.0 ml. Dilute each tube to 50 ml. with ammonia-free water. Add 1 ml of Nessler reagent and mix. After 20 minutes read the optical densities at 425 mμ against a compensating blank of nesslerized ammonia-free water. From the values obtained prepare a standard curve.



Determine the ammonia in the distillate by nesslerizing 50 ml or an aliquot diluted to 50 ml and reading the optical density at 425 mμ as described above for the Standards. Ammonia-nitrogen content is read from the standard curve.

#### 10. Calculations

(Tentative until a Standard Method for calculating results is adopted).

##### 10.1 Titrimetric

$$\text{mg/l NH}_3\text{-N} = \frac{A \times 0.28 \times 1000}{S}$$

in which:

A = ml 0.02 N H<sub>2</sub>SO<sub>4</sub> used

S = ml sample

##### 10.2 Spectrophotometric

$$\text{mg/l NH}_3\text{-N} = \frac{A \times 1000}{0.8 S}$$

in which:

A = mg NH<sub>3</sub>-N read from standard curve

S = volume of distillate nesslerized

#### 11. Precision

11.1 Precision and accuracy data are not available at this time.

Federal Water Pollution Control Administration

Analytical Quality Control Branch

OFFICIAL INTERIM METHODS

for

Analyses of Surface Water Samples

Storet Parameter No. 00625

Parameter : Nitrogen, Kjeldahl, Total (mg/l)

Method : Acid digestion and distillation, with titration  
or nesslerization, modified.

Reference : Standard Methods for the Examination of Water and  
Wastewater, 12th ed., APHA, Inc., N.Y., 1965,  
403-404.

Modifications: See method write-up.

Date: September 1968

Federal Water Pollution Control Administration

Analytical Quality Control Branch

OFFICIAL INTERIM METHOD

Nitrogen-Kjeldahl Total

Scope

1. This method covers the determination of total Kjeldahl nitrogen in fresh and estuarine waters. Two alternatives are listed for the determination of ammonia after distillation in the official method. The Kjeldahl procedure converts the nitrogen of most components of biological origin, such as amino acids, peptides and proteins, but may not convert the nitrogeneous matter in many industrial wastes, such as azines, hydrazones, nitro compounds, oximes, semi carbazones, and some refractory tertiary amines. The titrimetric method is applicable to concentrations above 2 mg N per liter and possibly to lower concentrations if reagent blanks are consistent enough. The nesslerization method is applicable to concentrations above 0.1 mg N per liter. The lower limit can be extended by concentration of the distillate prior to nesslerization. While the official method is outlined for a macro system, the same chemistry applied in a micro system (Standard Methods for the Examination of Water and Wastewater, 11th Edition, pg 305) is considered to be the same as the official method.

Definitions

2. (a) Total Kjeldahl nitrogen is defined as the sum of free ammonia and of organic nitrogen compounds which are converted to  $(\text{NH}_4)_2\text{SO}_4$  under the conditions of digestion which are specified below.

(b) Organic Kjeldahl nitrogen is defined as the difference obtained by subtracting the free ammonia value (reference to be cited) from the total Kjeldahl nitrogen value. This may be determined directly by removal of ammonia before digestion.

(c) Organic nitrogen is defined as the nitrogen derived from all organic substances in the sample and shall include Kjeldahl nitrogen.

## Purity of Reagents

3. (a) Reagent grade chemicals shall be used in all tests. Unless otherwise indicated, it is intended that all reagents shall conform to the specifications of the committee on Analytical Reagents of the American Chemical Society, where such specifications are available. Other reagents may be used, provided it is first ascertained that the reagent is of sufficiently high purity to permit its use without lessening the accuracy of the determination. Sulfuric acid, in particular, is subject to absorption of ammonia and should be protected from possible ammonia contamination.

(b) Water shall be understood to mean distilled water which is free of ammonia. Such water is best prepared by the passage of distilled water through an ion-exchange column containing a strongly acidic cation-exchange resin mixed with a strongly basic anion-exchange resin. These resins should be selected so that organic compounds which might subsequently interfere with the determination will be removed. (Note 1)

Note 1: The regeneration of the ion-exchange column should be carried out according to the instruction of the manufacturer.

## 4. Sampling and Preservation

(a) Collect the samples in accordance with the applicable methods recommended by the Committee on Sampling.

(b) The samples can be preserved for analysis at ice temperature for a period not exceeding 48 hours. Samples can be preserved with 1 ml conc.  $H_2SO_4$  per liter of sample and retained for longer periods provided that the relationship between organic nitrogen and ammonia is not of interest. The  $H_2SO_4$  will retain ammonia in solution; however, it accelerates the conversion of organic nitrogen to ammonia. Samples treated with  $H_2SO_4$  are also subject to gain ammonia from the air if not tightly sealed.

## Digestion Method

### Application

5. This method is applicable to all types of fresh and estuarine waters, containing from 0 to 100 mg N per liter.

### Summary of Method

6. The sample is heated in the presence of concentrated sulfuric acid,  $K_2SO_4$  and  $HgO$  and evaporated until  $SO_3$  fumes are obtained and the solution becomes colorless or pale yellow. The residue is cooled, diluted and is treated and made alkaline with a hydroxide-thiosulfate solution. The ammonia is distilled and determined after distillation either by nesslerization (see appropriate references) or titrimetrically.

### Apparatus

#### 7. (a) Digestion Apparatus

Kjeldahl digestion apparatus with 800 ml flasks and suction takeoff to remove water and  $SO_3$  fumes.

#### (b) Distillation Apparatus

The Kjeldahl flask is connected to a condenser and the adaptor is so arranged that the distillate can be collected for nesslerization or in indicating  $H_3BO_3$  solution for titration.

(c) Colorimeter of Nessler tubes as required for nesslerization (see ammonia nitrogen).

### Reagents

#### 8. (a) Mercuric Sulfate Solution

Dissolve 8 g red mercuric oxide,  $HgO$ , in 50 ml 1:5  $H_2O$ - $H_2SO_4$  solution and dilute to 100 ml with  $H_2O$ .

(b) Sulfuric Acid - Mercuric Sulfate - Potassium Sulfate Solution

Dissolve 267g  $K_2SO_4$  in 1,300 ml water and add 400 ml concentrated  $H_2SO_4$ . Add 50 ml mercuric sulfate solution and dilute to 2 liters.

(c) Sodium Hydroxide - Sodium Thiosulfate Solution

Dissolve 500g NaOH and 25g  $Na_2S_2O_3 \cdot 5H_2O$  in water and dilute to 1 liter.

(d) Phenolphthalein Indicator Solution

Dissolve 5g phenolphthalein in 500 ml 95% ethyl alcohol or isopropanol and add 500 ml water. Add 0.02 NaOH dropwise until a faint pink color appears.

(e) Mixed Indicator

Mix 2 volumes of 0.2% methyl red in 95% ethanol with 1 volume of 0.2% methylene blue in ethanol. Prepare fresh every 30 days.

(f) Boric Acid Solution

Dissolve 20g boric acid,  $H_2BO_3$ , in water and dilute to 1 liter with water.

(g) Sulfuric Acid Titrant, 0.020N.

In this strength 1.00 ml = 0.28 mg N.

Procedure

9. (a) Preparation of Apparatus

The distillation apparatus should be presteamed before use by distilling a 1:1 mixture of ammonia-free water and sodium hydroxide-sodium thiosulfate solution until the distillate is ammonia free. This operation should be repeated each time the apparatus is out of service long enough to accumulate ammonia (usually 4 hours or more).

(b) Digestion

Place a measured sample or the residue from the distillation in the ammonia determination (for Organic Kjeldahl only) into an 800 ml Kjeldahl flask. The sample size can be determined from the following table:

| <u>Kjeldahl Nitrogen</u><br><u>in sample, mg/l</u> | <u>Sample Size</u><br><u>ml</u> |
|--|---------------------------------|
| 0 - 5  | 500                             |
| 5 - 10   | 250                             |
| 10 - 20  | 100                             |
| 20 - 50  | 50.0                            |
| 50 - 100   | 25.0                            |

Dilute the sample, if required, to 500 ml, and add 100 ml sulfuric acid - mercuric sulfate - potassium sulfate solution (Note 2), and evaporate the mixture in the Kjeldahl apparatus until  $\text{SO}_3$  fumes are given off and the solution turns colorless or pale yellow. Cool the residue and add 300 ml water.

Note 2: Alternately digest the sample with 1 Kel-Pac (Olin-Matheson) and 20 ml  $\text{H}_2\text{SO}_4$ .

#### (c) Distillation

Make the digestate solution alkaline by carefully adding sodium hydroxide - thiosulfate solution without mixing. Connect a condenser to the Kjeldahl flask and connect the apparatus in such a manner that the tip of the condenser extends well below the level of 100 ml of boric acid. Mix and distill until 200 ml of distillate is collected. Add 1 ml of mixed indicator and titrate with 0.0200N  $\text{H}_2\text{SO}_4$  to a pale lavender endpoint. Run a blank on the reagents and correct as required.

#### Calculation

10. (a) Calculate total Kjeldahl nitrogen, in milligrams per liter, in the original sample as follows:

$$\text{total Kjeldahl nitrogen, mg/l} = \frac{(A-B) \times N \times F \times 1000}{S}$$

$$\text{or } \frac{A-B \times 280}{S}$$

where:

A = milliliters of standard 0.020N  $\text{H}_2\text{SO}_4$  solution used in titrating sample

B = milliliters of standard 0.020N  $\text{H}_2\text{SO}_4$  solution used in titrating blank

N = normality of sulfuric acid solution

F = millequivalent weight of nitrogen (14 mg)

S = milliliters of sample digested

(b) If nesslerization is used, follow ammonia procedure calculations.

(c) Calculated organic Kjeldahl nitrogen, in milligrams per liter, as follows:

organic Kjeldahl nitrogen, mg/l - C - D

where:

C = total Kjeldahl nitrogen in mg/l

D = ammonia nitrogen, in mg/l

#### Precision and Accuracy

11. The precision and accuracy will be established by FWPCA laboratories.



Federal Water Pollution Control Administration

Analytical Quality Control Branch

OFFICIAL INTERIM METHODS

for

Analyses of Surface Water Samples

Storet Parameter No. 00620

Parameter : Nitrogen, Nitrate (mg/l)

Method : Manual Method: Brucine Sulfate, colorimetric for fresh  
and salt water.  
Automated Method A: reduction, colorimetric for fresh water.  
Automated Method B: Brucine Sulfate, colorimetric for  
saline water. (to be added at later date)

Reference : 1. Standard Methods for the Examination of Water and  
Wastewater, 12th ed., APHA, Inc., N.Y., 1965,  
198-200.  
2. ASTM Book of Standards, Part 23, 1967,  
D992-52, pp. 138-140.

Modifications: New method write-ups. See attached.

Date: September 1968

Federal Water Pollution Control Administration

Analytical Quality Control Branch

OFFICIAL INTERIM METHOD

for

Nitrogen-Nitrate

1. Scope

1.1 The following methods are suitable for the determination of nitrogen-nitrate in water samples:

- a. Manual - Brucine Sulfate (fresh and salt water)
- b. Automated A, Hydrazine Reduction (fresh water)
- c. Automated B, Brucine Sulfate (saline water).  
(to be added at later date)

2. Purity of Reagents

2.1 Reagent grade chemicals shall be used in all tests. Unless otherwise indicated, it is intended that all reagents shall conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society where such specifications are available. Other grades of reagents may be used, provided it is first ascertained that the reagent is of sufficiently high purity to permit its use without reducing the accuracy of the determination. Distilled water free of nitrite and nitrate is to be used in preparation of all reagents and standards.

3. Sample Preservation

3.1 Until more conclusive data is obtained, samples may be preserved as follows:

- (a) Addition of 40 mg Hg/l (as  $\text{HgCl}_2$ ) and stored at 4° C.
- (b) Addition of 1 ml of  $\text{CHCl}_3$ /100 ml sample. Store at 4° C.

(c) Freezing.

Note 1. -- Data available at the present time indicate that in using the above methods the nitrate concentration is stable over a period of at least six weeks.

MANUAL METHOD<sup>(1)</sup>

4. Application and Principle of Method

4.1 This method is applicable to a wider variety of samples than either of the two automated methods, because modification can be made to remove or correct for turbidity, color, salinity, or dissolved organic compounds in the samples.

4.2 The principle of the method is based upon the reaction of the nitrate ion with brucine sulfate in a 13 N  $\text{H}_2\text{SO}_4$  solution at about 100° C. The optical density of the resulting colored complex is measured at 410 mμ.

4.3 Applicable range is 0.1 to 2 mg N- $\text{NO}_3$ /l.

5. Interferences

5.1 Dissolved organic matter will cause an off color in 13 N  $\text{H}_2\text{SO}_4$  and must be compensated for by additions of all reagents except the brucine-sulfanilic acid reagent. This also applies to natural color present not due to dissolved organics.

5.2 If turbidity is present, it must be removed by prior filtration, preferably through a 0.45 μ membrane filter.

5.3 The effect of salinity is eliminated by addition of sodium chloride to the blanks, standards and samples.

5.4 All strong oxidizing or reducing agents interfere. The presence of oxidizing agents may be determined by the addition of orthotolidine reagent.

5.5 Residual chlorine interference is eliminated by the addition of sodium arsenite.

5.6 Ferrous and Ferric iron and quadrivalent manganese give slight positive interference, but in concentrations less than 1 mg/l these are negligible.

## 6. Apparatus

6.1 Spectrophotometer or filter photometer suitable for measuring optical densities at 410 mμ and capable of accommodating 25 mm diameter cells.

6.2 Sufficient number of 25 mm diameter matched tubes for reagent blanks, standards, and samples.

6.3 Neoprene coated wire racks to hold 25 mm diameter tubes.

6.4 Water bath suitable for use at 100° C. This bath should contain a stirring mechanism so that all tubes are at same temperature.

6.5 Water bath suitable for use at 10-15°C.

## 7. Reagents

7.1 Sodium Chloride Solution (300 g/l). - Dissolve 300 g NaCl in distilled water and dilute to 1000 ml.

7.2 Sulfuric Acid Solution. - Carefully add 500 ml H<sub>2</sub>SO<sub>4</sub> (sp gr 1.84) to 125 ml distilled water. Cool and keep tightly stoppered to prevent absorption of atmospheric moisture.

7.3 Brucine-Sulfanilic Acid Reagent. - Dissolve 1 g brucine sulfate [(C<sub>23</sub> H<sub>26</sub> N<sub>2</sub>O<sub>4</sub>)<sub>2</sub> · H<sub>2</sub>SO<sub>4</sub> · 7 H<sub>2</sub>O] and 0.1 g sulfanilic acid (NH<sub>2</sub> C<sub>6</sub> H<sub>4</sub> SO<sub>3</sub>H · H<sub>2</sub>O) in 70 ml hot distilled water. Add 3 ml concentrated HCl, cool, mix and dilute to 100 ml. Store in a dark bottle at 5° C.

This solution is stable for several months; the pink color that develops slowly does not effect its usefulness. Mark bottle with warning:

CAUTION: Brucine Sulfate is toxic; take care to avoid ingestion.

7.4 Stock Potassium Nitrate Solution (1 ml = 0.1 mg NO<sub>3</sub>-N)

Dissolve 0.7218 g anhydrous KNO<sub>3</sub> in distilled water and dilute to 1 liter.

7.5 Standard Potassium Nitrate Solution (1 ml = 0.01 mg

NO<sub>3</sub>-N). - Dilute 100 ml of the stock solution to 1 liter. This standard solution should be prepared fresh weekly.

7.6 Acetic Acid (1 + 3) - Dilute 1 vol. glacial CH<sub>3</sub> COOH with 3 vol. distilled water.

8. Procedure

8.1 Adjust the pH of the samples to approximately pH 7 with 1+3 acetic acid and if necessary filter through a 0.45 μ membrane filter or Whatman No. 42 filter paper depending on the amount and type of suspended solids present.

8.2 Set up the required number of matched tubes in the rack to handle reagent blank, standards and samples. If it is necessary to correct for color or dissolved organic matter (which will cause color on heating), a set of duplicate tubes must be used to which all reagents except the brucine-sulfanilic acid has been added.

8.3 Pipet 10 ml or an aliquot of the samples diluted to 10 ml into the sample tubes.

8.4 If the samples are saline, add 2.0 ml of the 30 percent NaCl solution to the reagent blank, standards and samples. For fresh water samples NaCl may be omitted. Mix contents of tubes of swirling and place rack in cold water bath (0-10°C).

5.

8.5 Pipet 10 ml of  $\text{H}_2\text{SO}_4$  solution into each tube and mix by swirling. Allow tubes to come to thermal equilibrium in the cold bath.

8.6 Add 0.5 ml brucine-sulfanilic acid reagent to each tube (except the interference control tubes) and carefully mix by swirling, then place the rack of tubes in the boiling water bath for exactly 25 minutes.

8.7 Remove rack of tubes from the hot water bath and immerse in the cold water bath and allow to reach thermal equilibrium (20-25°C).

8.8 Dry tubes and read optical density against the reagent blank at 410 mμ.

## 9. Calculation

9.1 Obtain a standard curve by plotting the optical densities of standards run by the above procedure against mg  $\text{NO}_3\text{-N}$ . The color reaction does not always follow Beer's law.

9.2 Subtract the absorbance of the sample without the brucine-sulfanilic reagent from the absorbance of the sample containing brucine-sulfanilic acid and read the resultant absorbance in mg  $\text{NO}_3\text{-N}$ . Multiply by factor for converting mg per aliquot of sample to mg per liter.

$$\text{mg/l NO}_3\text{-N} = \frac{1000}{\text{ml sample}} \times \text{mg NO}_3\text{-N from curve}$$

## AUTOMATED METHOD A<sup>(2)</sup>

## 10. Application

10.1 This method is applicable to water samples which contain less than 500 mg/l calcium. The applicable range of this method is 0.05-10 mg/l nitrite or nitrate nitrogen. Approximately 20 samples per hour can be analyzed.

## 11. Summary of Method

11.1 This procedure, using the Technicon Auto Analyzer, determines  $\text{NO}_2\text{-N}$  by the conventional diazotization-coupling reaction. The  $\text{NO}_3\text{-N}$  is reduced with hydrazine sulfate in another portion of the sample and the nitrite thus formed is determined in the usual manner.

11.2 Subtraction of the  $\text{NO}_2\text{-N}$  originally present in the sample from the total  $\text{NO}_2\text{-N}$  found will give the original  $\text{NO}_3\text{-N}$  concentration in terms of  $\text{NO}_2\text{-N}$ .

## 12. Interferences

12.1 The following table lists the concentration of ions that cause no interference in the determination of nitrite and nitrate nitrogen. The same interfering ion concentration applies to either nitrite or nitrate:

| <u>Ion</u>             | <u>Mg/l ion not causing interference</u> |
|------------------------|--|
| $\text{Cl}^-$          | 30,000                                   |
| $\text{PO}_4^{-3}$     | 50                                       |
| $\text{S}^{-2}$        | Note                                     |
| $\text{NH}_3\text{-N}$ | 80                                       |
| $\text{Mg}^{+2}$       | 75                                       |
| $\text{Ca}^{+2}$       | 240                                      |
| $\text{Fe}^{+3}$       | 30                                       |
| ABS                    | 60                                       |

Note 2. -- The apparent  $\text{NO}_3$  and  $\text{NO}_2$  concentrations varied  $\pm$  10 percent with concentrations of sulfide ion up to 10 mg/l.

12.2 The pH of the samples should be between 6 and 9.

### 13. Apparatus

13.1 Technicon Auto Analyzer consisting of:

13.1.1 Two proportional pumps.

13.1.2 Two colorimeters each with an 8 mm flow-through cell and 520 mμ filters.

13.1.3 One continuous filter.

13.1.4 One sampler (large).

13.1.5 Two recorders.

13.1.6 One 38° C temperature bath.

13.1.7 Two time delay coils.

### 14. Reagents

14.1 Color developing reagent. - To approximately 3 liters of distilled water add 400 ml concentrated phosphoric acid (sp gr 1.834), 60 g sulfanilamide ( $\text{H}_2\text{N}-\text{C}_6\text{H}_4-\text{SO}_2-\text{NH}_2$ ) followed by 3.0 g N(1-Naphthyl)ethylene-diamine dihydrochloride. Dilute the solution to 4 liters with distilled water and store in a dark bottle in the refrigerator. This solution is stable for approximately 1 month.

Note 3. — It may be necessary to apply heat in order to dissolve the sulfanilamide.

14.2 Copper sulfate; stock solution. - Dissolve 2.5 g of copper sulfate ( $\text{CuSO}_4 \cdot 5 \text{H}_2\text{O}$ ) in distilled water and dilute to 1 liter.

14.3 Copper sulfate; dilute solution. - Dilute 20 ml of stock solution to 2 liters with distilled water.

14.4 Sodium hydroxide; stock solution. (10 N). - Dissolve 400 g NaOH in 750 ml distilled water, cool and dilute to 1 liter.



14.5 Sodium hydroxide (1.0 N). - Dilute 100 ml of stock NaOH solution to 1 liter.

14.6 Sodium hydroxide (0.3 N). - Dilute 60 ml of stock NaOH to 2 liters.

14.7 Hydrazine sulfate solution. - Dissolve 54.92 g of hydrazine sulfate ( $\text{N}_2\text{H}_4 \cdot \text{H}_2\text{SO}_4$ ) in 1800 ml of distilled water and dilute to 2000 ml. This solution is stable for approximately 6 months.

CAUTION: Toxic if ingested. Mark container with warning.

#### 14.8 Nitrate Standards

14.8.1 Potassium nitrate; stock standard (1000 mg/l  $\cdot \text{NO}_3\text{-N}$ ). Dissolve 7.2180 g of  $\text{KNO}_3$ , oven dried at 100-105° C for 2 hours, in distilled water and dilute to 1000 ml. Add 1 ml chloroform as a preservative. Stable for six months.

14.8.2 Potassium nitrate, dilute standard (100 mg/l  $\text{NO}_3\text{-N}$ ). Dilute 50 ml of stock  $\text{KNO}_3$  solution to 500 ml in a volumetric flask. From this dilute solution prepare the following standards in 500 ml volumetric flasks:

| <u>mg/l <math>\text{NO}_3\text{-N}</math></u> | <u>ml standard solution</u> |
|---|-----------------------------|
| 0.4   | 2.0                         |
| 1.0   | 5.0                         |
| 1.6   | 8.0                         |
| 3.0   | 15.0                        |
| 5.0   | 25.0                        |
| 7.0   | 35.0                        |
| 10.0  | 50.0                        |

#### 14.9 Nitrite Standards

##### 14.9.1 Potassium nitrite, stock standard (1000 mg/l $\text{NO}_2\text{-N}$ ).

Dissolve 4.9260 g  $\text{NaNO}_2$ , oven dried at 100–105° C for two hours, in distilled water and dilute to 1000 ml. Add 1 ml chloroform as preservative. Store in the refrigerator. Stable for one month.

##### 14.9.2 Potassium nitrite, dilute standard (100 mg/l).

Dilute 50 ml of stock  $\text{NaNO}_2$  solution to 500 ml in a volumetric flask. From this dilute solution prepare the same volumetric standards as in 15.3. Prepare fresh each week.

#### 15. Procedure

15.1 Set up the manifold as shown in Figures 1 and 2. Allow both colorimeter (with the proper filters) and recorder to warm up for 30 minutes, then run a base line with all reagents, feeding distilled water through the sample line. Adjust dark current and operative opening on each colorimeter. Adjust base line to 0.01 optical density. Place a distilled water wash tube in alternate openings on sampler and set sample timing at 1.5 minutes.

15.2 Run a 2.0 mg/l  $\text{NO}_3\text{-N}$  and a 2.0 mg/l  $\text{NO}_2\text{-N}$  standard through the system to check for 100% reduction of nitrate to nitrite. The two peaks should be of equal height. If the  $\text{NO}_3$  peak is lower than that of the  $\text{NO}_2$  peak, the temperature of the reduction bath should be increased until they are equal. If the  $\text{NO}_3$  peak is higher than the nitrate, the temperature should be reduced. When the correct temperature of the bath has been determined, no further adjustment should be necessary.

15.3 Arrange standards in sampler in  $\text{NO}_2$ - $\text{NO}_3$  order with increasing concentration of nitrogen. Place unknown samples in sampler tubes and place in alternate openings of sampler. A  $\text{NO}_2$  and  $\text{NO}_3$  standard of equal nitrogen concentration should be placed after every 10 samples as a further check on the system and to more easily identify peaks.

#### 16. Calculation

16.1 Subtract the  $\text{NO}_2$  concentration in the sample from the total  $\text{NO}_2$  found (nitrite plus nitrate) on the reduction side to calculate the  $\text{NO}_3$  concentration in the sample.

#### 17. Precision

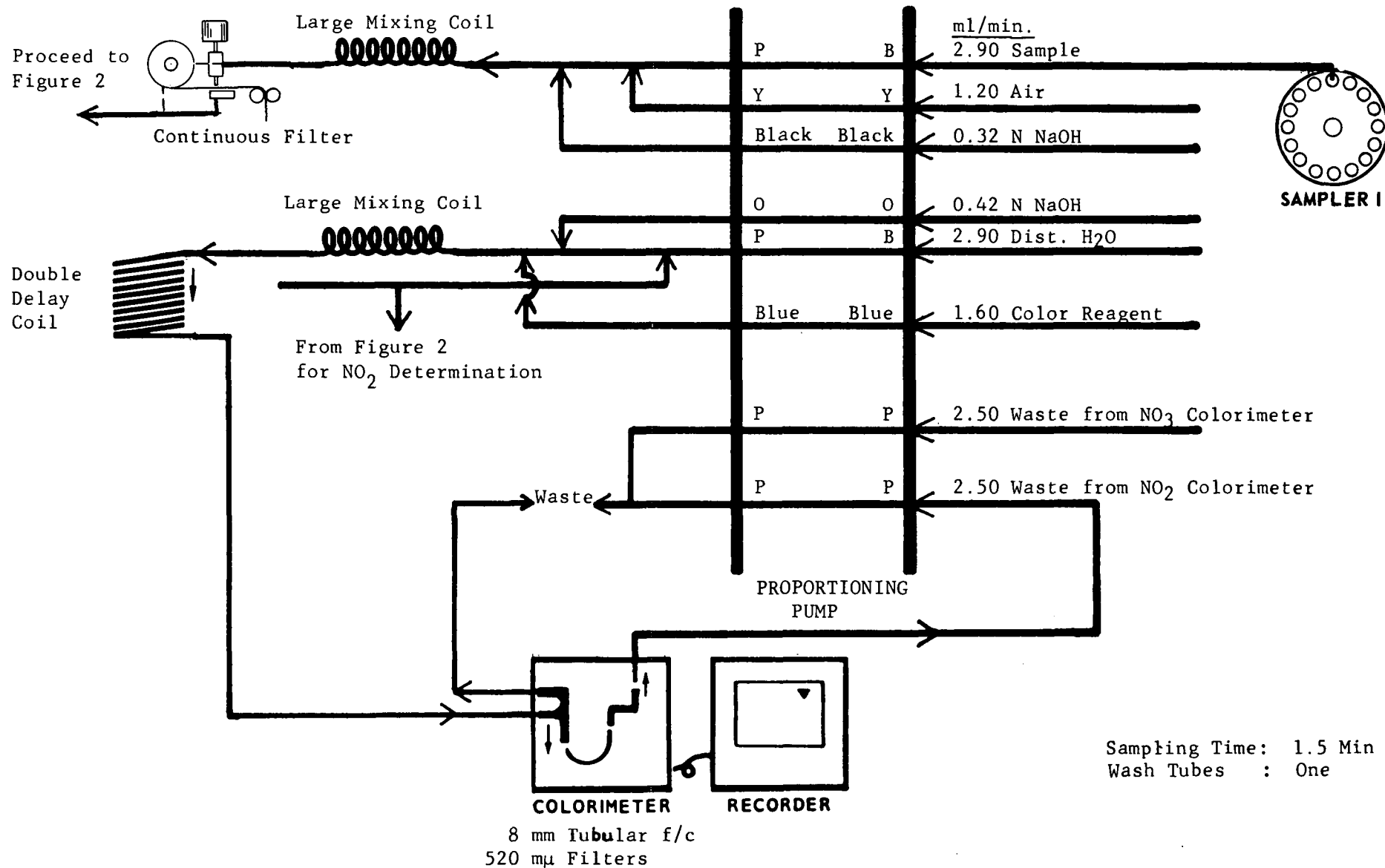
17.1 Precision and accuracy data are not available at this time.

#### References

1. D. Jenkins and L. Medsker, "Brucine Method for Determination of Nitrate in Ocean, Estuarine, and Fresh Waters". Anal. Chem., 36, 610 (1964).
2. L. Kamphake, S. Hannah, and J. Cohen, "Automated Analysis for Nitrate by Hydrazine Reduction". Water Research, 1, 205 (1967).

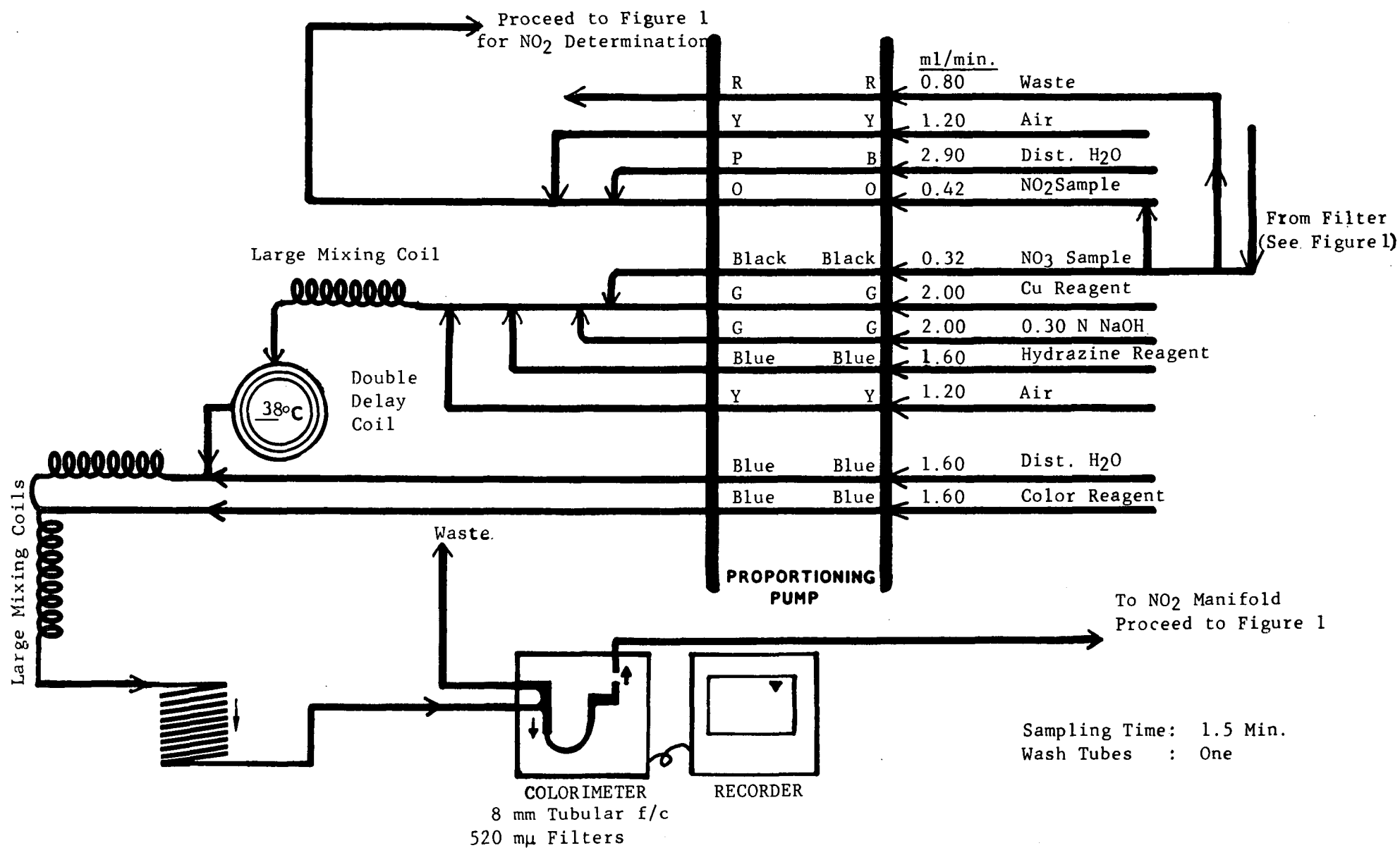
August 1968

Figure 1. Nitrate-Nitrite Manifold



August 1968

Figure 2. Nitrate-Nitrite Manifold



Federal Water Pollution Control Administration

Analytical Quality Control Branch

OFFICIAL INTERIM METHODS

for

Analyses of Surface Water Samples

Storet Parameter No. 00615

Parameter : Nitrogen, Nitrite (mg/l)

Method : Manual Method: colorimetric diazotization, modified.  
Manual Automated Method: same as manual.  
Automated Method: included in automated nitrate method  
for fresh water.

Reference : 1. Standard Methods for the Examination of Water and  
Wastewater, 12th ed., APHA, Inc., N.Y., 1965,  
205-208.  
2. ASTM Book of Standards, Part 23, 1967  
D1254-67, pp. 256-260.

Modifications: New method write-up. See attached.

Date: September 1968

Federal Water Pollution Control Administration

Analytical Quality Control Branch

OFFICIAL INTERIM METHOD

for

Nitrogen-Nitrite

Scope

1. These methods are applicable for the determination of nitrite ion in water, wastewater, sewage, sludges, and saline water by colorimetric methods.  
Official Method - Colorimetric method diazotization with sulfanilamide and N-(1-naphthyl)-ethylenediamine.  
Official Method - Automated - same chemistry as manual - to be developed for .010 mg/l sensitivity.\*

Preservation

2. Samples should be preserved at time of collection with 1 ml of chloroform per 100 ml sample or 40 mg Hg/ml as mercuric chloride. Store at 4°C. DO NOT PRESERVE WITH SULFURIC ACID.

Summary of Method

3. The diazonium compound formed by diazotation of sulfanilamide by nitrite ion in water under acid conditions is coupled with N-(1-naphthyl)-

\*Automated nitrite method is included in the automated nitrate method for fresh waters.

ethylenediamine to produce a reddish-purple color which is read in a spectrophotometer at 520 m $\mu$ .

#### Interferences

4. There are very few known interferences at concentrations less than 1000 times that of the nitrite; however, recent addition of strong oxidant or reductants to the sample will readily affect the nitrite concentration.

#### Determination of Nitrite-Nitrogen Ion in Aqueous Medium

##### Reagents

5. a) Color reagent: To 400 ml of distilled water, while stirring on a magnetic mixer, add 50 ml conc. HCl, 5.0 g of sulfanilamide and 0.5 g of N-(1-naphthyl)-ethylenediamine dihydrochloride. Stir until dissolved and dilute to 500 ml.
- b) Sodium acetate buffer, 2M: To 50 ml, while stirring on a magnetic mixer, add 27.4 g of  $\text{NaC}_2\text{H}_3\text{O}_2 \cdot 3 \text{H}_2\text{O}$ . Stir until dissolved and dilute to 100 ml.
- c) Stock nitrite-nitrogen standard (100 mg/l  $\text{NO}_2\text{-N}$ ): Dissolve 0.4926 g sodium nitrite, anhydrous  $\text{NaNO}_2$ , and dilute to 1000 ml with distilled water. Preserved with 2 ml chloroform per liter. Stable one week.



## Apparatus

6. a) Spectrophotometer or filter photometer suited for use in range of 515 to 530 mμ.
- b) Nessler tubes of 50 ml volume.

## Calibration

7. a) Prepare in 50 ml Nessler tubes a reagent blank and five standards in the desired concentration range from the 100 mg/l NO<sub>2</sub>-N standard and dilute to about 40 ml. The slope of the curve should be checked each day with a blank and one standard.
- b) To each add 1.0 ml of color reagent and 1.0 ml of acetate buffer. Dilute to 50 ml and allow color to develop for 10 minutes. The color reaction medium should be between pH 2.0 and 2.5.
- c) An estimate of the color density which will permit approximately 25% transmission in various size cells can be obtained from the following:

| ml stock<br>standard | mg/50 ml<br>NO <sub>2</sub> -N | mg/l<br>NO <sub>2</sub> -N | cell length<br>cm |
|----------------------|--------------------------------|----------------------------|-------------------|
| 2.0                  | .002                           | .040                       | 10.               |
| 4.0                  | .004                           | .080                       | 5.                |
| 20.0                 | .020                           | .40                        | 1.                |

- d) Read in spectrophotometer at 520 mμ against reagent blank.

## Procedure

8. a) If the sample has a pH greater than 10, adjust it to approximately pH 7 with acetic acid (1:3).
- b) Filter sample through Whatman No. 42 paper or .45  $\mu$  membrane filter, depending on the amount of suspended solids in sample.
- c) To 40 ml (or aliquot diluted to 40 ml) add 1.0 ml color reagent and 1.0 ml of buffer. Dilute to 50 ml mark and mix.
- d) Read color after 10-30 minutes in spectrophotometer at 520 m $\mu$  against reagent blank in same size cells as used with nitrite-nitrogen standards.

## Calculations

9. a) The colorimetric reaction obeys Beer-Lambert's law so that in plotting the absorbancy of the standards against the concentration, a straight line results.
- b) Calculate the concentration of nitrite-nitrogen ion in the sample in milligram per liter as follows:  

$$\text{mg/l NO}_2\text{-N} = \text{absorbance of sample} \times \frac{\text{mg/l standard} \times \frac{1000}{\text{ml sample}}}{\text{absorbance standard}}$$

## Precision

10. To be evaluated by "round robin" testing.

Federal Water Pollution Control Administration

Analytical Quality Control Branch

OFFICIAL INTERIM METHODS

for

Analyses of Surface Water Samples

Storet Parameter No. 00300

Parameter : Oxygen Dissolved (mg/l)

Method : Volumetric, Winkler azide, modified.

Reference : 1. Standard Methods for the Examination of Water and  
Wastewater, 12th ed., APHA, Inc., N.Y., 1965.  
406-410.  
2. ASTM Book of Standards, Part 23, 1967  
D888, pp. 114-115.

Modifications: Full bottle technique with normality adjusted  
to 0.0375N sodium thiosulfate. See new method  
write-up.

Date: September 1968

Federal Water Pollution Control Administration

Analytical Quality Control Branch

OFFICIAL INTERIM METHODS

for

Analyses of Surface Water Samples

Storet Parameter No. 00666

Parameter : Phosphorus, Soluble (mg/l)

Method : Colorimetric, mixed reagent, filtered with persulfate digestion.

Reference : 1. Gales, M. E. Jr., Julian, E. C., and Kroner, R. C.,  
"Method for Quantitative Determination of Total  
Phosphorus in Water." J. AWWA, 58(10), 1363-1368  
(1966).  
2. Murphy, J. and Riley, J. P., "A Modified Single  
Solution Method for the Determination of Phosphate  
in Natural Waters." Anal. Chim. Acta, 27, 31-36 (1962).  
Modifications: New method write-up.

Date: September 1968

Federal Water Pollution Control Administration

Analytical Quality Control Branch

OFFICIAL INTERIM METHODS

for

Analyses of Surface Water Samples

Storet Parameter No. to be assigned

Parameter : Phosphorus, Soluble, Ortho (mg/l)

Method : Colorimetric, mixed reagent, filtered.

Reference : Murphy, J. and Riley, J. P., "A Modified Single  
Solution Method for the Determination of Phosphate  
in Natural Waters." Anal. Chim. Acta, 27, 31-36 (1962).

Modifications: New method write-up.

Date: September 1968

Federal Water Pollution Control Administration

Analytical Quality Control Branch

OFFICIAL INTERIM METHODS

for

Analyses of Surface Water Samples

Storet Parameter No. 00665

Parameter : Phosphorus, Total (mg/l)

Method : Colorimetric, mixed reagent, with persulfate digestion

Reference : 1. Gales, M. E. Jr., Julian, E. C., and Kroner, R. C.,  
"Method for Quantitative Determination of Total  
Phosphorus in Water." J. AWWA, 58(10), 1363-1368  
(1966).  
2. Murphy, J. and Riley, J. P., "A Modified Single  
Solution Method for the Determination of Phosphate  
in Natural Waters." Anal. Chim. Acta, 27, 31-36 (1962).

Modifications: New method write-up.

Date: September 1968

Federal Water Pollution Control Administration

Analytical Quality Control Branch

OFFICIAL INTERIM METHODS

for

Analyses of Surface Water Samples

Storet Parameter No. to be assigned

Parameter : Phosphorus, Total, Ortho (mg/l)

Method : Colorimetric, mixed reagent.

Reference : Murphy, J. and Riley, J. P., "A Modified Single  
Solution Method for the Determination of Phosphate  
in Natural Waters." Anal. Chim. Acta, 27, 31-36 (1962).

Modifications: New method write-up.

Date: September 1968

Analytical Quality Control Branch

FWPCA OFFICIAL INTERIM METHOD

PHOSPHORUS

1. Scope

1.1 These methods cover the determination of specified forms of phosphorus in surface waters, saline waters, industrial waters, and sewage-type water samples. They may be applicable to sediment-type samples, sludges, algal blooms etc., but sufficient data is not available at this time to warrant such usage when measurements for total phosphorus content are required.

1.2 The methods are based on reactions that are specific for the orthophosphate ion. Thus, depending on the prescribed pre-treatment of the sample, the various forms of phosphorus given in Figure 1 may be determined. These forms are, in turn, defined in Table 1.

1.2.1 Except for in-depth and detailed studies, the most commonly measured forms of phosphorus are total and soluble phosphorus, and total and soluble orthophosphate. Hydrolyzable phosphorus is normally found only in sewage-type samples and insoluble forms of phosphorus, as noted, are determined by calculation.

1.3 The methods are usable in the 0.01 to 0.5 mg/l P range.

2. Definitions

2.1 The various forms of phosphorus are defined in Table 1.



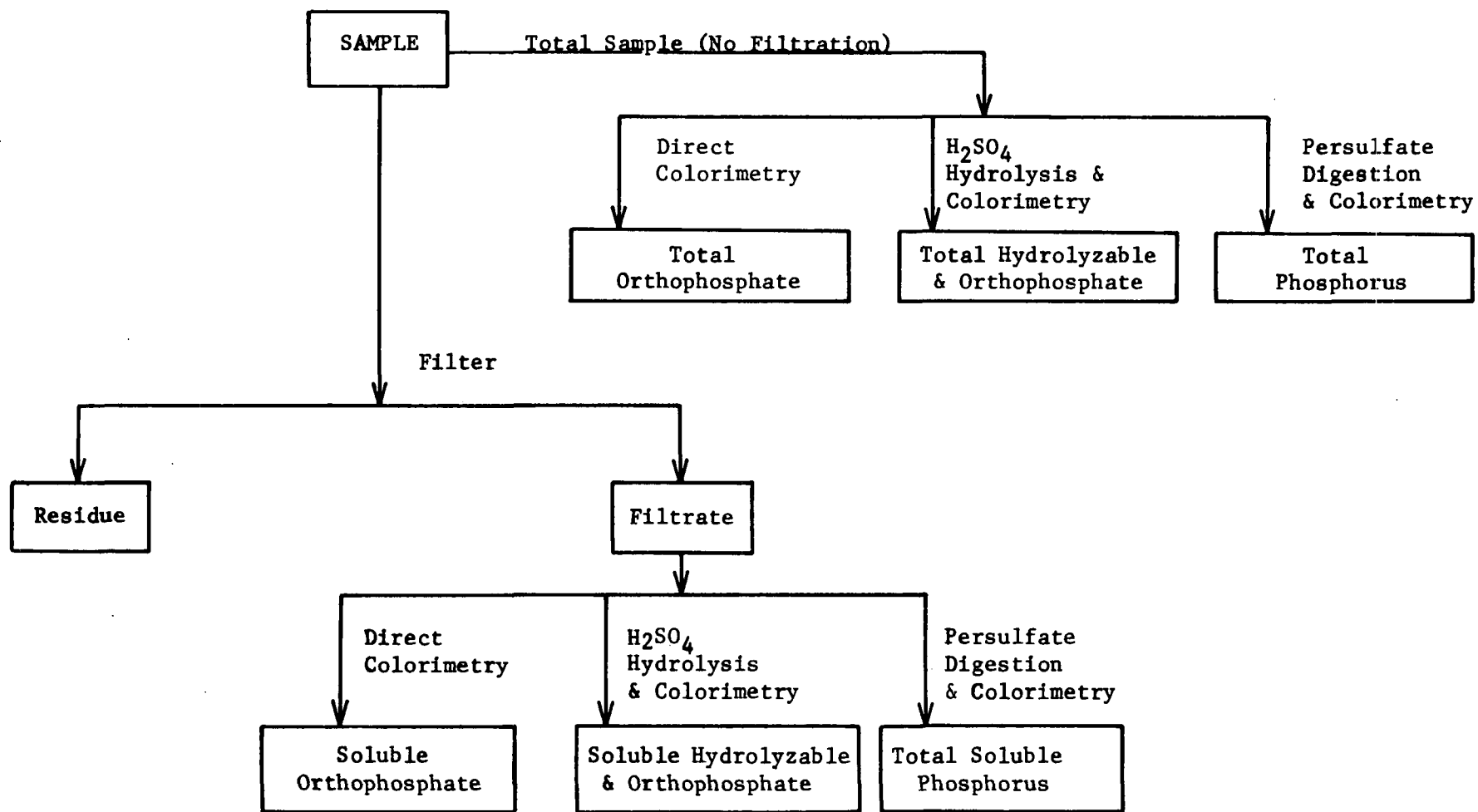


Figure 1. Analytical Scheme For Differentiation of Phosphorus Forms.

TABLE I

PHOSPHORUS TERMINOLOGY

1. Total Phosphorus (P-T) - all of the phosphorus present in the sample, regardless of form, as measured by the persulfate digestion procedure.
  - a. Total Orthophosphate (P-T,ortho) - inorganic phosphorus  $[(\text{PO}_4)^{-3}]$  in the sample as measured by the direct colorimetric analysis procedure.
  - b. Total Hydrolyzable Phosphorus (P-T,hydro) - phosphorus in the sample as measured by the sulfuric acid hydrolysis procedure, and minus pre-determined total orthophosphates. This hydrolyzable phosphorus includes polyphosphates  $[(\text{P}_2\text{O}_7)^{-4}, (\text{P}_3\text{O}_{10})^{-5}, \text{etc.}]$  + some organic phosphorus.
  - c. Total Organic Phosphorus (P-T,org) - phosphorus (inorganic + oxidizable organic) in the sample as measured by the persulfate digestion procedure, and minus total hydrolyzable phosphorus and orthophosphate.
2. Total Soluble Phosphorus (P-S,T) - all of the phosphorus present in the filtrate of a sample filtered through a phosphorus-free filter of 0.45 micron pore size and measured by the persulfate digestion procedure.
  - a. Soluble Orthophosphate (P-S,ortho) - as measured by the direct colorimetric analysis procedure.

TABLE I (Contd.)

- b. Soluble Hydrolyzable Phosphorus (P-S,hydro) - as measured by the sulfuric acid hydrolysis procedure and minus pre-determined soluble orthophosphates.
  - c. Soluble Organic Phosphorus (P-S,org) - as measured by the persulfate digestion procedure, and minus soluble hydrolyzable phosphorus and orthophosphate.
3. The following forms, when sufficient amounts of phosphorus are present in the sample to warrant such consideration, may be calculated:
- a. Total Insoluble Phosphorus  $(P-I,T) = (P-T) - (P-S,T)$ .
    - (1) Insoluble Orthophosphate  $(P-I,ortho) = (P-T,ortho) - (P-S,ortho)$ .
    - (2) Insoluble Hydrolyzable Phosphorus  $(P-I,hydro) = (P-T,hydro) - (P-S,hydro)$ .
    - (3) Insoluble Organic Phosphorus  $(P-I,org) = (P-T,org) - (P-S,org)$ .
4. All phosphorus forms shall be reported as P, mg/l.

### 3. Sampling

- 3.1 Samples should be taken in a location that is the most representative of the waters in the area being sampled. If benthic deposits are present in the area being sampled, great care should be taken not to include these deposits.
- 3.2 Sample containers may be of plastic material, such as cubitainers, or of Pyrex glass. In both cases, high iron concentrations interfere through the formation of clumps in the bottom of the sample.
- 3.3 If the analysis cannot be performed the same day of collection, the sample should be preserved in one of the following manners (Note 1):
  - 3.3.1 Five ml of chloroform per liter of sample.
  - 3.3.2 Acidification with sulfuric acid (used only when not measuring for all forms of phosphorus).
  - 3.3.3 Quick-freezing of sample.
  - 3.3.4 Five ml of saturated solution of mercury chloride per gallon of sample.

Note 1 - Sufficient data is not available on these suggested preservatives to state a preference at this time.

### 4. Summary of Method [Colorimetric Single Reagent Method]<sup>(1)</sup>

- 4.1 Ammonium molybdate and potassium antimonyl tartrate react in an acid medium with dilute solutions of phosphorus to

form an antimony-phosphate-molybdate complex. This complex is reduced to an intensely blue-colored complex by ascorbic acid. The color is proportional to the phosphorus concentration.

- 4.2 Only orthophosphate forms a blue color in this test. Polyphosphates (and some organic phosphorus compounds) may be converted to the orthophosphate form by sulfuric-acid-hydrolysis. Organic phosphorus compounds may be converted to the orthophosphate form by persulfate digestion.<sup>(2)</sup>

## 5. Interferences

- 5.1 It is reported<sup>(1)</sup> that no interference is caused by copper, iron, or silicate at concentrations many times greater than their greatest reported concentration in sea water.
- 5.2 The salt error for samples ranging from 5 to 20 percent salt content was found to be less than 1 percent<sup>(1)</sup>.
- 5.3 Arsenate, in concentrations greater than found in sea water, does not interfere<sup>(1)</sup>:

TABLE 2

Effect of Other Ions on Determination of Phosphate

| Ion        | Concentration<br>of Element<br>mg/l | Optical density at 822 mμ (4-cm cells) |                           |            |
|------------|-------------------------------------|--|---------------------------|------------|
|            |                                     | No added PO <sub>4</sub> /P            | + 10 μgPO <sub>4</sub> /P | Difference |
| -          | -                                   | 0.012                                  | 0.593                     | 0.581      |
| Copper(II) | 10                                  | 0.018                                  | 0.585                     | 0.567      |
| Iron(III)  | 50                                  | 0.017                                  | 0.598                     | 0.581      |
| Silicate   | 10                                  | 0.014                                  | 0.594                     | 0.580      |
| Arsenate   | 1.0                                 | 1.144 <sup>a</sup>                     | 1.752 <sup>a</sup>        | 0.608      |
| Arsenate   | 0.02                                | 0.020                                  | 0.614                     | 0.594      |

<sup>a</sup>Measured in 1-cm cell calculated for 4-cm cells.

## 6. Apparatus

6.1 Photometer - A spectrophotometer or filter photometer suitable for measurements at 880 mμ, and providing a light path of 1 inch (2.54 cm) or longer, should be used.

6.2 Acid-washed glassware: All glassware used in the determination should be washed with hot 1:1 HCl and rinsed with distilled water. The acid-washed glassware should be filled with distilled water and treated with all the reagents to remove the last traces of phosphorus that might be adsorbed on the glassware. Preferably, this glassware should be used only for the determination of phosphorus and after use it should be rinsed with distilled water and kept covered until needed again. If this is done, the treatment with 1:1 HCl and reagents is only required occasionally. Commercial detergents should never be used.

## 7. Reagents

- 7.1 Sulfuric acid solution, 5N: Dilute 70 ml of conc.  $\text{H}_2\text{SO}_4$  with distilled water to 500 ml.
- 7.2 Potassium antimonyl tartrate solution: Weigh 1.3715 g  $\text{K}(\text{SbO})\text{C}_4\text{H}_4\text{O}_6 \cdot 1/2 \text{H}_2\text{O}$ , dissolve in 400 ml distilled water in 500 ml volumetric flask, dilute to volume. Store in glass-stoppered bottle.
- 7.3 Ammonium molybdate solution: Dissolve 20 g  $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24} \cdot 4 \text{H}_2\text{O}$  in 500 ml distilled water. Store in a plastic bottle at 4° C.
- 7.4 Ascorbic acid, 0.1M: Dissolve 1.76 g of ascorbic acid in 100 ml of distilled water. The solution is stable for about a week if stored at 4° C.
- 7.5 Combined reagent: Mix the above reagents in the following proportions for 100 ml of the mixed reagent: 50 ml of 5N  $\text{H}_2\text{SO}_4$ , 5 ml of potassium antimonyl tartrate solution, 15 ml of ammonium molybdate solution, and 30 ml of ascorbic acid solution. Mix after addition of each reagent. All reagents must reach room temperature before they are mixed and must be mixed in the order given. If turbidity forms in the combined reagent, shake and let it stand for a few minutes until the turbidity disappears before proceeding. The reagent is stable for one week if stored at 4° C.
- 7.6 Primary phosphorus standard: Dissolve in distilled water 0.2197 g of potassium dihydrogen phosphate,  $\text{KH}_2\text{PO}_4$ , which

has been dried in an oven at 105° C. Dilute the solution to 1,000 ml; 1.00 ml equals 0.05 mg P.

7.7 Working phosphorus standard: Dilute 10.0 ml of stock phosphorus solution to 1,000 ml with distilled water; 1.00 ml equals 0.5 µg P.

7.8 Strong-acid solution: Slowly add 310 ml conc.  $H_2SO_4$  to 600 ml distilled water. When cool, dilute to 1 liter.

7.9 Ammonium persulfate.

## 8. Calibration

8.1 Standard curve: Prepare a series of at least nine standard phosphorus solutions to cover the range from 0 to 0.50 P mg/l. Make up the standards by diluting suitable volumes of working phosphorus solution to 50 ml with distilled water. The following dilutions are suggested:

| <u>ml of Working<br/>Phosphorus Standard</u> | <u>Conc., mg/l</u> |
|--|--------------------|
| 0  | 0.00               |
| 1.0  | 0.01               |
| 3.0  | 0.03               |
| 5.0  | 0.05               |
| 10.0   | 0.10               |
| 20.0   | 0.20               |
| 30.0   | 0.30               |
| 40.0   | 0.40               |
| 50.0   | 0.50               |

8.2 Develop color in the series of standards and blank of distilled water as directed in 9. Procedure. Measure the color absorbance of each standard at 880 mµ with a spectrophotometer, using the reagent blank as the reference solution.



Plot the absorbance values as ordinates and the corresponding phosphorus concentrations as abscissas.

8.3 Process standards and blank exactly as the samples.

Run at least a blank and two standards with each series of samples. If the standards do not agree within  $\pm 2\%$  of the true value, prepare a new calibration curve.

9. Procedure

9.1 Total Phosphorus

9.1.1 Add 1 ml of strong-acid solution to a 50-ml sample in a 125-ml Erlenmeyer flask.

9.1.2 Add 0.4 gram of ammonium persulfate.

9.1.3 Boil gently on a pre-heated hot plate for approximately 30-40 minutes or until a final volume of about 10 ml is reached. Do not allow sample to go to dryness. Alternatively, heat for 30 minutes in an autoclave at 121° C (15-20 psi).

9.1.4 Cool and dilute the sample to 50 ml.

9.1.5 The sample is now ready for determination of phosphorus as outlined in 9.3 Orthophosphate.

9.2 Hydrolyzable Phosphorus

9.2.1 Add 1 ml of strong-acid solution to a 50-ml sample in a 125-ml Erlenmeyer Flask.

9.2.2 Boil gently on a pre-heated hot plate for approximately 30-40 minutes or until a final volume of about 10 ml is reached. Do not allow sample to go to dryness. Alternatively, heat for 30 minutes in an autoclave at 121° C (15-20 psi).

9.2.3 Cool and dilute the sample to 50 ml.

9.2.4 The sample is now ready for determination of phosphorus as outlined in 9.3 Orthophosphate.

### 9.3 Orthophosphate

9.3.1 Add 1 drop of phenolphthalein indicator to the 50.0 ml sample. If a red color develops, add strong-acid solution drop-wise to just discharge the color.

9.3.2 Add 8.0 ml of combined reagent to sample and mix thoroughly. After a minimum of ten minutes, but no longer than thirty minutes, measure the color absorbance of each sample at 880 mμ with a spectrophotometer, using the reagent blank as the reference solution.

## 10. Calculation

10.1 Obtain concentration value of sample directly from prepared standard curve. Report results as P, mg/l.

## 11. Precision and Accuracy

11.1 Complete precision and accuracy data are not available

at this time. In a comparative study of three modifications of the Single Reagent Method,<sup>(3)</sup> however, the following results were obtained.

11.1.1 On a variety of natural water samples, both salt and fresh, a precision of 1.70% (coefficient of variation) and an accuracy of 0.43% (deviation from amount added) were obtained at a 0.2 mg/l P concentration.

#### References

1. J. Murphy and J. Riley, "A Modified Single Solution Method for the Determination of Phosphate in Natural Waters." Anal. Chim. Acta., 27, 31 (1962).
2. M. Gales, Jr., E. Julian, and R. Kroner, "Method for Quantitative Determination of Total Phosphorus in Water." Jour AWWA, 58, No. 10, 1363 (1966).
3. J. Winter and R. Booth, "A Comparison of Three Modifications of the Single Reagent Method for Phosphorus, Ortho, Soluble." Analytical Quality Control Branch, Division of Research, Federal Water Pollution Control Administration (August 1968).

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Federal Water Pollution Control Administration

Analytical Quality Control Branch

OFFICIAL INTERIM METHODS

for

Analyses of Surface Water Samples

Storet Parameter No. 00085

Parameter : Odor, Threshold, Hot (60 C)

Method : Dilution Series, modified.

Reference : Standard Methods for the Examination of Water and  
Wastewater, 12th ed., APHA, Inc., N.Y., 1965,  
304-311.

Modifications: Method in preparation. Use reference method until  
ready.

Date: September 1968

Federal Water Pollution Control Administration

Analytical Quality Control Branch

OFFICIAL INTERIM METHODS

for

Analyses of Surface Water Samples

Storet Parameter No. to be assigned

Parameter : Odor, Threshold, Room Temperature

Method : Dilution Series, modified.

Reference : Standard Methods for the Examination of Water and  
Wastewater, 12th ed., APHA, Inc., N.Y., 1965,  
304-311.

Modifications: Method in preparation. Use reference method until  
ready.

Date: September 1968

Federal Water Pollution Control Administration

Analytical Quality Control Branch

OFFICIAL INTERIM METHODS

for

Analyses of Surface Water Samples

Storet Parameter No. 00550

Parameter : Oil and Grease (mg/l)

Method : Soxhlet Extraction Method .

Reference : Standard Methods for the Examination of Water and  
Wastewater, 12th ed., APHA, Inc., N.Y., 1965,  
384-385.

Modifications: Page 384 Delete only the heading, "1. General Discussion".

Insert the following heading and paragraph:

1. Scope and Application

In the determination of grease, an absolute quantity of a specific substance is not measured. Rather, groups of substances with similar physical characteristics are determined quantitatively, based on their mutual solubility in the solvent used. Grease, therefore, can be said to include fats, waxes, oils, and any other nonvolatile material extracted by hexane from an acidified sample of water or waste water.

Sampling and Storage: When possible, collect representative samples in a wide-mouth bottle calibrated to hold a measured volume, and perform the initial steps of the procedure in the sample bottle. When information is required concerning the average grease concentration of a waste over an extended period, the examination of individual portions collected at prescribed time intervals can be used to eliminate losses of grease on sampling equipment during the collection of a composite sample.

Date: September 1968

Federal Water Pollution Control Administration  
OFFICIAL INTERIM METHODS

Modifications Cont'd:

Page 385 Delete paragraph 4.1.

Insert as paragraph 4.1:

Collect sample in a wide-mouth bottle and acidify  
pH 1.0 with conc. HCl.

Page 385 Section 6. Precision and Accuracy

Delete paragraph entirely.

Insert the following sentence:

Precision and accuracy will be determined by round  
robin testing.

Federal Water Pollution Control Administration

Analytical Quality Control Branch

OFFICIAL INTERIM METHODS

for

Analyses of Surface Water Samples

Storet Parameter No. 00681

Parameter : Organic Carbon, Dissolved (mg/l)

Method : Dow Beckman-type organic carbon analyzer.

Reference : ASTM Book of Standards, Part 23, 1967  
D2579-67T, pp. 716-719.

Modifications: None

Date: September 1968



Federal Water Pollution Control Administration

Analytical Quality Control Branch

OFFICIAL INTERIM METHODS

for

Analyses of Surface Water Samples

Storet Parameter No. 00680

Parameter : Organic Carbon, Total (mg/l)

Method : Dow Beckman-type organic carbon analyzer.

Reference : ASTM Book of Standards, Part 23, 1967  
D2579-67T, pp. 716-719.

Modifications: None

Date: September 1968

Federal Water Pollution Control Administration

Analytical Quality Control Branch

OFFICIAL INTERIM METHODS

for

Analyses of Surface Water Samples

Storet Parameter No. 00400

Parameter : pH

Method : Instrumental, glass/standard calomel electrodes.

Reference : 1. Standard Methods for the Examination of Water and  
Wastewater, 12th ed., APHA, Inc., N.Y., 1965,  
226-228.  
2. ASTM Book of Standards, Part 23, 1967  
289-299.

Modifications: None

Date: September 1968

Federal Water Pollution Control Administration

Analytical Quality Control Branch

OFFICIAL INTERIM METHODS

for

Analyses of Surface Water Samples

Storet Parameter No. 32730

Parameter : Phenolics (mg/l)

Method : "Phenolic Compounds in Industrial Water and  
Industrial Waste Water  
Method A. Chloroform Extraction Method  
Method B. Direct Colorimetric Method"

Reference : ASTM Book of Standards, Part 23, 1967  
D1783-62, pp. 430-436.

Modifications: None

Date: September 1968

Federal Water Pollution Control Administration

Analytical Quality Control Branch

OFFICIAL INTERIM METHODS

for

Analyses of Surface Water Samples

Storet Parameter No. 00935

Parameter : Potassium, (mg/l)

Method : 1. Atomic absorption.  
2. Flame photometry.

Reference : 1. Method is specific to the particular instrument.  
General procedure is being selected.  
2. Standard Methods for the Examination of Water and  
Wastewater, 12th ed., APHA, Inc., N.Y., 1965,  
238-240.

Modifications: None

Date: September 1968

Federal Water Pollution Control Administration

Analytical Quality Control Branch

OFFICIAL INTERIM METHODS

for

Analyses of Surface Water Samples

Storet Parameter No. to be assigned

Parameter : Selenium, Dissolved ( $\mu\text{g/l}$ )

Method : Filtration through 0.45  $\mu$  membrane filter.  
Measurement by diaminobenzidine colorimetric method.

Reference : Standard Methods for the Examination of Water and  
Wastewater, 12th ed., APHA, Inc., N.Y., 1965,  
251-253.

Modifications: Use of 0.45  $\mu$  membrane filter only.

Date: September 1968

Federal Water Pollution Control Administration

Analytical Quality Control Branch

OFFICIAL INTERIM METHODS

for

Analyses of Surface Water Samples

Storet Parameter No. 01145

Parameter : Selenium, Total ( $\mu\text{g/l}$ )

Method : Diaminobenzidine, colorimetric.

Reference : Standard Methods for the Examination of Water and  
Wastewater, 12th ed., APHA, Inc., N.Y., 1965,  
251-253.

Modifications: None

Date: September 1968

Federal Water Pollution Control Administration

Analytical Quality Control Branch

OFFICIAL INTERIM METHODS

for

Analyses of Surface Water Samples

Storet Parameter No. to be assigned

Parameter : Silicon (Silica), Dissolved ( $\mu\text{g/l}$ )

Method : Filtration through 0.45  $\mu$  membrane filter.  
Measurement by molybdate blue.

Reference : "Methods for Collection of Analysis of Water Samples",  
Geological Survey Water-Supply Paper 1454, 1960,  
pp. 259-261.

Modifications: Use of 0.45  $\mu$  membrane filter only.

Date: September 1968

Federal Water Pollution Control Administration

Analytical Quality Control Branch

OFFICIAL INTERIM METHODS

for

Analyses of Surface Water Samples

Storet Parameter No. 01140

Parameter : Silicon (Silica), Total ( $\mu\text{g/l}$ )

Method : Molybdate blue

Reference : "Methods for Collection of Analysis of Water Samples",  
Geological Survey Water-Supply Paper 1454, 1960,  
pp. 259-261.

Modifications: None

Date: September 1968



Federal Water Pollution Control Administration

Analytical Quality Control Branch

OFFICIAL INTERIM METHODS

for

Analyses of Surface Water Samples

Storet Parameter No. 00930

Parameter : Sodium (mg/l)

Method : 1. Atomic absorption.  
2. Flame photometry.

Reference : 1. Method is specific to the particular instrument.  
General procedure is being selected.  
2. Standard Method for the Examination of Water and  
Wastewater, 12th ed., APHA, Inc., N.Y., 1965,  
274-277.

Modifications: None

Date: September 1968

Federal Water Pollution Control Administration

Analytical Quality Control Branch

OFFICIAL INTERIM METHODS

for

Analyses of Surface Water Samples

Storet Parameter No. 00520

Parameter : Solids, Dissolved, Volatile (mg/l)

Method : Gravimetric by difference, modified.

Reference : Standard Methods for the Examination of Water and  
Wastewater, 12th ed., APHA, Inc., N.Y., 1965,  
247-248.

Modifications: Filter by 0.45  $\mu$  membrane filter for dissolved/suspended  
volatile solids.

Date: September 1968

Federal Water Pollution Control Administration

Analytical Quality Control Branch

OFFICIAL INTERIM METHODS

for

Analyses of Surface Water Samples

Storet Parameter No. 00500

Parameter : Solids, Total (mg/l)

Method : Gravimetric, modified.

Reference : Standard Methods for the Examination of Water and  
Wastewater, 12th ed., APHA, Inc., N.Y., 1965,  
244-245.

Modifications: Evaporate at 103-105°C only.

Date: September 1968

Federal Water Pollution Control Administration

Analytical Quality Control Branch

OFFICIAL INTERIM METHODS

for

Analyses of Surface Water Samples

Storet Parameter No. 00515

Parameter : Solids, Total Dissolved (mg/l)

Method : Gravimetric, modified.

Reference : Standard Methods for the Examination of Water and  
Wastewater, 12th ed., APHA, Inc., N.Y., 1965,  
247-248.

Modifications: Use of 0.45  $\mu$  membrane filter only, for filtrations.  
Glass pre-filter may be used to speed filtration.  
Evaporate at 103-105°C only.

Date: September 1968

Federal Water Pollution Control Administration

Analytical Quality Control Branch

OFFICIAL INTERIM METHODS

for

Analyses of Surface Water Samples

Storet Parameter No. 00530

Parameter : Solids, Total Suspended (mg/l)

Method : Gravimetric, modified.

Reference : Standard Methods for the Examination of Water and  
Wastewater, 12th ed., APHA, Inc., N.Y., 1965,  
246-247.

Modifications: Filter by 0.45  $\mu$  membrane filter only,  
evaporate at 103-105°C only.

Date: September 1968

Federal Water Pollution Control Administration

Analytical Quality Control Branch

OFFICIAL INTERIM METHODS

for

Analyses of Surface Water Samples

Storet Parameter No. 00535

Parameter : Solids, Suspended, Volatile (mg/l)

Method : Gravimetric by difference, modified.

Reference : Standard Methods for the Examination of Water and  
Wastewater, 12th ed., APHA, Inc., N.Y., 1965,  
247-248.

Modifications: Filter by 0.45  $\mu$  membrane filter for dissolved/suspended  
volatile solids.

Date: September 1968

Federal Water Pollution Control Administration

Analytical Quality Control Branch

OFFICIAL INTERIM METHODS

for

Analyses of Surface Water Samples

Storet Parameter No. 00505

Parameter : Solids, Total, Volatile (mg/l)

Method : Gravimetric, modified.

Reference : Standard Methods for the Examination of Water and  
Wastewater, 12th ed., APHA, Inc., N.Y., 1965,  
247-248.

Modifications: Filter by 0.45  $\mu$  membrane filter only for  
filterable/non-filterable volatile solids.

Date: September 1968

Federal Water Pollution Control Administration

Analytical Quality Control Branch

OFFICIAL INTERIM METHODS

for

Analyses of Surface Water Samples

Storet Parameter No. 00945

Parameter : Sulfate (mg/l)

Method : Turbidimetric, modified.

Reference : Standard Methods for the Examination of Water and  
Wastewater, 12th ed., APHA, Inc., N.Y., 1965,  
291-293.

Modifications: Use of proprietary reagents is acceptable.

Date: September 1968



Federal Water Pollution Control Administration

Analytical Quality Control Branch

OFFICIAL INTERIM METHODS

for

Analyses of Surface Water Samples

Storet Parameter No. 00746

Parameter : Sulfide, Dissolved (mg/l)

Method : In preparation.

Reference :

Modifications:

Date: September 1968

Federal Water Pollution Control Administration

Analytical Quality Control Branch

OFFICIAL INTERIM METHODS

for

Analyses of Surface Water Samples

Storet Parameter No. 00010

Parameter : Temperature (°Centigrade)

Method : Thermometer, (mercury, dial, or thermistor).

Reference : Standard Methods for the Examination of Water and  
Wastewater, 12th ed., APHA, Inc., N.Y., 1965,  
433.

Modifications: None

Date: September 1968

Federal Water Pollution Control Administration

Analytical Quality Control Branch

OFFICIAL INTERIM METHODS

for

Analyses of Surface Water Samples

Storet Parameter No. 00076

Parameter : Turbidity, Nephelometric

Method : Selected instrument such as Hach 2100, based on  
method specifications.

Reference : New method write-up. See attached.

Modifications: None

Date: September 1968

Federal Water Pollution Control Administration

Analytical Quality Control Branch

OFFICIAL INTERIM METHOD

for

Turbidity

Method Selection

To be measured by selected turbidimeter only. COMVAQC, FWPCA has developed the following specifications for a turbidimeter acceptable for use in the Administration. Instruments are now coming on to the market which can meet these specifications. No instrument listing is made since the instrument companies make quick model and design changes and any listing would be unintentionally incomplete and possibly incorrect.

Background

Clear water is important in those industries where the product is destined for human consumption or for a large number of industrial uses. Beverage producers, food processors, and treatment plants drawing upon a surface water supply commonly rely on coagulation, settling, and filtration measures to insure an acceptable effluent.

Turbidity in water is caused by the presence of suspended matter, such as clay, silt, finely divided organic and inorganic matter, plankton, and other microscopic organisms. Turbidity should be clearly understood to be an expression of the optical property of a sample which causes light to be scattered and absorbed rather than transmitted in straight lines through the sample. Attempts to correlate turbidity

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with the weight concentration of suspended matter are impractical, as the size, shape, and refractive index of the particulate materials are of great importance optically but bear little direct relationship to the concentration and specific gravity of the suspended matter.

The standard method for the determination of turbidity has been based on the Jackson Candle turbidimeter. However, the lowest turbidity value which can be measured directly on this instrument is 25 units. With turbidities of treated water generally falling within the range 0-5 units, indirect, secondary methods have been required to obtain turbidities on such samples. Unfortunately no instrument has been devised which will duplicate the results obtained on the Jackson Candle turbidimeter for all samples. Owing to fundamental differences in optical systems, the results obtained with different types of secondary instruments will frequently not check closely with one another even though the instruments are all pre-calibrated against the Jackson Candle turbidimeter.

A further cause of discrepancies in turbidity analysis is the use of suspensions of different types of particulate matter for preparation of instrumental calibration curves. As with the water samples, prepared suspensions have different optical properties depending upon the particle size distributions, shapes, and refractive indices. Most commercial turbidimeters available for measuring low

turbidities give comparatively good indications of the intensity of light scattered in one particular direction, predominately at right angles to the incident light. Since there is no direct relationship between the Jackson Candle turbidity and the intensity of light scattered at  $90^\circ$ , there is no valid basis for the practice of calibrating the  $90^\circ$  turbidimeters in terms of Jackson units.

## 1. General Discussion

1.1. Principle: The method presented below is based upon a comparison of the intensity of light scattered by the sample under defined conditions with the intensity of light scattered by a standard reference suspension under the same conditions. The higher the intensity of scattered light, the higher the turbidity. Formazin polymer, which has gained acceptance as the turbidity standard reference suspension in the brewing industry, is also used as the turbidity standard reference suspension for water. It is easy to prepare and is more reproducible in its light scattering properties than the clay or turbid natural water standards previously used. The turbidity of a particular concentration of Formazin suspension is defined as 40 units. This same suspension of Formazin has an approximate turbidity of 40 units when measured on the Jackson Candle turbidimeter, therefore turbidity units based on the Formazin

preparation will approximate those derived from the Jackson Candle turbidimeter but will not be identical to them.

1.2. Interference: The determination of turbidity is applicable to any water sample that is free of debris and coarse sediments which settle out rapidly, although dirty glassware, the presence of air bubbles, and the effects of vibrations which disturb the surface visibility of the sample will lead to false results. The presence of "true color", that is the color of the water which is due to dissolved substances which absorb light, will cause measured turbidities to be low. This effect is generally not significant with treated water.

1.3. Storage: It is preferable to determine turbidity on the same day the sample is taken. If longer storage is unavoidable, however, samples may be stored in the dark up to 24 hr. For even longer storage, treat 1 liter of sample with 1g mercuric chloride. Prolonged storage before measurement is not recommended as irreversible changes in turbidity may occur. All samples should be vigorously shaken before examination.

## 2. Apparatus

2.1 The turbidimeter shall consist of a nephelometer with light source for illuminating the sample and one or more photoelectric detectors with a readout device to indicate the intensity of light scattered at right angles to the path of the incident light. The turbidimeter should be so designed that little stray light reaches the detector in the absence of turbidity and should be free from significant drift after a short warm-up period. The sensitivity of the instrument should permit detection of turbidity differences of 0.02 unit or less in waters having turbidities less than 1 unit. The instrument should SEP

measure from 0-40 units turbidity. Several ranges will be necessary to obtain both adequate coverage and sufficient sensitivity for low turbidities.

The sample tubes to be used with the available instrument must be of clear, colorless glass. They should be kept scrupulously clean, both inside and out, and discarded when they become scratched or etched. They must not be handled at all where the light strikes them, but should be provided with sufficient extra length, or with a protective case, so that they may be handled. The tubes should be filled with samples and standards which have been thoroughly agitated, and sufficient time should be allowed for bubbles to escape.

Differences in physical design of turbidimeters will cause differences in measured values for turbidity even though the same suspension is used for calibration. To minimize such differences, the following design criteria should be observed:

- a. Light source - tungsten lamp operated at not less than 85% of rated voltage or more than rated voltage.
- b. Distance traversed by incident light and scattered light within the sample tube - total not to exceed 10 cm.
- c. Angle of light acceptance of the detector - centered at 90° to the incident light path and not to exceed  $\pm 30^\circ$  from 90°.
- d. Maximum turbidity to be measured - 40 units.

### 3. Reagents

3.1. Turbidity-free water: Pass distilled water through a membrane filter having a pore size no greater than 100  $\mu$  if such filtered water shows a lower turbidity than the distilled water. Discard



the first 200 ml collected. Otherwise, use the distilled water.

3.2. Stock turbidity suspension:

- a. Solution (I): Dissolve 1.000g hydrazine sulfate,  $(\text{NH}_2)_2\cdot\text{H}_2\text{SO}_4$ , in distilled water and dilute to 100 ml in a volumetric flask.
- b. Solution (II): Dissolve 10.00g hexamethylenetetramine in distilled water and dilute to 100 ml in a volumetric flask.
- c. In a 100 ml volumetric flask, mix 5.0 ml solution (I) with 5.0 ml solution (II). Allow to stand 24 hours at  $25 \pm 3^\circ \text{C}$ , then dilute to the mark and mix.

3.3. Standard turbidity suspension: Dilute 10.00 ml stock turbidity suspension to 100 ml with turbidity free water. The turbidity of this suspension is defined as 40 units.

3.4. Dilute turbidity standards: Dilute portions of the standard turbidity suspension with turbidity-free water as required.

A new stock turbidity suspension should be prepared each month. The standard turbidity suspension and dilute turbidity standards should be prepared weekly by dilution of the stock turbidity suspension.

4. Procedure:

4.1. Turbidimeter calibration: The manufacturer's operating instructions should be followed. Measure standards on the turbidimeter covering the range of interest. If the instrument is already calibrated in standard turbidity units, this procedure will check the accuracy of the calibration scales. At least one standard should be run in each instrument range to be used. Some instruments permit adjustment of sensitivity so that scale values will correspond to turbidities.

Reliance on a manufacturer's solid scattering standard for setting overall instrument sensitivity for all ranges is not an acceptable practice unless the turbidimeter has been shown to be free of drift on all ranges. If a pre-calibrated scale is not supplied, then calibration curves should be prepared for each range of the instrument.

4.2. Turbidities less than 40 units: Shake the sample to thoroughly disperse the solids. Wait until air bubbles disappear then pour the sample into the turbidimeter tube. Read the turbidity directly from the instrument scale or from the appropriate calibration curve.

4.3. Turbidities exceeding 40 units: Dilute the sample with one or more volumes of turbidity-free water until the turbidity falls below 40 units. The turbidity of the original sample is then computed from the turbidity of the diluted sample and the dilution factor. For example, if 5 volumes of turbidity-free water were added to 1 volume of sample, and the diluted sample showed a turbidity of 30 units, then the turbidity of the original sample was 180 units.

## 5. Interpretation of Results

5.1 Turbidity readings are reported in accordance with the following:

| Turbidity<br>Range,<br>units | Record<br>to nearest: |
|------------------------------|-----------------------|
| 0.0-1.0                      | 0.05                  |
| 1-10                         | 0.1                   |
| 10-40                        | 1                     |
| 40-100                       | 5                     |
| 100-400                      | 10                    |
| 400-1000                     | 50                    |
| >1000                        | 100                   |

5.2. For comparison of water treatment efficiencies, it may be desirable to estimate more closely than is specified in the table: but, because of the uncertainties and discrepancies in turbidity measurements, it cannot be expected that two or more laboratories will duplicate results on the same sample more closely than specified.

Federal Water Pollution Control Administration

Analytical Quality Control Branch

OFFICIAL INTERIM METHODS

for

Analyses of Surface Water Samples

Storet Parameter No. to be assigned

Parameter : Zinc, Dissolved

Method : Filtration through 0.45  $\mu$  membrane filter .  
Measurement by atomic absorption.

Reference : Method is specific to the particular instrument.  
General procedure is being selected.

Modifications: None

Date: September 1968

Federal Water Pollution Control Administration

Analytical Quality Control Branch

OFFICIAL INTERIM METHODS

for

Analyses of Surface Water Samples

Storet Parameter No. 01090

Parameter : Zinc, Total

Method : Atomic absorption.

Reference : Method is specific to the particular instrument.  
General procedure is being selected.

Modifications: None

Date: September 1968