# COMBINED WORK/QUALITY ASSURANCE PROJECT PLAN (CW/QAPP)

*for*

## DETAILED EFFLUENT CHARACTERIZATION: 1995-1997

**Task 8**
**MWRA Harbor and Outfall Monitoring Project**

*submitted to*


MASSACHUSETTS WATER RESOURCES AUTHORITY
**Environmental Quality Department**
**100 First Avenue**
**Charlestown Navy Yard**
**Boston, MA 02129**
**(617) 242-6000**


*prepared by*


**Eric Butler**
**Mark Hasegawa**
**Debra McGrath**
ENSR Consulting and Engineering


*submitted by*


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**May, 1995**

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**ms-35**

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## 1.0 PROJECT NAME

MWRA Harbor and Outfall Monitoring Project
Task 8
Detailed Effluent Characterization

## 2.0 PROJECT REQUESTED BY

Massachusetts Water Resources Authority

## 3.0 DATE OF REQUEST

November 2, 1994

## 4.0 DATE OF PROJECT INITIATION

November 2, 1994

## 5.0 PROJECT MANAGEMENT

Dr. Michael Connor, MWRA Director of Environmental Quality Department
Dr. Michael Mickelson, MWRA Harbor and Outfall Monitoring Project Manager
Mr. Ken Keay, MWRA Harbor and Outfall Monitoring Deputy Project Manager
Mr. Maury Hall, MWRA Detailed Effluent Characterization Task Manager

Dr. James Blake, ENSR Project Manager for Harbor and Outfall Monitoring
Dr. James Bowen, ENSR Technical Director for Harbor and Outfall Monitoring
Dr. Eric Butler, ENSR Detailed Effluent Characterization Area Manager

## 6.0 QUALITY ASSURANCE MANAGEMENT

Ms. Debra McGrath, ENSR Project QA Director

# 7.0 PROJECT DESCRIPTION

## 7.1 Objective and Scope

The overall objective of the Detailed Effluent Characterization Task (Task 8) is to measure the concentrations of trace metals, nutrients, *Clostridium perfringens*, and organic contaminants and stable isotopes in the Massachusetts Water Resources Authority (MWRA) sewage treatment plant effluent to obtain an accurate estimate of discharge loads and a chemical "fingerprint" to help trace the discharge in the environment. This work is intended to supplement routine measurements of effluent constituents conducted as part of the National Pollutant Discharge Elimination System (NPDES) permit compliance monitoring and other effluent monitoring conducted to evaluate treatment plant performance and to set local limits for industrial dischargers. This study is explicitly required as part of the Outfall Monitoring Program, which itself is required by United States Environmental Protection Agency (EPA) and Executive Office of Environmental Affairs (EOEA). It is also incorporated into the court order governing the Harbor Project. The regular routine monitoring analyses do not include many contaminants that are important for assessing the transport, fate, and effects of the effluent discharge. In addition, the analytical detection limits reported for the NPDES monitoring are too high to detect many of the organic and metal contaminants of concern and are often higher than the water quality criteria that might be used to assess potential adverse effects of the effluent discharge. The analytical methods employed under this task will provide significantly lower detection limits than those used for NPDES monitoring for the organics and metals and will provide measurements of additional contaminants and sewage tracers that may be important for source identification and contaminant transport modeling.

A secondary objective of this task is to provide data on the concentrations of selected trace metals and organic contaminants and nutrients in the influent, primary and secondary effluent of the Pilot Secondary Treatment Plant as well as other as-needed sampling and analysis of influents and effluents to support Authority needs in assessing the performance of this treatment process in removing toxic contaminants from the effluent discharge.

The scope of this task includes transporting effluent samples collected by MWRA staff to the ENSR subcontractor laboratories, measuring the concentrations of selected analytes in the effluent, and reporting the data in interim (covering 4 months of data per report) and annual data reports and for interpretation under Task 33.2 (Detailed Effluent Characterization Annual Synthesis Report). At the direction of MWRA, only the total recoverable concentrations of organic and metal contaminants will be measured; discrete dissolved, particulate, or colloidal fractions will not be measured at this time. In addition, stable isotopes, nutrients, and related compounds, and *Clostridium perfringens* will be measured in influent and effluent samples. In general, stable isotopes and *Clostridium perfringens* will be measured in the samples supplementing the routine NPDES monitoring, but not in samples from the Pilot Secondary Treatment Plant.

This Combined Work/Quality Assurance Project Plan (CW/QAPP) presents the organization, objectives, functional activities, and specific quality assurance (QA) and quality control (QC) activities with the Detailed Effluent Characterization Task. This document also describes the specific protocols that will be followed for sampling, sample handling and storage, chain of custody, and laboratory and field analyses. The CW/QAPP was prepared in accordance with EPA guidance documents on CW/QAPP preparation (EPA 1984, 1988) and is based on the CW/QAPP produced previously under a contract between MWRA and Battelle Ocean Sciences (Shea, 1993).

## 7.2 Data Usage

The Detailed Effluent Characterization Task will provide data on effluent contaminant concentrations at very low levels that will be used to

- Obtain more accurate estimates of contaminant discharge loads.
- Estimate short-term (day to week) and long-term (month to year) variability and temporal patterns in discharge loads.
- Estimate the annual mean discharge load of toxic contaminants and effluent tracers.
- Compare to NPDES monitoring data collected each month.
- Establish an effluent source "fingerprint" based on the distribution of contaminants and chemical tracers that are unique to this source.
- Support Authority special studies of influent and effluent quality or removal efficiencies (e.g., Pilot Secondary Treatment Plant Studies).

Data from this task and other tasks of the Harbor and Outfall Monitoring (HOM) Project will be integrated and used to produce, under Task 33, synthesis reports describing the relation between contaminant discharge loads and measured contaminant distributions in the environment. Concentrations of toxic contaminants will be compared to water quality criteria to evaluate the potential impact of discharging effluent into Massachusetts Bay. Data on various nutrient phases and species will contribute to refined water quality models evaluating effects of nutrient discharge in Massachusetts Bay.

## 7.3 Technical Approach

To accomplish the objectives, samples will be collected by MWRA staff using their regular procedures for collecting 24-h composite samples; aliquots of these samples will be poured into sample containers supplied by ENSR (Table 1). Organic contaminants, metals, and *Clostridium perfringens* will be measured in composite samples. The other analyses (Table 2) will be performed on grab samples. Samples will

## TABLE 1

## Sample Containers and Preservation

| Parameter | Sample Volume and Container | Sample Preservation/Processing[0] |
|---|---|---|
| Organic Contaminants | 2 2-L amber glass bottles | Refrigerate |
| Metals (Ag, Cd, Cu, Cr, Mo, Ni, Pb, Zn) | 1 500-mL polyethylene bottle in double plastic bag | 2.5 mL $HNO_3$, refrigerate |
| Mercury | 1 500-mL Teflon bottle in double plastic bag | 2.5 mL $HNO_3$, refrigerate |
| *C. perfringens* | 1 250-mL amber glass bottle | Sodium thiosulfate[1], refrigerate, ship immediately |
| Stable isotopes | | |
| - sulfur ($\delta^{34}$ S) | 4 1-L polyethylene bottles | Filter onto glass fiber filters (0.7 µm nominal pore size), rinse, dry, store over desiccant |
| - nitrogen ($\delta^{15}$ N) | 1 1-L polyethylene bottle | Filter onto glass fiber filters (0.7 µm nominal pore size), rinse, dry, store over desiccant |
| Nutrients/DOC | 1 1-L polyethylene bottle | Filter; retain filtrate for dissolved inorganic nutrients[2], TDN[3], TDP[3], DOC[3] analysis; retain filter for PP |
| Urea | 1 50 ml polyethylene bottles | Filter, freeze |
| Particulate Carbon and Particulate Nitrogen | 2 50 ml polyethylene bottles | Filter onto glass fiber filters (0.7 µm nominal pore size), rinse, dry, store over dessicant |
| Biogenic Silica | 2 50 ml polyethylene bottles | Filter, rinse, dry over dessicant |
| Total Suspended Solids | 1 1-L polyethylene bottle | Refrigerate |

[0]All samples are chilled immediately upon collection.
[1]Neutralizes chlorine.
[2]Chilled, except ammonia sample which is preserved with sulfuric acid.
[3]Preserved with sulfuric acid.

## TABLE 2

### Laboratory Analyses and Methods

| Parameter | Units | Methodology [1] (EPA Method No.) | Storage (Holding Time [3]) |
|---|---|---|---|
| **Organic** | | | |
| Polychlorinated biphenyls | ng/L | GC/ECD (modified 8080) | Refrigerate (7 days/40 days) |
| Polynuclear Aromatic Hydrocarbons | ng/L | GC/MS (SIM) (modified 8270) | Refrigerate (7 days/40 days) |
| Pesticides | ng/L | GC/ECD (modified 8080) | Refrigerate (7 days/40 days) |
| Linear alkyl benzenes | ng/L | GC/MS (SIM) (modified 8270) | Refrigerate (7 days/40 days) |
| **Trace Metals** | | | |
| Ag, Cd, Cu, Cr, Mo, Ni, Pb, Zn | µg/L | ICP-MS (modified EPA Series 200.8) | Refrigerate (6 months) |
| Hg | µg/L | CVAAS (modified 245.1) | Refrigerate (28 days) |
| **Stable Isotopes** | | | |
| $\delta^{15}N$, $\delta^{34}S$ | 0/00 (parts per thousand) | mass spectrometry | Dry at 60°C, store in desiccator (6 months) |
| ***Clostridium perfringens*** | #/100mL | Incubation/spore counting (Bisson and Cabelll, 1979 | Refrigerate (24 hours) |
| **Dissolved Nutrients** | | | |
| Ammonia | µg/L | EPA 350.2 | 28 days |
| Nitrate | µg/L | EPA 353.3 | 28 days |
| Nitrite | µg/L | EPA 354.1 | 2 days |
| Phosphate | µg/L | EPA 365.2 | 2 days |
| Silicate | µg/L | EPA 370.1 | 28 days |
| Total Dissolved Nitrogen | µg/L | EPA 351.3 | 28 days |
| Total Dissolved Phosphorus | µg/L | EPA 365.2 | 28 days |
| Urea | mg/L | Rahmatullah and Boyd (1980) | 3 months |

## TABLE 2 (Cont'd)

## Laboratory Analyses and Methods

| Parameter | Units | Methodology [1] (EPA Method No.) | Storage (Holding Time [2]) |
|---|---|---|---|
| Particulate Phosphorus | µg/L | EPA 365.2 | 28 days |
| Particulate Carbon | µM | Lambert and Oviatt (1986) | 3 months |
| Particulate Nitrogen | µM | Lambert and Oviatt (1986) | 3 months |
| Total Suspended Solids | mg/L | EPA 160.2 | 7 days |
| Dissolved Organic Carbon | µg/L | EPA 415.1 | 3 months |
| Biogenic Silica | µM | Knauss et al. (1983) | 3 months |

**[1] No EPA-published methods exist with the required detection limits for some analyses (see Table 4). See Section 12 for discussion of modified EPA methods and literature references.**
**[2] Where two times are given, the first refers to the maximum time prior to extraction of sample; the second refers to the maximum time prior to instrumental analysis after extraction.**
**[3] Filtration for nutrients and associated measurements will be performed as soon as possible after sample collection on the day of sample collection.**

be collected twice each month during the regular NPDES monitoring sample collection (samples collected Wednesday and Friday). These data can be compared to NPDES monitoring data for two of the three NPDES samples analyzed each month and will provide information on the short-term variability of discharge loads. These procedures are similar to procedures used in a previous study of organic contaminants in the MWRA effluent (Shea, 1992a and 1992b and Uhler et. al., 1994) and in a study of trace metals in the effluents of municipal discharges in the metropolitan New York area (Battelle, 1991).

The organic and metal analytical methods to be used (Table 2) are modifications of existing EPA methods and are comparable to those used in previous studies (Shea, 1993, 1992a, and 1992b; Battelle, 1991). They will provide data that are comparable to related studies of the same contaminants in water, sediment, and animal tissue. Nutrient analyses for both the effluent and pilot treatment plant samples will include dissolved inorganic nutrients (ammonia [$NH_3$], nitrate [$NO^-_3$], nitrite [$NO^-_2$], phosphate [$PO_4$], silicate [$SiO_4$]), total dissolved nitrogen [TDN], total dissolved phosphorus [TDP], and dissolved urea, particulate carbon [PC], particulate nitrogen [PN], particulate phosphorus [PP], and biogenic silica [BioSi]. Dissolved organic carbon (DOC) and total suspended solids (TSS), and *clostridium perfringens* will also be determined.

Stable isotope analyses will include $\delta^{15}$ N and $\delta^{34}$ S ratios in particulate matter.

The study of pilot plant treatment efficiency has not been designed although it is anticipated that the MWRA will request that one set of pilot plant samples (i.e., influent, primary effluent, and secondary effluent) will be collected each month. When requested by MWRA, ENSR will receive samples from MWRA and ship them to the appropriate laboratory for the requested analyses. Laboratory techniques described for the monthly effluent monitoring will be employed as needed for the pilot plant study. Any specific deviations from this CW/QAPP (e.g., measuring a subset of parameters, changing the number of sample replicates, or other sample design changes) will be discussed with MWRA and documented in a letter to the MWRA Project Manager. The pilot plant study will not be discussed further in this CW/QAPP.

Details of the sampling and analytical procedures to be used in this task are provided in Section 12.

### 7.4 Monitoring Parameters and Collection Frequency

The types of samples, sample containers, and sample preservation requirements are summarized in Table 1. The frequency of sample collection will be two sets of samples collected every month, one set on Wednesday and the other on the following Friday. Sampling will begin in January 1995 and end in December 1997. The sampling frequency may be altered by MWRA to meet the study objectives. Additional samples from special studies will be analyzed at the request of MWRA.

### 7.5 Parameter Tables

The chemical parameters to be analyzed in the laboratory and the methods to be used are summarized in Table 2. A more detailed list of the organic analytes is presented in Table 3. The standard EPA methods that will be used for some of the analyses (nutrients, DOC, TSS) are presented in Appendix A.

## 8.0 PROJECT FISCAL INFORMATION

This project is being carried out under the Harbor and Outfall Monitoring contract (Contract No. S186) between MWRA and ENSR Consulting and Engineering.

## 9.0 SCHEDULE OF ACTIVITIES AND DELIVERABLES

Detailed effluent characterization activities will span the period from the date of project initiation (see Section 4.0) until February 1998, when the last annual Effluent Characterization Data Report is due. Activities include sampling and laboratory analyses, with deliverables consisting of associated data reports. Effluent sampling will be conducted every month, normally in the second week of the month, beginning January 1995 and continuing through December 1997. MWRA staff are responsible for scheduling sample collection and for notifying ENSR when samples are available. Annual Effluent Characterization Data Reports are due in January 1996, January 1997, and February 1998 covering the preceding year. Two Interim Data Reports will be provided each year as well, covering the months January through April and May through August. These will be due in May and October, respectively.

## 10.0 PROJECT ORGANIZATION

The project organization is shown in Figure 1. Dr. Michael Mickelson is the MWRA Project Manager. He will be informed of all matters pertaining to work described in this CW/QAPP. Mr. Maurice Hall is the MWRA Task Manager and will be the MWRA contact for sample collection and transfer. Mr. Ken Keay is the MWRA Deputy Project Manager and serves as back-up to both Mr. Mickelson and Mr. Hall. Dr. James Blake is the ENSR Project Manager responsible for the overall performance of this project. Dr. James Bowen is the ENSR Technical Director responsible for the technical performance of this project. Dr. Eric Butler will be the Project Area Manager and will have overall responsibility for the Task. Mr. Dave Cameron will be the ENSR Task Manager responsible for sample coordination with MWRA and the laboratories. Analyses will be performed by ENSR's subcontractors:

- Biological Analytical Laboratories, Inc. (BAL), North Kingston, RI - *Clostridium perfringens* spores,

## TABLE 3

### Effluent Chemistry Analytes

**Metals**
- Ag silver
- Cd cadmium
- Cu copper
- Cr chromium
- Hg mercury
- Mo molybdenum
- Ni nickel
- Pb lead
- Zn zinc

**Polychlorinated biphenyls**
- 2,4,-$Cl_2$(8)
- 2,2′,5-$Cl_3$(18)
- 2,4,4′-$Cl_3$(28)
- 2,2′,3,5′-$Cl_4$(44)
- 2,2′,5,5′-$Cl_4$(52)
- 2,3′,4,4′-$Cl_4$(66)
- 3,3′,4,4′-$Cl_4$(77)
- 2,2′4,5,5′-$Cl_5$(101)
- 2,3,3′,4,4′-$Cl_5$(105)
- 2,3′,4,4′5-$Cl_5$(118)
- 3,3′,4,4′,5-$Cl_5$(126)
- 2,2′,3,3,4,4′-$Cl_6$(128)
- 2,2′,3,4,4′,5-$Cl_6$(138)
- 2,2′4,4′,5,5′-$Cl_6$(153)
- 2,2′3,3,4,4′,5-$Cl_7$(170)
- 2,2′,3,4,4′,5,5′-$Cl_7$(180)
- 2,2′,3,4,5,5′,6-$Cl_7$(187)
- 2,2′,3,3′,4,4′,5,6-$Cl_8$(195)
- 2,2′,3,3′4,4′,5,5′,6-$Cl_9$(206)
- Decachlorobiphenyl-$Cl_{10}$(209)

**Linear alkyl benzenes (LAB)**
- phenyl decanes
- phenyl undecanes
- phenyl dodecanes
- phenyl tridecanes
- phenyl tetradecanes

**Polynuclear aromatic hydrocarbons (PAH)**
- naphthalene
- $C_1$-naphthalenes
- $C_2$-naphthalenes
- $C_3$-naphthalenes
- acenaphthylene
- acenaphthene
- fluorene
- $C_1$-fluorenes
- $C_2$-fluorenes
- $C_3$-fluorenes

**PAH (continued)**
- anthracene
- phenanthrene
- $C_1$-phenanthrenes/anthracene
- $C_2$-phenanthrenes/anthracene
- $C_3$-phenanthrenes/anthracene
- $C_4$-phenanthrenes/anthracene
- dibenzothiophene
- $C_1$-dibenzothiophenes
- $C_2$-dibenzothiophenes
- $C_3$-dibenzothiophenes
- fluoranthene
- pyrene
- $C_1$-fluoranthenes/pyrenes
- benzo[*a*]anthracene
- chrysene
- $C_1$-chrysene
- $C_2$-chrysene
- $C_3$-chrysene
- $C_4$-chrysene
- benzo[*b*]fluoranthene
- benzo[*k*]fluoranthene
- benzo[*a*]pyrene
- dibenzo[*a,h*]anthracene
- benzo[*g,h,i*]perylene
- indeno[1,2,3-*c,d*]pyrene
- perylene
- biphenyl
- benzo[*e*]pyrene
- dibenzofuran
- benzothiazole

**Pesticides**
- hexachlorobenzene
- lindane
- heptachlor
- aldrin
- endrin
- heptachlorepoxide
- alpha-chlordane
- trans-Nonachlor
- dieldrin
- mirex
- o,p′-DDD
- p,p′-DDD
- o,p′-DDE
- p,p′-DDE
- o,p′-DDT
- p,p′-DDT
- DDMU

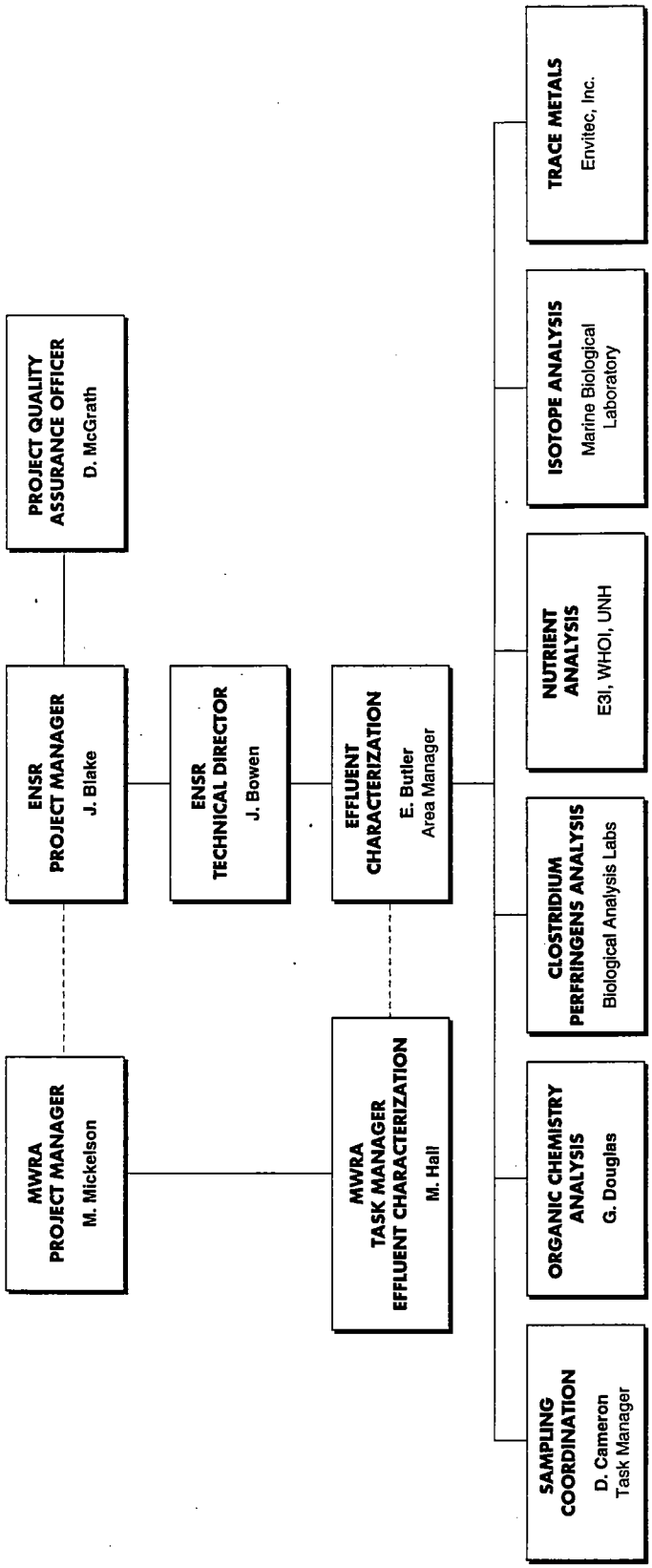


**FIGURE 1**
Effluent Characterization Team

- University of New Hampshire (UNH) Estuarine/Coastal Chemistry Laboratory, Institute for the Study of Earth, Oceans, and Space (EOS), Durham, NH - biogenic silica,
- Arthur D. Little, Inc. (ADL), Cambridge, MA - linear alkyl benzenes, PCBs, PAHs, and pesticides,
- Energy & Environmental Engineering, Inc. (E3I), Somerville, MA, - dissolved inorganic nutrients, DOC, TDN, TDP, TSS and PP analyses,
- Woods Hole Oceanographic Institution (WHOI), Woods Hole, MA, - urea, PC, and PN analyses,
- Marine Biological Laboratory, Woods Hole, MA, - $\delta^{34}S$ and $\delta^{15}N$ stable isotope analyses,
- Envitec, Inc., Northboro, MA, - metal analyses.

## 11.0 DATA QUALITY REQUIREMENTS AND ASSESSMENTS

The quality of the data produced for the detailed effluent characterization depends on the accuracy, precision, representativeness, comparability, and completeness of the data. In addition, method detection limits (MDLs) must be sufficiently low to measure the organic analytes at ng/L concentrations or lower and the metals at µg/L concentrations or lower. The MDL goals for chemical contaminants are listed in Table 4, along with typical MDLs from the MWRA NPDES monitoring program using standard EPA methods and some water quality criteria for comparison. Data quality objectives, other than MDLs, are presented in Table 5 for the chemical contaminants.

There is little precedent for establishing data quality requirements and assessments for stable isotope and *C. perfringens* analyses because they are non-routine analyses that have rarely been measured in effluent samples. Data quality requirements and assessments for these analyses are discussed below.

Deviations from the analytical scheme and data quality requirements presented in this CW/QAPP will be noted in the laboratory records associated with each analytical batch and in project files and reports to MWRA. All quality control (QC) data will be reported with the sample data. All corrective actions will be documented in reports to MWRA. When a sample does not meet the data quality objectives and is not reanalyzed, the justification for this decision will be documented.

## TABLE 4

### Method Detection Limit (MDL) Goals

| Parameter | MDL Goal[1] | NPDES MDL[2] | Water Quality Criteria[3] |
|---|---|---|---|
| **Metals** | (µg/L) | (µg/L) | (µg/L) |
| Ag | 0.50 | 10.0 | 2.3 |
| Cd | 0.50 | 4.0 | 9.3 |
| Cu | 0.50 | 10.0 | 2.9 |
| Cr | 1.0 | 10.0 | 50.0[4] |
| Hg | 0.005 | 0.2 | 0.025 |
| Mo | 0.50 | 80 | NA |
| Ni | 1.00 | 10.0 | 8.3 |
| Pb | 0.50 | 1.0 | 5.6 |
| Zn | 2.00 | 6.0 | 86 |
| **Organic Analytes** | (ng/L) | (ng/L) | (ng/L) |
| PCBs | 1 | 500 | 30 |
| LABs | 50 | NA | NA |
| PAH | 10 | 10,000 | 16-710 |
| Pesticides | 1 | 50-100 | 1-30 |
| **Dissolved Nutrients** | µg/L | µg/L | µg/L |
| Ammonia | 11 | NA | NA |
| Nitrate | 13 | NA | NA |
| Nitrite | 10 | NA | NA |
| Phosphate | 0.86 | NA | NA |
| Silicate | 2000 | NA | NA |
| Total Dissolved Nitrogen | 13 | NA | NA |
| Total Dissolved Organic Phosphorus | 6.2 | NA | NA |
| Urea | 500 | NA | NA |
| Dissolved Organic Carbon | 48 | NA | NA |
| Particulate Carbon | 4 | NA | NA |
| Particulate Nitrogen | 3 | NA | NA |
| Particulate Phosphorus | .6 | NA | NA |
| Biogenic Silica | .05 | NA | NA |

[1] MDL goals are based on past project performance and the goal of detecting concentrations extant in the effluent or at least 5 times less than the corresponding lowest salt water aquatic life criteria.
[2] NPDES MDLs are typical MDLs reported by MWRA in their NPDES monitoring reports; the listed MDLs meet the EPA Contract Laboratory Program (CLP) requirements.
[3] Water quality criteria listed are the lowest salt water aquatic life criteria published by EPA. Criteria listed for PAH and pesticides are the range of individual values; PAH criteria are lowest observed effects levels. Human health criteria are generally lower than the aquatic life criteria.
[4] As chromium VI.
NA means Not Available.

**TABLE 5**
**Data Quality Objectives for Effluent Samples[1]**

| Quality Control Sample Type and Frequency | Data Quality Objective | Corrective Action |
|---|---|---|
| **Procedural Blank** | | Reextraction, reanalysis, and/or blank substraction |
| Organics: 1/20 samples | < 5 x MDL | |
| Metals: 1/20 samples | < 5 x MDL | |
| Nutrients: 1/20 samples | < 5 x MDL | |
| **EPA Performance Sample** | | Performance documented |
| Organics: 1/year | ± 30% difference vs. known values | |
| Metals: 1/year | ± 30% difference vs. known values | |
| Nutrients: 1/year | Meet WP or WS EPA criteria | |
| **Matrix Spikes/Lab Duplicates** | | Report results |
| Organics: 1 MS/MSD/20 samples | 50-150% recovery<br>≤ 30% RPD | |
| Metals: 1 MS/20 samples | 65-135% recovery | |
| 1 Lab Duplicate/20 samples | ≤20% RPD | |
| Nutrients: 1 spike/20 samples | 75-125% recovery | |
| Stable Isotopes: | | |
| Lab duplicate 1/20 samples | Absolute difference ≤ 0.5 ‰ | |
| SRM 1/20 samples | Absolute difference ≤ 0.5 ‰ | |
| *Clostridium perfringens* | | |
| Lab duplicate 1/20 samples | ≤ 25% RPD | |
| **Surrogate Internal Standards (SIS)** | | Results examined; possible re-extraction and/or reanalysis. |
| Every organics sample | 50-150% recovery (one PAH SIS may exceed) | |
| **Calibrations, Initial** | | Reanalyze or document and justify |
| Organics: As needed | Organics:<br>± 30% RSD individual analyte (1 PAH may exceed)<br>± 15% RSD average of all analytes (1 PAH may exceed) | |
| Metals: Daily | Metals:<br>Calibration regression coeff (r) > 0.99 | |
| Nutrients: Daily | Nutrients:<br>Calibration regression coeff (r) > 0.99 (> 0.97 for Urea) | |
| **Calibrations, Check** | | Remedial maintenance, new initial calibration, possible reanalysis of samples. Decision documented and/or justified. |
| Organics: at least every 24 hours | Organics:<br>± 30% %D individual analyte<br>± 15% %D average of all analytes | |
| Metals: one per 10 samples | Metals:<br>± 10% of true value | |
| Nutrients: one per batch of 20 samples or fewer | Nutrients (Lab Control Sample):<br>95% confidence interval | |

[1]See text in Section 11.0 for explanation.

## 11.1 Precision and Accuracy

### 11.1.1 Chemical Constituents

Assessment of the precision and accuracy of the standard EPA methods used in this study appear in the methods themselves in Appendix A. Specific criteria appear in Table 5.

Precision and accuracy goals for non-standard methods are as follows: Analytical precision for organics will be determined using the concentrations of matrix spike (MS) and matrix spike duplicate (MSD) samples, with the relative percent difference (RPD) between duplicate analyses serving as the measure of precision. The RPD goal for MS/MSD samples is 30%. The RPD is calculated by

$$RPD = [\, 2\,(D_1 - D_2) \,/\, (D_1 + D_2)] \times 100$$

where $D_1$ = concentration of the first duplicate sample and
$D_2$ = concentration of the second duplicate sample.

Laboratory duplicates for metals analyses will be performed at a frequency of not fewer than one per 20 samples. The RPD goal for these analyses will be 20%.

Analytical accuracy will be evaluated based on percent recoveries of analytes in MS and MSD (organics only) samples (not fewer than one set of MS/MSD samples with every 20 samples), the recovery of surrogate internal standards (SIS) that are added to every sample (organics only), as well as the results of the procedural blanks which will be analyzed with every 20 samples. The percent recovery is calculated by:

$$\%\text{Recovery} = \text{([spiked result - unspiked result]/spike amount) x 100}$$

The data quality objective for accuracy is 50-150% recovery for the organic matrix spike analyses and 65-135% for the metals analyses. Procedural blanks are to contain less than five times the method detection limit (MDL) which are found in Table 4 of any target analyte (except that any one analyte may exceed this limit in the PAH analysis).

All effluent samples and associated QC samples processed for organic analysis will be spiked with the appropriate SIS before extraction. Quantification of the SIS will be based on the recovery internal standards (RIS) added to the final extract just before instrumental analysis. The acceptable SIS recovery range is 50%-150%; one of the PAH surrogate internal standards can be outside this range as long as the others are within the acceptable range. The samples are quantified using the surrogate recoveries as had been done in previous years of the program. Because samples are quantified relative to the recovery of the SIS which is added before extraction, any loss of analytes during processing is corrected by a comparable loss of the SIS. Therefore, recoveries of less than 50% may be considered acceptable. Each

sample showing low recoveries will be individually examined by the laboratory manager and/or task leader to determine the necessity of reextraction or reanalysis and the proposed action discussed with the ENSR Project Area Manager. The final determination will be reported to MWRA (in reports) in the QA/QC Corrective Action log (Section 18.0).

No standard reference materials (SRM) exist for organic analyses effluent. However, ADL will participate in the annual interlaboratory comparison exercise sponsored by the National Oceanic and Atmospheric Administration National Status and Trends Program (NOAA NS&T Program) for analysis of water, sediment, and tissue. The results of the exercise will be included in Task 8 annual data reports.

No SRM exists for the metals analyses of effluent samples, however, calibration check samples (NIST-certified aqueous sample 1643c or EPA Performance Evaluation samples) will be analyzed every 10 samples (see Section 14.1.2). The results of these check samples will be reported to MWRA.

### 11.1.2 Stable Isotopes

Standard Reference Materials (SRMs) will be used for stable isotopic analysis ($\delta^{15}N$, $\delta^{34}S$) of particulate effluent samples. SRMs are used for obtaining isotope ratios and for determining precision and accuracy.

A stable isotopic measurement is obtained as an isotope ratio (sample relative to a standard of known isotopic composition). For sulfur isotopic measurements ($\delta^{34}S$) of any substance, the standard reference is Canyon Diablo Troilite (CDT), National Bureau of Standards, with a $\delta^{34}S$ value of 0‰ (parts per thousand). Results of isotopic measurement are expressed as $\delta^{34}S$ values in ‰ relative to CDT (Canyon Diablo Troilite). For nitrogen isotopic measurements ($\delta^{15}N$) of any substance, the standard reference is atmospheric nitrogen gas (National Bureau of Standards), with a $\delta^{15}N$ value of 0‰. Results are expressed as $\delta^{15}N$ values in ‰ relative to atmospheric nitrogen gas.

Other SRMs are used to measure precision and accuracy. For particulate organic matter, SRMs obtained from the National Bureau of Standards will be used to determine accuracy. A citrus leaf standard (SRM 1524) and an internal laboratory standard of glycine are used by the Marine Biological Laboratory (MBL) Ecosystems Stable Isotope Laboratory (subcontracted by ENSR) for nitrogen isotope analyses. For sulfur isotopic analyses of organic matter, a precipitated barium sulfate standard is used. Choice of suitable SRMs will take into account the need for comparability of results with previous studies such as those of Giblin and Hopkinson (1994).

The precision of stable isotope analyses will be measured through replicate analysis of samples that are split in the laboratory (1 per 20). Precision for particulate samples generally ranges from ± 0.1 - 0.3‰ for $\delta^{15}N$ analyses (Muramoto et al., 1991) and ± 0.3‰ for $\delta^{34}S$ analyses (Fry et al., 1991). Accuracy will be determined by measuring the isotopic composition of an SRM and comparing it with the known composition. Accuracy and precision goals for this project are ± 0.5‰ absolute difference between duplicates and between laboratory SRM results and known SRM composition.

#### 11.1.3 Clostridium perfringens

The precision of *C. perfringens* analyses will be measured through replicate analysis of samples that are split in the laboratory (1 per 20 samples). Precision for particulate and sediment samples generally ranges from 5 to 25%. A direct measure of accuracy is not possible because of a lack of standards, but results from a recent interlaboratory comparison indicate that agreement between two laboratories can range from 25 to 55%, or possibly higher if the sample is unusually heterogeneous (Parmenter and Bothner, 1993).

#### 11.1.4 Nutrients, DOC, and TSS

The data quality objectives for these measurements are presented in Tables 4 and 5 or in Appendix A. In Table 5, 'EPA Performance Samples' refers to the ampuolized aqueous samples of known concentrations that EPA provides to laboratories as part of EPA's laboratory certification program. EPA sets acceptable criteria for the results that laboratories submit on an analyte by analyte basis. It is these criteria that are referred to in Table 5 for nutrients.

### 11.2 Completeness

The completeness of analyses will be ensured by comparing the samples received by the laboratory with the samples analyzed. Unless otherwise requested by the Authority, all samples will be analyzed for the parameters listed in Tables 2 and 3. The data quality objective is 95% completion. Completeness will be calculated as:

Completeness = ([Valid data obtained]/[Total data planned]) x 100

### 11.3 Comparability

Sample collection will remain the responsibility of the MWRA. MWRA personnel will use methods comparable to the methods previously used to collect effluent samples.

All data developed for this project must be demonstrated to be comparable to similar data generated by other laboratories or by other similar studies. To accomplish this, subcontractor laboratories will employ methods that are modifications of EPA methods and that are comparable to those used on previous effluent characterization studies (Shea, 1992a and 1992b; Battelle, 1991) except for the nutrient analyses for which

standard EPA methods are appropriate. These methods are comparable to those being used in other related studies of water, sediment, and animal tissue [e.g., for the MWRA, Massachusetts Bays Program (MBP), and NOAA NS&T Program]. In addition, ADL participates in an interlaboratory calibration exercise for analysis of PAHs, PCBs, and pesticides in water, sediment, and tissue using methods that are similar to those proposed for this task (see Section 11.1.1).

Comparability of the isotopic measurements will be ensured by using the same methods and laboratory that has performed similar measurements on MWRA sludge samples and on samples for other sewage disposal studies.

Comparability of *C. perfringens* determinations will be ensured by using methods used previously to measure *C. perfringens* in MWRA effluent and sludge samples, sediment samples from Boston Harbor and Massachusetts Bay, and on samples for other sewage disposal studies.

### 11.4 Representativeness

Representativeness has been addressed primarily in the sample collection design through the use of 24-h composite sampling, twice each month (except for nutrients and isotopes, which will be grab samples). Representativeness will also be ensured by proper handling, storage, and analysis of samples so that the material analyzed reflects the material collected as accurately as possible.

## 12.0 SAMPLING AND ANALYTICAL PROCEDURES

### 12.1 Effluent Sample Collection

Samples will be collected by MWRA staff using their regular procedures for collecting 24-h composite samples. Aliquots of these samples will be poured into sample containers (Table 1) supplied by ENSR. All bottles will be supplied with appropriate preservation. Labels and chain-of-custody forms will also be provided. Samples for nutrient and stable isotope analysis will be collected as grab samples. Effluent samples will be chilled as soon as possible after sampling, remaining at 4 °C until sample processing begins. Samples will be collected twice each month during the regular NPDES monitoring sample collection: on Wednesday and Friday. MWRA staff should note the sample's pH and temperature on the chain-of-custody.

All sample containers supplied by ENSR will be cleaned as appropriate to the measurement parameter. Metals sample containers will be cleaned in 10% acid bath, and Hg sample containers will be soaked in hot nitric acid overnight, followed by rinsing with deionized water. Bottles for the other analyses will be precleaned I-Chem bottles or equivalent.

Bottle drop-off and sample pick-up will be in the Toxic Reduction and Control office at the MWRA's Charlestown Navy Yard headquarters or at the Deer Island Central Laboratory. Bottle delivery will take place by noon on Tuesday of the sampling week. Sample pick-up will be by 3:00 PM on the day of sample collection. All organic and metal samples will be held by MWRA for Friday pick-up.

MWRA personnel will be responsible for filtering nutrient and stable isotope samples. Detailed instructions for sample collection and processing are attached as Appendix B.

## 12.2 Laboratory Analytical Procedures

The analytical methods to be employed on this task are modifications of existing EPA methods (see also NOAA 1993a and 1993b) that are comparable to those used on previous effluent characterization studies (see Section 11.0). The analytical methods are listed in Table 2; copies of standard EPA methods for nutrient analysis are presented in Appendix A; and specific organic analytes of interest are listed in Table 3. Brief descriptions of the analytical methods are given below.

### 12.2.1 Organic Analysis

Effluent samples will be serially extracted for PAH, LAB, chlorinated pesticides, and PCB following a modification to EPA Method 3510. This is the same extraction method used previously for characterization of the MWRA effluent (Shea, 1992a and 1992b). Each 2-L effluent sample will be transferred to a 3-L separatory funnel (measuring the volume with a graduated cylinder). The sample bottle and graduated cylinder will be rinsed with dichloromethane (DCM) and the rinseate added to the separatory funnel. The appropriate surrogate internal standards will be added to the sample and the sample will be serially extracted three times with 120 mL of DCM. The extract will be passed through a 20-g alumina column, eluting with 50 mL of DCM. The filtrate will be reduced in volume to about 1 mL using Kuderna-Danish and nitrogen concentration techniques. The concentrated extract will be further cleaned using size-exclusion (gel permeation) high-performance liquid chromatography (HPLC), which is a modification of EPA Method 3640. This procedure will remove common contaminants (including elemental sulfur) that interfere with instrumental analysis. The post-HPLC extract will be concentrated to approximately 0.5 mL under nitrogen and the RIS will be added after concentration to quantify extraction efficiency. The final extract will be split for analysis, one half remaining in DCM for PAH and LAB analysis, and the other half solvent-exchanged with isooctane for PCB and pesticide analysis.

Sample extracts will be analyzed for PAH and LAB compounds by gas chromatography/mass spectrometry (GC/MS) using a modification of EPA Method 8270. The modifications are (1) operating the mass spectrometer in the selected-ion-monitoring (SIM) mode and (2) tuning the mass spectrometer with PFTBA. Concentrations of LAB compounds will be determined as five separate LAB groups (those with alkyl chains containing 10, 11, 12, 13, and 14 carbon atoms) by monitoring the m/z 91 molecular fragment ion during the GC/MS analysis following the method of Eganhouse *et al.* (1983). LAB will be quantified

versus the surrogate internal standard 1-phenylnonane. Pesticides and PCB congeners will be analyzed by gas chromatography/electron capture detection (GC/ECD) using EPA Method 8080, modified to include additional analytes and a second column for qualitative confirmation.

### 12.2.2 Metal Analysis

The sample preparation procedures for determining total recoverable metals are defined by EPA (Section 4.4 of 600-4-91-010, June, 1991). For all metals except mercury, 100 mL of the sample will be spiked with 1 mL of hydrochloric acid and 1 ml of nitric acid and the sample reduced in volume to about 10-20 mL by evaporation. The solution will then be filtered through a Nuclepore 0.4 μm membrane and brought back to 100 mL. To reduce sample contamination, all sample preparation will be performed in a Class 100 clean room and all sample containers and sample preparation equipment will be rigorously cleaned according to the procedures of Patterson and Settle (1976). All effluent samples are directly measured by ICP-MS for silver, cadmium, chromium, copper, nickel, lead, molybdenum, and zinc.

The EPA method for total recoverable mercury (EPA Method 245.1) will be modified to achieve lower detection limits (0.005 μg/L). Mercury will be analyzed using a flow injection cold vapor technique with atomic absorption detection following preconcentration on gold amalgam as described by McIntosh *et al.*, (1993).

### 12.2.3 *Clostridium perfringens*

The enumeration of *C. perfringens* spore densities will be performed on selected effluent samples by membrane filtration, using serial half-log dilutions of the effluent according to the procedure developed by Bisson and Cabelli (1979). The effluent will be filtered using sterile filtration apparatus and membrane filters that have been rinsed with sterile phosphate-buffered saline (PBS). The filters will be incubated for 18 to 24 h at 44.5 °C, exposed to ammonium hydroxide, and the *C. perfringens* colonies will be counted and recorded. All final data will be reported in units of spores per 100 mL of filtered effluent.

### 12.2.4 Stable Isotopes

The analysis of stable isotopes nitrogen ($\delta^{15}N$) will be performed by mass spectrometry. Sulfur isotope ($\delta^{34}S$) measurements will be made on a separate sample using a different sample preparation method and mass spectrometer. All effluent samples will be filtered with precombusted 0.7-μm glass fiber filter prior to analysis; stable isotope analysis will be performed on the retained particulate material. The filters containing particulate material will be saved for isotopic analyses, rinsed with deionized or distilled water to remove sulfate present in seawater, dried at 60°C overnight and stored over desiccant until analysis. In the lab, samples will be homogenized by grinding to a fine powder in a mortar and pestle cleaned between each use with 10% HCl. Additional fractionation of the samples may be requested by MWRA

to determine $\delta^{15}N$ in dissolved nitrogen species (e.g., ammonia, nitrate, organic nitrogen). If MWRA requests these analyses, the fractionation procedures will be submitted as an addendum to this CW/QAPP.

Samples for $\delta^{15}N$ analysis will be combusted over Cu in a commercial elemental analyzer and the combustion products $CO_2$, $N_2$ and $H_2O$ trapped (the $N_2$ in molecular sieves) and cryogenically separated, while excess $O_2$ will be trapped as CuO. The molecular sieves containing trapped $N_2$ will be heated to release the $N_2$ after the other gases have been cryogenically separated, and a helium carrier gas will transport the $N_2$ gas to a second cryogenic trap to concentrate it. The concentrated $N_2$ will then be reheated and then transported via the carrier gas to an isotope ratio mass spectrometer (Finnegan Mat Delta S) where its isotopic composition will be measured against an $N_2$ gas standard. Results will be expressed as $\delta^{15}N$ in parts per thousand relative to atmospheric $N_2$.

Samples for organic sulfur isotopic analysis will be oven-dried and 200-300 mg weighed out. The sediment sample will be mixed in a 1:10 ratio with powdered $KNO_3$. The mixture will be vacuum sealed in Pyrex tubes and combusted in a muffle furnace under increasing temperature, frozen in liquid nitrogen, cracked and thawed. The thawed sample will be digested in 0.1N HCl, filtered to remove coarse particles, acidified with 6 M HCl and then heated to boiling with addition of $BaCl_2$ to precipitate sulfur as $BaSO_4$. This $BaSO_4$ precipitate will be filtered, combusted to remove impurities and then decomposed to $SO_2$ gas over the oxidant $V_2O_5$ for isotope ratio mass spectrometric analysis using a Finnegan Mat Delta S. Results will be expressed as $\delta^{34}S$ in parts per thousand relative to the Canyon Diablo troilite standard.

### 12.2.5 Nutrients, DOC, and TSS

The analytical methods for dissolved inorganic nutrients (nitrate, nitrite, ammonia, phosphate, and silica) are listed in Table 2 and are presented in Appendix A as are the analytical techniques for DOC, PP, and TSS.

Samples for TDN and TDP will be first oxidized, converting all N and P to inorganic forms, and analyzed as described in Table 2.

Particulate samples retained by a 0.4-micron membrane filter will be analyzed for biogenic silica. The filter and particulates will be digested with 0.2 N NaOH and neutralized with 0.2 N HCl. Dissolved silica will be measured with Technicon II Autoanalyzer and biogenic silica calculated.

Methods for analysis of PC and PN are described in Lambert and Oviatt (1986). Particulate matter collected on a pre-combusted glass fiber filter will be ignited at high temperature in a CHN elemental analyzer. The combustion releases total carbon and nitrogen in gaseous form. These products will be quantified by the analyzer using gas chromatography with a thermal conductivity detector.

Samples for PC, nitrogen, phosphorus and biogenic silica will not be diluted. Amounts sufficient for analysis will be obtained by filtering appropriate volumes of effluent. Thus, for a seawater sample, 60

ml may have to be filtered, whereas only 5 ml of effluent would be required to obtain sufficient particulate carbon and nitrogen for analysis.

The urea analysis is a modification of the method used by Rahmatullah and Boyd (1980). Urea will be determined in filtered samples colorimetrically, upon heating the sample with diacetyl monoxime and thiosemicarbazide under acidic conditions.

## 13.0 SAMPLE CUSTODY

The field sampler will be personally responsible for the care and custody of the samples from the time they are collected until they are transferred or dispatched properly. As few people as possible should handle the samples. Sample labels and chain-of-custody forms will be provided by ENSR (examples of these appear in Appendix C).

All sample containers will be labeled with a unique identifier as follows.

The first character will be 'E' designating the study (Effluent). The next two characters will be numbers designating the year, e.g., '95'. The next character will be a letter designating the month. For example, 'A' will be January, and 'K' will be November. The next character will be a number and signifies the number of samples collected that month. The next character will be a letter and signifies the type of analysis that the sample will undergo. For example, 'A' will signify a full suite of organic analyses, and a 'B' will signify particulate carbon and particulate nitrogen analysis. The next character is also a letter and will designate the type of sample, e.g., 'B' will signify a field duplicate sample. The sample will also be labeled with an MWRA sample identification number, which will be used when reporting the data to MWRA.

Samples will be accompanied by a properly completed chain-of-custody form. The MWRA's Central Laboratory will be given a chain-of-custody with the laboratory address and list of parameters to be analyzed already provided. The chain-of-custody record also includes fields for entering pertinent information about each sample collection, such as date and time collected, and general comments. This same information will be provided by the sample collector along with the MWRA ID. Labels will be filled out containing this information and will be attached to each sample container.

When transferring the possession of samples, the individuals relinquishing and receiving will sign, date, and note the time on the record. This record documents the transfer of custody of samples from the sampler, to another person, to the laboratory, or to/from a secure storage location. Samples will be packaged properly for shipment and dispatched to the laboratory for analysis with a separate signed custody record enclosed in each sample cooler.

Copies of all chain-of-custody forms will be returned to ENSR's Task Manager and filed.

Upon completion of the monthly sampling, custody of samples will be transferred to the appropriate laboratory. If a third party (i.e., commercial courier) is used to transfer the samples, chain-of-custody seals will be required. Coolers will be locked or secured with strapping tape and sealed with custody seals by the sample collectors. The preferred procedure is to attach a custody seal to the front right and back left of the cooler. The cooler will be taped closed with fiberglass tape covering the chain-of-custody seals. Commercial couriers will not be required to sign the chain-of-custody forms. However, the airbill will be maintained as part of the custody records.

Laboratory custody of all samples will be the responsibility of the subcontractor. Upon receipt of samples at the laboratory, the recipient will examine the samples received, verify that the information recorded on the copy of the chain-of-custody forms is accurate, and log the samples into the laboratory by signing the chain-of-custody form on the *Received By* line, and by entering the date and time of sample receipt. Any inconsistencies between samples listed as having been released and samples that were actually received, or any damage to containers, labels, etc., will be noted in the laboratory sample log book and immediately communicated to the ENSR Task Manager. Sample numbers that include the complete field ID number will be used to track the samples through the laboratory. All archived samples will remain in the custody of the appropriate subcontractor laboratory for a period of 1 year after sample collection, at which time the MWRA will be contacted about their disposition. All data generated for this study will be maintained for 6 years, after which time MWRA will be contacted.

## 14.0 CALIBRATION PROCEDURES AND PREVENTIVE MAINTENANCE

Logs of maintenance, calibrations, and repairs made to analytical instruments will be kept by the laboratory. Maintenance of and repair of instruments will be in accordance with manufacturers' manuals and laboratory SOPs. Any deviations to this policy will be noted.

### 14.1 Calibration Procedures and Response Factor Stability

#### 14.1.1 Organic Analysis

Analytical instruments will be calibrated before sample analysis. Response factors (RF) will be generated for each target analyte using the following equation:

$$RF = \frac{A_x}{A_{IS}} \times \frac{C_{IS}}{C_x}$$

where: $A_x$ = peak area of the analyte in the calibration standard
$A_{is}$ = peak area of the appropriate internal standard in the calibration standard
$C_x$ = concentration of the analyte in the calibration standard
$C_{is}$ = concentration of the appropriate internal standard in the calibration standard.

Three concentrations of standard solutions that encompass the expected range in sample concentrations will be analyzed. Initial calibrations will be acceptable if the relative standard deviations (RSD) are ≤30% of the mean for each individual analyte, and the mean of all analyte RSDs is ≤15%. One PAH compound may exceed these criteria.

The system calibration will be verified a minimum of once every 24 h using a mid-range calibration check. Using the mean RF of each analyte from the initial calibration, the percent difference between those mean values and the RFs from the midrange calibration checks will be calculated. The percent difference is calculated by:

$$\% \text{ Difference} = [(RF_i - RF_r) / RF_i] \times 100$$

where $RF_i$ = average response factor from the initial calibration, and
$RF_r$ = response factor from the midrange calibration check.

The calibration checks will be acceptable under the same criteria as the initial calibration (i.e., 30% for individual analytes, 15% for the means). If the percent difference between the RFs is greater than the acceptability criteria, remedial maintenance will be performed on the instrument, a new initial calibration will be performed, and the affected batch of samples may be reanalyzed. Because GC/ECD and GC/MS analyses are multicomponent analyses, it may not be necessary to reanalyze all samples. For example, if only certain analytes are detected in a sample, and the calibration is acceptable for those particular analytes, the sample should not require reanalysis. The decision as to whether reanalysis is necessary will be made by the laboratory task manager, with the approval of the ENSR Area Manager. Deviations from calibration or data objectives will be documented in the project files.

Samples analyzed by GC/ECD and GC/MS will be bracketed by two acceptable calibrations, initial or check. Analytes will be quantified by using the average RFs for that individual analyte generated from the initial calibration unless otherwise stated.

### 14.1.2 Metal Analysis

Calibration standards will be prepared each day and effluent sample digestion solutions will be quantified by ICP-MS for all metals (except possibly mercury) using the method of standard additions to avoid inaccuracies resulting from chemical interferences. Calibration standard check samples (as NIST-certified aqueous sample 1643c or EPA Performance Evaluation samples) will be analyzed every 10 samples to ensure continued accuracy. Measurements that are not bracketed by an accuracy check standard within 10% of its true value will be rejected and reanalyzed after corrective action is taken (as needed). ICP-MS measurements will be made in triplicate for each sample; if the RSD between triplicate injections is greater than 5%, then the sample measurement will be rejected unless the absorbance values are very low and small differences (<0.004 abs units) result in high RSD values. Sample quantitations will only be accepted if the standard additions quantitation curve has a correlation coefficient of 0.99 or better. If adequate quantification of Hg is accomplished by the ICP-MS, then the CVAAS measurement of Hg, described below, will not be carried out.

The CVAAS measurements of mercury will be quantified by standard comparisons; mercury calibration standards will be prepared the day of analysis, and samples will be quantified within the linear range of the instrument and below the highest calibration standard. Instrument performance will be monitored using continuing accuracy check standards (with a 10% acceptance criteria), prepared by an analyst other than the analyst that prepares the calibration standards. Samples will be analyzed once for quantitation; all duplication exercises will be laboratory or field duplicates. Sample quantitations will proceed only if the calibration standard curve is linear with a correlation coefficient of 0.99 or better.

If the target correlation coefficient for the calibration curve is not obtained for the atomic absorption instrumentation, then the instrument operation and instrument integrity will be assessed and analytical standards evaluated. Necessary remedial action will be taken, and the calibration procedure repeated until a satisfactory calibration for each trace metal can be obtained. Any sample concentrations that are above the highest calibration atomic absorption standard will be reanalyzed (after appropriate dilution if necessary).

### 14.1.3 Nutrient, DOC, and TSS Analysis

The calibration procedures for these determinations are contained in the methods in Appendix A.

## 14.2 Instrument Maintenance

Analytical instrumentation will be properly calibrated and maintained in accordance with laboratory SOPs, manufacturers' instructions, and analytical methods. A log will be kept for each analytical instrument and will contain a record of all routine maintenance and repairs. Procedures for maintenance of the more complex analytical equipment are described below.

### 14.2.1 Gas Chromatograph Mass Spectrometer

Detector response (electron-capture detectors and mass spectrometer) and capillary column performance will be monitored/calibrated daily by injection of GC standards containing known amounts of targeted compounds (e.g., PAH mixture, pesticides, PCB mixtures, and LAB calibrations). Both the responses per unit amount and the resolution of specific components will be monitored. If any evidence of chromatographic column performance deterioration is observed, the column will be replaced.

### 14.2.2 ICP-MS

Maintenance of the ICP-MS instrumentation will include complete cleaning of sample and skimmer cones, replacing sampling tubes, and optimizing the instrument sensitivity by adjusting and cleaning the lenses. The base vacuum, operating vacuum, and gas flow rates will also be checked.

## 15.0 DOCUMENTATION, DATA REDUCTION, AND REPORTING

### 15.1 Documentation

Documentation will include chain-of-custody forms and laboratory records. Sample collection information (i.e., sample location, time and date, sampler's identification, pH and temperature of the samples and ENSR and MWRA sample ID numbers) will be recorded on the chain-of-custody forms. Chain-of-custody records are discussed in Section 13.0.

Initially, all laboratory data will be recorded either (1) electronically onto computer storage media from laboratory data systems or (2) manually into laboratory notebooks or on established data forms. All notes will be written in ink. Corrections to hand-entered data will be initialed, dated, and justified. Completed forms, laboratory notebooks, or other forms of hand-entered data will be signed and dated by the individual entering the data. It will be the responsibility of the laboratory managers to ensure that all data entries and hand calculations are verified. Laboratory records of sample preparation will be maintained.

Data loading documentation will include diskettes received from subcontractor laboratories, SQL* Loader files, and Microsoft Access files used for loading, as well as results of checks made during loading and scripts or Access files fully documenting any corrections made during loading.

## 15.2 Data Reduction

Data reduction involves the process of converting raw numbers into data that have direct chemical meaning or can be compared statistically.

GC/MS data will be acquired and reduced on Hewlett-Packard A-series minicomputers with dedicated chromatography software. GC/ECD data will be acquired and reduced on a VG Minichrome Data Acquisition System. Data generated during metals analyses will be transferred from the instruments to PCs, where analyte concentrations will be calculated. Organic analyte data will be reported in units of ng/L; metals concentrations will be reported in µg/L; stable isotope data will be reported as ‰ for $\delta^{15}N$ and $\delta^{34}S$; *C. perfringens* data will be reported as spores/100 mL; TSS and DOC data will be reported in mg/l; and nutrient data will be reported as µg/L, or µM as appropriate (see Table 2).

In addition to analyte concentrations in field samples, statistical evaluations will be performed on all quality control samples as discussed in Section 11.1. Quality control objectives for these calculations are presented in Table 5.

## 15.3 Reporting

Three formats will be used to report the effluent chemistry data to MWRA

(1) Data submitted for inclusion in the Harbor Studies Database
(2) Data presented in annual and interim data reports
(3) Data summarized and interpreted in annual synthesis reports.

### 15.3.1 Harbor Studies Database

Only data that have been designated as final by the Project Area Manager will be loaded into ENSR's copy of the Harbor Studies Database. All data will be loaded into the database by ENSR data management staff following the formats described below. Upon receipt, each diskette will be logged in and assigned an unique log in identifier. Any changes or additions to data, necessary for loading into the database, will be made using well-documented scripts that indicate the original values. The original diskette, scripts, and data-loading documentation will be filed at ENSR according to the log in identifier. The data sources notebook will contain the chain-of-custody forms and data entry information.

**Sample Collection Data**

Sample collection data contained on the sample chain-of-custody form will be included in the EFF_CHEM Oracle table. Columns will include sample_id (MWRA ID), study, event_id, location, collect_date, and anal_lab_id.

**Analytical Data**

All data generated by ENSR subcontractors will be either electronically transferred from the instrument to Oracle tables or a PC-based spreadsheet, or read from the instrument display (or optical field or a microscope) and manually entered into laboratory notebooks or data sheets. Data in laboratory notebooks or data sheets will be manually entered into a PC-based spreadsheet or into Oracle through a Microsoft Access interface. Subcontractor spreadsheet data will be loaded into Oracle and checked by ENSR data management staff. Columns include sample_id, param_code, value, val_qual, unit_code, meth_code, detect_limit, instr_code, lab_sample_id, batch_no, qc_code, and anal_date.

### 15.3.2 Annual and Interim Data Reports

Data reports will be submitted to MWRA in both hard-copy and electronic forms. Data will be presented in tables containing the results of individual sample analysis plus QC data.

Following complete laboratory analysis of samples from each year, a data report that provides a tabular summary of results of the analyses will be submitted to MWRA. The due dates for the draft and final data reports are listed in Section 9. Interim data reports will be submitted in May and September of each year, and will present data from the previous 4 months.

### 15.3.3 Annual Synthesis Reports

Annual synthesis reports for the detailed effluent characterization task will include tables and graphics presenting summaries of results. These presentations may show temporal trends in effluent constituent concentrations and distribution. The objective of these data presentations will be to communicate our understanding of the relevance of measured effluent constituents to the task objectives and data usage discussed above.

## 16.0 DATA EVALUATION

All data reported for this project will be reviewed to check for errors in transcription, calculation, or computer input by the technical staff of the appropriate laboratory. The validation procedures that will be performed are:

- 100% of data that are hand-entered into a database or spreadsheet will be verified for accuracy either by (1) printing the spreadsheet and proofreading against the original hand entry or by (2) duplicate entry into the database and comparison of the entries to detect any differences. These tasks will be carried out by two people and documented for each data set.

- All manual calculations will be checked for accuracy by a second staff member.

- Calculations performed by software will be checked by the technical staff member at a frequency sufficient to ensure the accuracy of the calculations. All data-reduction algorithms will be verified prior to final data submission.

- Subsets of the analytical data will be reviewed by in-house or subcontractor data validators. The data will be reviewed for adherence to analytical protocols and to pre-established criteria (e.g., for holding times, surrogate recoveries, initial and continuing calibration, matrix spikes, laboratory duplicates, blank contamination, SRM recoveries).

- Database staff will check the received data and associated documentation for completeness, freedom from errors, and technical reasonableness.

- All new software developed for this task will be validated before entry of data.

The ENSR Project Area Manager will be responsible for validation of all data generated by ENSR to ensure that the data are accurate, complete, and scientifically reasonable. Subcontractors will be responsible for conducting similar data validations. As an additional data validation step, the ENSR Project Area Manager will review all subcontractor data for technical reasonableness.

## 17.0 PERFORMANCE AND SYSTEM AUDITS

This project will be monitored by the ENSR Project QA Director. All tabular and graphic data reported in deliverables and associated raw data generated by ENSR will be reviewed by the Project QA Director or his/her designee. Raw data will be reviewed for traceability, accuracy, completeness, and proper documentation.

All deliverables generated during the course of this project will be submitted to an internal review prior to delivery of drafts to MWRA.

Audits of the subcontractor laboratory data-collection programs will be the responsibility of the subcontractor. During the time work is in progress, an inspection will be conducted by the subcontractor QA officer or their designee to evaluate the laboratory data-production process. All data must be reviewed by the Subcontractor QA Officer prior to submission to the ENSR Project Area Manager and must be accompanied by a signed QA statement that describes the types of audits and reviews conducted and any outstanding issues that could affect data quality.

Performance audits, procedures used to determine quantitatively the accuracy of the total measurement system or its components, will be the responsibility of subcontractor laboratories and may include internal performance evaluation samples and participation in external certification programs.

## 18.0 CORRECTIVE ACTION

Identification of problems regarding technical performance is the responsibility of all staff members working on this project. Responsibility for overall conduct of the project, including schedule, costs, and technical performance lies with the ENSR Project Manager. The Project Manager is responsible for identifying and resolving problems that (1) have not been addressed promptly or successfully at a lower level, (2) influence other components of the project, (3) require changes in this CW/QAPP, or (4) require consultation with ENSR management or with MWRA.

Technical problems relating to sample collection (schedule changes, modifications to the sampling plan, etc.) will be resolved through discussion with the MWRA Task Manager and ENSR Project Area Manager. Problems relating to the overall successful completion of the project will be reported to the MWRA Task Manager in a timely manner for discussion and resolution between the ENSR and MWRA managers.

Identification of problems and corrective action at the laboratory level will be resolved by the laboratory staff. Issues that affect schedule, cost, technical performance, or data quality will be reported to the ENSR Project Area Manager or the ENSR Project Manager. They will be responsible for evaluating the overall impact to the project and for discussing corrective actions with the MWRA Task Manager.

A QA/QC Corrective Action Log will be maintained by the ENSR Project QA Director and submitted to MWRA Task Manager at quarterly intervals. The log will include documentation of QA/QC activities as they occur, descriptions of the methods and procedures recommended to prevent the problem from reoccurring, and verification that these actions have corrected the problem.

## 19.0 REPORTS

Reports related to the detailed effluent characterization task include annual and interim data reports and annual synthesis reports. These are described in Sections 15.3.2 and 15.3.3, respectively.

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# APPENDIX A

# ANALYTICAL METHODS

# RESIDUE, NON-FILTERABLE

## Method 160.2 (Gravimetric, Dried at 103–105°C)

## STORET NO. 00530

1. Scope and Application
   - 1.1 This method is applicable to drinking, surface, and saline waters, domestic and industrial wastes.
   - 1.2 The practical range of the determination is 4 mg/1 to 20,000 mg/1.
2. Summary of Method
   - 2.1 A well-mixed sample is filtered through a glass fiber filter, and the residue retained on the filter is dried to constant weight at 103–105°C.
   - 2.2 The filtrate from this method may be used for Residue, Filterable.
3. Definitions
   - 3.1 Residue, non-filterable, is defined as those solids which are retained by a glass fiber filter and dried to constant weight at 103–105°C.
4. Sample Handling and Preservation
   - 4.1 Non-representative particulates such as leaves, sticks, fish, and lumps of fecal matter should be excluded from the sample if it is determined that their inclusion is not desired in the final result.
   - 4.2 Preservation of the sample is not practical; analysis should begin as soon as possible. Refrigeration or icing to 4°C, to minimize microbiological decomposition of solids, is recommended.
5. Interferences
   - 5.1 Filtration apparatus, filter material, pre-washing, post-washing, and drying temperature are specified because these variables have been shown to affect the results.
   - 5.2 Samples high in Filterable Residue (dissolved solids), such as saline waters, brines and some wastes, may be subject to a positive interference. Care must be taken in selecting the filtering apparatus so that washing of the filter and any dissolved solids in the filter (7.5) minimizes this potential interference.
6. Apparatus
   - 6.1 Glass fiber filter discs, without organic binder, such as Millipore AP-40, Reeves Angel 934-AH, Gelman type A/E, or equivalent.
     **NOTE:** Because of the physical nature of glass fiber filters, the absolute pore size cannot be controlled or measured. Terms such as "pore size", collection efficiencies and effective retention are used to define this property in glass fiber filters. Values for these parameters vary for the filters listed above.
   - 6.2 Filter support: filtering apparatus with reservoir and a coarse (40–60 microns) fritted disc as a filter support.

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**NOTE:** Many funnel designs are available in glass or porcelain. Some of the most common are Hirsch or Buchner funnels, membrane filter holders and Gooch crucibles. All are available with coarse fritted disc.

6.3 Suction flask.

6.4 Drying oven, 103–105°C.

6.5 Desiccator.

6.6 Analytical balance, capable of weighing to 0.1 mg.

7. Procedure

7.1 Preparation of glass fiber filter disc: Place the glass fiber filter on the membrane filter apparatus or insert into bottom of a suitable Gooch crucible with wrinkled surface up. While vacuum is applied, wash the disc with three successive 20 ml volumes of distilled water. Remove all traces of water by continuing to apply vacuum after water has passed through. Remove filter from membrane filter apparatus or both crucible and filter if Gooch crucible is used, and dry in an oven at 103–105°C for one hour. Remove to desiccator and store until needed. Repeat the drying cycle until a constant weight is obtained (weight loss is less than 0.5 mg). Weigh immediately before use. After weighing, handle the filter or crucible/filter with forceps or tongs only.

7.2 Selection of Sample Volume

For a 4.7 cm diameter filter, filter 100 ml of sample. If weight of captured residue is less than 1.0 mg, the sample volume must be increased to provide at least 1.0 mg of residue. If other filter diameters are used, start with a sample volume equal to 7 ml/cm$^2$ of filter area and collect at least a weight of residue proportional to the 1.0 mg stated above.

**NOTE:** If during filtration of this initial volume the filtration rate drops rapidly, or if filtration time exceeds 5 to 10 minutes, the following scheme is recommended: Use an unweighed glass fiber filter of choice affixed in the filter assembly. Add a known volume of sample to the filter funnel and record the time elapsed after selected volumes have passed through the filter. Twenty-five ml increments for timing are suggested. Continue to record the time and volume increments until fitration rate drops rapidly. Add additional sample if the filter funnel volume is inadequate to reach a reduced rate. Plot the observed time versus volume filtered. Select the proper filtration volume as that just short of the time a significant change in filtration rate occurred.

7.3 Assemble the filtering apparatus and begin suction. Wet the filter with a small volume of distilled water to seat it against the fritted support.

7.4 Shake the sample vigorously and quantitatively transfer the predetermined sample volume selected in 7.2 to the filter using a graduated cylinder. Remove all traces of water by continuing to apply vacuum after sample has passed through.

7.5 With suction on, wash the graduated cylinder, filter, non-filterable residue and filter funnel wall with three portions of distilled water allowing complete drainage between washing. Remove all traces of water by continuing to apply vacuum after water has passed through.

**NOTE:** Total volume of wash water used should equal approximately 2 ml per cm$^2$. For a 4.7 cm filter the total volume is 30 ml.

7.6 Carefully remove the filter from the filter support. Alternatively, remove crucible and filter from crucible adapter. Dry at least one hour at 103–105°C. Cool in a desiccator and weigh. Repeat the drying cycle until a constant weight is obtained (weight loss is less than 0.5 mg).

8. Calculations

8.1 Calculate non-filterable residue as follows:

$$\text{Non-filterable residue, mg/l} = \frac{(A - B) \times 1{,}000}{C}$$

where:

A = weight of filter (or filter and crucible) + residue in mg
B = weight of filter (or filter and crucible) in mg
C = ml of sample filtered

9. Precision and Accuracy

9.1 Precision data are not available at this time.

9.2 Accuracy data on actual samples cannot be obtained.

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# NITROGEN, AMMONIA

## Method 350.2 (Colorimetric; Titrimetric; Potentiometric – Distillation Procedure)

**STORET NO. Total 00610**
**Dissolved 00608**

1. Scope and Application
   1.1 This distillation method covers the determination of ammonia-nitrogen exclusive of total Kjeldahl nitrogen, in drinking, surface and saline waters, domestic and industrial wastes. It is the method of choice where economics and sample load do not warrant the use of automated equipment.
   1.2 The method covers the range from about 0.05 to 1.0 mg $NH_3$–N/l for the colorimetric procedure, from 1.0 to 25 mg/l for the titrimetric procedure, and from 0.05 to 1400 mg/l for the electrode method.
   1.3 This method is described for macro glassware; however, micro distillation equipment may also be used.
2. Summary of Method
   2.1 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 colorimetrically by nesslerization, titrimetrically with standard sulfuric acid with the use of a mixed indicator, or potentiometrically by the ammonia electrode. The choice between the first two procedures depends on the concentration of the ammonia.
3. Sample Handling and Preservation
   3.1 Samples may be preserved with 2 ml of conc. $H_2SO_4$ per liter and stored at 4°C.
4. Interferences
   4.1 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 (i.e., without distillation), has been discarded as an official method.
   4.2 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 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 (approximately 2 to 3) prior to distillation and nesslerization.
   4.3 Residual chlorine must also be removed by pretreatment of the sample with sodium thiosulfate before distillation.

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5. Apparatus

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

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

5.3 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.

5.4 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.

6. Reagents

6.1 Distilled water should be free of ammonia. Such water is best prepared by passage through an ion exchange column containing a strongly acidic cation exchange resin mixed with a strongly basic anion exchange resin. Regeneration of the column should be carried out according to the manufacturer's instructions.

**NOTE 1:** All solutions must be made with ammonia-free water.

6.2 Ammonium chloride, stock solution: 1.0 ml = 1.0 mg $NH_3$–N. Dissolve 3.819 g $NH_4Cl$ in distilled water and bring to volume in a 1 liter volumetric flask.

6.3 Ammonium chloride, standard solution: 1.0 ml = 0.01 mg. Dilute 10.0 ml of stock solution (6.2) to 1 liter in a volumetric flask.

6.4 Boric acid solution (20 g/1): Dissolve 20 g $H_3BO_3$ in distilled water and dilute to 1 liter.

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

**NOTE 2:** Specially denatured ethyl alcohol conforming to Formula 3A or 30 of the U.S. Bureau of Internal Revenue may be substituted for 95% ethanol.

6.6 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 3:** 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).

6.7 Borate buffer: Add 88 ml of 0.1 N NaOH solution to 500 ml of 0.025 M sodium tetraborate solution (5.0 g anhydrous $Na_2B_4O_7$ or 9.5 g $Na_2B_4O_7 \cdot 10H_2O$ per liter) and dilute to 1 liter.

6.8 Sulfuric acid, standard solution: (0.02 N, 1 ml = 0.28 mg $NH_3$–N). Prepare a stock solution of approximately 0.1 N acid by diluting 3 ml of conc. $H_2SO_4$ (sp. gr. 1.84) to 1 liter with $CO_2$-free distilled water. Dilute 200 ml of this solution to 1 liter with $CO_2$-free distilled water.

**NOTE 4:** An alternate and perhaps preferable method is to standardize the approximately 0.1 N $H_2SO_4$ solution against a 0.100 N $Na_2CO_3$ solution. By proper dilution the 0.02 N acid can then be prepared.

6.8.1 Standardize the approximately 0.02 N acid against 0.0200 N $Na_2CO_3$ solution. This last solution is prepared by dissolving 1.060 g anhydrous $Na_2CO_3$, oven-dried at 140°C, and diluting to 1000 ml with $CO_2$-free distilled water.

6.9 Sodium hydroxide, 1 N: Dissolve 40 g NaOH in ammonia-free water and dilute to 1 liter.

6.10 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 $Na_2S_2O_3 \cdot 5H_2O$ in distilled 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 $NaAsO_2$ in distilled water and dilute to 1 liter.

7. Procedure

7.1 Preparation of equipment: Add 500 ml of distilled 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.

7.2 Sample preparation: Remove the residual chlorine in the sample by adding dechlorinating agent equivalent to the chlorine residual. To 400 ml of sample add 1 N NaOH (6.9), until the pH is 9.5, checking the pH during addition with a pH meter or by use of a short range pH paper.

7.3 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 (6.7). Distill 300 ml at the rate of 6–10 ml/min. into 50 ml of 2% boric acid (6.4) contained in a 500 ml Erlenmeyer flask.

**NOTE 5:** The condenser tip or an extension of the condenser tip must extend below the level of the boric acid solution.

Dilute the distillate to 500 ml with distilled water and nesslerize an aliquot to obtain an approximate value of the ammonia-nitrogen concentration. For concentrations above 1 mg/l the ammonia should be determined titrimetrically. For concentrations below this value it is determined colorimetrically. The electrode method may also be used.

7.4 Determination of ammonia in distillate: Determine the ammonia content of the distillate titrimetrically, colorimetrically or potentiometrically as described below.

7.4.1 Titrimetric determination: Add 3 drops of the mixed indicator to the distillate and titrate the ammonia with the 0.02 N $H_2SO_4$, matching the end point against a blank containing the same volume of distilled water and $H_3BO_3$ solution.

7.4.2 Colorimetric determination: Prepare a series of Nessler tube standards as follows:

| ml of Standard 1.0 ml = 0.01 mg $NH_3$–N | mg $NH_3$–N/50.0 ml |
|---|---|
| 0.0 | 0.0 |
| 0.5 | 0.005 |
| 1.0 | 0.01 |
| 2.0 | 0.02 |
| 3.0 | 0.03 |
| 4.0 | 0.04 |
| 5.0 | 0.05 |
| 8.0 | 0.08 |
| 10.0 | 0.10 |

Dilute each tube to 50 ml with distilled water, add 2.0 ml of Nessler reagent (6.6) and mix. After 20 minutes read the absorbance at 425 nm against the blank. From the values obtained plot absorbance vs. mg $NH_3$–N for the standard curve. Determine the ammonia in the distillate by nesslerizing 50 ml or an aliquot diluted to 50 ml and reading the absorbance at 425 nm as described above for the standards. Ammonia-nitrogen content is read from the standard curve.

7.4.3 Potentiometric determination: Consult the method entitled Nitrogen, Ammonia: Selective Ion Electrode Method (Method 350.3) in this manual.

7.5 It is not imperative that all standards be distilled in the same manner as the samples. It is recommended that at least two standards (a high and low) be distilled and compared to similar values on the curve to insure that the distillation technique is reliable. If distilled standards do not agree with undistilled standards the operator should find the cause of the apparent error before proceeding.

8. Calculations

8.1 Titrimetric

$$\text{mg/l } NH_3 - N = \frac{A \times 0.28 \times 1{,}000}{S}$$

where:

A = ml 0.02 N $H_2SO_4$ used.

S = ml sample.

8.2 Spectrophotometric

$$\text{mg/l } NH_3 - N = \frac{A \times 1{,}000}{D} \times \frac{B}{C}$$

where:

A = mg $NH_3$–N read from standard curve.

B = ml total distillate collected, including boric acid and dilution.

C = ml distillate taken for nesslerization.

D = ml of original sample taken.

8.3 Potentiometric

$$\text{mg/l } NH_3 - N = \frac{500}{D} \times A$$

where:

A = mg $NH_3$–N/l from electrode method standard curve.

D = ml of original sample taken.

9. Precision and Accuracy

9.1 Twenty-four analysts in sixteen laboratories analyzed natural water samples containing exact increments of an ammonium salt, with the following results:

| Increment as Nitrogen, Ammonia mg N/liter | Precision as Standard Deviation mgN/liter | Accuracy as Bias, % | Accuracy as Bias, mg N/liter |
|---|---|---|---|
| 0.21 | 0.122 | -5.54 | -0.01 |
| 0.26 | 0.070 | -18.12 | -0.05 |
| 1.71 | 0.244 | +0.46 | +0.01 |
| 1.92 | 0.279 | -2.01 | -0.04 |

(FWPCA Method Study 2, Nutrient Analyses)

## Bibliography


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2. Annual Book of ASTM Standards, Part 31, "Water", Standard D1426–74, Method A, p 237 (1976).

# NITROGEN, KJELDAHL, TOTAL

## Method 351.3 (Colorimetric; Titrimetric; Potentiometric)

## STORET NO. 00625

1. Scope and Application
   1.1 This method covers the determination of total Kjeldahl nitrogen in drinking, surface and saline waters, domestic and industrial wastes. The procedure converts nitrogen components of biological origin such as amino acids, proteins and peptides to ammonia, but may not convert the nitrogenous compounds of some industrial wastes such as amines, nitro compounds, hydrazones, oximes, semicarbazones and some refractory tertiary amines.
   1.2 Three alternatives are listed for the determination of ammonia after distillation: the titrimetric method which is applicable to concentrations above 1 mg N/liter; the Nesslerization method which is applicable to concentrations below 1 mg N/liter; and the potentiometric method applicable to the range 0.05 to 1400 mg/1.
   1.3 This method is described for macro and micro glassware systems.
2. Definitions
   2.1 Total Kjeldahl nitrogen is defined as the sum of free-ammonia and organic nitrogen compounds which are converted to ammonium sulfate $(NH_4)_2SO_4$, under the conditions of digestion described below.
   2.2 Organic Kjeldahl nitrogen is defined as the difference obtained by subtracting the free-ammonia value (Method 350.2, Nitrogen, Ammonia, this manual) from the total Kjeldahl nitrogen value. This may be determined directly by removal of ammonia before digestion.
3. Summary of Method
   3.1 The sample is heated in the presence of conc. sulfuric acid, $K_2SO_4$ and $HgSO_4$ 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 by Nesslerization, titration or potentiometry.
4. Sample Handling and Preservation
   4.1 Samples may be preserved by addition of 2 ml of conc. $H_2SO_4$ per liter and stored at 4°C. Even when preserved in this manner, conversion of organic nitrogen to ammonia may occur. Preserved samples should be analyzed as soon as possible.
5. Interference
   5.1 High nitrate concentrations (10X or more than the TKN level) result in low TKN values. The reaction between nitrate and ammonia can be prevented by the use of an anion exchange resin (chloride form) to remove the nitrate prior to the TKN analysis.

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6. Apparatus

6.1 Digestion apparatus: A Kjeldahl digestion apparatus with 800 or 100 ml flasks and suction takeoff to remove $SO_3$ fumes and water.

6.2 Distillation apparatus: The macro Kjeldahl flask is connected to a condenser and an adaptor so that the distillate can be collected. Micro Kjeldahl steam distillation apparatus is commercially available.

6.3 Spectrophotometer for use at 400 to 425 nm with a light path of 1 cm or longer.

7. Reagents

7.1 Distilled water should be 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. Regeneration of the column should be carried out according to the manufacturer's instructions.

**NOTE 1:** All solutions must be made with ammonia-free water.

7.2 Mercuric sulfate solution: Dissolve 8 g red mercuric oxide (HgO) in 50 ml of 1:4 sulfuric acid (10.0 ml conc. $H_2SO_4$ : 40 ml distilled water) and dilute to 100 ml with distilled water.

7.3 Sulfuric acid-mercuric sulfate-potassium sulfate solution: Dissolve 267 g $K_2SO_4$ in 1300 ml distilled water and 400 ml conc. $H_2SO_4$. Add 50 ml mercuric sulfate solution (7.2) and dilute to 2 liters with distilled water.

7.4 Sodium hydroxide-sodium thiosulfate solution: Dissolve 500 g NaOH and 25 g $Na_2S_2O_3 \cdot 5H_2O$ in distilled water and dilute to 1 liter.

7.5 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.

7.6 Boric acid solution: Dissolve 20 g boric acid, $H_3BO_3$, in water and dilute to 1 liter with distilled water.

7.7 Sulfuric acid, standard solution: (0.02 N) 1 ml = 0.28 mg $NH_3$–N. Prepare a stock solution of approximately 0.1 N acid by diluting 3 ml of conc. $H_2SO_4$ (sp. gr. 1.84) to 1 liter with $CO_2$-free distilled water. Dilute 200 ml of this solution to 1 liter with $CO_2$-free distilled water. Standardize the approximately 0.02 N acid so prepared against 0.0200 N $Na_2CO_3$ solution. This last solution is prepared by dissolving 1.060 g anhydrous $Na_2CO_3$, oven-dried at 140°C, and diluting to 1 liter with $CO_2$-free distilled water.

**NOTE 2:** An alternate and perhaps preferable method is to standardize the approximately 0.1 N $H_2SO_4$ solution against a 0.100 N $Na_2CO_3$ solution. By proper dilution the 0.02 N acid can the be prepared.

7.8 Ammonium chloride, stock solution: 1.0 ml = 1.0 mg $NH_3$–N. Dissolve 3.819 g $NH_4Cl$ in water and make up to 1 liter in a volumetric flask with distilled water.

7.9 Ammonium chloride, standard solution: 1.0 ml = 0.01 mg $NH_3$–N. Dilute 10.0 ml of the stock solution (7.8) with distilled water to 1 liter in a volumetric flask.

7.10 Nessler reagent: Dissolve 100 g of mercuric iodide and 70 g potassium iodide in a small volume of distilled water. Add this mixture slowly, with stirring, to a cooled solution of 160 g of NaOH in 500 ml of distilled water. Dilute the mixture to 1 liter. The solution is stable for at least one year if stored in a pyrex bottle out of direct sunlight.

**NOTE 3:** Reagents 7.7, 7.8, 7.9, and 7.10 are identical to reagents 6.8, 6.2, 6.3, and 6.6 described under Nitrogen, Ammonia (Colorimetric; Titrimetric; Potentiometric-Distillation Procedure, Method 350.2).

8. Procedure

8.1 The distillation apparatus should be pre-steamed before use by distilling a 1:1 mixture of distilled water and sodium hydroxide-sodium thiosulfate solution (7.4) 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).

8.2 Macro Kjeldahl system

8.2.1 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:

| Kjeldahl Nitrogen in Sample, mg/l | Sample Size ml |
|---|---|
| 0–5 | 500 |
| 5–10 | 250 |
| 10–20 | 100 |
| 20–50 | 50.0 |
| 50–500 | 25.0 |

Dilute the sample, if required, to 500 ml with distilled water, and add 100 ml sulfuric acid-mercuric sulfate-potassium sulfate solution (7.3). Evaporate the mixture in the Kjeldahl apparatus until $SO_3$ fumes are given off and the solution turns colorless or pale yellow. Continue heating for 30 additional minutes. Cool the residue and add 300 ml distilled water.

8.2.2 Make the digestate alkaline by careful addition of 100 ml of sodium hydroxide – thiosulfate solution (7.4) without mixing.

**NOTE 5:** Slow addition of the heavy caustic solution down the tilted neck of the digestion flask will cause heavier solution to underlay the aqueous sulfuric acid solution without loss of free-ammonia. Do not mix until the digestion flask has been connected to the distillation apparatus.

8.2.3 Connect the Kjeldahl flask to the condenser with the tip of condenser or an extension of the condenser tip below the level of the boric acid solution (7.6) in the receiving flask.

8.2.4 Distill 300 ml at the rate of 6–10 ml/min., into 50 ml of 2% boric acid (7.6) contained in a 500 ml Erlenmeyer flask.

8.2.5 Dilute the distillate to 500 ml in the flask. 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. For concentrations above 1 mg/1, the ammonia can be determined titrimetrically. For concentrations below this value, it is determined colorimetrically. The potentiometric method is applicable to the range 0.05 to 1400 mg/1.

8.3 Micro Kjeldahl system

8.3.1 Place 50.0 ml of sample or an aliquot diluted to 50 ml in a 100 ml Kjeldahl flask and add 10 ml sulfuric acid-mercuric sulfate-potassium sulfate solution (7.3). Evaporate the mixture in the Kjeldahl apparatus until $SO_3$ fumes are given off and the solution turns colorless or pale yellow. Then digest for an additional 30 minutes. Cool the residue and add 30 ml distilled water.

8.3.2 Make the digestate alkaline by careful addition of 10 ml of sodium hydroxide-thiosulfate solution (7.4) without mixing. Do not mix until the digestion flask has been connected to the distillation apparatus.

8.3.3 Connect the Kjeldahl flask to the condenser with the tip of condenser or an extension of the condenser tip below the level of the boric acid solution (7.6) in the receiving flask or 50 ml short-form Nessler tube.

8.3.4 Steam distill 30 ml at the rate of 6–10 ml/min., into 5 ml of 2% boric acid (7.6).

8.3.5 Dilute the distillate to 50 ml. For concentrations above 1 mg/1 the ammonia can be determined titrimetrically. For concentrations below this value, it is determined colorimetrically. The potentiometric method is applicable to the range 0.05 to 1400 mg/1.

8.4 Determination of ammonia in distillate: Determine the ammonia content of the distillate titrimetrically, colorimetrically, or potentiometrically, as described below.

8.4.1 Titrimetric determination: Add 3 drops of the mixed indicator (7.5) to the distillate and titrate the ammonia with the 0.02 N $H_2SO_4$ (7.7), matching the endpoint against a blank containing the same volume of distilled water and $H_3BO_3$ (7.6) solution.

8.4.2 Colorimetric determination: Prepare a series of Nessler tube standards as follows:

| ml of Standard 1.0 ml = 0.01 mg $NH_3$–N | mg $NH_3$–N/50.0 ml |
|---|---|
| 0.0 | 0.0 |
| 0.5 | 0.005 |
| 1.0 | 0.010 |
| 2.0 | 0.020 |
| 4.0 | 0.040 |
| 5.0 | 0.050 |
| 8.0 | 0.080 |
| 10.0 | 0.10 |

Dilute each tube to 50 ml with ammonia free water, add 1 ml of Nessler Reagent (7.10) and mix. After 20 minutes read the absorbance at 425 nm against the blank. From the values obtained for the standards plot absorbance vs. mg $NH_3$-N for the standard curve. Develop color in the 50 ml diluted distillate in exactly the same manner and read mg $NH_3$-N from the standard curve.

8.4.3 Potentiometric determination: Consult the method entitled Nitrogen, Ammonia: Potentiometric, Ion Selective Electrode Method, (Method 350.3) in this manual.

8.4.4 It is not imperative that all standards be treated in the same manner as the samples. It is recommended that at least 2 standards (a high and low) be digested, distilled,

and compared to similar values on the curve to insure that the digestion-distillation technique is reliable. If treated standards do not agree with untreated standards the operator should find the cause of the apparent error before proceeding.

9. Calculation

9.1 If the titrimetric procedure is used, calculate Total Kjeldahl Nitrogen, in mg/l, in the original sample as follows:

$$\text{TKN, mg/l} = \frac{(A - B)N \times F \times 1{,}000}{S}$$

where:
A = milliliters of standard 0.020 N $H_2SO_4$ solution used in titrating sample.
B = milliliters of standard 0.020 N $H_2SO_4$ solution used in titrating blank.
N = normality of sulfuric acid solution.
F = milliequivalent weight of nitrogen (14 mg).
S = milliliters of sample digested.

If the sulfuric acid is exactly 0.02 N the formula is shortened to:

$$\text{TKN, mg/l} = \frac{(A - B) \times 280}{S}$$

9.2 If the Nessler procedure is used, calculate the Total Kjeldahl Nitrogen, in mg/l, in the original sample as follows:

$$\text{TKN, mg/l} = \frac{A \times 1{,}000}{D} \times \frac{B}{C}$$

where:
A = mg $NH_3$–N read from curve.
B = ml total distillate collected including the $H_3BO_3$.
C = ml distillate taken for Nesslerization.
D = ml of original sample taken.

9.3 Calculate Organic Kjeldahl Nitrogen in mg/l, as follows:
Organic Kjeldahl Nitrogen = TKN –($NH_3$–N.)

9.4 Potentiometric determination: Calculate Total Kjeldahl Nitrogen, in mg/1, in the original sample as follows:

$$\text{TKN, mg/l} = \frac{B}{D} \times A$$

where:
A = mg $NH_3$–N/1 from electrode method standard curve.
B = volume of diluted distillate in ml.
D = ml of original sample taken.

10. Precision

10.1 Thirty-one analysts in twenty laboratories analyzed natural water samples containing exact increments of organic nitrogen, with the following results:

| Increment as Nitrogen, Kjeldahl mg N/liter | Precision as Standard Deviation mg N/liter | Accuracy as Bias, % | Accuracy as Bias, mg N/liter |
|---|---|---|---|
| 0.20 | 0.197 | +15.54 | +0.03 |
| 0.31 | 0.247 | + 5.45 | +0.02 |
| 4.10 | 1.056 | + 1.03 | +0.04 |
| 4.61 | 1.191 | - 1.67 | -0.08 |

(FWPCA Method Study 2, Nutrient Analyses)

## Bibliography


1. Standard Methods for the Examination of Water and Wastewater, 14th Edition, p 437, Method 421 (1975).
2. Schlueter, Albert, "Nitrate Interference In Total Kjeldahl Nitrogen Determinations and Its Removal by Anion Exchange Resins", EPA Report 600/7–77–017.

# NITROGEN, NITRATE-NITRITE

## Method 353.3 (Spectrophotometric, Cadmium Reduction)

## STORET NO. Total 00630

1. Scope and Application
   1.1 This method is applicable to the determination of nitrite singly, or nitrite and nitrate combined in drinking, surface and saline waters, domestic and industrial wastes. The applicable range of this method is 0.01 to 1.0 mg/1 nitrate-nitrite nitrogen. The range may be extended with sample dilution.
2. Summary of Method
   2.1 A filtered sample is passed through a column containing granulated copper-cadmium to reduce nitrate to nitrite. The nitrite (that originally present plus reduced nitrate) is determined by diazotizing with sulfanilamide and coupling with N-(1-naphthyl)-ethylenediamine dihydrochloride to form a highly colored azo dye which is measured spectrophotometrically. Separate, rather than combined nitrate-nitrite, values are readily obtained by carrying out the procedure first with, and then without, the Cu-Cd reduction step.
3. Sample Handling and Preservation
   3.1 Analysis should be made as soon as possible. If analysis can be made within 24 hours, the sample should be preserved by refrigeration at 4°C. When samples must be stored for more than 24 hours, they should be preserved with sulfuric acid (2 ml $H_2SO_4$ per liter) and refrigeration.
   Caution: Samples for reduction column must not be preserved with mercuric chloride.
4. Interferences
   4.1 Build up of suspended matter in the reduction column will restrict sample flow. Since nitrate-nitrogen is found in a soluble state, the sample may be pre-filtered through a glass fiber filter or a 0.45$u$ membrane filter. Highly turbid samples may be pretreated with zinc sulfate before filtration to remove the bulk of particulate matter present in the sample.
   4.2 Low results might be obtained for samples that contain high concentrations of iron, copper or other metals. EDTA is added to the samples to eliminate this interference.
   4.3 Samples that contain large concentrations of oil and grease will coat the surface of the cadmium. This interference is eliminated by pre-extracting the sample with an organic solvent.
   4.4 This procedure determines both nitrate and nitrite. If only nitrate is desired, a separate determination must be made for nitrite and subsequent corrections made. The nitrite may be determined by the procedure below without the reduction step.

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5. Apparatus

5.1 Reduction column: The column in Figure I was constructed from a 100 ml pipet by removing the top portion. This column may also be constructed from two pieces of tubing joined end to end. A 10 mm length of 3 cm I.D. tubing is joined to a 25 cm length of 3.5 mm I.D. tubing.

5.2 Spectrophotometer for use at 540 nm, providing a light path of 1 cm or longer.

6. Reagents

6.1 Granulated cadmium: 40-60 mesh (MCB Reagents).

6.2 Copper-Cadmium: The cadmium granules (new or used) are cleaned with dilute HCl and copperized with 2% solution of copper sulfate in the following manner:

6.2.1 Wash the cadmium with dilute HCl (6.10) and rinse with distilled water. The color of the cadmium should be silver.

6.2.2 Swirl 25 g cadmium in 100 ml portions of a 2% solution of copper sulfate (6.11) for 5 minutes or until blue color partially fades, decant and repeat with fresh copper sulfate until a brown colloidal precipitate forms.

6.2.3 Wash the copper-cadmium with distilled water (at least 10 times) to remove all the precipitated copper. The color of the cadmium so treated should be black.

6.3 Preparation of reaction column: Insert a glass wool plug into the bottom of the reduction column and fill with distilled water. Add sufficient copper-cadmium granules to produce a column 18.5 cm in length. Maintain a level of distilled water above the copper-cadmium granules to eliminate entrapment of air. Wash the column with 200 ml of dilute ammonium chloride solution (6.5). The column is then activated by passing through the column 100 ml of a solution composed of 25 ml of a 1.0 mg/l $NO_3$–N standard and 75 ml of ammonium chloride – EDTA solution (6.4). Use a flow rate between 7 and 10 ml per minute.

6.4 Ammonium chloride – EDTA solution: Dissolve 13 g ammonium chloride and 1.7 g disodium ethylenediamine tetracetate in 900 ml of distilled water. Adjust the pH to 8.5 with conc. ammonium hydroxide (6.9) and dilute to 1 liter.

6.5 Dilute ammonium chloride-EDTA solution: Dilute 300 ml of ammonium chloride-EDTA solution (6.4) to 500 ml with distilled water.

6.6 Color reagent: Dissolve 10 g sulfanilamide and 1 g N(1-naphthyl)–ethylene-diamine dihydrochloride in a mixture of 100 ml conc. phosphoric acid and 800 ml of distilled water and dilute to 1 liter with distilled water.

6.7 Zinc sulfate solution: Dissolve 100 g $ZnSO_4 \cdot 7H_2O$ in distilled water and dilute to 1 liter.

6.8 Sodium hydroxide solution, 6N: Dissolve 240 g NaOH in 500 ml distilled water, cool and dilute to 1 liter.

6.9 Ammonium hydroxide, conc.

6.10 Dilute hydrochloric acid, 6N: Dilute 50 ml of conc. HCl to 100 ml with distilled water.

6.11 Copper sulfate solution, 2%: Dissolve 20 g of $CuSO_4 \cdot 5H_2O$ in 500 ml of distilled water and dilute to 1 liter.

6.12 Stock nitrate solution: Dissolve 7.218 g $KNO_3$ in distilled water and dilute to 1000 ml. Preserve with 2 ml of chloroform per liter. This solution is stable for at least 6 months. 1.0 ml = 1.00 mg $NO_3$–N.

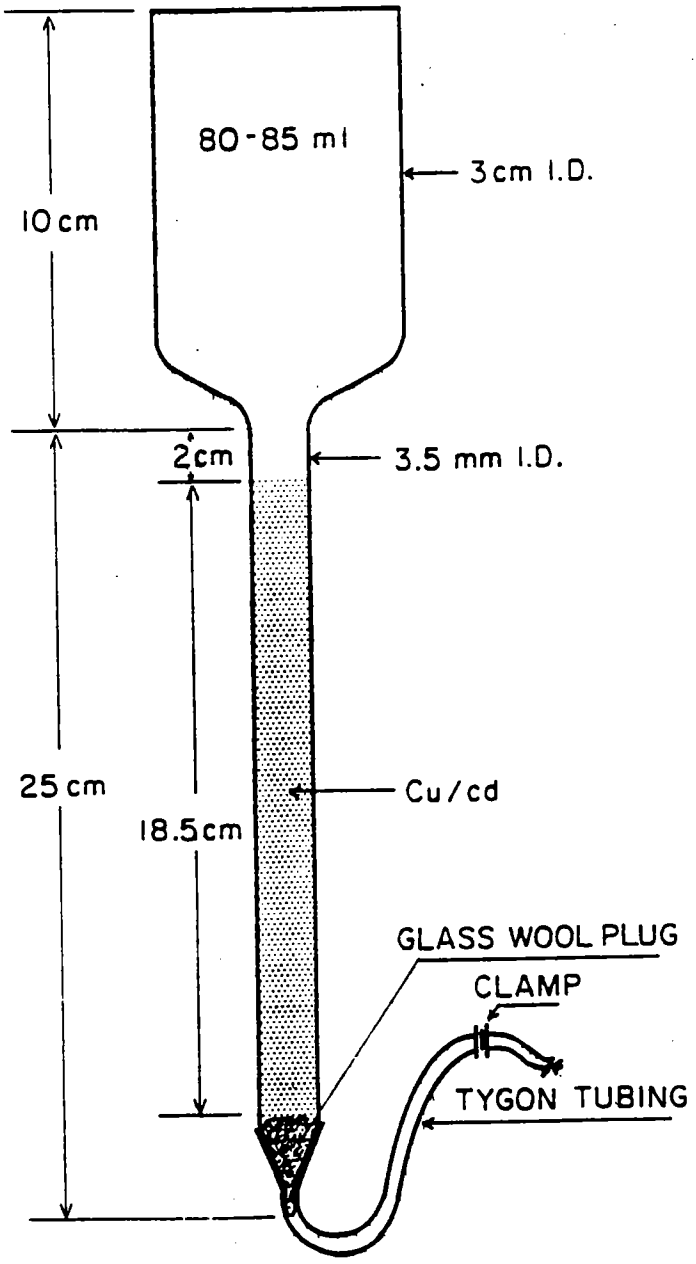


**FIGURE 1. REDUCTION COLUMN**

6.13 Standard nitrate solution: Dilute 10.0 ml of nitrate stock solution (6.12) to 1000 ml with distilled water. 1.0 ml = 0.01 mg $NO_3$–N.

6.14 Stock nitrite solution: Dissolve 6.072 g $KNO_2$ in 500 ml of distilled water and dilute to 1000 ml. Preserve with 2 ml of chloroform and keep under refrigeration. Stable for approximately 3 months. 1.0 ml = 1.00 mg $NO_2$–N.

6.15 Standard nitrite solution: Dilute 10.0 ml of stock nitrite solution (6.14) to 1000 ml with distilled water. 1.0 ml = 0.01 mg $NO_2$–N.

6.16 Using standard nitrate solution (6.13) prepare the following standards in 100 ml volumetric flasks:

| Conc., mg-$NO_3$–N/l | ml of Standard Solution/100.0 ml |
|---|---|
| 0.00 | 0.0 |
| 0.05 | 0.5 |
| 0.10 | 1.0 |
| 0.20 | 2.0 |
| 0.50 | 5.0 |
| 1.00 | 10.0 |

7. Procedure

7.1 Turbidity removal: One of the following methods may be used to remove suspended matter.

7.1.1 Filter sample through a glass fiber filter or a 0.45*u* membrane filter.

7.1.2 Add 1 ml zinc sulfate solution (6.7) to 100 ml of sample and mix thoroughly. Add 0.4–0.5 ml sodium hydroxide solution (6.8) to obtain a pH of 10.5 as determined with a pH meter. Let the treated sample stand a few minutes to allow the heavy flocculent precipitate to settle. Clarify by filtering through a glass fiber filter or a 0.45*u* membrane filter.

7.2 Oil and grease removal: Adjust the pH of 100 ml of filtered sample to 2 by addition of conc. HCl. Extract the oil and grease from the aqueous solution with two 25 ml portions of a non-polar solvent (Freon, chloroform or equivalent).

7.3 If the pH of the sample is below 5 or above 9, adjust to between 5 and 9 with either conc. HCl or conc. $NH_4OH$. This is done to insure a sample pH of 8.5 after step 7.4.

7.4 To 25.0 ml of sample or an aliquot diluted to 25.0 ml, add 75 ml of ammonium chloride-EDTA solution (6.4) and mix.

7.5 Pour sample into column and collect sample at a rate of 7–10 ml per minute.

7.6 Discard the first 25 ml, collect the rest of the sample (approximately 70 ml) in the original sample flask. Reduced sample should not be allowed to stand longer than 15 minutes before addition of color reagent, step 7.7.

7.7 Add 2.0 ml of color reagent (6.6) to 50.0 ml of sample. Allow 10 minutes for color development. Within 2 hours measure the absorbance at 540 nm against a reagent blank. **NOTE:** If the concentration of sample exceeds 1.0 mg $NO_3$–N/1, the remainder of the reduced sample may be used to make an appropriate dilution before proceeding with step 7.7.

7.8 Standards: Carry out the reduction of standards exactly as described for the samples. At least one nitrite standard should be compared to a reduced nitrate standard at the same concentration to verify the efficiency of the reduction column.

8. Calculation

8.1 Obtain a standard curve by plotting the absorbance of standards run by the above procedure against $NO_3$–N mg/l. Compute concentration of samples by comparing sample absorbance with standard curve.

8.2 If less than 25 ml of sample is used for the analysis the following equation should be used:

$$\text{mg}NO_2 + NO_3 - N/l = \frac{A \times 25}{\text{ml sample used}}$$

where:

A = Concentration of nitrate from standard curve.

9. Precision and Accuracy

9.1 In a single laboratory (EMSL), using sewage samples at concentrations of 0.04, 0.24, 0.55 and 1.04 mg $NO_3 + NO_2$-N/1, the standard deviations were ±0.005, ±0.004, ±0.005 and ±0.01, respectively.

9.2 In a single laboratory (EMSL), using sewage samples at concentrations of 0.24, 0.55, and 1.05 mg $NO_3 + NO_2$–N/1, the recoveries were 100%, 102% and 100%, respectively.

## Bibliography


1. Standard Methods for the Examination of Water and Wastewater, 14th Edition, p 423, Method 419C (1975).
2. Henrikson, A., and Selmer-Olsen, "Automatic Methods for Determining Nitrate and Nitrite in Water and Soil Extracts". Analyst, May 1970, Vol. 95, p 514–518.
3. Grasshoff, K., "A Simultaneous Multiple Channel System for Nutrient Analysis in Sea Water with Analog and Digital Data Record", "Advances in Automated Analysis", Technicon International Congress, 1969, Vol. 11, p 133–145.
4. Brewer, P. G., Riley, J. P., "The Automatic Determination of Nitrate in Sea Water", Deep Sea Research, 1965, Vol. 12, p 765–772.

# NITROGEN, NITRITE

## Method 354.1 (Spectrophotometric)

## STORET NO. Total 00615

1. Scope and Application
   - 1.1 This method is applicable to the determination of nitrite in drinking, surface and saline waters, domestic and industrial wastes.
   - 1.2 The method is applicable in the range from 0.01 to 1.0 mg $NO_2$–N/1.
2. Summary of Method
   - 2.1 The diazonium compound formed by diazotation of sulfanilamide by nitrite in water under acid conditions is coupled with N–(1-naphthyl)–ethylenediamine dihydrochloride to produce a reddish-purple color which is read in a spectrophotometer at 540 nm.
3. Sample Handling and Preservation
   - 3.1 Samples should be analyzed as soon as possible. They may be stored for 24 to 48 hours at 4°C.
4. Interferences
   - 4.1 There are very few known interferences at concentrations less than 1,000 times that of the nitrite; however, the presence of strong oxidants or reductants in the samples will readily affect the nitrite concentrations. High alkalinity (> 600 mg/1) will give low results due to a shift in pH.
5. Apparatus
   - 5.1 Spectrophotometer equipped with 1 cm or larger cells for use at 540 nm.
   - 5.2 Nessler tubes, 50 ml or volumetric flasks, 50 ml.
6. Reagents
   - 6.1 Distilled water free of nitrite and nitrate is to be used in preparation of all reagents and standards.
   - 6.2 Buffer-color reagent: To 250 ml of distilled water, add 105 ml conc. hydrochloric acid, 5.0 g sulfanilamide and 0.5 g N–(1-naphthyl) ethylenediamine dihydrochloride. Stir until dissolved. Add 136 g of sodium acetate ($CH_3COONa \cdot 3H_2O$) and again stir until dissolved. Dilute to 500 ml with distilled water. This solution is stable for several weeks if stored in the dark.
   - 6.3 Nitrite stock solution: 1.0 ml = 0.10 mg $NO_2$–N. Dissolve 0.1493 g of dried anhydrous sodium nitrite (24 hours in desiccator) in distilled water and dilute to 1000 ml. Preserve with 2 ml chloroform per liter.
   - 6.4 Nitrite standard solution: 1.0 ml = 0.001 mg $NO_2$–N. Dilute 10.0 ml of the stock solution (6.3) to 1000 ml.
7. Procedure
   - 7.1 If the sample has a pH greater than 10 or a total alkalinity in excess of 600 mg/1, adjust to approximately pH 6 with 1:3 HCl.

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7.2 If necessary, filter the sample through a 0.45 *u* pore size filter using the first portion of filtrate to rinse the filter flask.

7.3 Place 50 ml of sample, or an aliquot diluted to 50 ml, in a 50 ml Nessler tube; hold until preparation of standards is completed.

7.4 At the same time prepare a series of standards in 50 ml Nessler tubes as follows:

| ml of Standard Solution 1.0 ml = 0.001 mg $NO_2$-N | Conc., When Diluted to 50 ml, mg/l of $NO_2$–N |
|---|---|
| 0.0 | (Blank) |
| 0.5 | 0.01 |
| 1.0 | 0.02 |
| 1.5 | 0.03 |
| 2.0 | 0.04 |
| 3.0 | 0.06 |
| 4.0 | 0.08 |
| 5.0 | 0.10 |
| 10.0 | 0.20 |

7.5 Add 2 ml of buffer-color reagent (6.2) to each standard and sample, mix and allow color to develop for at least 15 minutes. The color reaction medium should be between pH 1.5 and 2.0.

7.6 Read the color in the spectrophotometer at 540 nm against the blank and plot concentration of $NO_2$–N against absorbance.

8. Calculation

8.1 Read the concentration of $NO_2$–N directly from the curve.

8.2 If less than 50.0 ml of sample is taken, calculate mg/l as follows:

$$NO_2 - N, \text{ mg/l} = \frac{\text{mg/l from std. curve} \times 50}{\text{ml sample used}}$$

9. Precision and Accuracy

9.1 Precision and Accuracy data are not available at this time.

## Bibliography

1. Standard Methods for the Examination for Water and Wastewater, 14th Edition, p 434, Method 420, (1975).

# PHOSPHORUS, ALL FORMS

## Method 365.2 (Colorimetric, Ascorbic Acid, Single Reagent)

## STORET NO. See Section 4

1. Scope and Application
   - 1.1 These methods cover the determination of specified forms of phosphorus in drinking, surface and saline waters, domestic and industrial wastes.
   - 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 defined in Section 4.
     - 1.2.1 Except for in-depth and detailed studies, the most commonly measured forms are phosphorus and dissolved phosphorus, and orthophosphate and dissolved orthophosphate. Hydrolyzable phosphorus is normally found only in sewage-type samples and insoluble forms of phosphorus are determined by calculation.
   - 1.3 The methods are usable in the 0.01 to 0.5 mg P/1 range.
2. Summary of Method
   - 2.1 Ammonium molybdate and antimony potassium tartrate react in an acid medium with dilute solutions of phosphorus to form an antimony-phospho-molybdate complex. This complex is reduced to an intensely blue-colored complex by ascorbic acid. The color is proportional to the phosphorus concentration.
   - 2.2 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[2].
3. Sample Handling and Preservation
   - 3.1 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.
   - 3.3 If the analysis cannot be performed the day of collection, the sample should be preserved by the addition of 2 ml conc. $H_2SO_4$ per liter and refrigeration at 4°C.
4. Definitions and Storet Numbers
   - 4.1 Total Phosphorus (P) — all of the phosphorus present in the sample, regardless of form, as measured by the persulfate digestion procedure. (00665)
     - 4.1.1 Total Orthophosphate (P, ortho) — inorganic phosphorus $[(PO_4)^{-3}]$ in the sample as measured by the direct colorimetric analysis procedure. (70507)
     - 4.1.2 Total Hydrolyzable Phosphorus (P, hydro) - phosphorus in the sample as measured by the sulfuric acid hydrolysis procedure, and minus pre-determined orthophosphates. This hydrolyzable phosphorus includes polyphosphorus. $[(P_2O_7)^{-4}$, $(P_3O_{10})^{-5}$, etc.] plus some organic phosphorus. (00669)

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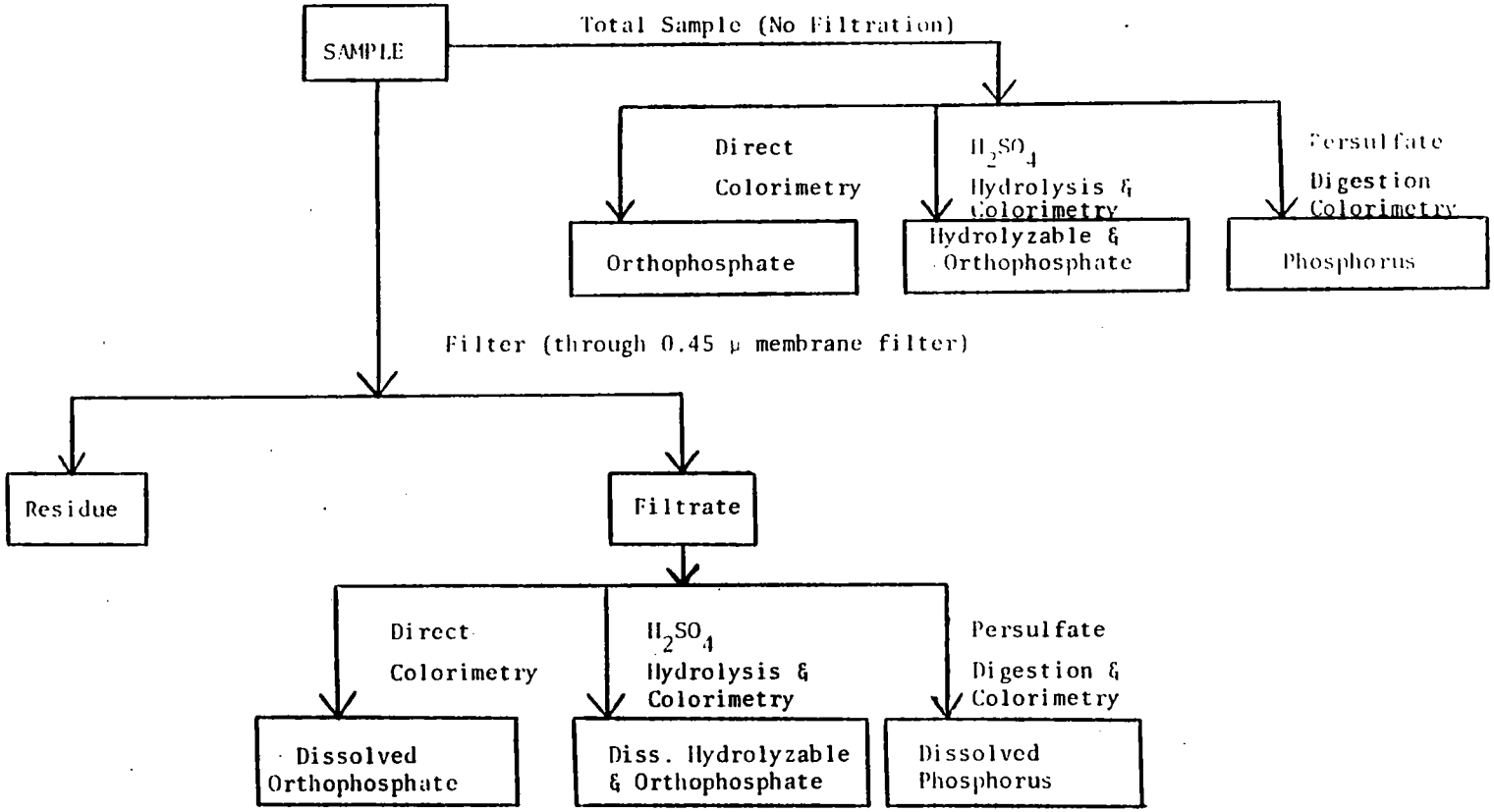


**FIGURE 1. ANALYTICAL SCHEME FOR DIFFERENTIATION OF PHOSPHORUS FORMS**

4.1.3 Total Organic Phosphorus (P, org) — phosphorus (inorganic plus oxidizable organic) in the sample measured by the persulfate digestion procedure, and minus hydrolyzable phosphorus and orthophosphate. (00670)

4.2 Dissolved Phosphorus (P–D) — 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. (00666)

4.2.1 Dissolved Orthophosphate (P–D, ortho) — as measured by the direct colorimetric analysis procedure. (00671)

4.2.2 Dissolved Hydrolyzable Phosphorus (P–D, hydro) — as measured by the sulfuric acid hydrolysis procedure and minus pre-determined dissolved orthophosphates. (00672)

4.2.3 Dissolved Organic Phosphorus (P–D, org) — as measured by the persulfate digestion procedure, and minus dissolved hydrolyzable phosphorus and orthophosphate. (00673)

4.3 The following forms, when sufficient amounts of phosphorus are present in the sample to warrant such consideration, may be calculated:

4.3.1 Insoluble Phosphorus (P-I)=(P)-(P-D). (00667)

4.3.1.1 Insoluble orthophosphate (P-I, ortho)=(P, ortho)-(P-D, ortho). (00674)

4.3.1.2 Insoluble Hydrolyzable Phosphorus (P-I, hydro)=(P, hydro)-(P-D, hydro). (00675)

4.3.1.3 Insoluble Organic Phosphorus (P-I, org)=(P, org) – (P-D, org). (00676)

4.4 All phosphorus forms shall be reported as P, mg/1, to the third place.

5. Interferences

5.1 No interference is caused by copper, iron, or silicate at concentrations many times greater than their reported concentration in sea water. However, high iron concentrations can cause precipitation of and subsequent loss of phosphorus.

5.2 The salt error for samples ranging from 5 to 20% salt content was found to be less than 1%.

5.3 Arsenate is determined similarly to phosphorus and should be considered when present in concentrations higher than phosphorus. However, at concentrations found in sea water, it does not interfere.

6. Apparatus

6.1 Photometer – A spectrophotometer or filter photometer suitable for measurements at 650 or 880 nm with a light path of 1 cm or longer.

6.2 Acid-washed glassware: All glassware used 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. $H_2SO_4$ with distilled water to 500 ml.

7.2 Antimony potassium tartrate solution: Weigh 1.3715 g $K(SbO)C_4H_4O_6 \cdot 1/2H_2O$, dissolve in 400 ml distilled water in 500 ml volumetric flask, dilute to volume. Store at 4°C in a dark, glass-stoppered bottle.

7.3 Ammonium molybdate solution: Dissolve 20 g $(NH_4)_6Mo_7O_{24} \cdot 4H_2O$ in 500 ml of 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 $H_2SO_4$, (7.1), 5 ml of antimony potassium tartrate solution (7.2), 15 ml of ammonium molybdate solution (7.3), and 30 ml of ascorbic acid solution (7.4). 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 stand for a few minutes until the turbidity disappears before proceeding. Since the stability of this solution is limited, it must be freshly prepared for each run.

7.6 Sulfuric acid solution, 11 N: Slowly add 310 ml conc. $H_2SO_4$ to 600 ml distilled water. When cool, dilute to 1 liter.

7.7 Ammonium persulfate.

7.8 Stock phosphorus solution: Dissolve in distilled water 0.2197 g of potassium dihydrogen phosphate, $KH_2PO_4$, which has been dried in an oven at 105°C. Dilute the solution to 1000 ml; 1.0 ml = 0.05 mg P.

7.9 Standard phosphorus solution: Dilute 10.0 ml of stock phosphorus solution (7.8) to 1000 ml with distilled water; 1.0 ml = 0.5 ug P.

7.9.1 Using standard solution, prepare the following standards in 50.0 ml volumetric flasks:

| ml of Standard Phosphorus Solution (7.9) | Conc., mg/l |
|---|---|
| 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 |

7.10 Sodium hydroxide, 1 N: Dissolve 40 g NaOH in 600 ml distilled water. Cool and dilute to 1 liter.

8. Procedure

8.1 Phosphorus

8.1.1 Add 1 ml of $H_2SO_4$ solution (7.6) to a 50 ml sample in a 125 ml Erlenmeyer flask.

8.1.2 Add 0.4 g of ammonium persulfate.

8.1.3 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).

8.1.4 Cool and dilute the sample to about 30 ml and adjust the pH of the sample to 7.0 ±0.2 with 1 N NaOH (7.10) using a pH meter. If sample is not clear at this point, add 2–3 drops of acid (7.6) and filter. Dilute to 50 ml.
Alternatively, if autoclaved see **NOTE 1.**

8.1.5 Determine phosphorus as outlined in 8.3.2 Orthophosphate.

8.2 Hydrolyzable Phosphorus

8.2.1 Add 1 ml of $H_2SO_4$ solution (7.6) to a 50 ml sample in a 125 ml Erlenmeyer flask.

8.2.2 Boil gently on a pre-heated hot plate for 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).

8.2.3 Cool and dilute the sample to about 30 ml and adjust the pH of the sample to 7.0 ±0.2 with NaOH (7.10) using a pH meter. If sample is not clear at this point, add 2–3 drops of acid (7.6) and filter. Dilute to 50 ml.
Alternatively, if autoclaved see **NOTE 1.**

8.2.4 The sample is now ready for determination of phosphorus as outlined in 8.3.2 Orthophosphate.

8.3 Orthophosphate

8.3.1 The pH of the sample must be adjusted to 7±0.2 using a pH meter.

8.3.2 Add 8.0 ml of combined reagent (7.5) 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 650 or 880 nm with a spectrophotometer, using the reagent blank as the reference solution.
**NOTE 1:** If the same volume of sodium hydroxide solution is not used to adjust the pH of the standards and samples, a volume correction has to be employed.

9. Calculation

9.1 Prepare a standard curve by plotting the absorbance values of standards versus the corresponding phosphorus concentrations.

9.1.1 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 ±2% of the true value, prepare a new calibration curve.

9.2 Obtain concentration value of sample directly from prepared standard curve. Report results as P, mg/1. SEE **NOTE 1.**

10. Precision and Accuracy

10.1 Thirty-three analysts in nineteen laboratories analyzed natural water samples containing exact increments of organic phosphate, with the following results:

| Increment as Total Phosphorus mg P/liter | Precision as Standard Deviation mg P/liter | Accuracy as Bias, % | Accuracy as Bias mg P/liter |
|---|---|---|---|
| 0.110 | 0.033 | +3.09 | +0.003 |
| 0.132 | 0.051 | +11.99 | +0.016 |
| 0.772 | 0.130 | +2.96 | +0.023 |
| 0.882 | 0.128 | –0.92 | –0.008 |

(FWPCA Method Study 2, Nutrient Analyses)

10.2 Twenty-six analysts in sixteen laboratories analyzed natural water samples containing exact increments of orthophosphate, with the following results:

| Increment as Orthophosphate mg P/liter | Precision as Standard Deviation mg P/liter | Accuracy as Bias, % | Accuracy as Bias, mg P/liter |
|---|---|---|---|
| 0.029 | 0.010 | –4.95 | –0.001 |
| 0.038 | 0.008 | –6.00 | –0.002 |
| 0.335 | 0.018 | –2.75 | –0.009 |
| 0.383 | 0.023 | –1.76 | –0.007 |

(FWPCA Method Study 2, Nutrient Analyses)

## Bibliography


1. Murphy, J., and Riley, J., "A modified Single Solution for the Determination of Phosphate in Natural Waters", Anal. Chim. Acta., 27, 31 (1962).
2. Gales, M., Jr., Julian, E., and Kroner, R., "Method for Quantitative Determination of Total Phosphorus in Water", Jour. AWWA, 58, No. 10, 1363 (1966).
3. Annual Book of ASTM Standards, Part 31, "Water", Standard D515–72, Method A, p 389 (1976).
4. Standard Methods for the Examination of Water and Wastewater, 14th Edition, p 476 and 481, (1975).

# SILICA, DISSOLVED

## Method 370.1 (Colorimetric)

## STORET NO. Dissolved 00955

1. Scope and Application
   - 1.1 This method is applicable to drinking, surface and saline waters, domestic and industrial wastes.
   - 1.2 The working range of the method is approximately 2 to 25 mg silica/1. The upper range can be extended by taking suitable aliquots; the lower range can be extended by the addition of amino-naphthol-sulfonic acid solution, as described in (6.8).
2. Summary of Method
   - 2.1 A well-mixed sample is filtered through a 0.45 *u* membrane filter. The filtrate, upon the addition of molybdate ion in acidic solution, forms a greenish-yellow color complex proportional to the dissolved silica in the sample. The color complex is then measured spectrophotometrically.
   - 2.2 In the low concentration modification the yellow (410 nm) molybdosilicic acid color is reduced by 1-amino-2-naphthol-4-sulfonic acid to a more intense heteropoly blue (815 nm or 650 nm).
3. Interferences
   - 3.1 Excessive color and/or turbidity interfere. Correct by running blanks prepared without addition of the ammonium molybdate solution. See (6.7).
   - 3.2 Tannin interference may be eliminated and phosphate interferences may be decreased with oxalic acid.
   - 3.3 Large amounts of iron and sulfide interfere.
   - 3.4 Contact with glass should be minimized, silica free reagents should be used as much as possible. A blank should be run.
4. Apparatus
   - 4.1 Platinum dishes, 100 ml.
   - 4.2 Colorimetric equipment–one of the following:
     - 4.2.1 Spectrophotometer for use at 410 nm, 650 nm and/or 815 nm with a 1 cm or longer cell.
     - 4.2.2 Filter photometer with a violet filter having maximum transmittance as near 410 nm as possible and a 1 cm or longer cell.
     - 4.2.3 Nessler tubes, matched, 50 ml, tall form.
5. Reagents
   - 5.1 Use chemicals low in silica and store in plastic containers.
   - 5.2 Sodium bicarbonate, $NaHCO_3$, powder.
   - 5.3 Sulfuric acid, $H_2SO_4$, 1 N.

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5.4 Hydrochloric acid, HCl, 1 + 1.

5.5 Ammonium molybdate reagent: Place 10 g $(NH_4)_6Mo_7O_{24}\cdot 4H_2O$ in distilled water in a 100 ml volumetric. Dissolve by stirring and gently warming. Dilute to the mark. Filter if necessary. Adjust to pH 7 to 8 with silica free $NH_4OH$ or NaOH. Store in plastic bottle.

5.6 Oxalic acid solution: Dissolve 10 g $H_2C_2O_4\cdot 2H_2O$ in distilled water in a 100 ml volumetric flask, dilute to the mark. Store in plastic.

5.7 Stock silica solution: Dissolve 4.73 g sodium metasilicate nonahydrate, $Na_2SiO_3\cdot 9H_2O$, in recently boiled and cooled distilled water. Dilute to approximately 900 ml. Analyze 100.0 ml portions by gravimetry (ref. 1, p. 484). Adjust concentration to 1.000 mg/l $SiO_2$. Store in tightly stoppered plastic bottle.

5.8 Standard silica solution: Dilute 10.0 ml stock solution to 1 liter with recently boiled and cooled distilled water. This is 10 mg/l $SiO_2$ (1.00 ml = 10.0 *ug* $SiO_2$). Store in a tightly stoppered plastic bottle.

5.9 Permanent color solutions

5.9.1 Potassium chromate solution: Dissolve 630 mg $K_2CrO_4$ in distilled water in a 1 liter volumetric flask and dilute to the mark.

5.9.2 Borax solution: Dissolve 10 g sodium borate decahydrate, $(Na_2B_4O_7\cdot 10H_2O)$ in distilled water in a 1 liter volumetric flask and dilute to the mark.

5.10 Reducing agent: Dissolve 500 mg of 1-amino-2-naphthol-4-sulfonic acid and 1 g $Na_2SO_3$ in 50 ml distilled water with gentle warming if necessary. Dissolve 30 g $NaHSO_3$ in 150 ml distilled water. Mix these two solutions. Filter into a plastic bottle. Refrigerate and avoid exposure to light. Discard when it darkens. If there is incomplete solubility or immediate darkening of the aminonaphthosulfonic acid solution do not use.

6. Procedure

6.1 Filter sample through a 0.45 u membrane filter.

6.2 Digestion: If molybdate unreactive silica is present and its inclusion in the analysis is desired, include this step, otherwise proceed to 6.3.

6.2.1 Place 50 ml, or a smaller portion diluted to 50 ml, of filtered (6.1) sample in a 100 ml platinum dish.

6.2.2 Add 200 mg silica-free $NaHCO_3$ (5.2) and digest on a steam bath for 1 hour. Cool.

6.2.3 Add slowly and with stirring 2.4 ml $H_2SO_4$ (5.3).

6.2.4 Immediately transfer to a 50 ml Nessler tube, dilute to the mark with distilled water and proceed to 6.3 without delay.

6.3 Color development

6.3.1 Place 50 ml sample in a Nessler tube.

6.3.2 Add rapidly 1.0 ml of 1 + 1 HCl (5.4) and 2.0 ml ammonium molybdate reagent (5.5).

6.3.3 Mix by inverting at least 6 times.

6.3.4 Let stand 5 to 10 minutes.

6.3.5 Add 1.5 ml oxalic acid solution (5.6) and mix thoroughly.

6.3.6 Read color (spectrophotometrically or visually) after 2 minutes but before 15 minutes from the addition of oxalic acid.

6.4 Preparation of Standards

6.4.1 If digestion (6.2) was used add 200 mg $NaHCO_3$ (5.2) and 2.4 ml $H_2SO_4$ (5.3) to standards to compensate for silica introduced by these reagents and for effect of the salt on the color intensity.

6.5 Photometric measurement

6.5.1 Prepare a calibration curve using approximately six standards to span the range shown below with the selected light path.

Selection of Light Path Length for Various Silica Concentrations

| Light Path cm | Silica in 54.5 ml final volume (*ug*) |
|---|---|
| 1 | 200–1300 |
| 2 | 100–700 |
| 5 | 40–250 |
| 10 | 20–130 |

6.5.2 Carry out the steps in 6.3 using distilled water as the reference. Read a blank.

6.5.3 Plot photometric reading versus *ug* of silica in the final solution of 54.5 ml. Run a reagent blank and at least one standard with each group of samples.

6.6 Visual Comparison

6.6.1 Prepare a set of permanent artificial color standards according to the table. Use well stoppered, properly labelled 50 ml Nessler tubes.

| Silica value mg | Potassium chromate solution (5.9.1) ml | Borax solution (5.9.2) ml | Distilled water ml |
|---|---|---|---|
| 0.00 | 0.0 | 25 | 30 |
| 0.10 | 1.0 | 25 | 29 |
| 0.20 | 2.0 | 25 | 28 |
| 0.40 | 4.0 | 25 | 26 |
| 0.50 | 5.0 | 25 | 25 |
| 0.75 | 7.5 | 25 | 22 |
| 1.00 | 10.0 | 25 | 20 |

6.6.2 Verify permanent standards by comparison to color developed by standard silica solutions.

6.6.3 These permanent artificial color standards are only for color comparison procedure, not for photometric procedure.

6.7 Correction for color or turbidity

6.7.1 A special blank is run using a portion of the sample and carrying out the procedure in 6.1, 6.2 if used, and 6.3 except for the addition of ammonium molybdate (6.3.2).

6.7.2 Zero the photometer with this blank before reading the samples.

6.8 Procedure for low concentration ( < 1000 ug/1)

6.8.1 Perform steps 6.1 and 6.2 if needed.

6.8.2 Place 50 ml sample in a Nessler tube.

6.8.3 In rapid succession add 1.0 ml of 1 + 1 HCl (5.4).

6.8.4 Add 2.0 ml ammonium molybdate reagent (5.5).

6.8.5 Mix by inverting at least six times.

6.8.6 Let stand 5 to 10 minutes.

6.8.7 Add 1.5 ml oxalic acid solution (5.6).

6.8.8 Mix thoroughly.

6.8.9 At least 2, but not more than 15 minutes after oxalic acid addition, add 2.0 ml reducing agent (5.10).

6.8.10 Mix thoroughly.

6.8.11 Wait 5 minutes, read photometrically or visually.

6.8.12 If digestion (6.2) was used see (6.4).

6.8.13 Photometric measurement

6.8.13.1 Prepare a calibration curve using approximately 6 standards and a reagent blank to span the range shown below with the selected light path.

Selection of Light Path Length for Various Silica Concentrations

| Light Path cm | Silica in 56.5 ml Final volume, ug | |
|---|---|---|
| | 650 nm | 815 nm |
| 1 | 40–300 | 20–100 |
| 2 | 20–150 | 10–50 |
| 5 | 7–50 | 4–20 |
| 10 | 4–30 | 2–10 |

6.8.13.2 Read versus distilled water.

6.8.13.3 Plot photometric reading at 650 nm or at 815 nm versus ug of si... in 56.5 ml.

6.8.13.4 For turbidity correction use 6.1, 6.2 if used and 6.8.2–6.8.11 omitting 6.8.4 and 6.8.9.

6.8.13.5 Run a reagent blank and at least one standard (to check calibration curve drift) with each group of samples.

6.8.14 Visual comparison

6.8.14.1 Prepare not less than 12 standards covering the range of 0 to 120 ug $SiO_2$ by placing the calculated volumes of standard silica (5.8) in 50 ml Nessler tubes, diluting to the mark and develop the color as in 6.8.2–6.8.11.

7. Calculations

7.1 Read *ug* $SiO_2$ from calibration curve or by visual comparison

7.2 mg/l $SiO_2$ = $\frac{ug/SiO_2}{ml\ sample}$

7.3 Report whether $NaHCO_3$ digestion (6.2) was used

8. Precision and Accuracy

8.1 A synthetic unknown sample containing 5.0 mg/l $SiO_2$, 10 mg/l chloride, 0.200 mg/l ammonia N, 1.0 mg/l nitrate N, 1.5 mg/l organic N, and 10.0 mg/l phosphate in distilled water was analyzed in 19 laboratories by the molybdosilicate method, with a relative standard deviation of 14.3% and a relative error of 7.8%.

8.2 Another synthetic unknown sample containing 15.0 mg/l $SiO_2$, 200 mg/l chloride, 0.800 mg/l ammonia N, 1.0 mg/l nitrate N, 0.800 mg/l organic N, and 5.0 mg/l phosphate in distilled water was analyzed in 19 laboratories by the molybdosilicate method, with a relative standard deviation of 8.4% and a relative error of 4.2%.

8.3 A third synthetic unknown sample containing 30.0 mg/l $SiO_2$, 400 mg/l chloride, 1.50 mg/l ammonia N, 1.0 mg/l nitrate N, 0.200 mg/l organic N, and 0.500 mg/l phosphate in distilled water was analyzed in 20 laboratories by the molybdosilicate method, with a relative standard deviation of 7.7% and a relative error of 9.8%. All results were obtained after sample digestion with $NaHCO_3$.

8.4 Photometric evaluations by the amino-naphthol-sulfonic acid procedure have an estimated precision of ±0.10 mg/l in the range from 0 to 2 mg/l (ASTM).

8.5 Photometric evaluations of the silico-molybdate color in the range from 2 to 50 mg/l have an estimated precision of approximately 4% of the quantity of silica measured (ASTM).

## Bibliography


1. Annual Book of ASTM Standards, Part 31, "Water", Standard D859–68, p 401 (1976).
2. Standard Methods for the Examination of Water and Wastewater, 14th Edition, p 487, Method 426B, (1975).

# ORGANIC CARBON, TOTAL

## Method 415.1 (Combustion or Oxidation)

**STORET NO. Total 00680**
**Dissolved 00681**

1. Scope and Application
   1.1 This method includes the measurement of organic carbon in drinking, surface and saline waters, domestic and industrial wastes. Exclusions are noted under Definitions and Interferences.
   1.2 The method is most applicable to measurement of organic carbon above 1 mg/1.
2. Summary of Method
   2.1 Organic carbon in a sample is converted to carbon dioxide ($CO_2$) by catalytic combustion or wet chemical oxidation. The $CO_2$ formed can be measured directly by an infrared detector or converted to methane ($CH_4$) and measured by a flame ionization detector. The amount of $CO_2$ or $CH_4$ is directly proportional to the concentration of carbonaceous material in the sample.
3. Definitions
   3.1 The carbonaceous analyzer measures all of the carbon in a sample. Because of various properties of carbon-containing compounds in liquid samples, preliminary treatment of the sample prior to analysis dictates the definition of the carbon as it is measured. Forms of carbon that are measured by the method are:
      A) soluble, nonvolatile organic carbon; for instance, natural sugars.
      B) soluble, volatile organic carbon; for instance, mercaptans.
      C) insoluble, partially volatile carbon; for instance, oils.
      D) insoluble, particulate carbonaceous materials, for instance; cellulose fibers.
      E) soluble or insoluble carbonaceous materials adsorbed or entrapped on insoluble inorganic suspended matter; for instance, oily matter adsorbed on silt particles.
   3.2 The final usefulness of the carbon measurement is in assessing the potential oxygen-demanding load of organic material on a receiving stream. This statement applies whether the carbon measurement is made on a sewage plant effluent, industrial waste, or on water taken directly from the stream. In this light, carbonate and bicarbonate carbon are not a part of the oxygen demand in the stream and therefore should be discounted in the final calculation or removed prior to analysis. The manner of preliminary treatment of the sample and instrument settings defines the types of carbon which are measured. Instrument manufacturer's instructions should be followed.

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4. Sample Handling and Preservation

4.1 Sampling and storage of samples in glass bottles is preferable. Sampling and storage in plastic bottles such as conventional polyethylene and cubitainers is permissible if it is established that the containers do not contribute contaminating organics to the samples.
**NOTE 1:** A brief study performed in the EPA Laboratory indicated that distilled water stored in new, one quart cubitainers did not show any increase in organic carbon after two weeks exposure.

4.2 Because of the possibility of oxidation or bacterial decomposition of some components of aqueous samples, the lapse of time between collection of samples and start of analysis should be kept to a minimum. Also, samples should be kept cool (4°C) and protected from sunlight and atmospheric oxygen.

4.3 In instances where analysis cannot be performed within two hours (2 hours) from time of sampling, the sample is acidified ($pH \leq 2$) with HCl or $H_2SO_4$.

5. Interferences

5.1 Carbonate and bicarbonate carbon represent an interference under the terms of this test and must be removed or accounted for in the final calculation.

5.2 This procedure is applicable only to homogeneous samples which can be injected into the apparatus reproducibly by means of a microliter type syringe or pipette. The openings of the syringe or pipette limit the maximum size of particles which may be included in the sample.

6. Apparatus

6.1 Apparatus for blending or homogenizing samples: Generally, a Waring-type blender is satisfactory.

6.2 Apparatus for total and dissolved organic carbon:

6.2.1 A number of companies manufacture systems for measuring carbonaceous material in liquid samples. Considerations should be made as to the types of samples to be analyzed, the expected concentration range, and forms of carbon to be measured.

6.2.2 No specific analyzer is recommended as superior.

7. Reagents

7.1 Distilled water used in preparation of standards and for dilution of samples should be ultra pure to reduce the carbon concentration of the blank. Carbon dioxide-free, double distilled water is recommended. Ion exchanged waters are not recommended because of the possibilities of contamination with organic materials from the resins.

7.2 Potassium hydrogen phthalate, stock solution, 1000 mg carbon/liter: Dissolve 0.2128 g of potassium hydrogen phthalate (Primary Standard Grade) in distilled water and dilute to 100.0 ml.
**NOTE 2:** Sodium oxalate and acetic acid are not recommended as stock solutions.

7.3 Potassium hydrogen phthalate, standard solutions: Prepare standard solutions from the stock solution by dilution with distilled water.

7.4 Carbonate-bicarbonate, stock solution, 1000 mg carbon/liter: Weigh 0.3500 g of sodium bicarbonate and 0.4418 g of sodium carbonate and transfer both to the same 100 ml volumetric flask. Dissolve with distilled water.

7.5 Carbonate-bicarbonate, standard solution: Prepare a series of standards similar to step 7.3.

**NOTE 3:** This standard is not required by some instruments.

7.6 Blank solution: Use the same distilled water (or similar quality water) used for the preparation of the standard solutions.

8. Procedure

8.1 Follow instrument manufacturer's instructions for calibration, procedure, and calculations.

8.2 For calibration of the instrument, it is recommended that a series of standards encompassing the expected concentration range of the samples be used.

9. Precision and Accuracy

9.1 Twenty-eight analysts in twenty-one laboratories analyzed distilled water solutions containing exact increments of oxidizable organic compounds, with the following results:

| Increment as TOC mg/liter | Precision as Standard Deviation TOC, mg/liter | Accuracy as Bias, % | Accuracy as Bias, mg/liter |
|---|---|---|---|
| 4.9 | 3.93 | +15.27 | +0.75 |
| 107 | 8.32 | + 1.01 | +1.08 |

(FWPCA Method Study 3, Demand Analyses)

## Bibliography


1. Annual Book of ASTM Standards, Part 31, "Water", Standard D 2574–79, p 469 (1976).
2. Standard Methods for the Examination of Water and Wastewater, 14th Edition, p 532, Method 505, (1975).

# APPENDIX B

# INSTRUCTIONS FOR SAMPLE COLLECTION AND PROCESSING

## APPENDIX B

## INSTRUCTIONS FOR SAMPLE COLLECTION AND PROCESSING

All samples will be chilled immediately upon collection and will be shipped or delivered on the same day they are collected with the exception of trace metal, mercury, and organics samples. These samples may be stored 5 days in a refrigerator before shipment. They will be shipped for overnight delivery or delivered by courier. All sample holding times are shown in Table 2.

***Clostridium Sample Collection.*** *Clostridium perfringens* samples will be collected in 250-mL amber glass bottles. The bottles contain sodium thiosulfate, a chlorine neutralizer. The bottles should be filled to the bend in the neck of the bottle leaving ½ inch of air space. The samples should be shipped on ice the same night of the date of collection and marked for next day delivery. Ship samples to:

Gerri Miceli
Biological Analytical Laboratories, Inc.
610 Ten Rod Road
North Kingstown, RI 02852

In addition, please call Gerri Miceli at (401) 294-6677 with the shipping number so that coolers may be tracked if the need arises.

***Metals and Mercury Sample Collection.*** Metals samples will be collected in 500-mL polyethylene bottles and the mercury samples in 500-mL Teflon bottles. Each of the bottles will contain 2.5 mL of 50% nitric acid; handle with caution. Fill the bottles with sample up to the shoulder of the bottle, cap tightly, and invert the bottle at least twice to mix the acid with the sample. Double bag the sample and refrigerate.

Note: To avoid contamination of the bottle or sample:

Handle the bottles with clean gloves (supplied with bottles).
While wearing the gloves avoid touching objects other than the bottle and cap, especially metal objects.
While sampling, hold the cap with clean gloves, avoiding the inner surface. If it is not possible to hold the cap, place it in a clean bag.
Leave the bottle uncovered for as little time as possible.

***Organic Sample Collection.*** Organic samples will be collected in two 2-L amber glass bottles. Fill the bottles with sample up to the handle on the neck, cap, and refrigerate.

***Stable Isotope Sample Collection.*** The stable isotope samples will be initially collected in 5 1-L polyethylene bottles or in a single, 10-L glass jar. Two of the bottles will be marked for sulfur and one will be marked for nitrogen. Fill each of the bottles to the base of the neck. The stated amount is assumed to provide adequate amounts of sample for analysis.

The volume of sample water necessary will be dependent upon the concentration of filterable material in the sample water. It is expected that a total of 10 to 15 4.7 cm GF/F filters per sample are required to have enough sample material for $\delta^{34}S$ measurements. It is expected that between one to three 4.7 cm GFF filters per sample are required to obtain sufficient nitrogen for $\delta^{15}N$ measurement. Additional effluent samples may be required to have sufficient material for stable isotope determination. Additional effluent samples will be labeled as additional samples and have the same procedures performed upon them.

1) Assemble vacuum filtration apparatus. Rinse filter funnel with distilled water (under vacuum) and inspect the funnel to make sure that there are no adhering particulates.

2) Using the provided filter forceps and with gloves, place one of the fiber filters into the filter funnel housing. Grab the filter by the edge and avoid touching the center of the filter. Do not use filters that have been damaged in any way or dropped.

3) Record the Date, Sample Type (whether Primary, Influent, etc.), and volume filtered in the spaces provided on the label on the filter petri dishes. Also record the same information with the sample dish or vial number on the sample label to be placed on the corresponding sample plastic baggie.

4) Shake bottle containing the effluent sample before removing the volume to be filtered. The sample should be placed in a graduated cylinder and the volume should be recorded. The entire volume of the graduate cylinder must be filtered (due to settling problems). the sample volume filtered needs to be sufficient to cause a significant slowing of the rate of filtration (due to the particle accumulation on the filter), otherwise there will not be sufficient signal for analysis. Attempt a minimum of 25 ml for pilot plant influent, 30 ml for pilot plant primary effluent, and 35 ml for pilot and full scale plant secondary effluent.

5) The filter and funnel should be rinsed three times lightly with deionized water (DI) and filtered dry. Turn off vacuum and equalize pressure within the filtration system before removing the filter/sample with the forceps to prevent tearing of the filter. Place filters in the NOW LABELED petri dishes. Place filtered sample in corresponding plastic baggie with label attached.

6) Dry filters (in their petri dishes) at 60 degrees C overnight.

7) Store dried filters in a dessiccator.

***Dissolved Inorganic Nutrients***

Samples will be shaken and a measured amount of sample filtered through a 0.7 micron glass fiber filter (GFF) and then through a 0.45 micron membrane filter and the filtrate collected. The filtrate will then be poured into the appropriate sample bottles provided by the laboratory. The sample for silicate analysis will only be filtered through a membrane filter, not a GFF filter.

***TDN and TDP***

A measured amount of shaken sample will be filtered through a 0.45 micron membrane filter and the filtrate collected. The filtrate will then be digested as per the method (Lambert and Oviatt, 1986) and analyzed appropriately (see Table 2).

***Biogenic Silica***

1. Shake sample so it is well mixed each time a sample is withdrawn.
2. Draw up 5-mL portions of the sample using a pipette with a fresh pipette tip rinsed with DI.
3. Deliver the 5-mL portions into a plastic filter holder funnel containing a 25-mm diam. 0.45m Poretics or Nuclepore polycarbonate filter.
4. Filter a total of 20 mL of sample or more if the filter is not clogged. Here the analyst must use their own judgment. The goal is to obtain enough material on the filter for the analysis, but not totally clog the filter. Thus samples with very high particulate matter may require only 5-10 mL portions. Record the volume used for each sample on bottle and in sample log.
5. Pull the sample through the filter using a vacuum pump set no higher than 5 psi.
6. Rinse the filter funnel walls with 5 mL of DI and draw air through the sample filter until it appears dry.
7. Remove filter with forceps and place at the bottom of a screw-cap plastic scintillation vial to be used for the digestion.
8. The vials should be precleaned by soaking in a NaOH solution(used for digestion), rinsing with DI and dried in a dust free place.
9. Blanks:
   a. Place a fresh filter in filter holder prior to any sample filtration.
   b. Add 5 ml of DDW with clean pipette tip and draw through the filter.
   c. Draw air through the filter for approx. 30 sec. to dry filter.
   d. Remove filter and place in plastic scintillation vial for digestion.
   e. Repeat for all blanks.

*DOC*

A measured amount of shaken sample will be filtered through a pre-combusted 0.7 micron glass fiber filter. The filtrate will then be processed as per EPA Method 415.1

*PP*

A measured amount of shaken sample will be filtered through a 0.7 micron GFF. The filter will be rinsed with deionized water, digested, and analyzed as per EPA method 365.2

*PC AND PN*

A measured amount of shaken sample will be filtered through pre-combusted 0.7 micron GFF. The filter and particulate matter is then rinsed, dried, and analyzed as per Lambert and Oviatt (1986).

# APPENDIX C

# EXAMPLE OF CHAIN-OF-CUSTODY AND OF SAMPLE LABEL

M901376

ENSR

# CHAIN OF CUSTODY RECORD

Page ____ of ____

| | |
|---|---|
| Client/Project Name: | Project Location: |
| Project Number: | Field Logbook No.: |
| Sampler: (Print Name) /Affiliation: | Chain of Custody Tape No.: |
| Signature: | Send Results/Report to: |

Analysis Requested

| Field Sample No./ Identification | Date | Time | Grab | Comp | Sample Container (Size/Matl) | Sample Type (Liquid, Sludge, Etc.) | Preservative | Field Filtered | | | | | | | | Lab I.D. | Remarks |
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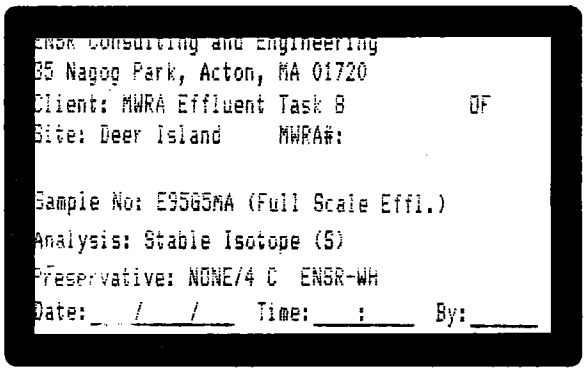
|---|---|---|---|---|
| Relinquished by: (Print Name) | Date: | Received by: (Print Name) | Date: | Analytical Laboratory (Destination): |
| Signature: | Time: | Signature: | Time: | |
| Relinquished by: (Print Name) | Date: | Received by: (Print Name) | Date: | |
| Signature: | Time: | Signature: | Time: | |
| Relinquished by: (Print Name) | Date: | Received by: (Print Name) | Date: | |
| Signature: | Time: | Signature: | Time: | Serial No. 18987 |


ENSR Consulting and Engineering
35 Nagog Park, Acton, MA 01720
Client: MWRA Effluent Task B OF
Site: Deer Island MWRA#:
Sample No: E95G5MA (Full Scale Effl.)
Analysis: Stable Isotope (5)
Preservative: NONE/4 C ENSR-WH
Date: / / Time: : By: