STATE OF MICHIGAN
DEPARTMENT OF NATURAL RESOURCES

QUALITY ASSURANCE MANUAL FOR WATER SEDIMENT AND BIOLOGICAL SAMPLING 1994

Prepared By:
Surface Water Quality Division

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MICHIGAN DEPARTMENT OF NATURAL RESOURCES

INTRODUCTION

Environmental data are used daily by Surface Water Quality Division (SWQD) staff to make decisions about National Pollutant Discharge Elimination System (NPDES) permit compliance, sources of pollution, water quality standards violations and other concerns. The overall data quality management system used by the SWQD is described in the Surface Water Quality Division Quality Assurance Management Plan. This document is limited to the actual step by step procedures used by SWQD staff and ERD lab staff to aquire environmental data including collecting and analyzing samples, and storing the results. Also included in this manual are the procedures used by the Land and Water Management Division, Inland Lakes Management Unit to collect and analyze lake samples.

This document replaces the former DNR Environmental Protection Bureau document (Quality Assurance for Water and Sediment Sampling July 1981 publication # 3730-0028), for Surface Water Quality Programs in the Michigan Department of Natural Resources.

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CHAPTER 1. LABORATORY QUALITY ASSURANCE

1.A. INTRODUCTION

The Environmental Laboratory provides analytical and technical services to the State's environmental and resource management programs. Laboratory analyses are an integral part of environmental law enforcement, environmental monitoring and surveillance, pollution control, facility planning and operation, and management of air, water, and land resources of the State of Michigan.

The Environmental laboratory operates as three laboratory units, General Chemistry, Inorganics, and Organics. Their respective responsibilities and quality assurance procedures are described in Sections 1.D. through 1.F.

1.A.1. QUALITY CONTROL vs. QUALITY ASSURANCE

The terms quality control (QC) and quality assurance (QA) are often misunderstood and incorrectly used interchangeably. Laboratory quality control consists of those internal operations which are routinely performed during the measurement process to document data quality (e.g., replicate analyses, spiked samples, reagent blanks, instrument calibration checks, etc.). Laboratory quality assurance consists of those activities which are performed with less frequency to obtain independent assessments of operating conditions (e.g., independent reference samples, interlabooratory comparison studies, laboratory evaluation samples, etc.).

1.B. GLOSSARY

1.B.1. ACCURACY

The ability to measure a sample constituent, compared to a standard or true value, without bias or error.

1.B.2. APPROVED ANALYTICAL METHOD

An analytical method which has gone through the complete Environmental Laboratory procedure for methodology approval (Appendix 1.C.-1) including the Lab Director's signature.

"EPA approved" refers to a method promulgated under the Clean Water Act, the Resource Conservation Recovery Act and the Clean Air Act.

1.B.3. BETWEEN-RUN DUPLICATES (REPEATS)

Two separate aliquots of a single sample analyzed in two separate batches of analyses to evaluate between-run variability.

1.B.4. CALIBRATION

The process of defining the relationship between the output of an analytical system (some value) and the input. Analysis of several different standards will define a calibration curve.

1.B.5. CALIBRATION CHECK

A sample, usually a standard of known concentration, which is not used in the calibration process, but is used as an external check on the accuracy of the calibration.

1.B.6. CONTROL LIMIT

The established level which, when exceeded, determines that a system is not in control and requires re-evaluation.

1.B.7. DETECTION LIMIT

The lowest concentration of an analyte that the analytical process can reliably detect.

1.B.8. FIELD BLANK

A sample submitted by field personnel to measure contamination from sample containers, chemical preservatives, and sample handling techniques.

1.B.9. FIELD REPLICATE

The second of two separate samples from a single source submitted to the laboratory to evaluate combined overall precision due to source, sampling and analytical variability.

1.B.10. INTERLABORATORY COMPARISON STUDY

A study, usually performed by an independent agency, to assess the comparability of data submitted by participating laboratories.

1.B.11. LABORATORY EVALUATION STUDY

A study, usually performed by an external agency, to evaluate the accuracy of results from a specific lab. Unknown standards are usually analyzed.

1.B.12. METHOD DETECTION LIMIT (MDL)

The minimum concentration of a substance that can be analyzed with 99% confidence that the analyte is actually present (based on a one tailed Student's t distribution).

1.B.13. METHODOLOGY APPROVAL

The laboratory procedure for evaluating and approving an analytical method for use in the Environmental Laboratory (Appendix 1.C.-1).

1.B.14. PRECISION

The ability to replicate a value within which random deviations can usually be expected to fit.

1.B.15. QUALITY ASSURANCE

Laboratory quality assurance consists of activities periodically performed to obtain independent assessments of data quality (e.g. reference samples, interlaboratory studies, laboratory evaluation samples, laboratory inspections, etc.).

1.B.16. QUALITY CONTROL

Laboratory quality control consists of the internal operations routinely performed during the measurement process to document data quality (e.g., replicate analyses, spiked samples, calibration checks, etc.).

1.B.17. QUALITY CONTROL AUDIT

Any routine check of a system to determine the adequacy of the system's performance.

1.B.18. QUALITY CONTROL CHART

A graphic presentation of quality control data. The classic approach has been the plotting of a variable, such as a value for a QC audit, against time.

1.B.19. REAGENT BLANK

A sample of water (distilled, deionized, or equivalent) which is taken through the entire analytical procedure to establish the zero intercept of the calibration curve and to check for contamination.

1.B.20. REFERENCE SAMPLE

A sample, usually a verified standard, supplied by an independent entity, to be used as an external check on the accuracy of an analytical procedure.

1.B.21. REPORTED DETECTION LIMIT (RDL)

The detection limit used to routinely report laboratory data, based on the method detection limit but usually slightly higher than the MDL.

1.B.22. SPIKED BLANK

A reagent blank which has had added to it a known volume of a standard of known concentration. It is generally used to measure the recovery of a process as a check on calibration.

1.B.23. SPIKED SAMPLE

A sample to which a known volume of a standard of known concentration has been added to measure accuracy, recovery, or matrix effects.

1.B.24. STANDARD

A known concentration of analyte in a non-interfering matrix.

1.B.25. WARNING LIMIT

The established level which, when exceeded, indicates that an analytical system may be near an out-of-control situation and may require a review.

1.B.26. WITHIN-RUN DUPLICATES

Two separate aliquots of a single sample analyzed within a single batch of samples to evaluate the precision of the system.

1.C. GENERAL LABORATORY QA PROGRAM

1.C.1. MANAGEMENT OF THE LABORATORY QA PROGRAM

1.C.1.a. Laboratory Management Team

The laboratory director and the supervisors of the three laboratory units form the Laboratory Management Team. The Lab Management Team is responsible for establishing the quality assurance policy of the Environmental Laboratory. The laboratory director, as the team leader, has the ultimate responsibility for adminstration of all laboratory programs, including the quality assurance program. The Lab Management Teams meets about once a pay period.

1.C.1.b. Laboratory Quality Assurance Coordinator

One of the laboratory unit supervisors is also assigned as the Laboratory Quality Assurance Coordinator. The Quality Assurance Coordinator is responsible for internal and external coordination of the quality assurance program. The additional functions include:

-- Serving as the Laboratory Quality Assurance Team Leader. The activities of the Lab QA Team must be planned, organized and controlled for effective operation.

-- Serving as a member of the Data Quality Work Group of the International Joint Commission's Water Quality Programs Committee.

-- Serving as a resource person for quality assurance problems within the laboratory.

-- Serving as a contact person at the laboratory for quality assurance problems outside the laboratory.

1.C.1.c. Laboratory Quality Assurance Team

The Laboratory Quality Assurance Team consists of the Laboratory Quality Assurance Coordinator as team leader and a representative from each of the three laboratory units as team members. The members are appointed by and are accountable to their respective supervisors. The Bureau Quality Assurance Coordinator also serves on the Laboratory Quality Assurance Team. The responsibilities and authority of the Lab QA Team include:

-- Review of revisions to the laboratory quality assurance program annually.

-- Development and revision of quality assurance procedures through normal administrative practices.

-- Review of the quality control audit program performed by each laboratory unit with reporting of deficiencies to the Lab Management Team.

1.C.1.d. Laboratory Supervisors

The laboratory supervisors are responsible for the interpretation, implementation, and maintenance of approved quality assurance policy and procesures in their respective laboratory units. Some of their specific functions related to quality assurance include:

-- Development and implementation of detailed quality control procedures and practices according to approved quality assurance policy.

-- Approval of routine quality control audits and control limits proposed by the analyst.

-- Review and approval of all laboratory results generated by the laboratory unit.

1.C.1.e. Laboratory Analysts

All laboratory analysts are responsible for understanding laboratory quality assurance policy and following the directions of their immediate supervisor on all quality assurance concerns. Duties include:

-- Preparation of methodology write-ups and method addenda.

-- Performance of QC audits on instruments and maintenance of equipment log books.

-- Performance of QC audits on analytical runs with reporting of out-of-control systems to the lead worker or unit supervisor.

1.C.2. LABORATORY QA POLICY

Laboratory Quality Assurance Policy is described in Chapter 9. According to this policy, all analyses or methods are placed into one of three categories (quantitative, semi-quantitative, or qualitative) dependent upon the level of quality assurance documentation. The purpose of this policy is to ensure that:

- An approved analytical method is being used,
- The method has been shown to be suitable for the sample types requiring analysis,
- The method as used is fully documented,
- The analyst performing the analysis has demonstrated competency,
- The method has the detection capabilities necessary to quantify the constituents of interest,
- The equipment used to perform the analyses are capable of the task, are properly maintained, and are operating properly,
- The sample as analyzed is representative of the sample source,
- The chemicals and supplies are of suitable quality for their intended use,
- Standards and control samples indicate normal operating conditions,
- Samples are properly collected, received and distributed to the appropriate lab units,
- The reference sample program periodically evaluates analytical performance,
- The laboratory participates in pertinent interlaboratory comparison studies (IJC) and performance evaluation studies (EPA),
- Laboratory results are adequately reviewed and properly reported.

1.C.2.a. Approved Methods

The U.S. Environmental Protection Agency lists the analytical methods approved for use with NPDES compliance monitoring in 40 CFR Part 136. Approved analytical methods for use in testing waste materials under the Resource Conservation Recovery Act (RCRA) are listed in 40 CFR, Part 261, Appendix III.

If a method other than an "EPA approved" procedure listed in 40 CFR Part 136 is to be used (because of better accuracy, improved efficiency, lower sensitivity, better precision, or lower operating costs), there must be a formal evaluation and submittal to the EPA. The method must be shown to be equivalent to the approved method. The use of alternative test procedures is much more restrictive in the RCRA program and requires formal changes to federal regulations.

1.C.2.b. Methodology Approval

Appendix 1.C.-1 is the internal laboratory procedure for evaluating and approving a method for use in the Environmental Laboratory. In brief, the procedure consists of:

- Literature search,
- standardization procedure,

-- detection limit determination,
-- precision measurement,
-- accuracy measurement,
-- reference sample evaluation,
-- check for interferences,
-- procedure for documentation,
-- approval policy, and
-- reporting of unapproved results.

1.C.2.c. Methodology Write-Up Format

So that all laboratory methods are documented in a uniform manner, a procedure for methodology documentation was developed and is included as Appendix 1.C.-3. The sections to be included in a written laboratory procedure include:

-- Scope and Application,
-- Summary of Method,
-- Sample Collection, Handling, and Preservation,
-- Interferences and Biases,
-- Apparatus,
-- Reagents,
-- Procedure,
-- Quality Control Audits,
-- Calculation,
-- Method Validation,
-- Reported Detection Limit
-- References, and
-- Approval.

The procedure for documenting and adding significant changes to existing methods appears as Appendix 1.C.-1.

1.C.2.d. Detection Limit

The laboratory procedure for quantifying the detection limit of a method appears as Appendix 1.C.-6. Laboratory detection limit used to report data are listed in Appendix 1.C.-7.

1.C.2.e. Equipment Logbook

Each piece of major laboratory equipment has a logbook for the recording of monitored variables and other pertinent information.

1.C.2.f. Representative Sample

The laboratory has little control over whether the sample is actually representative of the sample source, but tries to maintain the integrity of the sample as received from field personnel. This means maintaining proper sample preservation which was initiated in the field and attempting to analyze all samples within their respective holding times. If this is not possible, it is the responsibility of the appropriate unit supervisor to not report results or report coded values.

1.C.2.g. Quality of Chemicals and Supplies

Only chemicals meeting specifications necessary for an analytical procedure are used. It is the responsibility of each unit to ensure their suitability. When chemicals are received from a lab supply company, they are dated. Each analyst is responsible for dating a chemical bottle when it is opened if it will not be consumed in a short period of time. If it is unstable, an expiration date should also be added at that time. Chemicals are not to be used past their expiration date.

When standards are prepared, the container that they are stored in should contain:

-- the concentration and name of the analyte,
-- the type and amount of the compound it was prepared from,
-- the substrate it is prepared in,
-- who it was prepared by,
-- date it was prepared, and
-- expiration date.

Information found on reagent bottles should include:

-- the reagent name,
-- what test the reagent is for,
-- the quantity of each chemical used in its preparation,
-- who it was prepared by,
-- an expiration date.

Laboratory supplies should be checked when they are received from stock to make sure that they are appropriate for the intended analysis. Even new supplies should be thoroughly cleaned before use unless lack of contamination has been sufficiently documented.

1.C.2.h. Standards and Control Samples

Each analytical batch must be in documented control through the use and evaluation of standards for calibration and quality control samples for precision and accuracy estimation. The types and frequency of these will vary with each method and should be fully documented with each methodology.

1.C.2.h.1. Calibration

Proper instrument calibration must be established or confirmed with each batch of analyses or more often as necessary. The type of instrument response (linear or otherwise) and the degree of its variability will tend to dictate calibration needs. Anything from a two point slope and intercept regression to replicate analyses of multiple points may be necessary.

1.C.2.h.2. Accuracy

The accuracy of a method must be measured and evaluated with each analytical batch. Spiked samples or other appropriate audits may be used.

Generally, five to ten percent of the samples in a batch should be for the determination of accuracy.

1.C.2.h.3. Precision

Precision is an estimate of procedural variability. It is generally derived from the analysis of replicates. The replicates may be within-run duplicates, between-run duplicates, or field replicates. Each type of audit should indicate different degrees of variability and must be evaluated separately. Five to ten percent of the samples in a batch should be for the measurement of precision.

1.C.2.h.4. Quality Control Charts

Quality control charts (Shewhart type or similar) are very useful for the graphic display of QC data and very helpful for identifying trends. QC charts should be used wherever applicable.

1.C.2.h.5. Precision and Accuracy Summaries

The precision and accuracy of each quantitative analytical method is summarized annually and reported to users of the lab. This summary provides basic performance information to laboratory users and allows them to use and interprete lab results within limits of data quality. The Lab procedure for preparing this summary is included in Appendix 1.C.-2.

1.C.2.i. Requesting Sample Containers and Preservatives

To facilitate the ordering of sample containers and preservatives, a "Sample Bottle and Preservative Request" form (Appendix 1.C.-8) should be used. This form should be completed by field personnel and received by the laboratory at least one week prior to the planned pick-up time. If there remains insufficient time for proper notification, bottle requests should be prepared and phoned into the proper designee in the General Chemistry Unit with as much advanced notice as possible.

Additional sample containers may be required for non-routine analyses not listed. It is better to make sure that the lab has sufficient sample in the proper container than to risk not receiving the desired analyses.

The chemical preservative and dechlorinating agents are available from the laboratory either as a kit or as individual preservatives. Field personnel who routinely collect samples will find it more convenient to have a kit assigned to them and restock chemicals as needed. Certain preservatives have an expiration date to notify field personnel when the preservative must be restocked. If there is no expiration date, the preservative should be restocked at least every six months. Personnel who do not frequently collect samples may find it more convenient to request preservatives with each survey or batch of samples and return the preservative when samples are submitted to the laboratory. A preservative kit which is not frequently used should be carefully stored to prevent contamination of the chemicals. Field blanks should be requested

with bottles and set according to instructions provided in Chapter 5, Section 5.B., Field Blanks.

The laboratory will attempt to supply sample bottles with caps on. If caps and bottles are received separately by field personnel, caps should be added to the bottles as soon as possible to prevent contamination of sample bottles.

1.C.2.j. Laboratory Sample Blanks (Parameter Request Sheets)

The laboratory attempts to maintain a stock of analysis request sheet forms at the laboratory. These are updated periodically to correspond with laboratory unit reorganization, changes in bottles or preservatives, or the addition or deletion of parameters. The laboratory has posted a list of current forms which should be reviewed at the time that sample bottles are picked up.

For easier identification, the water sheets are white, leachate sheets are blue, tissue sheets are pink, sediment sheets are goldenrod, and wastes and oil sheets are canary. Some white blanks may exist due to lack of colored paper at the time of printing.

Sample blank forms may be requested from the laboratory, allow at least two weeks for delivery of larger orders. Special forms may be prepared for projects if existing forms are not suitable and sufficient advance notification (about one month) is given.

1.C.2.k. Laboratory Receipt of Samples

1.C.2.k.1. Receiving Hours

The Environmental Laboratory is generally open to receive samples from 8:00 a.m. until 12 noon and from 12:30 p.m. until 5:00 p.m. on Monday through Friday (except during holiday weeks). The lab may be able to receive samples at other times with prior notification and approval.

1.C.2.k.2. Laboratory Check-In Policy

The sample receiving entrance is at the rear of the lab (west end of the building). A buzzer is by the receiving door to notify the proper laboratory personnel that there are samples to be received.

Field personnel should set up samples on the available tables (from left to right in the order they appear from top to bottom on the sample sheets). A single sample is defined as being from one location and depth and having a common sampling time. A single sample may have more than one sample container with various preservatives. Each individual sample should be maintained in a column. The rows should be lined up by the separate sample containers for different parameter groups. Using the same order, from front to back, as appears on the Collection and Preservation Table (Table 3.B.-1) (top to bottom) will expedite sample check-in.

Personnel from the General Chemistry Unit have been specifically trained to receive samples from all laboratory units. The laboratory sample receiver checks the sample sheets for the proper matrix and to verify that they are not outdated. The person submitting the samples will have to fill out the proper sample sheets if incorrect forms have been used. The lab sample receiver then checks that the forms are properly completed and requests any missing information (collected by, transferred to, location sampled, sample remarks, send results to, field ID, description, cost center, STORET location number (optional), sampling date and time, etc.). The requested parameters are then checked against the sample containers submitted to verify that the necessary bottles with proper preservatives exist. The sample bottle label is reviewed by lab receiver to ensure that the information on the label is complete, accurate and clearly understood. Descriptions on sample labels should match as exactly as possible those on the sample sheets to avoid any confusion. Any discrepancies are immediately brought to the attention of the field personnel and noted on the appropriate sample sheet.

Field personnel are responsible for submitting the sample that they want analyzed. Samples composed of more than one matrix or stratum should be clearly identified as to the portion which is to be analyzed. And if practical, the portion requiring analysis should be separated and submitted by itself for analysis. If more than one matrix is to be analyzed (oil and water sample or water and sediment sample), separation of matrices and separate sample submittal is requested.

The laboratory sample receiver then writes the date and time of receipt on the analysis request sheet. The Environmental Laboratory Logbook is filled out with the date and time of receipt, the assignment of a log number for that sample batch, name of the person delivering the samples, initials of the lab person receiving the samples, project code, lab sample numbers, priority assignment, and the source of the samples. Samples from one laboratory log number should be from the same sample source or run, should be chargeable to one project code and cost center, should contain only one sample matrix, and should be submitted at the same time. Special priority may be assigned by responsible Division Chief or his designee. Any inquires about a batch of samples should reference the lab log number.

The sample receiver enters the lab log number, project code, priority, and their initials on the analysis request sheets. Consecutive sample numbers are assigned to each individual sample. The laboratory sample numbers are stamped on the appropriate request sheets. The sample number labels are carefully attached to the sample containers. Field personnel should assist in wiping off wet, dirty, or oily bottles so that the labels will adhere properly. Bottles suspected of containing listed or other hazardous wastes should be identified upon receipt by completing the Sample Hazard Information Form on the backside of the Analysis Request Sheet. Stickers designating special handling or analytical techniques are affixed by the receiver.

The copy of the analysis request sheet is given to the field personnel for immediate review and future reference. The original is filed at the lab. Since future laboratory identification by analysts will be based

mainly on the sample number tag, field personnel should check the sample bottles for proper tagging.

1.C.2.k.3. Non-Aqueous Samples and Shared Samples

The General Chemistry Unit is responsible for the handling of non-aqueous samples and shared samples. The laboratory sample receiver places a yellow sticker on non-aqueous or shared samples. The initials of all units using the samples are written on the yellow sticker. These samples are entered in a special log book kept by the General Chemistry Unit. Samples are stored numerically in trays in the cold room. Lab employees needing these samples refer to the sediment log book for sample location and check out the sample for use. When finished with the samples, they are returned to trays in the cold room.

Every three months, the General Chemistry Unit circulates a list of old samples. The unit supervisors authorize disposal of completed samples and identify which samples require special disposal precautions.

1.C.2.k.4. Preparatory Analyses

Each laboratory unit is responsible for sample preparation steps specific to their analyses.

Sample preparation for sediment, soil, sludge and other solid samples is described in Section 1.C.2.q. of this manual. Fish tissues sample handling procedures are described in Section 4.J.4. of this manual.

When more than one bottle of the same non-aqueous sample is delivered each bottle will receive a number tag and yellow sticker. Bottles will be suffixed "A", "B", "C", etc. If the sample requires a % TS analysis, each unit will perform its % TS analysis. The % TS will be reported with other sample results.

1.C.2.k.5. Distribution of Samples

A designated person in each laboratory unit is notified by the laboratory sample receiver when samples are ready for distribution. Each unit should then recheck the samples for proper tagging and the existence of all necessary bottles. Any corrections should be brought to the immediate attention of the laboratory sample receiver. Corrections should be carefully noted on all pertinent forms (analysis request sheets, laboratory log book, etc.). Appropriate field personnel should be promptly notified of serious problems so that additional sample can be collected and submitted. The respective lab units should then properly store samples until analyses are initiated. Analysts responsible for the most time dependent analyses should be immediately notified.

1.C.2.l. Laboratory Sample Handling

Each laboratory unit is responsible for the handling of the samples they have received. Their procedures are found in Sections 1.D. through 1.F. It is imperative that the integrity of each sample is maintained through

continued preservation, timely controlled analysis, and proper sample handling.

1.C.2.m. Laboratory Data Handling

Each laboratory unit is responsible for the handling of data within their unit. All original data must be properly filed in a permanent manner. Transcription of data should be minimized to reduce errors. Proper review of data and QC audits at each level is imperative. Each analyst's data should be concise and clear enough that any trained analyst could easily interpret the results. Ink should be used whenever practical. Any corrections or changes to data should be done by drawing a single line through the old value such that it can still be read and writing in the new value. An explanation of any changes should be included if necessary to clarify results.

1.C.2.n. Laboratory Reporting of Data

Each laboratory supervisor, or his designee, is responsible for the final review and reporting of data. Data which have not meet all laboratory criteria for optimum quality may be reported with proper qualifier codes. Appendix 1.C.-9 contains three lists of laboratory result remark codes which may presently appear with results. Coded values may generally be considered reliable and usable. A three letter code with no value is reported for highly questionable data or when an analysis is not performed.

Data should be reported with proper attention to significant figures and rounding of values.

An Administrative Unit clerk logs-out sample sheets from all the laboratory units and sends results to the appropriate person.

1.C.2.o. Reference Sample Program

The Environmental Laboratory has an established schedule for the analysis of reference samples. Reference samples are special samples which have been developed by an outside source for internal evaluation of analytical performance. Analysts are supposed to perform analyses using routine procedures without prior knowledge of the expected results. If more than one method of analysis is routinely employed or more than one analyst commonly performs certain analyses, each method and analyst should be evaluated separately. The results are submitted to and evaluated by the Quality Assurance Coordinator. Bias and % bias are calculated based on the "true" or "mean" values supplied with the samples.

When evaluated results are returned to the responsible laboratory unit, they should be reviewed carefully. Poor performance should be investigated and corrective action taken whenever possible. A memo indicating the reason for poor performance and the results of corrective measures should be sent to the Laboratory Director. This should be reviewed, commented upon if necessary, and filed with the original results. Continued poor performance should be investigated by the Laboratory Quality Assurance Team.

The Environmental Laboratory presently analyzes reference sample sets provided by the U.S. Environmental Protection Agency (EPA). Sets are scheduled for analysis every three months and are also available upon special request from unit supervisors.

1.C.2.p. Interlaboratory Comparison and Evaluations

The laboratory should participate in all interlaboratory comparisons and evaluations when the parameters and matrices under study are routine laboratory analyses. The International Joint Commission (IJC) periodically conducts interlaboratory comparisons covering a variety of parameters in different matrices. The EPA annually conducts laboratory evaluation studies. When the results have been evaluated and returned by the originating agency (which may take several months), the conclusions of the studies should be confirmed and any necessary corrective measures taken. Usually the organization originating the study (IJC or EPA) would appreciate general feedback and notification of corrective action taken.

Values for non-routine laboratory parameters should not be reported for evaluations. These results do not reflect routine laboratory performance and may create incorrect impressions as to the quality of results reported by the laboratory. It should also be remembered that any accurate evaluation of actual laboratory performance cannot be obtained from infrequent evaluation studies. A short-term problem can easily be interpreted as a long-term problem. Also, interferences or matrix problems encountered on actual environmental samples may not appear in special evaluation samples.

1.C.2.q. Sediment, Soil, Sludge and Other Solid Samples

Sediment, soil and sludge samples are collected in 250 ml wide mouth glass jars or 40 ml purgeable vials, refrigerated and transported to the laboratory. Other than refrigeration, no other preservation is employed. The General Chemistry Unit receives and logs all samples into the laboratory. All 250 ml samples are placed in the sample receiving cold room (4°C). When more than one bottle of the same sample is delivered, each bottle receives a numbered tag and yellow sticker. Each bottle is then suffixed "A", "B", "C", etc. If the sample requires a % TS analysis, each unit will perform this analysis on its own bottle. Purgeable 40 ml vials are provided directly to the Organic Unit.

Samples for determination of purgeable compounds in soil, sediment and sludge are submitted to the laboratory in 40 ml septum seal vials (5 grams of sample covered with contaminant-free water) and are provided to the Organic Unit. Dry weight is determined on the solid portion of the sample after purgeable analysis of the leachate. These procedures are described in laboratory methods (Scan 1 and 2 leachate procedures).

Samples submitted to the laboratory in 250 ml wide mouth glass bottles may require a number of different sample preparatory steps and analyses. Each unit is responsible for sample preparation procedures. For those parameters that are determined from a wet sediment, sludge or soil, (cyanide, COD, Total Phosphorus, Kjeldahl-Nitrogen, Mercury, Oil and Grease, Total Recoverable Phenol and trace organic analyses) the unit

responsible for analysis removes the sample from the cold room and removes an appropriate quantity of sample. Less stable parameters (COD, Mercury and Phenolics) are analyzed as soon as possible and promulgated holding times for water samples are followed as a guideline. For those analyses conducted on wet or air dried samples, the percent dry weight (percent moisture) is determined to allow conversion and reporting of sample results as dry weight. Percent dry weight is reported to allow conversion back to wet weight, if requested. A separate 250 ml sample is preferred for the E.P. Toxicity Procedure. Separate aliquots are required for determination of percent total solids, the ASTM Leachate Procedure, General Chemistry Unit parameters, mercury, metals, extractable organics, and Freon extractables. The aliquots and sample preparation needs for these aliquots are described below.

When it is necessary to take an aliquot from a soil, sediment or sludge sample, the sample is thoroughly stirred with a spatula and an appropriate amount of sample is removed (depending on the purposes of the aliquot) by selecting a small amount of sample from several locations throughout the container and compositing the material in a suitable container or drying dish.

1.C.2.q.1. Percent Total Solids Analysis

A wet or air dried sediment, sludge or soil sample is dried according to the PERCENT TOTAL SOLIDS procedure. The purpose of the percent solids determination is to provide a factor for calculating results on a dry weight basis when a wet or air dried sample is analyzed. At least 10 grams of wet sample are required. The determination is made by the appropriate unit and results are provided to the sample requestor.

1.C.2.q.2. Analysis of Leachate

When sediment, soil or sludge samples are submitted for analysis of leachate, the units responsible for such analyses leach a suitable sized sediment aliquot according to the ASTM LEACHATE PROCEDURE.

1.C.2.q.3. Extraction Procedure Toxicity Analysis

When sediment, soil, or sludge samples are submitted to the laboratory for E.P. Toxicity analysis, a separate sample is desirable to provide the approximate 100 gram quantity required by the test. The Inorganic Unit is responsible for all steps in the procedure from sample extraction to analysis of the extract. The EXTRACTION PROCEDURE TOXICITY method describes these steps in detail.

1.C.2.q.4. General Chemistry Unit Analyses

When a sediment sample is submitted for analysis of parameters analyzed by the General Chemistry Unit (Chemical Oxygen Demand, Kjeldahl-Nitrogen, Total Phosphorus, Phenolics and Cyanide) a suitable quantity of wet sediment is taken from the sample by the General Chemistry Unit. Percent total solids is provided so that dry weight results can be reported.

1.C.2.q.5. Metals Analyses

When a sediment sample is submitted for analysis of metals (excluding mercury), the Inorganic Unit prepares an oven dried aliquot. Procedures for drying sediment samples are described in the SEDIMENT DRYING PROCEDURE FOR METALS. Depending on the desired sample turn around time, drying may be in two steps (air dried-oven dried) or completely oven dried. The oven dried aliquot is digested and analyzed and results are reported as dry weight.

1.C.2.q.6. Mercury Analyses

When a sediment, sludge, or soil sample is submitted for mercury analysis, a wet sample aliquot is removed from the sample by the Inorganic Unit. At least 1 gram or wet sample is digested and analyzed. Results are converted to dry weight based on the percent solids in the sample. The percent solids of the sample is also reported.

1.C.2.q.7. Extractable Organic Analyses

When a sediment, sludge, or soil or other solid sample is submitted for analysis of base/neutral extractables (Scan 3 and GC/MS Base/Neutrals) the organic Unit uses a 20 gram aliquot of wet sample. The Organic Unit is also responsible for extracting the sample according to procedures identified in individual methods. After extraction and analysis, results are corrected to dry weight (based on percent moisture) and reported.

1.C.2.q.8. Wet Analyzed Organic Parameters

Solid samples for analysis of freon extractable compounds are analyzed directly from a wet sample. Results are reported on a wet weight basis.

1.C.2.r. Method Development Requests

When laboratory users desire additional analytical services not presently available from the laboratory, these services may be requested through, "Method Development Request Procedures" outlined in Environmental Laboratory Procedure No. PD-26 (Appendix 1.C.-5). The purpose of the Method Development Request Procedure is to estimate the demand for the new service and the cost of developing the new service. The laboratory will usually develop needed methodology if sufficient demand exists and if the requesting division can provide the necessary resources.

1.C.2.s. Analytical Costs

The laboratory periodically estimates costs for each analysis. Cost estimates are based on expenditures (salaries, equipment, overhead and etc.) divided by the number of analyses for a given time period (usually the fiscal year). Analytical cost estimates enable users to estimate the total cost of monitoring programs, amount of grant funds to apply for, and to compare cost to commercial lab costs. Appendix 1.C.-4 lists analytical costs for each analysis.

1.D. GENERAL CHEMISTRY UNIT QUALITY ASSURANCE PROGRAM

1.D.1. INTRODUCTION

The General Chemistry (GC) Unit is responsible for the analysis of nutrients, BOD, COD, TOC, dissolved gases, cyanides, phenolics, residues, flashpoint, turbidity, microbiology, and chlorophyll from water, leachate, sediment, and other environmental samples. The GC Unit presently consists of a unit supervisor, lead workers, professional analysts and paraprofessional analysts. Additionally, temporary analysts (Student Interns) are usually employed during summer months due to a considerable seasonal increase in the Unit's workload.

1.D.2. UNIT QA/QC MANAGEMENT

Each position in the General Chemistry Unit has a minimum time commitment of approximately 15% to quality assurance and/or quality control activities.

1.D.2.a. Unit Supervisor

The unit supervisor has the responsibility of establishing the general QA policy for the GC unit. The unit supervisor also identifies the QC audits for each parameter and has the ultimate responsibility of reviewing program effectiveness. Additional duties include staff assignments, approving methodology documentation and modifications, control limits, control audits and reviewing and approving GC unit results.

1.D.2.b. Lead Workers

The lead workers' general responsibilities include technical supervision of the analysts, development of new methods, sample analyses with more complex procedures, and maintenance of the daily operations of the unit. The lead workers are also responsible for reviewing each analyst's output to ensure that QC procedures are properly interpreted and followed. The frequency of review depends upon the complexity of the method and the familiarity of the analyst with the method. This equates to a 20% minimum time commitment.

1.D.2.c. Quality Assurance Coordinator

One of the laboratory scientists is assigned the duty of being the unit's quality assurance coordinator. The additional responsibilities include serving as the unit's representative on the Laboratory Quality Assurance Team. The QA coordinator is also responsible for assisting with the periodic review and assessment of the unit's QC/QC program and for the performance of special related projects. A 15% minimum time allotment is necessary.

1.D.2.d. Analysts

Each analyst is responsible for understanding the laboratory's QA policy. They must also understand and perform the QC audits which have been

identified for the analytical procedures they perform. All QC audits are immediately reviewed to verify that they are within the specified control limits. Out-of-control audits indicate that some aspect of the analytical procedure is not performing properly. The problem should be located and corrected. This may be a very complicated task. The analytical batch may then be repeated. This may not be possible if the holding time has been exceeded or insufficient sample volume remains.

The lead worker and the unit supervisor have authority to approve the reporting of a batch of results when control limits are exceeded based on the other audits. Questionable audits must be discussed with the lead worker or the unit supervisor. Only data with acceptable audits are reported without a qualifier such as an appropriate laboratory remark code. Highly doubtful data are not reported. Each analyst allots a 10% minimum time commitment for QC.

1.D.2.e. Total Time Commitment

The minimum total time commitment for QA/QC functions in the General Chemistry Laboratory Unit is approximately 15%.

1.D.3. PARAMETERS ANALYZED BY THE GENERAL CHEMISTRY UNIT

1.D.3.a. Analytical Responsibilities

Table 1.D.-1 contains the parameters for which the General Chemistry Unit has primary responsibility and the matrices for which analyses are practical.

1.D.3.b. Primary Analysts

Primary assignment of parameters to laboratory scientists or laboratory technicians is based on the difficulty of the procedure, the complexity of the instrumentation involved, quantity of workload anticipated, and the degree of methodology documentation. In addition to primary analytical responsibilities each analyst has secondary parameter assignments which are made to provide depth and flexibility to the GC Unit, increase each analyst's area of expertise, and promote new insight into established laboratory procedures.

1.D.4. METHODOLOGY STATUS

1.D.4.a. Documentation of Methods

The General Chemistry Unit recognizes the necessity of documenting the ability to perform analyses by suitable established methodologies. Table 1.D.-1 contains a brief summary of the most common parameters analyzed, matrices, method descriptions and method references.

1.D.5. ANALYST PROFICIENCY

The General Chemistry Unit recognizes the necessity of having qualified analysts with demonstrated competency performing all analyses. The exhibition of proficiency is especially important when new analysts are

TABLE 1.D.-1
ANALYTICAL RESPONSIBILITIES OF THE GENERAL CHEMISTRY UNIT

PARAMETER NAME	METHOD DESCRIPTION	MATRICES*	METHOD	REFERENCE
Dissolved Oxygen	Azide modified Winkler	W	360.2	2
Chemical Oxygen Demand	Low test tube-colorimetric 450 nm	WL		3
Chemical Oxygen Demand	High test tube-titrimetric FAS	WLS	410.1	2
Total Organic Carbon	Dohrmann DC-80 auto. UV Digestion	WL	415.2	2
Nitrate plus Nitrite	Automated Cadmium reduction	WL	353.2	2
Nitrite	Automated diazotization	WL	353.2	2
Ammonia	Automated phenolate	WL	350.1	2
Kjeldahl Nitrogen	Block digestor, auto. salicylate	WLS	351.2	2
Ortho (Reactive) Phosphate	Automated ascorbic acid reduction	WL	365.1	2
Total Phosphorus	Block Dig., auto. ascorbic acid red.	WLS	365.4	2
Reactive Silicates	Automated molybdosilicate	W	370.1	2
Sulfide	Methylene blue colorimetric	W	376.2	2
Sulfide	Titrimetric, Iodine	WH	9030	1
Total Rec. Phenolics	Man. distillation, auto. color. 4AAP	WLS	420.1	2
Total Rec. Phenolics	Auto. distillation, colorimetric 4AAP	WL	420.2	2
Total Cyanide	Man. distillation, pyridine-barbituric acid	WLSH	335.2	2
Free Cyanide	Chlorination, man. dist., P-B acid	WLH	335.1	2
Biochemical Oxygen Demand	Electrode	W	405.1	2
Microbiology	Membrane Filter	W		3
Residues (solids)	Glass fiber filter, gravimetric	W	160	2
Turbidity	Nephelometric	W	180.1	2
Chlorophyll	Fluorometric	W		3
TSP-HiVol	Gravimetric	A		3
Filter Wt. Gain (Stack Studies)	Gravimetric, 105°C	A		3
Water Volume (SS)	Volumetric	A		3
Silica Gel Wt. Gain (SS)	Gravimetric	A		3
Solids, Washes, Impingers	Gravimetric	A		3
% TS, % VS	Gravimetric, 105°C, 550°C	S		3
Sample Leaching	48 hr. shaker, filter, preserve	S		3
Flash Point	TTC Pensky-Martens	H	1010	1

*Matrices: W = Water; L = Leachate; S = Sed./Soil; H = Hazardous Waste; A = Misc. Air Monitoring

1. EPA, Test Methods for Evaluating Solid Waste, SW-846, 1982.
2. EPA-600/4-79-020, Method for Chemical Analysis of Water and Wastes.
3. Internal Lab Method.

being trained or existing analysts learn or develop new procedures. Generally two or more trained analysts are maintained for each routine parameter. This is particularly important if the holding time for the parameter is short. The unit supervisor, with the consultation of the responsible lead worker, makes final decisions as to when an analyst is capable of performing a methodology. The degree of competency demonstration necessary depends upon the difficulty of the particular analysis and the analyst's background with similar methodologies.

1.D.6. EQUIPMENT LOG BOOKS

1.D.6.a. Log Book Information

Equipment log book information is maintained for most major instruments with variables which could affect analytical results. The pertinent information for each instrument will vary but the type of information which should be documented may include:

-- Name, address, and phone numbers of supplier and service personnel.

__ Location of instrument's operating and service manuals.

__ A schedule of routine maintenance required to ensure proper instrument operation.

__ Various audits and control limits used to ensure proper instrument operation.

1.D.6.b. Major General Chemistry Unit Instruments

__ Auto Analyzer II Systems

Auto Analyzer II Systems generally require checks with each batch for standard calibration (absorbance), temperature of the heating coil (may not be present), and baseline drift and noise. Control limits are listed with each method.

__ BOD Incubators

Incubators for biochemical oxygen demand samples require daily checks for temperature (20° $\pm$ 1°C).

-- Distillation Apparatus

Distillation apparatus require checks for proper heating and recovery of standards.

-- Oxygen Meter

Dissolved oxygen meters require calibration against air saturated water with a periodic check against a Winkler set DO sample.

-- Ovens and Heating Blocks

The temperature of ovens and heating blocks should be checked with each use.

-- Spectrophotometers

Absorbance of standards and blanks and their drift must be monitored on UV-VIS spectrophotometers.

-- Titrators

Titrators must be checked for proper operation and stable normality of titrants with each use.

-- TOC Analyzers

Total organic carbon analyzers must be checked for proper response of the NDIR detector and proper flow of gas(es) and reagents.

-- Autoclave

The autoclave is checked each time it is used for proper pressure (minimum 15 psi) and temperature (250°F). Sterilizer strips or tape are used with each batch. The batch is resterilized if the indicator does not change color indicating proper sterilization conditions.

-- Balances, Analytical

Analytical balances are checked daily against standard weights which must weigh within 0.0010g. of their certified weight. They are cleaned and checked annually by company service person.

-- Incubator (microbiology)

The microbiology incubator is maintained within 0.5°C. It is checked daily with a standard thermometer with an additional weekly check with a certified thermometer. Results are not reported if the temperature is not within the control limits.

-- Ovens, Drying

Drying ovens are checked daily to maintain temperatures within 5°C.

-- Refrigerator

Microbiology refrigerators are checked daily and adjusted to their proper temperatures as needed.

-- Filter Fluorometer

The fluorescence curve is recalibrated three times a year with standards on the filter fluorometer.

-- Turbidimeter

A standard is set with each batch for each scale used on the turbidimeter.

-- Water Bath (microbiology)

The microbiology water bath is maintained within 0.2°C. It is checked daily with a standard thermometer with an extra check each week with a certified thermometer. Results are not reported if they are not within the control limits.

-- Cold Room

The Cold Room's temperature is monitored by the telephone alarm system, which notifies the lab if the temperature rises above 50°F.

-- Water Deionizer

Pretreatment tanks and the pre-filter, organic, and fine filter cartridges are replaced on an as necessary basis, as indicated by pre-set lights on the pretreatment tanks.

1.D.7. SAMPLE AND DATA HANDLING

1.D.7.a. Sample Receiving

Samples are received at the Environmental Services Laboratory by specially trained personnel in the General Chemistry Unit. They receive, review, number and log the samples. If any samples require analyses by the General Chemistry Unit, usually a lead worker is notified that samples have been received. If a lead worker is not present or available, the unit supervisor or a laboratory scientist assumes the responsibility. The unit sample receiver reviews the sample sheets and checks that all necessary sample bottles are present and properly numbered. Any errors or questions are brought to the immediate attention of the sample receiver and corrected. Samples are then either delivered to the responsible analyst (particularly very short holding time parameters) or stored numerically by laboratory sample number in the cold room or sample refrigerator.

1.D.7.b. Sample Logging

At the earliest convenience, samples are entered in the General Chemistry Unit Record Book by the individual receiving samples for the GC Unit. The project header should include laboratory log number, date of receipt, and a project name. Blue or black ink is to be used unless otherwise stated. If the project has a high priority, is to be charged to a special cost center, or has special requirements or instructions, these are entered in red ink for higher visibility. Any special instructions should also be brought to the attention of the appropriate analyst(s).

For each project or log number, a grid of sample numbers versus parameters to be analyzed is then made. Information to be included is:

-- the assigned laboratory number,
-- field sample identification information,
-- the parameters requested by the field personnel,
-- additional parameters required to calculate the requested parameters,
-- additional parameters which may be automatically obtained from multi-channel analytical systems, and
-- any additional pertinent sample information.

For leachate and sediment samples which require special sample preparation, the appropriate sheet is filled out and submitted to the appropriate analyst.

1.D.7.c. Assignment of Workload

Each analyst is responsible for reviewing the projects entered in the GC Record Book and making their own work assignments. Factors considered are holding time, priority assignment, sample backlog, and workload volume. The unit supervisor or a lead worker may modify assignments as deemed necessary for efficient unit operation.

1.D.7.d. Record Keeping

Benchsheets, sample record books, equipment log books, and/or QC records are to be filled out in ink with all pertinent information. There should be sufficient clarity that any trained analyst could easily interpret the results. All original information should be stored in accordance with laboratory policy. Transcription of raw data should be avoided. Any sample peculiarities or interferences should be noted and clearly stated.

1.D.7.e. Review of Data

Each analyst immediately reviews the instrument and QC audits for compliance with control limits. Problems are addressed according to laboratory procedures. The analyst then records and initials the valid results in the GC Lab Record book. Any qualifying remarks should be footnoted.

The unit supervisor, or lead workers during his absences, reviews the values. Items to be considered may include:

-- proper correlation of related parameters,
-- reasonable trends within batches of related samples, and
-- comparison with previous results from the same sampling location, if readily available.

Questionable data is investigated as thoroughly as possible and reanalyzed if deemed necessary and possible.

1.D.7.f. Data Reporting

Values are then recorded by the reviewer on the sample sheets with rounding to the appropriate number of significant figures. Any pertinent laboratory remark codes are also reported with the data. Sample sheets

are then signed by the individual reporting the data and submitted for transmittal to the appropriate data user.

1.E.1. INORGANIC UNIT QUALITY ASSURANCE PROGRAM

1.E.1. INTRODUCTION

The Inorganic Unit is responsible for the analysis of inorganic contaminants in various environmental substrates. The lab is also responsible for the calibration of air monitoring instrumentation.

1.E.2. UNIT QA/QC MANAGEMENT

1.E.2.a. Unit Supervisor

The Unit supervisor is responsible for establishing, assuring compliance with, reviewing and updating the Inorganic Unit's quality assurance program. The unit supervisor also defines and/or approves the quality control acceptance limits for each analytical parameter. The supervisor is ultimately responsible for the approval of each analytical batch of samples. The supervisor reviews the analyst's run evaluation, QC audit values and run comparisons before approving or rejecting the sample run.

The supervisor is also responsible for approving all analytical sample results. He again reviews the quality control audits, analytical run comparisons, various parameter relationships and field sampling patterns before approving or repeating the sample results.

The supervisor invests a 15% minimum time commitment for quality assurance.

1.E.2.b. Quality Assurance Coordinator

The Inorganic Unit's quality assurance coordinator serves as the unit's representative on the Laboratory Quality Assurance Team. Duties include statistical review of quality control data, recommendation of improved QC techniques, and special related projects.

These duties require an investment of a 10% minimum time commitment.

1.E.2.c. Professional Analyst's Responsibilities

The unit's professional analyst, or laboratory scientists, are responsible for the accurate calibration of the analytical instruments. Duties include the preparation and verification of accurate standards and the evaluation and approval of instrument calibration curves. Quality control audits include minimum absorbance values, limits on "feedback" concentration for standards, and professional judgment on proper calibration and instrument functions. Each professional analyst is also responsible for the evaluation of problem samples and possible interferences. The accuracy of the results is either verified or coded with an appropriate qualifier.

The laboratory scientists evaluate quality control parameters and limits. The analyst complies and reviews all the quality control data. This includes blanks, check standards, mixed control samples, and spike samples. Each quality control audit is evaluated against acceptable limits.

The analyst evaluates the entire analytical run and recommends approval or rejection of the entire run or specific samples. Questionable runs are also submitted to the unit supervisor for a final determination. The analyst's evaluation and decision is based on instrument calibration, the quality control evaluation, and his/her professional judgment and experience.

The analyst's time and workload investment in quality control is substantial. Ten samples in a batch of forty samples are devoted to quality control. This equates to each analyst investing a 25% minimum time commitment for quality assurance.

1.E.2.d. Technical Analyst's Responsibilities

The technical analysts are responsible for the accurate set up of each analytical run. Duties include assuring proper parameter analyses, expediting priority samples and alerting laboratory scientists of possible problem samples.

Technical analysts are also responsible for the accurate preparation of analytical standards for the controls, spikes and mixed control samples. They must assure that proper quality control audits are available on each analytical run. The technical analysts also verify that the samples are digested using the proper digestion procedure.

Technical analysts invest a 25% minimum time commitment for quality control.

1.E.2.e. Total Time Commitment

The time commitment for QA/AC functions in the Inorganic Unit is about 25% of the unit's manpower.

1.E.3. PARAMETERS ANALYZED BY THE INORGANIC UNIT

Table 1.E.-1 includes the parameters analyzed by the Inorganic Unit. Also listed are the matrices and the corresponding EPA or other method referenes.

1.E.4. ANALYST PROFICIENCY

The Inorganic Unit recognizes the necessity of having qualified analysts with demonstrated competency performing all analyses. Proficiency is especially important when new analysts are being trained or existing analysts learn or develop new procedures. Generally, two or more trained analysts are maintained for each routine parameter. This is particularly important if the holding time for the parameter is short. The unit supervisor, with the consultation of the responsible lead worker, makes

TABLE 1.E.-1
ANALYTICAL RESPONSIBILITIES OF THE INORGANIC UNIT

PARAMETER	METHOD DESCRIPTION	MATRIX	METHOD	REFERENCE
Hardness	Total, Titirmetric EDTA	W	130.2	2
Calcium	Flame AA, Acet/Air	WLS	215.1	2
Magnesium	Flame AA, Acet/Air	WLS	242.1	2
Sodium	Flame AA, Acet/Air	WLS	273.1	2
Potassium	Flame Emission	WLS	258.1	2
Cadmium	Flame AA, Acet/Air	WLSOT	213.1	2
Cadmium	Flameless AA, Graphite Furnace	WT	213.2	2
Cadmium	Flame AA, Acet/Air, with Std. Add.	H	7130	1
Cadmium	Inductively Coupled Plasma	E	200.7	2
Chromium	Flame AA, Acet/Nitrous Oxide	WLSOT	218.1	2
Chromium	Flameless AA, Graphite Furnace	WT	218.2	2
Chromium	Flame AA, Acet/Air, with St. Add	H	7190	1
Chromium	Industively Coupled Plasma	E	200.7	2
Copper	Flame AA, Acet/Air	WLSOT	220.1	2
Copper	Flameless AA, Graphite Furnace	W	220.1	2
Copper	Flame AA, Acet/Air, with St. Add.	H	220.1	2
Copper	Inductively Coupled Plasma	E	200.7	2
Nickel	Flame AA, Acet/Air	WLSOT	249.1	2
Nickel	Flameless AA, Graphite Furnace	WT	249.2	2
Nickel	Flame AA, Acet/Air, with St. Add.	H	7520	1
Nickel	Inductively Coupled Plasma	E	200.7	2
Lead	Flame AA, Acet/Air	WLSOT	239.1	2
Lead	Flame AA, Acet/Air, with Std. Add.	H	7420	1
Lead	Industively Coupled Plasma	E	200.7	2
Lead	Flameless AA, Graphite Furnace	WT	239.2	2
Zinc	Flame AA, Acet/Air	WLSOT	289.1	2
Zinc	Flame AA, Acet/Air with Std. Add.	H	7950	1
Zinc	Inductively Coupled Plasma	E	200.7	2
Zinc	Flameless AA, Graphite Furnace	W	289.2	2
Silver	Flameless AA, Graphite Furnace	WH	272.2	2
Aluminum	Inductively Coupled Plasma	WLSOT	200.7	2
Beryllium	Flame AA, Acet/Nitrous Oxide	WLSOT	210.1	2
Beryllium	Inductively Coupled Plasma	E	200.7	2
Cobalt	Flame AA, Acet/Air	WLS	219.1	2

TABLE 1.E.-1 Continued

PARAMETER	METHOD DESCRIPTION	MATRIX	METHOD	REFERENCE
Cobalt	Inductively Coupled Plasma	E		
Lithium	Flame AA, Acet/Air	WLS	--	3
Lithium	Inductively Coupled Plasma	WLSOT		
Manganese	Flame AA, Acet/Air	WLS	243.1	2
Iron	Flame AA, Acet/Air	WLSOT	236.1	2
Molybdenum	Inductively Coupled Plasma	WLSOT	200.7	2
Titanium	Inductively Coupled Plasma	WLSOT	283.1	2
Vanadium	Flame AA, Acet/Nitrous Oxide	WLSOT	286.1	2
Mercury	Cold Vapor Flameless AA	WLS	245.1	2
Arsenic	Borohydride, Hydride	WLS	206.3	2
Selenium	Borohydride, Hydride	W	--	3
Antimony	Borohydride, Hydride	W	204.1	2
Barium	Inductively Coupled Plasma	WLSOT	208.1	3
pH	Electrometric	W	150.1	2
Cond	Probe	W	120.1	2
Hex Cr	DPC Colorimetric Method	W	E690000WF	3
Chloride	Titrimetric, Mercuric Nitrate	W	325.3	2
Alkalinity	Colorimetric, Auto, Methyl Orange	W	310.2	2
Sulfate	Colorimetric, Auto Methyl Thymol Blue	W	375.2	2

*Matrices: W = Water; L = Leachate (ASTM); S = Sed./Soil; O = Organic/Oil; T = Tissue; H = Hazardous Waste;
E = E.P. Tox. Leachate

1. EPA, Test Methods for Evaluating Solid Waste, SW-846, 1982.
2. EPA-600/4-79-020, Methods for Chemical Analysis of Water and Wastes.
3. Internal Lab Method.

final decisions as to when an analyst is capable of performing a methodology.

1.E.5. EQUIPMENT LOG BOOKS

An equipment log record is maintained for each major instrument. All pertinent information is recorded. The log records for each atomic absorption spectrophotometer include:

-- Standard curve absorbance readings and minimum absorbance limits.

-- Instrument calculated concentration values for each standard and acceptable QC limits.

-- Other pertinent information such as date, analyst, run ID number, and comments.

1.E.6. SAMPLE AND DATA HANDLING

Incoming samples are recorded in the Inorganic Unit log records. Recorded information includes:

-- date of receipt,
-- log number,
-- project code,
-- cost center,
-- priority,
-- person results are sent to,
-- sample matrix,
-- location sampled,
-- laboratory sample number,
-- field ID numbers,
-- analyses requested,
-- final sample results,
-- analytical run ID number, and
-- analyst date reported.

Analytical run sheets list the samples and parameters for analysis. Each run sheet includes:

-- run ID number,
-- sample matrix,
-- date samples digested,
-- technician performing digestion,
-- date samples analyzed,
-- analyst performing analysis,
-- laboratory sample number,
-- parameters requested for analysis,
-- zero and standard curve checks,
-- direct instrument reading,
-- dilution factors,
-- final results,
-- comments, and
-- all quality control data and evaluation.

Approved sample results are transferred into the unit computer for report generation. The unit supervisor approves all analytical results before they are reported.

The samples are sorted by matrix and stored chronologically. Samples are held for a minimum of three months before disposal. Samples involved in legal action are stored indefinitely.

1.F. ORGANIC UNIT QUALITY ASSURANCE PROGRAM

1.F.1. INTRODUCTION

The Organic Unit is responsible for the detection and measurement of organic contaminants in water, sediment, biological tissue, and other environmental substrates. The unit is involved in the analysis of volatile and extractable organic compounds using gas and liquid chromatography, mass spectrometry and infrared spectrophotometry. The lab is also responsible for the identification and matching with possible sources of spilled and abandoned organic materials.

The unit is divided into three groups:

-- One group is involved in the analysis of extractable, semi-volatile compounds using gas chromatography following extraction and purification steps. This group is also involved in GC/MS analysis and confirmation of the identifies of compounds found by the other group.

-- A second group is responsible for the analysis of volatile compounds via gas chromatography, aromatic amines via liquid chromatography, air toxics via gas chromatography, infrared characterization, and various colorimetric and gravimetric determinations.

-- A third group is responsible for the preparation of tissue samples and analysis of trace organics in fish tissue for the Department Fish Monitoring Program.

The staff consists of two lead workers, senior level worker (GC/MS specialist), laboratory scientists, and laboratory technicians.

1.F.2. UNIT QA/QC MANAGEMENT

All positions in Organic Unit have commitments to quality assurance activities. Time commitments vary depending on the position and type of analysis.

1.F.2.a. Unit Supervisor

The unit supervisor is responsible for applying general laboratory quality assurance policy to the Organic Unit. This includes determining the frequency and type of QC audit for each group of parameters. The unit supervisor is also responsible for reviewing all results produced by

the unit. A minimum of 15% of the unit supervisor's time is allotted to QA/QC activities.

1.F.2.b. Lead Worker

Each lead worker is responsible for reviewing each analyst's output in order to ensure that QC procedures are followed as part of his/her technical supervision in the group. In addition, the lead workers are responsible for understanding the laboratory's quality assurance policy and the quality control audits which apply to the analytical procedures that they are performing. The result is a minimum commitment of 15% of a leadworker's time to QC/QA activities.

1.F.2.c. Analysts

Each laboratory scientist and technician is responsible for understanding the quality assurance policy of the laboratory and the quality control audits which apply to the analytical procedures they perform. QC audits are reviewed immediately to verify that the data produced are in control. When the audits are out of control, the analyst works with the lead worker or unit supervisor to determine what part of the method is causing the problem. Once the problem is corrected, the set of analyses is repeated if possible. If the analyses cannot be repeated, the supervisor may report results with a qualifying remark indicating the problem (e.g., low recovery, high blank, etc.), using an appropriate result remark code (Appendix 1.C.-9) or not report the results. Annually, each analyst prepares a precision and accuracy summary of the past calendar year's data. Each analyst in the Organic Unit has a minimum time commitment of 15% to QA/QC functions.

1.F.2.d. Total Time Commitment

The minimum total time commitment for the Organic Unit to QA/QC functions is approximately 15% of the unit's manpower.

1.F.3. PARAMETERS ANALYZED BY THE ORGANIC UNIT

A list of the parameter groups analyzed is found in Table 1.F.-1. Also shown are the substrates in which these groups can be analyzed as well as a brief description of each parameter or parameter group. The methods generally conform to those proposed by U.S. EPA for NPDES compliance or RCRA monitoring. The specific compounds routinely determined by these methods (scans) are listed in Appendix 1.C.-10. Since the compounds vary according to the matrix type, separate lists are used for water, sediment/soil, oil and tissue.

1.F.4. ANALYST PROFICIENCY

Analysts in the Organic Laboratory must demonstrate proficiency in the analyses they perform. The ability to properly perform the analysis is measured through QC audits, through the observations of the lead worker who technically supervises the analysis, and by the unit supervisor.

TABLE 1.F.-1
ANALYTICAL RESPONSIBILITIES OF THE ORGANIC UNIT

PARAMETER GROUP	METHOD DESCRIPTION	MATRICES	EPA METHOD	REFERENCE
Purgeable Halocarbons (Scan 1)	Purge & trap, GC, HECD	W, L, S, O	601	1
Purgeable Aromatic Hydrocarbons (Scan 2)	Purge & trap, GC, FID or PID	W, L, S, O	602	1
Halogenated Hydrocarbons, PCB's and Organochlorine Pesticides (Scan 3)	Neutral ext., GC	W, S, O, T	608/612	1
Phenols (Scan 8)	Acid extraction, GC/FID and GC/MS	W	604/625	1
Aromatic Amines (Scan 9)	Basic extraction, LC, electrochemical det.	W, S	605	1
Oil and Grease	Freon ext., gravimetric	W, S	413.1	2
B/N GC/MS Analysis	Basic extraction, GC/MS	W, S	625	1

*Matrices: W = Water; L = Soil/Leachate; S = Sed./Soil; O = Organic; T = Tissue.

1. Guidelines Establishing Test Procedures for Analysis of Pollutants Under the Clean Water Act, 40 CFR Part 136, October 26, 1984.
2. Methods for Chemical Analysis of Water and Wastes, March 1983. EPA-600/4-79-020.

1.F.5. EQUIPMENT LOG BOOKS

Instrument log books are maintained for each gas or liquid chromatograph. At the beginning of each day, standards are injected into each column in each instrument that is used that day. Pertinent data regarding the performance of the chromatograph (e.g., sensitivity, resolution) is recorded in the log book. If instrument performance is not satisfactory, then adjustments must be made or repair work done before the instrument can be used.

1.F.6. SAMPLE AND DATA HANDLING

1.F.6.a. Sample Receiving

Samples are received, logged in, and numbered by personnel in the General Chemistry Unit. Upon notification that samples are ready for distribution, a leadworker or the unit supervisor reviews the sample analysis request forms. He/she also checks that samples are accurately numbered and that all of the necessary sample bottles are present for the parameters requested. Any errors are resolved and corrected immediately.

The samples are then stored in the designated areas in the cold room or in appropriate refrigerators or freezers where analysts can find them when ready to proceed with the analysis. The samples are filed chronologically and analyzed "oldest first" except in the case of special priority samples.

1.F.6.b. Unit Sample Logging

The sample receiver then enters the samples in the Organic Unit result book. The laboratory log number, project code, date of receipt and the source of the samples are entered with each group of samples. Red ink is used for the log number and high priority assignments.

Also, a grid is made of sample numbers versus parameters requested. Enough field information to identify the sample is written adjacent to the sample number.

1.F.6.c. Assignment of Workload and Recordkeeping

The lead workers assign analyses to the analysts in their group. Results from qualitative analyses are entered in the Organic Unit result book by the lead worker or by the analyst with review by the lead worker. Individual scan results are entered, by the analyst, into the laboratory computer where they are combined with other sample results.

1.F.6.d. Data Review and Reporting

When all results for a log are completed, a report is generated with scan results for each sample. Detection limits are included when possible and remark codes when necessary. The unit supervisor reviews the results, signs the analysis request forms, and attaches a copy of the report.

CHAPTER 1

LABORATORY QUALITY ASSURANCE

Prepared by
State of Michigan
Department of Natural Resources
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APPENDICES

CHAPTER 1. LABORATORY QUALITY ASSURANCE

1.A. INTRODUCTION

The Environmental Laboratory provides analytical and technical services to the State's environmental and resource management programs. Laboratory analyses are an integral part of environmental law enforcement, environmental monitoring and surveillance, pollution control, facility planning and operation, and management of air, water, and land resources of the State of Michigan.

The Environmental laboratory operates as two laboratory units, Inorganic and Organic. Their respective responsibilities and quality assurance procedures are described in Section 1.D.

1.A.1. QUALITY CONTROL vs. QUALITY ASSURANCE

The terms quality control (QC) and quality assurance (QA) are often misunderstood and incorrectly used interchangeably. Laboratory quality control consists of those internal operations which are routinely performed during the measurement process to document data quality (e.g., replicate analyses, spiked samples, reagent blanks, instrument calibration checks, etc.). Laboratory quality assurance consists of those activities which are performed with less frequency to obtain independent assessments of operating conditions (e.g., independent reference samples, interlaboratory comparison studies, laboratory evaluation samples, etc.).

1.B. GLOSSARY

1.B.1. ACCURACY

The ability to measure a sample constituent, compared to a standard or true value, without bias or error.

1.B.2. APPROVED ANALYTICAL METHOD

An analytical method which has gone through the complete Environmental Laboratory procedure for methodology approval (Appendix 1.C.-1) including the Lab Director's signature.

"EPA approved" refers to a method promulgated under the Clean Water Act, the Resource Conservation Recovery Act and the Clean Air Act.

1.B.3. BETWEEN-RUN DUPLICATES (REPEATS)

Two separate aliquots of a single sample analyzed in two separate batches of analyses to evaluate between-run variability.

1.B.4. CALIBRATION

The process of defining the relationship between the output of an analytical system (some value) and the input. Analysis of several different standards will define a calibration curve.

1.B.5. CALIBRATION CHECK

A sample, usually a standard of known concentration, which is not used in the calibration process, but is used as an external check on the accuracy of the calibration.

1.B.6. CONTROL LIMIT

The established level which, when exceeded, determines that a system is not in control and requires re-evaluation.

1.B.7. DETECTION LIMIT

The lowest concentration of an analyte that the analytical process can reliably detect.

1.B.8. FIELD BLANK

A sample submitted by field personnel to measure contamination from sample containers, chemical preservatives, and sample handling techniques.

1.B.9. FIELD REPLICATE

The second of two separate samples from a single source submitted to the laboratory to evaluate combined overall precision due to source, sampling and analytical variability.

1.B.10. INTERLABORATORY COMPARISON STUDY

A study, usually performed by an independent agency, to assess the comparability of data submitted by participating laboratories.

1.B.11. LABORATORY EVALUATION STUDY

A study, usually performed by an external agency, to evaluate the accuracy of results from a specific lab. Unknown standards are usually analyzed.

1.B.12. METHOD DETECTION LIMIT (MDL)

The minimum concentration of a substance that can be analyzed and reported with 99% confidence that the analyte is greater than zero.

1.B.13. METHODOLOGY APPROVAL

The laboratory procedure for evaluating and approving an analytical method for use in the Environmental Laboratory (Appendix 1.C.-1).

1.B.14. PRECISION

The ability to replicate a value within which random deviations can usually be expected to fit.

1.B.15. QUALITY ASSURANCE

Laboratory quality assurance consists of activities periodically performed to obtain independent assessments of data quality (e.g. reference samples, interlaboratory studies, laboratory evaluation samples, laboratory inspections, etc.).

1.B.16. QUALITY CONTROL

Laboratory quality control consists of the internal operations routinely performed during the measurement process to document data quality (e.g., replicate analyses, spiked samples, calibration checks, etc.).

1.B.17. QUALITY CONTROL AUDIT

1.B.17. QUALITY CONTROL AUDIT

Any routine check of a system to determine the adequacy of the system's performance.

1.B.18. QUALITY CONTROL CHART

A graphic presentation of quality control data. The classic approach has been the plotting of a variable, such as a value for a QC audit, against time.

1.B.19. REAGENT BLANK

A sample of water (distilled, deionized, or equivalent) which is taken through the entire analytical procedure to establish the zero intercept of the calibration curve and to check for contamination.

1.B.20. REFERENCE SAMPLE

A sample, usually a verified standard, supplied by an independent entity, to be used as an external check on the accuracy of an analytical procedure.

1.B.21. REPORTED DETECTION LIMIT (RDL)

The detection limit used to routinely report laboratory data, based on the method detection limit but usually slightly higher than the MDL.

1.B.22. SPIKED BLANK

A reagent blank which has had added to it a known volume of a standard of known concentration. It is generally used to measure the recovery of a process as a check on calibration.

1.B.23. SPIKED SAMPLE

A sample to which a known volume of a standard of known concentration has been added to measure accuracy, recovery, or matrix effects.

1.B.24. STANDARD

A known concentration of analyte in a non-interfering matrix.

1.B.25. WARNING LIMIT

The established level which, when exceeded, indicates that an analytical system may be near an out-of-control situation and may require a review.

1.B.26. WITHIN-RUN DUPLICATES

Two separate aliquots of a single sample analyzed within a single batch of samples to evaluate the precision of the system.

1.C. GENERAL LABORATORY QA PROGRAM

1.C.1. MANAGEMENT OF THE LABORATORY QA PROGRAM

1.C.1.a. Laboratory Management Team

The laboratory director and the supervisors of the two laboratory units form the Laboratory Management Team. The Lab Management Team is responsible for establishing the quality assurance policy of the Environmental

Laboratory. The laboratory director, as the team leader, has the ultimate responsibility for administration of all laboratory programs, including the quality assurance program. The Lab Management Teams meets about once a every two weeks.

1.C.1.b. Laboratory Quality Assurance Coordinator

One of the laboratory senior staff members is assigned as the Laboratory Quality Assurance Coordinator. The Quality Assurance Coordinator is responsible for internal and external coordination of the quality assurance program. The additional functions include:

-- Serving as the Laboratory Quality Assurance Team Leader. The activities of the Lab QA Team must be planned, organized and controlled for effective operation.

-- Serving as a resource person for quality assurance problems within the laboratory.

-- Serving as a contact person at the laboratory for quality assurance problems outside the laboratory.

1.C.1.c. Laboratory Quality Assurance Team

The Laboratory Quality Assurance Team consists of the Laboratory Quality Assurance Coordinator as team leader and a representative from each of the laboratory units as team members. The members are appointed by and are accountable to their respective supervisors. The responsibilities and authority of the Lab QA Team include:

-- Review and revise, as needed, the laboratory quality assurance for water and sediment sampling program.

-- Develop and revise the quality assurance procedures and seek implementation through normal administrative practices.

-- Review the quality control audit program performed by each laboratory unit with reporting of deficiencies to the Lab Management Team on a quarterly basis.

-- Meet at least quarterly or more frequently as need arise.

-- Submit minutes of meetings to the Lab Management Team.

1.C.1.d. Laboratory Supervisors

The laboratory supervisors are responsible for the interpretation, implementation, and maintenance of approved quality assurance policy and procedures in their respective laboratory units. Some of their specific functions related to quality assurance include:

-- Development and implementation of detailed quality control procedures and practices according to approved quality assurance policy.

-- Approval of routine quality control audits and control limits proposed by the analyst.

-- Review and approval of all laboratory results generated by the laboratory unit.

1.C.1.e. Laboratory Analysts

All laboratory analysts are responsible for understanding laboratory quality assurance policy and following the directions of their immediate supervisor on all quality assurance concerns. Duties include:

-- Preparation of methodology write-ups and method addenda.

-- Performance of QC audits on instruments and maintenance of equipment log books.

-- Performance of QC audits on analytical runs with reporting of out-of-control systems to the lead worker or unit supervisor.

1.C.2. LABORATORY QA POLICY

Laboratory Quality Assurance Policy is described in Chapter 9. According to this policy, all analyses or methods are placed into one of three categories (quantitative, semi-quantitative, or qualitative) dependent upon the level of quality assurance documentation. The purpose of this policy is to ensure that:

-- An approved analytical method is being used,
-- The method has been shown to be suitable for the sample types requiring analysis,
-- The method as used is fully documented,
-- The analyst performing the analysis has demonstrated competency,
-- The method has the detection capabilities necessary to quantify the constituents of interest,
-- The equipment used to perform the analyses are capable of the task, are properly maintained, and are operating properly,
-- The sample as analyzed is representative of the sample source,
-- The chemicals and supplies are of suitable quality for their intended use,
-- Standards and control samples indicate normal operating conditions,
-- Samples are properly collected, received and distributed to the appropriate lab units,
-- The reference sample program periodically evaluates analytical performance,
-- The laboratory participates in pertinent interlaboratory comparison studies and performance evaluation studies,
-- Laboratory results are adequately reviewed and properly reported.

1.C.2.a. Approved Methods

The U.S. Environmental Protection Agency lists the analytical methods approved for use with NPDES compliance monitoring in 40 CFR Part 136. Approved analytical methods for use in testing waste materials under the Resource Conservation Recovery Act (RCRA) are listed in 40 CFR, Part 261, Appendix III.

If a method other than an "EPA approved" procedure listed in 40 CFR Part 136 is to be used (because of better accuracy, improved efficiency, lower sensitivity, better precision, or lower operating costs), there must be a formal evaluation and submittal to the EPA. The method must be shown to be equivalent to the approved method. The use of alternative test procedures is much more restrictive in the RCRA program and requires formal changes to federal regulations.

1.C.2.b. Methodology Approval

Appendix 1.C.-1 is the internal laboratory procedure for evaluating and approving a method for use in the Environmental Laboratory. In brief, the procedure consists of:

-- Literature search,
-- standardization procedure,
-- detection limit determination,
-- precision measurement,
-- accuracy measurement,
-- reference sample evaluation,
-- check for interference's,
-- procedure for documentation,
-- approval policy, and
-- reporting of unapproved results.

1.C.2.c. Methodology Write-Up Format

So that all laboratory methods are documented in a uniform manner, a procedure for methodology documentation was developed and is included as Appendix 1.C.-3. The sections to be included in a written laboratory procedure include:

-- EPA Method Number Reference in header
-- Scope and Application,
-- Summary of Method,
-- Sample Collection, Handling, and Preservation,
-- Interference's and Biases,
-- Apparatus,
-- Reagents,
-- Procedure,
-- Quality Control Audits,
-- Calculation,
-- Method Validation,
-- Reported Detection Limit
-- References, and
-- Approval.

The procedure for documenting and adding significant changes to existing methods appears as Appendix 1.C.-1.

1.C.2.d. Detection Limit

The laboratory procedure for quantifying the detection limit of a method appears as Appendix 1.C.-6. Laboratory detection limit used to report data are listed in Appendix 1.C.-7.

1.C.2.e. Equipment Logbook

Each piece of major laboratory equipment has a logbook for the recording of monitored variables and other pertinent information.

1.C.2.f. Representative Sample

The laboratory has little control over whether the sample is actually representative of the sample source, but tries to maintain the integrity of the sample as received from field personnel. This means maintaining proper sample preservation which was initiated in the field and attempting to analyze all samples within their respective holding times. If this is not possible, it is the responsibility of the appropriate unit supervisor to not report results or report coded values.

1.C.2.g. Quality of Chemicals and Supplies

Only chemicals meeting specifications necessary for an analytical procedure are used. It is the responsibility of each unit to ensure their suitability. When chemicals are received from a lab supply company, they are dated. Each analyst is responsible for dating a chemical bottle when it is opened if it will not be consumed in a short period of time. If it is unstable, an expiration date should also be added at that time. Chemicals are not to be used past their expiration date.

When standards are prepared, the container that they are stored in should contain:

-- the concentration and name of the analyte,
-- the type and amount of the compound it was prepared from,
-- the substrate it is prepared in,
-- who it was prepared by,
-- date it was prepared, and
-- expiration date.

Information found on reagent bottles should include:

-- the reagent name,
-- what test the reagent is for,
-- the quantity of each chemical used in its preparation,
-- who it was prepared by,
-- an expiration date.

Laboratory supplies should be checked when they are received from stock to make sure that they are appropriate for the intended analysis. Even new supplies should be thoroughly cleaned before use unless lack of contamination has been sufficiently documented.

1.C.2.h. Standards and Control Samples

Each analytical batch must be in documented control through the use and evaluation of standards for calibration and quality control samples for precision and accuracy estimation. The types and frequency of these will vary with each method and should be fully documented with each methodology.

1.C.2.h.1. Calibration

Proper instrument calibration must be established or confirmed with each batch of analyses or more often as necessary. The type of instrument response (linear or otherwise) and the degree of its variability will tend to dictate calibration needs. Anything from a two point slope and intercept regression to replicate analyses of multiple points may be necessary.

1.C.2.h.2. Accuracy

The accuracy of a method must be measured and evaluated with each analytical batch. Spiked samples or other appropriate audits may be used. Generally, five to ten percent of the samples in a batch should be for the determination of accuracy.

1.C.2.h.3. Precision

Precision is an estimate of procedural variability. It is generally derived from the analysis of replicates. The replicates may be within-run duplicates, between-run duplicates, or field replicates. Each type of audit should indicate different degrees of variability and must be

evaluated separately. Five to ten percent of the samples in a batch should be for the measurement of precision.

1.C.2.h.4. Quality Control Charts

Quality control charts (Shewhart type or similar) are very useful for the graphic display of QC data and very helpful for identifying trends. QC charts should be used wherever applicable.

1.C.2.h.5. Precision and Accuracy Summaries

The precision and accuracy of each quantitative analytical method is summarized annually and reported to users of the lab. This summary provides basic performance information to laboratory users and allows them to use and interpret lab results within limits of data quality. The Lab policy that requires this annual summary is included in Appendix 1.C.-2.

1.C.2.i. Requesting Sample Containers and Preservatives

To facilitate the ordering of sample containers and preservatives, a "Sample Bottle and Preservative Request" form (Appendix 1.C.-8) should be used. This form should be completed by field personnel and received by the laboratory at least one week prior to the planned pick-up time. If there remains insufficient time for proper notification, bottle requests should be prepared and phoned into the proper designee with as much advanced notice as possible.

Additional sample containers may be required for non-routine analyses not listed. It is better to make sure that the lab has sufficient sample in the proper container than to risk not receiving the desired analyses.

The chemical preservative and dechlorinating agents are available from the laboratory either as a kit or as individual preservatives. Field personnel who routinely collect samples will find it more convenient to have a kit assigned to them and restock chemicals as needed. Certain preservatives have an expiration date to notify field personnel when the preservative must be restocked. If there is no expiration date, the preservative should be restocked at least every six months. Personnel who do not frequently collect samples may find it more convenient to request preservatives with each survey or batch of samples and return the preservative when samples are submitted to the laboratory. A preservative kit which is not frequently used should be carefully stored to prevent contamination of the chemicals. Field blanks should be requested with bottles and set according to instructions provided in Chapter 5, Section 5.B., Field Blanks.

The laboratory will attempt to supply sample bottles with caps on. If caps and bottles are received separately by field personnel, caps should be added to the bottles as soon as possible to prevent contamination of sample bottles.

1.C.2.j. Analysis Request Sheets

The laboratory attempts to maintain a stock of analysis request sheet forms at the laboratory. These are updated periodically to correspond with laboratory unit reorganization, changes in bottles or preservatives, or the addition or deletion of parameters. The laboratory has posted a list of current forms which should be reviewed at the time that sample bottles are picked up.

For easier identification, the water sheets are white, leachate sheets are blue, tissue sheets are pink, sediment sheets are goldenrod, and

wastes and oil sheets are canary. Some white blanks may exist due to lack of colored paper at the time of printing.

Sample blank forms may be requested from the laboratory, allow at least two weeks for delivery of larger orders. Special forms may be prepared for projects if existing forms are not suitable and sufficient advance notification (about one month) is given.

1.C.2.k. Laboratory Receipt of Samples

1.C.2.k.1. Receiving Hours

The Environmental Laboratory is generally open to receive samples from 7:30 a.m. until 12 noon Monday through Friday, from 12:30 p.m. until 4:00 p.m. on Monday through Thursday and 12:30 p.m. until 3:00 on Friday (except during holiday weeks). The lab may be able to receive samples at other times with prior notification and approval.

1.C.2.k.2. Laboratory Check-In Policy

The sample receiving is located in building #44 of the Public Health Facility at 3500 N. Logan Street, Lansing, MI. The entrance is located on the third floor to the right of the elevator (Room #303). A telephone is located in the basement loading dock area if assistance is needed from sampling receiving staff.

Field personnel should set up samples on the available tables (from left to right in the order they appear from top to bottom on the sample sheets). A single sample is defined as being from one location and depth and having a common sampling time. A single sample may have more than one sample container with various preservatives. Each individual sample should be maintained in a column. The rows should be lined up by the separate sample containers for different parameter groups. Using the same order, from front to back, as appears on the Collection and Preservation Table (Table 3.B.-1) (top to bottom) will expedite sample check-in.

Personnel from Sample Receiving have been specifically trained to receive samples for all laboratory units. The laboratory sample receiver checks the sample sheets for the proper matrix and to verify that they are not outdated. The person submitting the samples will have to fill out the proper sample sheets if <u>incorrect</u> forms have been used. The lab sample receiver then checks that the forms are properly completed and requests any missing information (collected by, transferred to, location sampled, sample remarks, send results to, field ID, description, cost center, STORET location number (optional), sampling date and time, etc.). The requested parameters are then checked against the sample containers submitted to verify that the necessary bottles with proper preservatives exist. The sample bottle label is reviewed by lab receiver to ensure that the information on the label is complete, accurate and clearly understood. Descriptions on sample labels should match as exactly as possible those on the sample sheets to avoid any confusion. Any discrepancies are immediately brought to the attention of the field personnel and noted on the appropriate sample sheet.

Field personnel are responsible for submitting the sample that they want analyzed. Samples composed of more than one matrix or stratum should be clearly identified as to the portion which is to be analyzed. If practical, the portion requiring analysis should be separated and submitted by itself for analysis. If more than one matrix is to be analyzed (oil and water sample or water and sediment sample), separation of matrices and separate sample submittal is requested.

The laboratory sample receiver then writes the date and time of receipt on the analysis request sheet. The Environmental Laboratory Logbook is filled out with the date and time of receipt, the assignment of an order number for that sample batch, name of the person delivering the samples, initials of the lab person receiving the samples, lab sample numbers, priority assignment, and the source of the samples. Samples from one laboratory order number should be from the same sample source or run, should be chargeable to one project code and cost center, should contain only one sample matrix, and should be submitted at the same time. Special priority may be assigned by responsible Division Chief or his designee. Any inquires about a batch of samples should reference the lab order number.

The sample receiver enters the lab order number, date, time, priority, and their initials on the analysis request sheets. Consecutive sample numbers are assigned to each individual sample. The laboratory sample numbers are written on the appropriate request sheets and the pertinent sample data is entered into the Laboratory's LIM System. Computer generated sample labels are carefully attached to the corresponding sample containers. Field personnel should assist in wiping off wet, dirty, or oily bottles so that the labels will adhere properly. Bottles suspected of containing listed or other hazardous wastes should be identified upon receipt by completing the Sample Hazard Information Form on the backside of the Analysis Request Sheet. Stickers designating special handling or analytical techniques are affixed by the receiver.

The copy of the analysis request sheet is given to the field personnel for immediate review and future reference. The original is filed at the lab. Since future laboratory identification by analysts will be based mainly on the sample number tag, field personnel should check the sample bottles for proper tagging.

1.C.2.k.3. Non-Aqueous Samples and Shared Samples

Sample Receiving is responsible for the handling of non-aqueous samples and shared samples. These samples are entered in a sediment log book kept by the Sample Receiving. Samples are stored numerically in trays in the cold room. Lab employees needing these samples refer to the sediment log book for sample location. When finished with the samples, they are returned to the appropriate trays in the cold room.

Every three months, the Sample Receiving circulates a list of old samples. The unit supervisors authorize disposal of completed samples and identify which samples require special disposal precautions.

1.C.2.k.4. Preparatory Analyses

Each laboratory unit is responsible for sample preparation steps specific to their analyses.

Sample preparation for sediment, soil, sludge and other solid samples is described in Section 1.C.2.q. of this manual. Fish tissues sample handling procedures are described in Section 4.J.4. of this manual.

When more than one bottle of the same non-aqueous sample is delivered each bottle will receive a computer generated label for proper identification. Bottles will be suffixed "A", "B", "C", etc. If the sample requires a % TS analysis, each unit will perform its % TS analysis. The % TS will be reported with other sample results.

1.C.2.k.5. Distribution of Samples

A designated person in each laboratory unit is notified by the laboratory sample receiver when samples are ready for distribution.

Each unit should then recheck the samples for proper labeling and the existence of all necessary bottles. Any corrections should be brought to the immediate attention of the laboratory sample receiver. Corrections should be carefully noted on all pertinent forms (analysis request sheets, laboratory log book, etc.). Appropriate field personnel should be promptly notified of serious problems so that additional sample can be collected and submitted. The respective lab units should then properly store samples until analyses are initiated. Analysts responsible for the most time dependent analyses should be immediately notified.

1.C.2.l. Laboratory Sample Handling

Each laboratory unit is responsible for the handling of the samples they have received. Their procedures are found in Section 1.D. It is imperative that the integrity of each sample is maintained through continued preservation, timely controlled analysis, and proper sample handling.

1.C.2.m. Laboratory Data Handling

Each laboratory unit is responsible for the handling of data within their unit. All original data must be properly filed in a permanent manner. Transcription of data should be minimized to reduce errors. Proper review of data and QC audits at each level is imperative. Each analyst's data should be concise and clear enough that any trained analyst could easily interpret the results. Ink should be used whenever practical. Any corrections or changes to data should be done by drawing a single line through the old value such that it can still be read and writing in the new value. An explanation of any changes should be included if necessary to clarify results.

1.C.2.n. Laboratory Reporting of Data

Each laboratory supervisor, or his designee, is responsible for the final review and reporting of data. Data which have not meet all laboratory criteria for optimum quality may be reported with proper qualifier codes. Appendix 1.C.-9 contains a list of laboratory result remark codes which may presently appear with results. Coded values may generally be considered reliable and usable. A three letter code with no value is reported for highly questionable data or when an analysis is not performed.

Data should be reported with proper attention to significant figures and rounding of values.

1.C.2.o. Reference Sample Program

The Environmental Laboratory has an established schedule for the analysis of reference samples. Reference samples are special samples which have been developed by an outside source for internal evaluation of analytical performance. Analysts are supposed to perform analyses using routine procedures without prior knowledge of the expected results. If more than one method of analysis is routinely employed or more than one analyst commonly performs certain analyses, each method and analyst should be evaluated separately. The results are submitted to and evaluated by the Quality Assurance Coordinator. Bias and % bias are calculated based on the "true" or "mean" values supplied with the samples.

When evaluated results are returned to the responsible laboratory unit,

they should be reviewed carefully. Poor performance should be investigated and corrective action taken whenever possible. A memo indicating the reason for poor performance and the results of corrective measures should be sent to the Laboratory Director. This should be reviewed, commented upon if necessary, and filed with the original results. Continued poor performance should be investigated by the Laboratory Quality Assurance Team.

The Environmental Laboratory presently analyzes reference sample sets provided by the U.S. Environmental Protection Agency (EPA). Sets are scheduled for analysis every three months and are also available upon special request from unit supervisors.

1.C.2.p. Interlaboratory Comparison and Evaluations

The laboratory should participate in interlaboratory comparisons and evaluations when the parameters and matrices under study are routine laboratory analyses. The EPA annually conducts laboratory evaluation studies. When the results have been evaluated and returned by the originating agency (which may take several months), the conclusions of the studies should be confirmed and any necessary corrective measures taken. Usually the organization originating the study would appreciate general feedback and notification of corrective action taken.

Values for non-routine laboratory parameters should not be reported for evaluations. These results do not reflect routine laboratory performance and may create incorrect impressions as to the quality of results reported by the laboratory. It should also be remembered that any accurate evaluation of actual laboratory performance cannot be obtained from infrequent evaluation studies. A short-term problem can easily be interpreted as a long-term problem. Also, interference's or matrix problems encountered on actual environmental samples may not appear in special evaluation samples.

1.C.2.q. Sediment, Soil, Sludge and Other Solid Samples

Sediment, soil and sludge samples are collected in 250 ml (8 oz.) or 125 ml (4 oz.) wide mouth glass jars or 40 ml purgeable vials, refrigerated and transported to the laboratory. Other than refrigeration, no other preservation is employed. Sample Receiving receives and logs all samples into the laboratory. Samples in 250 ml and 125 ml wide mouth jars are placed in the sample receiving cold room (4°C). When more than one bottle of the same sample is delivered, each bottle receives a numbered label. Each bottle is then suffixed "A", "B", "C", etc. If the sample requires a % TS analysis, each unit will perform this analysis on its own bottle. Purgeable 40 ml vials are provided directly to the Organic Unit where they are refrigerated at 4 degrees C.

Samples submitted to the laboratory in 250 ml or 125 ml wide mouth glass jars may require a number of different sample preparatory steps and analyses. Each unit is responsible for sample preparation procedures. For those parameters that are determined from a wet sediment, sludge or soil, (cyanide, COD, Total Phosphorus, Kjeldahl-Nitrogen, Mercury, Oil and Grease, Total Recoverable Phenol and trace organic analyses) the unit responsible for analysis removes the sample from the cold room and removes an appropriate quantity of sample. Less stable parameters (COD, Mercury and Phenolics) are analyzed as soon as possible and promulgated holding times for water samples are followed as a guideline. For those analyses conducted on wet or air dried samples, the percent dry weight (percent moisture) is determined to allow conversion and reporting of

sample results as dry weight. Percent dry weight is reported to allow conversion back to wet weight, if requested. A separate 250 ml sample is preferred for the E.P. Toxicity Procedure, TCLP, and SPLP. Separate aliquots are required for determination of percent total solids, the ASTM Leachate Procedure, wet chemistry parameters, mercury, metals, extractable organics, and Freon extractables. The aliquots and sample preparation needs for these aliquots are described below.

When it is necessary to take an aliquot from a soil, sediment or sludge sample, the sample is thoroughly stirred with a spatula and an appropriate amount of sample is removed (depending on the purposes of the aliquot) by selecting a small amount of sample from several locations throughout the container and compositing the material in a suitable container or drying dish.

1.C.2.q.1. Percent Total Solids Analysis

A wet or air dried sediment, sludge or soil sample is dried according to the PERCENT TOTAL SOLIDS procedure. The purpose of the percent solids determination is to provide a factor for calculating results on a dry weight basis when a wet or air dried sample is analyzed. At least 10 grams of wet sample are required. The determination is made by the appropriate unit and results are provided to the sample requester.

1.C.2.q.2. Analysis of Neutral Leachate

When sediment, soil or sludge samples are submitted for analysis of leachate, the units responsible for such analyses leach a suitable sized sediment aliquot according to the ASTM LEACHATE PROCEDURE.

1.C.2.q.3. Extraction Procedure Toxicity, TCLP or SPLP Analysis

When sediment, soil, or sludge samples are submitted to the laboratory for E.P. Toxicity, TCLP or SPLP analysis, a separate sample is desirable for each to provide the approximate 100 gram quantity required by each test. The Inorganic Unit or Organic Unit is responsible for all steps in the procedure from sample extraction to analysis of the extract. The EXTRACTION PROCEDURE TOXICITY, TCLP and SPLP methods describes these steps in detail.

1.C.2.q.4. Inorganic Non-Metal Analyses

When a sediment sample is submitted for analysis of parameters analyzed for inorganic non-metals (Chemical Oxygen Demand, Kjeldahl-Nitrogen, Total Phosphorus, Phenolics and Cyanide) a suitable quantity of wet sediment is taken from the sample. Percent total solids is provided so that dry weight results can be reported.

1.C.2.q.5. Metals Analyses

When a sediment sample is submitted for analysis of metals (excluding mercury), the Inorganic Unit prepares an oven dried aliquot. Procedures for drying sediment samples are described in the SEDIMENT DRYING PROCEDURE FOR METALS. Depending on the desired sample turn around time, drying may be in two steps (air dried-oven dried) or completely oven dried. The oven dried aliquot is digested and analyzed and results are reported as dry weight.

1.C.2.q.6. Mercury Analyses

When a sediment, sludge, or soil sample is submitted for mercury analysis, a wet sample aliquot is removed from the sample by the Inorganic Unit. At least 1 gram or wet sample is digested and analyzed. Results are converted to dry weight based on the percent solids in the sample.

The percent solids of the sample is also reported.

1.C.2.q.7. Extractable Organic Analyses

When a sediment, sludge, or soil or other solid sample is submitted for analysis of base/neutral extractables (Scan 3 and GC/MS Base/Neutrals) the organic Unit uses a 10 gram aliquot of wet sample. The Organic Unit is also responsible for extracting the sample according to procedures

identified in individual methods. After extraction and analysis, results are corrected to dry weight (based on percent moisture) and reported.

1.C.2.q.8. Oil and Grease Analysis

Solid samples for analysis of freon extractable compounds are analyzed directly from a wet sample. Results are reported on a wet weight basis.

1.C.2.r. Method Development Requests

When laboratory users desire additional analytical services not presently available from the laboratory, these services may be requested through, "Method Development Request Procedures" outlined in Environmental Laboratory Procedure No. PD-26 (Appendix 1.C.-5). The purpose of the Method Development Request Procedure is to estimate the demand for the new service and the cost of developing the new service. The laboratory will usually develop needed methodology if sufficient demand exists and if the requesting division can provide the necessary resources.

1.C.2.s. Analytical Costs

The laboratory periodically estimates costs for each analysis. Cost estimates are based on expenditures (salaries, equipment, overhead and etc.) divided by the number of analyses for a given time period (usually the fiscal year). Analytical cost estimates enable users to estimate the total cost of monitoring programs, amount of grant funds to apply for, and to compare cost to commercial lab costs. Appendix 1.C.-4 lists analytical costs for each analysis.

1.D. DNR ENVIRONMENTAL LABORATORY UNITS QUALITY ASSURANCE PROGRAM

1.D.1. INTRODUCTION

The Inorganic Unit is responsible for the analysis of metals, nutrients, BOD, COD, TOC, dissolved gases, cyanides, phenolics, residues, flashpoint, turbidity, and chlorophyll from water, leachate, sediment, and other environmental samples. The Inorganic Unit presently consists of a unit supervisor, lead workers, laboratory scientists and technicians. Additionally, temporary analysts (Student Interns) are usually employed during summer months due to a considerable seasonal increase in the Unit's workload.

The Organic Unit is responsible for the detection and measurement of organic contaminants in water, sediment, and other environmental substrates. The unit is involved in the analysis of volatile and extractable organic compounds using gas and liquid chromatography and mass spectrometry. The organic compounds detected include chlorinated solvents such as methylene chloride, trichloroethylene, benzene, etc., chlorinated pesticides such as DDT, Dieldrin, chlordane, etc., and other

compounds such as PCB's, phenols and polynuclear aromatic hydrocarbons. The Unit is also responsible for the operation of the Mobile Laboratory. The Unit consists of a unit supervisor, lead workers, laboratory scientists and technicians.

1.D.2. UNIT QA/QC MANAGEMENT

Each position in the Laboratory has a minimum time commitment of approximately 25% to quality assurance and/or quality control activities.

1.D.2.a. Unit Supervisor

The unit supervisors have the responsibility of establishing the general QA policy for the their unit. The unit supervisor also identifies the QC audits for each parameter and has the ultimate responsibility of reviewing program effectiveness. Additional duties include staff assignments, approving methodology documentation and modifications, control limits, control audits and reviewing and approving unit results.

1.D.2.b. Lead Workers

The lead workers' general responsibilities include technical supervision of the analysts, development of new methods, sample analyses with more complex procedures, and maintenance of the daily operations of the unit. The lead workers are also responsible for reviewing each analyst's output to ensure that QC procedures are properly interpreted and followed. The frequency of review depends upon the complexity of the method and the familiarity of the analyst with the method. This equates to a 25% minimum time commitment.

1.D.2.c. Quality Assurance Coordinator

One of the laboratory scientists is assigned the duty of being the unit's quality assurance coordinator. The additional responsibilities include serving as the unit's representative on the Laboratory Quality Assurance Team. The QA coordinator is also responsible for assisting with the periodic review and assessment of the unit's QA/QC program and for the performance of special related projects. A 25% minimum time allotment is necessary.

1.D.2.d. Analysts

Each analyst is responsible for understanding the laboratory's QA policy. They must also understand and perform the QC audits which have been identified for the analytical procedures they perform. All QC audits are immediately reviewed to verify that they are within the specified control limits. Out-of-control audits indicate that some aspect of the analytical procedure is not performing properly. The problem should be located and corrected. This may be a very complicated task. The analytical batch may then be repeated. This may not be possible if the holding time has been exceeded or insufficient sample volume remains.

The lead worker and the unit supervisor have authority to approve the reporting of a batch of results when control limits are exceeded based on the other audits. Questionable audits must be discussed with the lead worker or the unit supervisor. Only data with acceptable audits are reported without a qualifier such as an appropriate laboratory

remark code. Highly doubtful data are not reported. Each analyst allots a 25% minimum time commitment for QC.

1.D.2.e. Total Time Commitment

The minimum total time commitment for QA/QC functions in the Units is approximately 25%.

1.D.3. PARAMETERS ANALYZED BY THE ENVIRONMENTAL LABORATORY UNITS

1.D.3.a. Analytical Responsibilities

Tables 1.D.-1, 1.E.-1, and 1.F.-1 contain the parameters for which the Environmental Laboratory UNITS have primary responsibility and the matrices for which analyses are practical. The methods generally conform to those proposed by the US EPA for NPDES compliance or RCRA monitoring.

1.D.3.b. Primary Analysts

Primary assignment of parameters to laboratory scientists or laboratory technicians is based on the difficulty of the procedure, the complexity of the instrumentation involved, quantity of workload anticipated, and the degree of methodology documentation. In addition to primary analytical responsibilities each analyst has secondary parameter assignments which are made to provide depth and flexibility to each unit, increase each analyst's area of expertise, and promote new insight into established laboratory procedures.

1.D.4. METHODOLOGY STATUS

1.D.4.a. Documentation of Methods

The Laboratory recognizes the necessity of documenting the ability to perform analyses by suitable established methodologies.
Tables 1.D,E,F.-1 contain a brief summary of the most common parameters analyzed, matrices, method descriptions and method references.

1.D.5. ANALYST PROFICIENCY

The Laboratory recognizes the necessity of having qualified analysts with demonstrated competency performing all analyses. The exhibition of proficiency is especially important when new analysts are being trained or existing analysts learn or develop new procedures. The ability to properly perform the analysis is measured through QC audits, observation of the lead worker who technically supervises the analysis, and by the unit supervisor. Generally two or more trained analysts are maintained for each routine parameter. This is particularly important if the holding time for the parameter is short. The degree of competency demonstration necessary depends upon the difficulty of the particular analysis and the analyst's background with similar methodologies.

1.D.6. EQUIPMENT LOG BOOKS

1.D.6.a. Log Book Information

Equipment log book information is maintained for major instruments with variables which could affect analytical results. The pertinent information for each instrument will vary but the type of information which should be documented may include:

-- Name, address, and phone numbers of supplier and service personnel.

__ Location of instrument's operating and service manuals.

__ A schedule of routine maintenance required to ensure proper instrument operation.

-- Any equipment servive that is performed

__ Various audits and control limits used to ensure proper instrument operation.

-- Comments on daily operation of instrument.

1.D.7. SAMPLE AND DATA HANDLING

1.D.7.a. Sample Receiving

Samples are received at the Environmental Laboratory by specially trained personnel in Sample Receiving. They receive, review, number and log the samples. The unit's representative reviews the sample sheets and checks that all necessary sample bottles are present and properly numbered. Any errors or questions are brought to the immediate attention of the sample receiver and corrected. Samples are then either delivered to the responsible analyst (particularly very short holding time parameters) or stored numerically by laboratory sample number in the cold room or sample refrigerator.

1.D.7.b. Sample Logging

Samples are entered in the Laboratory's LIM System by the appropriate staff after notification by Sample Receiving. The project header should include laboratory order number, date of receipt, and a project name. If the project has a high priority, is to be charged to a special cost center, or has special requirements or instructions, these are entered and brought to staffs attention. Any special instructions should also be brought to the attention of the appropriate analyst(s).

For each project or order number, the following information to be included is:

-- the assigned laboratory number,
-- field sample identification information,
-- the parameters requested by the field personnel,
-- additional parameters required to calculate the requested parameters,
-- additional parameters which may be automatically obtained from multi-channel analytical systems, and
-- any additional pertinent sample information.

Each batch of samples gets a unique log number and the samples in the batch are asigned sample numbers sequentially by the lab computer.

1.D.7.c. Assignment of Workload

Each analyst is responsible for reviewing their computer generated work sheets and making their own work assignments. Factors considered are holding time, priority assignment, sample backlog, and workload volume. The unit supervisor or a lead worker may modify assignments as deemed necessary for efficient unit operation.

1.D.7.d. Record Keeping

Bench sheets, sample record books, equipment log books, and/or QC records are to be filled out in ink with <u>all</u> pertinent information. There should be sufficient clarity that any trained analyst could easily interpret the results. All original information should be stored in

accordance with laboratory policy. Transcription of raw data should be avoided. Any sample peculiarities or interferences should be noted and clearly stated.

1.D.7.e. Review of Data

Each analyst immediately reviews the instrument and QC audits for compliance with control limits. Problems are addressed according to laboratory procedures.

The unit supervisor, or lead workers during his absences, reviews the values. Items to be considered may include:

-- proper correlation of related parameters,
-- reasonable trends within batches of related samples, and
-- comparison with previous results from the same sampling location, if readily available.

Questionable data is investigated as thoroughly as possible and reanalyzed if deemed necessary and possible.

1.D.7.f. Data Reporting

Analytical results are entered by automatic transfer or manually into the Lab's LIM System. Draft reports are printed when all data is recorder and distributed to the unit supervisor for review. Any pertinent laboratory remark codes are also reported with the data. After review the draft reports are signed by the unit supervisor and submitted to LIM's personnel. The reports are then entered as verified and a final report is printed. One copy of the final report is submitted for transmittal to the appropriate data user and a second is retained at the laboratory.

MICHIGAN DEPARTMENT OF NATURAL RESOURCES	PROCEDURE	NO.: PD-14
	ENVIRONMENTAL LABORATORY	DATE REV 11-3-92

SUBJECT: Methodology Approval

POLICY: Each quantitative analytical method used in environmental monitoring shall be evaluated and approved by the Laboratory.

EFFECTIVE DATE: November 3, 1992

Before any new or "alternate" test procedure can be used in analyzing samples for environmental monitoring, the method of analysis shall be evaluated by the analyst and approved by the unit supervisor and the Laboratory Director. The following steps are recommended but may not be practical for all parameters:

1. Literature Search - Lists of "EPA approved" methods (40 CFR 136) should be consulted where applicable. Standard references (Standard Methods. . ., EPA Methods. . ., ASTM. . ., etc.) and journal articles should be reviewed. Methods should be evaluated in relation to the availability of existing or cost of new equipment, lack of common interferences, complexity of analytical techniques required, detection capabilities of the method and suitability of the method for the type of sample normally analyzed. If a new or alternate method is not an EPA "approved" method, the procedure for alternate test procedure established by EPA must be followed and application for equivalency or approval must be made to EPA.

2. Standardization - Necessary equipment, reagents and standards should be prepared and a standard calibration curve made containing sufficient (a minimal of five points plus zero) points to establish the analytical working range of the method. Each point should be replicated to verify its accuracy.

3. Detection Limit - The detection limit of the method should be established using Environmental Laboratory Procedure No. PD-06.

4. Precision - The precision of the method should be determined by performing replicate analyses on natural (from actual samples) samples covering the analytical range of the method. Generally, about seven replicates each of a low (< 10% of full scale [f.s.]), medium (20-50% f.s.) and high (60-90% f.s.) sample are sufficient. Appropriate routine precision QC data may be substituted if available.

5. Accuracy - Where applicable, the accuracy of the method should be established by spiking known concentrations of analytes into actual sample matrixes as in (4) above and calculating

the % recovery. Again, use actual samples for accuracy as were used for precision. Two sets of at least seven replicate samples will be spiked. The first set should be low concentration (<10% of f.s.) spiked with low concentration analytes (about 5%-10% f.s.), and the second set should be medium concentration (20%-50% f.s.) and spiked with analytes in the concentration range of 25 to 40%.

$$\% \text{ Recovery} = \frac{(\text{conc. spiked sample} - \text{conc. original sample}) \times 100\%}{\text{theoretical spike conc.}}$$

6. Reference Samples - If available, reference samples (EPA, etc.) should be analyzed to check the method's performance against unknown standards.

7. Interferences - The effects of known or possible interferences should be evaluated by spiking suspect interferences into samples or standards with established values. The effects, if any, should be documented.

8. Written Procedure - The unit supervisor or lead worker and analyst should decide the suitability and practicality of the method. If found acceptable, the method should be written up following a standard format (PD-15) and submitted to the Laboratory Director for approval.

9. Final Approval - The Laboratory Director shall review and approve or reject (with comments) the method. Methods must be numbered appropriately for addition to the MDNR's "Analytical Methods for Environmental Samples". The Lab secretary shall maintain a file of the originals.

10. Use of unapproved Methods - If values from a method must be used before the method completes the approval process, these values shall be appropriately coded to indicate that the method has not yet been approved by the Laboratory.

Approved:

11/5/92

George Su, Laboratory Director

Appendix 1.C.-2

MICHIGAN DEPARTMENT OF NATURAL RESOURCES	POLICY	NO.: PC-04
	ENVIRONMENTAL LABORATORY	DATE: Rev. 10-20-92

SUBJECT: Minimal Requirements for an Analytical Quality Assurance Program

EFFECTIVE DATE: October 20, 1992

1. Commitment of Effort
   - 1.1 A minimum of 15% of the total analytical effort should be committed to quality control and quality assurance activities.
   - 1.2 To balance the workload demand and quality control, no more than 30% of the total analytical effort should be spent on routine quality control audits.
   - 1.3 Each laboratory unit should designate a member to the Quality Assurance Team who will spend not more than 10% of his/her time on team activities.

2. Type of Analysis
   - 2.1 Each laboratory analysis shall be classified into one of three types. The specific requirements for test procedure, quality control and reporting results are listed in Table 1.

3. Approved Analytical Methods
   - 3.1 Quantitative analyses (Type I) must be conducted using a laboratory approved method which is suitable for the matrix and applicable range.
   - 3.2 Semi-quantitative analyses (Type II) must be conducted according to a laboratory approved method or method validated for environmental analyses.

4. Routine Quality Control Audits
   - 4.1 All Type I quantitative analyses must have established quality control audits and control limits for calibration, precision and, where applicable, accuracy.
   - 4.2 Quality control audits must be suitable for the analyses so that an accurate determination of an in or out-of-control situation can be made.
   - 4.3 Once a reliable estimate of the population standard deviation is obtained, the control limits should not exceed 3 standard deviations.

5. Procedures for Preventing and Correcting Out-of-Control Situations
   - 5.1 Each laboratory unit shall develop guidelines for preventing and correcting out-of-control situations.

5.1.1 When a QC audit is outside the control limit, the analyst, the lead worker, or the supervisor must evaluate the situation and determine whether the system or the sample is out-of-control. The problem and the action taken must be brought to the attention of the lead worker or supervisor.

5.1.2 If the sample is out-of-control, the analysis should be repeated.

5.1.3 If the system is out-of-control, it must be stopped and corrected.

5.2 No on-going analyses shall be conducted when the system is out-of-control unless they are reclassified as a Type II or Type III analyses.

5.3 No result shall be reported when sample or system is out-of-control unless a proper result remark code is used.

6. Documentation of Performance

6.1 Performance on quality control audits shall be documented and statistically evaluated to determine control limits and updated as necessary.

6.2 A summary of precision and accuracy control data shall be made available to lab users so that reasonable estimations of confidence intervals can be made.

7. Equipment Log Book

7.1 The primary analyst and/or unit supervisor shall maintain an equipment log book for each major piece of analytical equipment and shall routinely record monitored variables.

Approved by:

George Su, Laboratory Director — 10/20/92 Date

TYPE OF ANALYSIS

	Test Procedure	Quality Control	Reporting Results
Type I Quantitative Analysis	Laboratory Approved Methods	Routine QC audits for the matrix and applicable concentration range, and Analytical system in control, and Properly collected and preserved sample and analyzed within maximum holding time.	Numerical
Type II Semi-quantitative Analysis	Laboratory Approved Methods or methods validated for environmental analysis	Insufficient or no routine QC audit for the matrix and applicable concentration range, or System out-of-control or unknown status, or Sample collection, preservation or holding time are different from the recommended procedure so that the accuracy of the results may be affected.	Numerical with appropriate result remark code
Type III Qualitative Analysis	May not have a Laboratory Approved Method or a validated method	No routine QC audits, or QC audits indicate a potential gross bias and source of bias unknown, or Sample collection, preservation or holding time are significantly different from the recommended procedures so that the accuracy of the results may be severely affected.	Statement or concentration range

MICHIGAN DEPARTMENT OF NATURAL RESOURCES	PROCEDURE	NO.: PD-15
	ENVIRONMENTAL LABORATORY	DATE REV. 11-5-92

SUBJECT: Methodology Write-Up Format

POLICY: Each method used by the Laboratory should be written using the following standard format. Each method should place particular emphasis on changes from referenced methods. Method addendums shall be added as necessary to identify methodology changes.

EFFECTIVE DATE: November 5, 1992

So that each analyst, data user or any other person requesting a Laboratory method will have a single reference for all procedures in use in the Laboratory, each method should be written in a standard format and updated when changes occur. Enough detail should be included so that other Laboratory personnel with similar equipment and knowledge of its proper operation could duplicate the method. The heading should contain "Michigan Department of Natural Resources-Environmental Laboratory", the parameter name, a method name and a STORET or SOROAD parameter code number, where applicable. Other information that should be included is as follows:

1. State method and EPA's reference method number or other reference number.

2. Scope and Application - A brief description including sample type, matrix, normal operating range, definition and significance of the parameter. Where appropriate, indicate circumstances in which this method may not be appropriate to use.

3. Summary of Method - A brief description of the method containing an explanation of the principles involved and the primary equipment used for analysis.

4. Sample Collection, Handling, Preservation and Holding Time - Include the volume or mass necessary for analysis, recommend sample container material and size, recommend physical or chemical preservatives, recommend maximum holding time and possible or probable effects of exceeding that holding time.

5. Interferences or Biases - Include possible interferences or biases to the method and how results would be affected, if present. Also discuss how interferences may be removed or the effects minimized.

6. Apparatus - List the equipment and laboratory supplies required to perform the method in the prescribed manner.

7. Reagents - Describe how all the necessary reagents and standards are prepared, for how long and under what conditions they may be stored. Specify any special safety concerns with each chemical.

8. Procedure - Include step by step instructions including normal instrument settings as to how to perform the test with sufficient detail that other knowledgeable Laboratory personnel with similar equipment could duplicate the method. Identify the routine calibration procedure. Note any special safety precautions which must be followed.

9. Quality Control Audits - Define the various quality control audits (and their frequency) which are used to determine whether the method and equipment are functioning properly and whether the analytical batch has sufficient precision and accuracy. The control limits used to determine when an out-of-control condition exists should be enumerated whenever practical (possibly in an appendix).

10. Calculation - Explain step-by-step instructions as to how the instrument output is reduced to meaningful data. Include necessary equations, etc.

11. Method Validation/Method Detection Limit - Include separate statements to define how the method is validated and specify the method detection limit, precision and accuracy of the method as evaluated during the methodology approval procedure (PD-14). Give specific information detailing how the statements were developed.

12. Report Detection Limit (See also PD-06) - Include the routine reported detection limit (RDL) that is used for data reporting purposes. If it differs from the method detection limit (MDL), identify the reason(s) for the difference(s).

13. References - List references which were used to obtain the method or could be used to check problems with it.

14. Approval - The analyst, unit supervisor and Laboratory Director should sign and date the method signifying acceptance of the procedure.

The method and pages must be numbered appropriately for inclusion in the Laboratory's methods manual. Any significant methodology changes should be documented in an addendum to the method. Major changes should be documented through a revised method.

APPROVED:

George Su, Laboratory Director — Date 11/5/92

EL 070
12/93
MATRIX = WATER

MICHIGAN DEPT OF NATURAL RESOURCES
ENVIRONMENTAL LABORATORY
ANALYSIS REQUEST SHEET

SAFETY WARNING
YES / NO - INFO ON B

##

COSTS FOR WATER SAMPLES

SAMPLE NUMBER	FIELD ID OR DESCRIPTION (25 Characters)	SAMPLE COLLECTED YY/MM/DD	HH:MM	SAMPLE INFORMATION
01				
02				
03				
04				
05				

GENERAL CHEMISTRY

DO	Diss Oxygen ...	8.30	
GN	NO2, o-Phos ...	9.50	
	Residue SS	13.30	
	Residue TDS ...	13.30	
	.....		
	BOD Tot 5 day	33.00	
	BOD Carb 5 day	33.00	
	.....		
CA	Chlorophyll ...	13.35	
GA	COD	19.70	
	TOC	15.90	
	NO3+NO2, NH3 ..	9.50/ea	
	KJEL N, Tot P .	13.30/ea	
	.....		
GG	Phenolics . .	13.30/33.00	
GB	Total CN.....	33.00	
	Free CN	53.30	
	.....		
	.....		

ORGANICS

PO1	#1 Halocarbons	33.00	
PO2	#2 Aromatic HC	33.00	
	.....		
ON	#3 Chloro HC + Pest & PCB .	160.00	
	.....		
OB	GC/MS Base Neut	142.50	
	.....		
OA	#8 Phenols	130.62	
	.....		
ADDITIONAL			
	8260	95.00	
	BTEX ONLY	60.00	

INORGANIC

MA	Total Metals		
MAD	Diss-Field Filtered ...		
MD	Diss-Lab Filtered	7.00	
	Ca Mg Na K	4.45/ea	
	Cd Cr Cu Ni Pb Zn	10.80/ea	
	Fe Co Li Mn	10.80/ea	
	Al Ba Be Mo Ti V	10.80/ea	
	.....		
	Hg - Mercury	26.70	
	As - Arsenic	26.70	
	Se - Selenium	26.70	
	Sb - Antimony	26.70	
	.....		
	LOW LEVEL Ag	15.90	
	" " Cd	15.90	
	" " Cr Cu Ni Pb ..	15.90	
	" " Zn Fe	13.30/ea	
MN	pH, Conductance	4.45/ea	
	Cl, SO4, Total Alk	5.70/ea	
	HCO3- CO3=	3.20/ea	
	CR+6	10.80	
	OIL & GREASE	33.00	

Appendix 1.C.-4 Continued

EL 099
9/93
MATRIX = AIR

MICHIGAN DEPT OF NATURAL RESOURCES
ENVIRONMENTAL LABORATORY
ANALYSIS REQUEST SHEET

SAFETY WARNING
YES / NO - INFO ON BACK

A I R C O S T S

SAMPLE NUMBER	FIELD ID OR DESCRIPTION	SAMPLE COLLECTED YY/MM/DD	HH:MM	SAMPLE INFORMATION
01				
02				
03				
04				
05				
06				
07				
08				

CANISTER	BAG SAMPLE	PUF SAMPLES	OTHERS (PREARRANGED)
Halocarbons 380.00/EA 1 2 3 4 5 6 7 8	Halocarbon 380.00/EA 1 2 3 4 5 6 7 8	(FUTURE USE)	_____ 1 2 3 4 5 6 7 8
Aromatics 380.00/EA 1 2 3 4 5 6 7 8	Aromatics 380.00/EA 1 2 3 4 5 6 7 8		_____ 1 2 3 4 5 6 7 8
Compound ID 380.00/EA 1 2 3 4 5 6 7 8	Compound ID 380.00/EA 1 2 3 4 5 6 7 8		_____ 1 2 3 4 5 6 7 8
Others _____ 1 2 3 4 5 6 7 8	Others _____ 1 2 3 4 5 6 7 8		_____ 1 2 3 4 5 6 7 8

EL 086
9/93
MATRIX = EP TOX / ASTM LEACHATE / TCLP / SP

MICHIGAN DEPT OF NATURAL RESOURCES
ENVIRONMENTAL LABORATORY
ANALYSIS REQUEST SHEET

SAFETY WARNING
YES / NO - INFO ON BACK

C O S T S

EP TOX / ASTM / LEACHATE / TCLP / SP

SAMPLE NUMBER	FIELD ID OR DESCRIPTION	SAMPLE COLLECTED YY/MM/DD	HH:MM	SAMPLE INFORMATION
01				
02				
03				
04				
05				
06				
07				
08				

GENERAL CHEMISTRY

GS	Ortho P, NO2 ..	7.00	/EA
	....		
A	COD	19.70	
S	....		
T	TOC	15.90	
M	....		
	NO3+NO2, NH3 ..	8.50	/EA
L	....		
E	KJEL N, Tot P .	13.30	/EA
A	....		
C	Phenolics	13.30	
H	....		
A	Total CN	33.00	
T	....		
E	% TS	4.45	
	....		
	....		
	ASTM	40.00	
	....		

ORGANICS

TCLP		
	VOLATILES	142.50
	.....extraction	66.70
	.... (×17)	

INORGANIC

MS	ASTM Leaching	40.00	
	....		
A	Cl, SO4, Alk	5.70	/EA
S	Cr+6	10.80	
T	Ca, Mg, Na, K	4.45	/EA
M	Cd Cr Cu Ni Pb Zn	10.80	/EA
	Fe Co Li Mn	10.80	/EA
	Al Ba Be Mo T..........	10.80	/EA
	Hg, As, Se, Sb	26.70	/EA

EP TOX/TCLP/SP	66.70	
....		
Cd Cr Cu Ni Pb Zn	13.30	/EA
Ag - Silver	19.70	
Ba - Barium	13.30	
Hg - Mercury	53.35	
As - Arsenic	53.35	
Se - Selenium..........	53.35	

EL 085
9/93
MATRIX = ORGANIC / OIL

MICHIGAN DEPT OF NATURAL RESOURCES
ENVIRONMENTAL LABORATORY
ANALYSIS REQUEST SHEET

SAFETY WARNING
YES / NO - INFO ON BACK

O I L C O S T S

SAMPLE NUMBER	FIELD ID OR DESCRIPTION	SAMPLE COLLECTED YY/MM/DD	SAMPLE COLLECTED HH:MM	SAMPLE INFORMATION
01				
02				
03				
04				
05				
06				
07				
08				

GENERAL CHEMISTRY

HW	FLASH POINT	26.70

ORGANICS

OL	#1 Halocarbons (Quantitative)	46.40
	#2 Aromatic HC (Quantitative)	46.40
	#3 Chloro HC + Pest & PCB	213.40
	PCB Only	186.70

INORGANIC

MO	Ca Mg Na K	7.00
	Cd Cr Cu Ni Pb Zn	13.30
	Fe Co Li Mn	13.30
	Al Ba Be Mo Ti V	13.30
	Hg - Mercury	33.00
	As - Arsenic	53.30
	% Cl	46.40
	BTU.....	33.00
	% Sulfur.....	19.70
	% Ash.....	26.70
	% H2O.....	19.70

EL 06B
9/93
MATRIX = SEDIMENT/ SOIL

MICHIGAN DEPT OF NATURAL RESOURCES
ENVIRONMENTAL LABORATORY
ANALYSIS REQUEST SHEET

SAFETY WARNING
YES / NO - INFO ON BACK

SEDIMENT COSTS

SAMPLE NUMBER	FIELD ID OR DESCRIPTION	SAMPLE COLLECTED YY/MM/DD	HH:MM	SAMPLE INFORMATION
01				
02				
03				
04				
05				
06				
07				
08				

GENERAL CHEMISTRY

GS	COD	40.00
	.....	
	KJEL N, Tot P .	15.90/EA
	.....	
	Phenolics	40.00
	.....	
	Total CN	46.40
	.....	
	% Total Solids	4.45
	.....	
	.....	
	.....	
	.....	
	.....	
	.....	
	.....	
	.....	

ORGANICS

POV	VOLATILES	
	8260 (Sc 1,2)...	95.00
	BTEX (only).....	60.00
DS	CHLORO HC +PEST & PCB	
	8081/8121.(Sc3).	266.70
	PCB (only).....	226.70
	8207 (BN)	237.50

SPECIAL REQUESTS

Lib Search	(Qualitative)	
	Volatives ...	142.50
	Base Neutral	95.00
	.....	
	.....	

INORGANIC

MS	Ca Mg Na K	7.00
	.....	
	Cd Cr Cu Ni Pb Zn	12.00
	.....	
	Fe Co Li Mn	12.00
	.....	
	Al Ba Be Mo Ti V	12.00
	.....	
	Hg - Mercury	33.00
	As - Arsenic	46.40
	Se - Selenium.....	47.00
	.....	
	.....	
	% Total Solids	4.50/EA
	.....	
	.....	

MICHIGAN DEPARTMENT OF NATURAL RESOURCES	PROCEDURE	NO. PD-26
	ENVIRONMENTAL LABORATORY	DATE: 8-1-83

SUBJECT: Method Development Request

EFFECTIVE DATE: August 1, 1983

In order that the Environmental Laboratory may best utilize its available resources for method development, it is necessary to prioritize the needs of the EPB for new or modified analyses. The following protocol will allow the Laboratory to maximize its ability to serve the Bureau in this area.

Step 1. The Program Manager should fill out Part I of the Method Development Request Form and send it to the Laboratory.

Step 2. The appropriate Laboratory personnel, usually the Unit Chief that would be in charge of the analysis and the Laboratory Director, review the request and fill out Part II of the form within two weeks and provide their recommendations to the Program Manager.

Step 3. The Program Manager replies, if necessary, within two weeks.

Step 4. When two or more requests are submitted by a single division, they should be prioritized by that division.

Step 5. The Laboratory Management Team compares the method development request with others received and prioritizes them.

Step 6. Any conflict in priority that arises will be resolved by the Environmental Services Division Chief or the Bureau Management Team.

Part 1

The program manager should first list the parameter or parameter group and the matrices or substances (e.g. water, sludge, tissue) for which he/she wants methods developed.

The significance of the parameter as a pollutant or contaminant should be described in the next section. Details on its effect on the environment including its toxicity, its persistence and its potential for getting into the water and air should be summarized. Information on whether it is manufactured in Michigan or how much is used in Michigan should also be noted. Data on the parameter's carcinogenicity, teratogenicity, etc. should be included in the persistance section of the form.

Information relating to whether the new chemical or group of chemicals is expected to be a one time problem or a continuing one should be included in the next section. An estimation of how many samples a month for how long a period should be made.

The required detection limit should be stated for each substrate. The precision or reproducibility needed should be noted and if there is a specific "cut off" value(s) about which the standard deviation is needed, this should be requested. If there are special accuracy or percent recovery requirements, these should also be noted.

A short summary should conclude the Program Manager's request for method development and a statement made relative to the impact to his/her program if a method cannot be developed.

Part 2

Once a request is received for a certain parameter(s) and substrate(s) the status of current methodology will be determined. The supervisor of the unit where the parameter will be analyzed, will check the box that best denotes the method status, briefly describe the method and list reference(s).

The next step will be to evaluate the additional resources needed in order to develop and utilize the method. New equipment and supplies needed should be listed with approximate costs. If special training is needed, the time and cost should be entered. If personnel need to be hired or transferred, this should also be noted with approximate costs.

The cost of providing laboratory space for the development work, whether through displacement of other work, renovation, or procurement of additional space, should be estimated. The amount of space needed should be described.

The availability of a private laboratory (contractor) that could provide the analysis should be determined. The cost of having a private lab(s) do the development work and the analyses should be compared to the cost of doing it in-house. The ability of the private lab to reach the required detection limit and satisfy the necessary recovery and repeatability limits should also be compared with the Environmental Laboratory.

Laboratory personnel should summarize the information and make the decision on whether or not to contract out the method development work. A detailed rationale should be given for the decision. An attempt should be made at comparing the importance of the method development request with other requests received so that they can be put in some kind of priority order.

Approved

Tung Kai Wu

Tung Kai Wu
Laboratory Director

Department of Natural Resources
Environmental Services Division

REQUEST FOR METHOD DEVELOPMENT

Part I - Program Manager

Name

Phone no.

Date

Parameter

Matrix

SIGNIFICANCE

Effect on environment

Toxicity

Potential for reaching the environment

Use in Michigan

Persistance in the environment

SCOPE

Long term or short term, if short term state duration

Estimated number of samples per month

REQUIREMENTS

Detection limit and concentration range

Precision (% RSD)

Accuracy (% Recovery)

Approval

Date

R 4415
6/83

APPENDIX 1.C.-5. continued

Department of Natural Resources
Environmental Services Division

REQUEST FOR METHOD DEVELOPMENT

Part II - Environmental Labortory

Lab Unit

Name

Target Date

Parameter

Matrix

STATUS

☐ Approved Method ☐ Validated Method ☐ Adaptable Method ☐ Literature Search ☐ From Scratch

Method

Reference

RESOURCE NEEDS

Equipment — Est. Costs

Personnel & Training

_____ hours

$ _____

Supplies — Est. Costs

Facility

Additional Space

_____ sq. ft.

Renovation

$ _____

EVALUATION

Cost Comparison

Quality Comparison

RECOMMENDATION

☐ Develop method in house ☐ Contract Out

Justification:

Approval

Date

MICHIGAN DEPARTMENT OF NATURAL RESOURCES	PROCEDURE	NO.: PD-06
	ENVIRONMENTAL LABORATORY	DATE: Rev. 10/12/84

SUBJECT: Estimation of Method Detection Limit (MDL) and Reported Detection Limit (RDL)

POLICY: Each routine quantitative (Type I) laboratory method shall have a detection limit. A method detection limit is the minimum concentration of a substance that can be analyzed with 99% confidence that the analyte is actually present (based on one tailed student t distribution). A reported detection limit may be used for reporting purposes if the MDL is not obtainable on routine samples.

EFFECTIVE DATE: October 15, 1984

Method Detection Limit

The attached procedure, "Appendix A: Definition and Procedure for the Determination of the Method Detection Limit" from Methods for Organic Chemical Analysis of Municipal and Industrial Wastewater, EPA-600/4-82-057, is to be used for calculating the MDL.

The MDL is initially calculated as part of the method validation procedure. The primary analyst should discuss with their lead worker and/or unit supervisor: 1) the matrix(es) to be used, 2) the expected MDL, 3) the number of replicates which should be analyzed, and 4) whether spiking with standards will be necessary. The MDL's should be documented with the methodology write-up (see PD-15, "Methodology Write-Up Format", Section 10, Validation).

The MDL may need to be reevaluated periodically, particularly if any significant changes are made to a method. Each method should also have a routine QC audit designed to monitor sensitivity, such as the response (absorbance, peak area count, etc.) of a low level standard, to verify that the MDL is approachable.

Reported Detection Limit

The reported detection limit is simply the detection limit used to report data. Frequently it may be impractical to expect a method to routinely achieve the method detection limit. In such cases the RDL may be substituted for the MDL to report data. The RDL shall be based on the MDL and the reason(s) for its use shall be documented (see PD-15, "Methodology Write-Up Format", Section 11, Reported Detection Limit). Typical reasons for using RDL's include: 1) rounding off to the nearest five or ten, 2) to facilitate reporting (i.e. adjusting a group of compounds in a GC scan to the least sensitive compound, or 3) accounting for common interferences, such as iron or phthalates, which may not have been practically reflected in the MDL determination.

In any case, the reported detection limit should be adjusted high enough to prevent a significant number of false positives, but low enough to prevent a significant number of false negatives.

Approved by:

Tung Kai Wu
Laboratory Director

Appendix A

Definition and Procedure for the Determination of the Method Detection Limit

The method detection limit (MDL) is defined as the minimum concentration of a substance that can be identified, measured and reported with 99% confidence that the analyte concentration is greater than zero and determined from analysis of a sample in a given matrix containing analyte.

Scope and Application

This procedure is designed for applicability to a wide variety of sample types ranging from reagent (blank) water containing analyte to wastewater containing analyte. The MDL for an analytical procedure may vary as a function of sample type. The procedure requires a complete, specific and well defined analytical method. It is essential that all sample processing steps of the analytical method be included in the determination of the method detection limit.

The MDL obtained by this procedure is used to judge the significance of a single measurement of a future sample.

The MDL procedure was designed for applicability to a broad variety of physical and chemical methods. To accomplish this, the procedure was made device- or instrument-independent.

Procedure

1. Make an estimate of the detection limit using one of the following:

   (a) The concentration value that corresponds to an instrument signal/noise ratio in the range of 2.5 to 5. If the criteria for qualitative identification of the analyte is based upon pattern recognition techniques, the least abundant signal necessary to achieve identification must be considered in making the estimate.
   (b) The concentration value that corresponds to three times the standard deviation of replicate instrumental measurements for the analyte in reagent water.
   (c) The concentration value that corresponds to the region of the standard curve where there is a significant change in sensitivity at low analyte concentrations, i.e., a break in the slope of the standard curve.
   (d) The concentration value that corresponds to known instrumental limitations.

   It is recognized that the experience of the analyst is important to this process. However, the analyst must include the above considerations in the estimate of the detection limit.

2. Prepare reagent (blank) water that is as free of analyte as possible. Reagent or interference free water is defined as a water sample in which analyte and interferent concentrations are not detected at the method detection limit of each analyte of interest. Interferences are defined as systematic errors in the measured analytical signal of an established procedure caused by the presence of interfering species (interferent). The interferent concentration is presupposed to be normally distributed in representative samples of a given matrix.

3. (a) If the MDL is to be determined in reagent water (blank), prepare a laboratory standard (analyte in reagent water) at a concentration which is at least equal to or in the same concentration range as the estimated MDL. (Recommend between 1 and 5 times the estimated MDL.) Proceed to Step 4.

(b) If the MDL is to be determined in another sample matrix, analyze the sample. If the measured level of the analyte is in the recommended range of one to five times the estimated MDL, proceed to Step 4.

If the measured concentration of analyte is less than the estimated MDL, add a known amount of analyte to bring the concentration of analyte to between one and five times the MDL. In the case where an interference is coanalyzed with the analyte:

If the measured level of analyte is greater than five times the estimated MDL, there are two options:

(1) Obtain another sample of lower level of analyte in same matrix if possible.
(2) The sample may be used as is for determining the MDL if the analyte level does not exceed 10 times the MDL of the analyte in reagent water. The variance of the analytical method changes as the analyte concentration increases from the MDL, hence the MDL determined under these circumstances may not truly reflect method variance at lower analyte concentrations.

4. (a) Take a minimum of seven aliquots of the sample to be used to calculate the MDL and process each through the entire analytical method. Make all computations according to the defined method with final results in the method reporting units. If blank measurements are required to calculate the measured level of analyte, obtain separate blank measurements for each sample aliquot analyzed. The average blank measurement is subtracted from the respective sample measurements.
(b) It may be economically and technically deirable to evaluate the estimated MDL before proceeding with 4a. This will: (1) prevent repeating this entire procedure when the costs of analyses are high and (2) insure that the procedure is being conducted at the correct concentration. It is quite possible that an incorrect MDL can be calculated from data obtained at many times the real MDL even though the background concentration of analyte is less than five times the calculated MDL. To insure that the estimate of the MDL is a good estimate, it is necessary to determine that a lower concentration of analyte will not result in a significantly lower MDL. Take two aliquots of the sample to be used to calculate the MDL and process each through the entire method, including blank measurements as described above in 4a. Evaluate these data:

(1) If these measurements indicate the sample is in the desirable range for determining the MDL, take five additional aliquots and proceed. Use all seven measurements to calculate the MDL.
(2) If these measurements indicate the sample is not in the correct range, reestimate the MDL, obtain new sample as in 3 and repeat either 4a or 4b.

5. Calculate the variance (S^2) and standard deviation (S) of the replicate measurements, as follows:

$$S^2 = \frac{1}{n-1}\left[\sum_{i=1}^{n} X_i^2 - \left(\sum_{i=1}^{n} X_i\right)^2 \Big/ n\right]$$

$$S = (S^2)^{1/2}$$

where: the x_i, i = 1 to n are the analytical results in the final method reporting units obtained from the n sample aliquots and $\sum_{i=1}^{n} X_i^2$ refers to the sum of the X values from i = 1 to n.

6. (a) Compute the MDL as follows:

$$MDL = t_{(n-1,\ 1-\alpha\ =\ .99)}(S) .$$

where:

MDL = the method detection

$t_{(n-1,\ 1-\alpha\ =\ .99)}$ = the students' t value appropriate for a 99% confidence level and a standard deviation estimate with n-1 degrees of freedom. See Table.

S = standard deviation of the replicate analyses.

(b) The 95% confidence limits for the MDL derived in 6a are computed according to the following equations derived from percentiles of the chi square over degrees of freedom distribution (X^2/df) and calculated as follows:

$MDL_{LCL} = 0.64\,MDL$
$MDL_{UCL} = 2.20\,MDL$

where MDL_{LCL} and MDL_{UCL} are the lower and upper 95% confidence limits respectively based on seven aliquots.

7. Optional iterative procedure to verify the reasonableness of the estimated MDL and calculated MDL of subsequent MDL determinations.

(a) If this is the initial attempt to compute MDL based on the estimated MDL in Step 1, take the MDL as calculated in Step 6, spike in the matrix at the calculated MDL and proceed through the procedure starting with Step 4.

(b) If the current MDL determination is an iteration of the MDL procedure for which the spiking level does not permit qualitative identification, report the MDL as that concentration between the current spike level and the previous spike level which allows qualitative identification.
If the current MDL determination is an iteration of the MDL procedure and the spiking level allows qualitative identification, use S^2 from the current MDL calculation and S^2 from the previous MDL calculation to compute the F ratio.

$$\text{if } \frac{S_A^2}{S_B^2} < 3.05$$

then compute the pooled standard deviation by the following equation:

$$S_{pooled} = \left[\frac{6S_A^2 + 6S_B^2}{12}\right]^{1/2}$$

if $\frac{S_A^2}{S_B^2} > 3.05$, respike at the last calculated MDL and process the samples through the procedure starting with Step 4.

(c) Use the S_{pooled} as calculated in 7b to compute the final MDL according to the following equation:

$MDL = 2.681\ (S_{pooled})$

where 2.681 is equal to $t_{(12,\ 1-\alpha\ =\ .99)}$.

(d) The 95% confidence limits for MDL derived in 7c are computed according to the following equations derived from percentiles of the chi squared over degrees of freedom distribution.

$MDL_{LCL} = 0.72\ MDL$
$MDL_{UCL} = 1.65\ MDL$

where LCL and UCL are the lower and upper 95% confidence limits respectively based on 14 aliquots.

Reporting

The analytical method used must be specifically identified by number or title and the MDL for each analyte expressed in the appropriate method reporting units. If the analytical method permits options which affect the method detection limit, these conditions must be specified with the MDL value. The sample matrix used to

determine the MDL must also be identified with the MDL value. Report the mean analyte level with the MDL. If a laboratory standard or a sample that contained a known amount analyte was used for this determination, report the mean recovery, and indicate if the MDL determination was iterated.

If the level of the analyte in the sample matrix exceeds 10 times the MDL of the analyte in reagent water, do not report a value for the MDL.

Reference

Glaser, J. A., Foerst, D. L., McKee, G. D., Quave, S. A., and Budde, W. L., "Trace Analysis for Wastewaters," *Environmental Science and Technology, 15,* 1426 (1981).

Table of Students' t Values at the 99 Percent Confidence Level

Number of Replicates	*Degrees of Freedom (n-1)*	$t_{(n-1,\ 1-\alpha\ =\ 99\%)}$
7	*6*	*3.143*
8	*7*	*2.998*
9	*8*	*2.896*
10	*9*	*2.821*
11	*10*	*2.764*
16	*15*	*2.602*
21	*20*	*2.528*
26	*25*	*2.485*
31	*30*	*2.457*
61	*60*	*2.390*
∞	∞	*2.326*

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DEPARTMENT OF NATURAL RESOURCES-ENVIRONMENTAL RESPONSE DIVISION LABORTORY

Table 1. Detection Levels for Environmental Contamination Detection, Compliance, and Response Activities

VOLATILE ORGANICS 624/8260 *PLUS*	GROUNDWATER DNR Lab Reported Detection Limits (ug/l)	SEDIMENT/SOILS DNR Lab Reported Detection Limits (ug/kg)	ANALYTICAL METHOD EPA / SW-846	MDNR TECHNIQUE	SAMPLING CONTAINERS
Acrylonitrile	5	5	624/8260	8260 +	2- 40 ML
Benzene	1	5	624/8260	8260 +	GLASS VIALS
Bromochloromethane	1	5	624/8260	8260 +	W/ TELFON SEAL
Bromodichloromethane	1	5	624/8260	8260 +	"
Bromoform	1	5	624/8260	8260 +	"
Bromomethane	5	10	624/8260	8260 +	"
2-Butanone (MEK)	(5)	(10)	624/8260	8260 +	"
Carbon Disulfide	5	10	624/8260	8260 +	"
Carbon Tetrachloride	1	5	624/8260	8260 +	"
Chlorobenzene	1	5	624/8260	8260 +	"
Chloroethane	5	10	624/8260	8260 +	"
Chloroform	1	5	624/8260	8260 +	"
Chloromethane	5	10	624/8260	8260 +	"
Dibromochloromethane	1	5	624/8260	8260 +	"
1,2-Dibromo-3-chloropropane	5	10	624/8260	8260 +	"
Dibromomethane	1	5	624/8260	8260 +	"
1,2-Dibromoethane	1	5	624/8260	8260 +	"
1,2-Dichlorobenzene	1	5	624/8260	8260 +	"
1,3-Dichlorobenzene	1	5	624/8260	8260 +	"
1,4-Dichlorobenzene	1	5	624/8260	8260 +	"
1,4-Dichloro-2 butene (trans)	1	5	624/8260	8260 +	"
Dichlorodifluoromethane	5	10	624/8260	8260 +	"
1,1-Dichloroethane	1	5	624/8260	8260 +	"
1,2-Dichloroethane	1	5	624/8260	8260 +	"
1,1-Dichloroethene	1	5	624/8260	8260 +	"
1,2-Dichloroethene (cis)	1	5	624/8260	8260 +	"
1,2-Dichloroethene (trans)	1	5	624/8260	8260 +	"
1,2-Dichloropropane	1	5	624/8260	8260 +	"
1,3-Dichloropropene (cis)	1	5	624/8260	8260 +	"
1,3-Dichloropropene (trans)	1	5	624/8260	8260 +	"
Diethyl ether	10	10	624/8260	8260+	"
Ethylbenzene	1	5	624/8260	8260 +	"
Hexachloroethane	1	5	624/8260	8260 +	"
2-Hexanone	5	10	624/8260	8260 +	"
Isopropylbenzene	1	5	624/8260	8260 +	"
Methylene Chloride	(5)	(10)	624/8260	8260 +	"
Methyl Iodide	1	5	624/8260	8260 +	"
2-Methylnaphthalene	5	10	624/8260	8260 +	"
4-Methyl-2-Propanone (MIBK)	5	10	624/8260	8260 +	"
Methyl Tertiary Butyl Ether (MTBE)	5	10	624/8260	8260 +	"
Naphthalene	5	10	624/8260	8260 +	"
2-Propanone (acetone)	5	50	624/8260	8260 +	"
n-Propylbenzene	1	5	624/8260	8260 +	"
Styrene	1	5	624/8260	8260 +	"
1,1,1,2 - Tetrachloroethane	1	5	624/8260	8260+	"
1,1,2,2-Tetrachloroethane	1	5	624/8260	8260 +	"
Tetrachloroethene	1	5	624/8260	8260 +	"
Toluene	1	5	624/8260	8260 +	"
1,1,1-Trichlorethane	1	5	624/8260	8260 +	"
1,2,4-Trichlorobenzene	5	10	624/8260	8260 +	"
1,1,2-Trichloroethane	1	5	624/8260	8260 +	"
Trichloroethene	1	5	624/8260	8260 +	"
Trichlorofluoromethane	5	10	624/8260	8260 +	"
1,2,3-Trichloropropane	1	5	624/8260	8260 +	"
1,2,4-Trimethylbenzene	1	5	624/8260	8260 +	"
1,3,5-Trimethylbenzene	1	5	624/8260	8260 +	"
*Vinyl acetate	1	10	624/8260	8260 +	"
Vinyl Chloride	5	10	624/8260	8260 +	"
o-Xylene	1	5	624/8260	8260 +	"
m &p-Xylene	2	5	624/8260	8260 +	"

* *Indicates semiquantitative analysis*

APPENDIX 1.C-7 (Cont.)

VOLATILE ORGANICS 624/8260	GROUNDWATER DNR Lab Reported Detection Limits (ug/l)	SEDIMENT/SOILS DNR Lab Reported Detection Limits (ug/kg)	ANALYTICAL METHOD RCRA SW-846	SAMPLING CONTAINERS (waters)	SAMPLING CONTAINERS (sediments)
Chloromethane	5	10	624/8260	2 - 40 ML	2-40 ML GLASS VIALS
Vinyl Chloride	5	10	624/8260	GLASS VIALS	OR
Bromomethane	5	10	624/8260	"	2 - 4 OZ GLASS JARS
Chloroethane	5	10	624/8260	"	WITH TEFLON SEALS
2-Propanone (acetone)	25	50	624/8260	"	"
1,1-Dichloroethene	1	5	624/8260	"	"
Methylene Chloride	(5)	(10)	624/8260	"	"
Carbon Disulfide	5	10	624/8260	"	"
1,2-Dichloroethene (trans)	1	5	624/8260	"	"
Methyl Terbary Butyl Ether (MTBE	5	10	624/8260	"	"
1,1-Dichloroethane	1	5	624/8260	"	"
2-Butanone (MEK)	(5)	(10)	624/8260	"	"
1,2-Dichloroethene (cis)	1	5	624/8260	"	"
Chloroform	1	5	624/8260	"	"
1,1,1-Trichloroethane	1	5	624/8260	"	"
1,2-Dichloroethane	1	5	624/8260	"	"
Benzene	1	5	624/8260	"	"
Carbon Tetrachloride	1	5	624/8260	"	"
1,2-Dichloropropane	1	5	624/8260	"	"
Trichloroethene	1	5	624/8260	"	"
Bromodichloromethane	1	5	624/8260	"	"
2-Hexanone	5	10	624/8260	"	"
1,3-Dichloropropene(cis)	1	5	624/8260	"	"
1,3-Dichloropropene (trans)	1	5	624/8260	"	"
Toluene	1	5	624/8260	"	"
1,1,2-Trichloroethane	1	5	624/8260	"	"
4-Methyl-2-Propanone (MIBK)	5	10	624/8260	"	"
Dibromochloromethane	1	5	624/8260	"	"
1,2-Dibromoethane	1	5	624/8260	"	"
Tetrachloroethene	1	5	624/8260	"	"
Chlorobenzene	1	5	624/8260	"	"
Ethylbenzene	1	5	624/8260	"	"
m & p-Xylene	2	5	624/8260	"	"
Bromoform	1	5	624/8260	"	"
Styrene	1	5	624/8260	"	"
o-Xylene	1	5	624/8260	"	"
1,1,2,2-Tetrachloroethane	1	5	624/8260	"	"

( ) = Detection limit dependent upon laboratory background level

PHENOLS
SCAN 8

2-Chlorophenol	10	625	Scan 8	1 LITER AMBER
4-Chloro-3-methylphenol	10	625	Scan 8	GLASS BOTTLE
M-Cresol & P-Cresol	20	625	Scan 8	"
O-Cresol	10	625	Scan 8	"
2,4-Dichlorophenol	10	625	Scan 8	"
2,4-Dimethylphenol	10	625	Scan 8	"
2,4-Dinitrophenol	50	625	Scan 8	"
2-Methyl-4,6-dinitrophenol	50	625	Scan 8	"
2-Nitrophenol	10	625	Scan 8	"
4-Nitrophenol	50	625	Scan 8	"
Pentachlorophenol	50	625	Scan 8	"
Phenol	10	625	Scan 8	"
2,4,5-Trichlorophenol	10	625	Scan 8	"
2,4,6-Trichlorophenol	10	625	Scan 8	"

APPENDIX 1.C-7 (Cont.)

CHLORINATED HYDROCARBON	GROUNDWATER DNR Lab Reported Detection Limits (ug/l)	SEDIMENT/SOIL DNR Lab Reported Detection Limits (ug/kg)	ANALYTICAL METHOD EPA / SW-846	MDNR TECHNIQUE	SAMPLING CONTAINERS (waters)	SAMPLING CONTAINERS (sediments)
2-Chloronaphthalene	2.0	200	625/8270	B/N	1 LITER AMBER	250 ML
	0.2	1,500	612/8120	Scan 3	GLASS BOTTLE	GLASS JAR
1,2-Dichlorobenzene	1.0	100	625/8270	B/N	"	"
	0.1	500	612/8120	Scan 3	"	"
1,3-Dichlorobenzene	1.0	100	625/8270	B/N	"	"
	(0.1)	500	612/8120	Scan 3	"	"
1,4-Dichlorobenzene	1.0	100	625/8270	B/N	"	"
	0.1	500	612/8120	Scan 3	"	"
Hexachlorobenzene	1.0	100	625/8270	B/N	"	"
	.01	50	612/8120	Scan 3	"	"
Hexachlorobutadiene	2.0	200	625/8270	B/N	"	"
	.01	50	612/8120	Scan 3	"	"
Hexachlorocyclopentadiene	2.0	200	625/8270	B/N	"	"
	.01		612/8120	Scan 3	"	"
Hexachloroethane	1.0	100	625/8270	B/N	"	"
	.01	50	612/8120	Scan 3	"	"
1,2,4-Trichlorobenzene	2.0	200	625/8270	B/N	"	"
	.01	500	612/8120	Scan 3	"	"

( ) = Detection limit dependent upon laboratory background level

HALOETHERS

Bis(2-chloroethyl)ether	1.0	100	625/8270	B/N	1 LITER AMBER	250 ML
Bis(2-chloroethoxy)methane	2.0	200	625/8270	B/N	GLASS BOTTLE	GLASS JAR
Bis(2-chloroisopropyl)ether	1.0	100	625/8270	B/N	"	"
4-Bromodiphenylether	2.0	200	625/8270	B/N	"	"
4-Chlorodiphenylether	1.0	100	625/8270	B/N	"	"

NITROSAMINES

N-Nitrosodiphenylamine	5.0	500	625/8270	B/N	1 LITER AMBER	250 ML
N-Nitroso-di-n-propylamine	2.0	200	625/8270	B/N	GLASS BOTTLE	GLASS JAR
1,2-Diphenylhydrazine	2.0	200	625/8270	B/N	"	"

NITROAROMATICS

2,4-Dinitrotoluene	5.0	500	625/8270	B/N	1 LITER AMBER	250 ML
2,6-Dinitrotoluene	5.0	500	625/8270	B/N	GLASS BOTTLE	GLASS JAR
Isophorone	1.0	100	625/8270	B/N	"	"
Nitrobenzene	2.0	200	625/8270	B/N	"	"

PHTHALATES BASE/NEUTRAL	GROUNDWATER DNR Lab Reported Detection Limits (ug/l)	SEDIMENT/SOIL DNR Lab Reported Detection Limits (ug/kg)	ANALYTICAL METHOD EPA or SW-846	MDNR TECHNIQUE	SAMPLING CONTAINERS (waters)	SAMPLING CONTAINERS (sediments)
Bis(2-ethylhexyl)phthalate	2.0	200	625/8270	B/N	1 LITER AMBER	250 ML
Butyl benzyl phthalate	1.0	100	625/8270	B/N	GLASS BOTTLE	GLASS JAR
Di-n-butyl phthalate	1.0	100	625/8270	B/N	"	"
Diethyl phthalate	1.0	100	625/8270	B/N	"	"
Dimethyl phthalate	2.0	200	625/8270	B/N	"	"
Di-n-octyl phthalate	2.0	200	625/8270	B/N	"	"
POLYNUCLEAR AROMATIC HYDROCARBONS B/N						
Acenaphthene	1.0	100	625/8270	B/N	1 LITER AMBER	250 ML
Acenaphthylene	1.0	100	625/8270	B/N	GLASS BOTTLE	GLASS JAR
Anthracene	1.0	100	625/8270	B/N	"	"
Benzo(a)anthracene	1.0	100	625/8270	B/N	"	"
Benzo(b)fluoranthene	2.0	200	625/8270	B/N	"	"
Benzo(k)fluoranthene	2.0	200	625/8270	B/N	"	"
Benzo(a)pyrene	2.0	200	625/8270	B/N	"	"
Benzo(g,h,i)perylene	5.0	500	625/8270	B/N	"	"
Chrysene	1.0	100	625/8270	B/N	"	"
Dibenzo(a,h)anthracene	5.0	500	625/8270	B/N	"	"
Fluoranthene	1.0	100	625/8270	B/N	"	"
Fluorene	1.0	100	625/8270	B/N	"	"
Indeno(1,2,3-c,d)pyrene	5.0	500	625/8270	B/N	"	"
Naphthalene	1.0	100	625/8270	B/N	"	"
Phenanthrene	1.0	100	625/8270	B/N	"	"
Pyrene	1.0	100	625/8270	B/N	"	"

APPENDIX 1.C-7 (Cont.)

PCB s and PESTICIDES SCAN 3	GROUNDWATER DNR Lab Reported Detection Limits (ug/l)	SEDIMENT/SOIL DNR Lab Reported Detection Limits (ug/kg)	ANALYTICAL METHOD EPA or SW-846	MDNR TECHNIQUE	SAMPLING CONTAINERS (waters)	SAMPLING CONTAINERS (sediments)
Aldrin	0.01	50	608/8081	Scan 3	1 LITER AMBER	250 ML
a-BHC	0.01		608/8081	Scan 3	GLASS BOTTLE	GLASS JAR
b-BHC	0.01		608/8081	Scan 3	"	"
d-BHC	0.01		608/8081	Scan 3	"	"
g-BHC (Lindane)	0.01	50	608/8081	Scan 3	"	"
BP-6 (PBB)	0.05	250	608/8081	Scan 3	"	"
a-Chlordane	0.01	50	608/8081	Scan 3	"	"
g-Chlordane	0.01	50	608/8081	Scan 3	"	"
4,4'-DDD	0.05	50	608/8081	Scan 3	"	"
4,4'-DDE	0.01	50	608/8081	Scan 3	"	"
4,4'-DDT	0.01	50	608/8081	Scan 3	"	"
Dieldrin	0.01		608/8081	Scan 3	"	"
Endosulfan I	0.01		608/8081	Scan 3	"	"
Endrin	0.01		608/8081	Scan 3	"	"
Heptachlor	0.01	50	608/8081	Scan 3	"	"
Heptachlor epoxide	0.01	50	608/8081	Scan 3	"	"
Hexabromobenzene	0.01	100	608/8081	Scan 3	"	"
Methoxychlor	0.05		608/8081	Scan 3	"	"
Mirex	0.01	50	608/8081	Scan 3	"	"
PCB 1016 *	0.1	500	608/8081	Scan 3	"	"
PCB 1221 *	0.1	500	608/8081	Scan 3	"	"
PCB 1232 *	0.1	500	608/8081	Scan 3	"	"
PCB 1242	0.1	500	608/8081	Scan 3	"	"
PCB 1248 *	0.1	500	608/8081	Scan 3	"	"
PCB 1254	0.1	500	608/8081	Scan 3	"	"
PCB 1260	0.1	500	608/8081	Scan 3	"	"
PCB 1262 *	0.1	500	608/8081	Scan 3	"	"
PCB 1268 *	0.1	500	608/8081	Scan 3	"	"
Pentachlorobenzene	0.01		612/8121	Scan 3	"	"
Pentachloronitrobenzene	0.01	50	612/8121	Scan 3	"	"
Toxaphene *	0.1	500	608/8081	Scan 3	"	"
1,2,3-Trichlorobenzene	0.01		8121	Scan 3	"	"
1,3,5-Trichlorobenzene	0.01		8121	Scan 3	"	"
1,2,3 4-Tetrachlorobenzene	0.01		8121	Scan 3	"	"
1,2 4 5-Tetrachlorobenzene	0.01		8121	Scan 3	"	"

Volatile 624/8260 Purge and Trap with high resolution capillary gas chromatography with mass spectrometry detection

Scan 3 Dual column high resolution capillary gas chromatography with dual electron capture detectors

Scan 8 High resolution capillary gas chromatography with mass spectrometry detection

B/N High resolution capillary gas chromatography with mass spectrometry detection

* Estimated RDL

Semi-quantitative analysis

APPENDIX 1.C-7 (Cont.)

METALS	GROUNDWATER DNR Lab Reported Detection Limits (ug/l)	SEDIMENT/SOILS DNR Lab Reported Detection Limits (ug/kg)	ANALYTICAL METHOD EPA/SW-846	MDNR TECHNIQUE	SAMPLING CONTAINERS (waters)	SAMPLING CONTAINERS (sediments)
Aluminum	50	5,000	200.7/6010	ICP	500 ML PLASTIC	250 ML GLASS JAR
Antimony	1.0		204.1/7040	Hydride	"	"
Arsenic	1.0	500	206.3/7061	Hydride	"	"
Arsenic	1.0		206.2/7060	Furnace	"	"
Barium	5	1,000	200.7/6010	ICP	"	"
Beryllium	1.0	200	200.7/6010	ICP	"	"
Boron	20		200.7/6010	ICP	"	
Cadmium	5	500	200.7/6010	ICP	"	"
Cadmium	20	2,000	213.1/7130	At. Abs.	"	"
Cadmium	0.2+		213.2	Furnace	"	"
Calcium	1,000	50,000	215.1/7140	At. Abs.	"	"
Chromium	20	2,000	200.7/6010	ICP	"	"
Chromium	1.0		218.2	Furnace	"	"
Chromium VI	5		7196	DPC	"	"
Cobalt	50	5,000	219.1/7200	At. Abs.	"	"
Cobalt	2		219.2	Furnace	"	"
Cobalt	15	5,000	200.7/6010	ICP	"	"
Copper	20	1,000	200.7/6010	ICP	"	"
Copper	20	2,000	220.1/7210	At. Abs.	"	"
Copper	1.0		220.2	Furnace	"	"
Iron	100	10,000	236.1/7380	At. Abs.	"	"
Iron	20	2,500	200.7/6010	ICP	"	"
Lead	50	5,000	239.1/7420	At. Abs.	"	"
Lead	50		200.7/6010	ICP	"	"
Lead	1.0		239.2	Furnace	"	"
Lithium	20	2,000	317 B *	Furnace	"	"
Lithium	8			ICP	"	"
Magnesium	1,000	50,000	242.1/7450	At. Abs.	"	"
Manganese	5	1,000	200.7/6010	ICP	"	"
Manganese	20	2,000	243.1/7460	At. Abs.	"	"
Mercury	0.2	100	245.1/7470,7471	At. Abs.	"	"
Molybdenum	25	5,000	200.7/6010	ICP	"	"
Nickel	50	5,000	249.1/7520	At. Abs.	"	"
Nickel	25	5,000	200.7/6010	ICP	"	"
Nickel	2		249.2	Furnace	"	"
Potasium	100	5,000	258.1/7610	At. Em.	"	"
Selenium	1.0	500	270.3/7740	Hydride	"	"
Silver	0.5+	0.25	272.2	Furnace	"	"
Sodium	1,000	50,000	273.1/7770	At. Abs.	"	"
Titanium	10	1,000	200.7/6010	ICP	"	"
Thallium	2.0		272.2	Furance	"	
Vanadium	10	1,000	200.7/6010	ICP	"	"
Zinc	4	1,000	200.7/6010	ICP	"	"
Zinc	50	5,000	289.1/7950	At. Abs.	"	"

At. Abs. = Atomic Absorption Spectroscopy

At. Em. = Atomic Emission Spectroscopy

ICP = Argon Plasma Emission Spectroscopy

DPC = Diphenylcarbazide

@ = Cold Vapor

* "Standard Methods For the Examination of Water and Wastewater"

+ = Matrix Dependent

~ = Furnace Method Required to Detect Act 307, Type B Levels

APPENDIX 1.C-7 (Cont.)

NON-METALS	GROUNDWATER DNR Lab Reported Detection Limits (ug/l)	ANALYTICAL METHOD EPA or SW-846	MDNR TECHNIQUE	SAMPLING CONTAINERS (waters)
Alkalinity	20,000	310.1	Auto Analyzer	500 ML
Alkalinity, Bicarbonate	5,000		Calculate	PLASTIC
Alkalinity, Carbonate	10,000		Calculate	"
Ammonia	10	350.1	Auto Phenolate	"
BOD-Carb.	2,000	405.1	5 Day-DO Probe	"
BOD-Total	2,000	405.1	5 Day-DO Probe	"
Chloride	1,000	325	Auto Analyzer	"
COD (High Level)	10,000	410	Titrimetric	"
COD (low level)	5,000	410	Colorimetric	"
Conductivity	1.0*		Bridge	"
Cyanide	5	335.2/9010	Man Dist. Man PBA Color	"
Dissolved Oxygen	100	360.2	Manual Titration	250 ML GLASS W / GLASS STOPPER
Hardness (Ca2CO3)	5,000	130.2	Calculate	500 ML
Nitrate + Nitrite	10	353.2	Auto CD Reduction	PLASTIC
Nitrite	10	353.2	Auto Diazotization	"
Nitrogen, Kjeldahl	100	351.2	BD, Auto Salicylate	"
OrthoP	10	365	Auto Ascorbic Acid Redu	"
Phenolics	1.0	420.2	Auto Dist., Auto 4AAP	GLASS
Phenolics	10	420.2/9066	Manual Dist., Auto 4AAP	"
Phosphorous, Total	10	365.4	BD Auto Ascorbic Acid R	PLASTIC
Residue	20,000	160.1	Total Filt-TDS 180C	"
Residue	4,000	160.2	Non Filt-Susp Sol 105C	"
Silicates	50	370.1	Auto Ascorbic Acid Redu	"
Sulfate	2,000	375.4	Auto Analyzer	"
TOC	500	415.1	UV/Persulfate (DC-80)	"
Turbidity	0.40#	180.1	Turbidimeter	"

* = umhos/cm

= NTU

Calculate = Value is calculated from existing data

Bridge = Conductivity meter

DO Probe = Dissolved Oxygen (YSI) Probe

CD Reduc = Cadmium Reduction

BD = Block Digester

Man. Dist. = Manual Distillation

4AAP = 4 Amino Antipyrene

BOD = Biochemical Oxygen Demand

COD = Chemical Oxygen Demand

TOC = Total Organic Carbon

TDS = Total Dissolved Solids

Auto Dist = Automated Distillation

DNR LABORATORY

SAMPLE BOTTLES AND PRESERVATIVES REQUESTS

PHONE (517) 321-2241 FAX (517) 323-9084

PLEASE ALLOW 1 WEEK FOR PREPARATION

EMPLOYEE NAME:

DIVISION/UNIT:

TODAY'S DATE / /

PICK-UP DATE / / AM PM

Bottle code	Parameter Group	Plastic Containers: 500 ml White	250 ml White	250 ml Brown	Glass Containers: 40 ml Septum	1000 ml Brown	250 ml Wide	125 ml Septum	250 ml Narrow	250 ml SC CAP	Field Blanks	Field Replicates	Preservatives	Need	Prepared
DO	Dissolved Oxygen												DO KIT		
GN	Gen Chem/Neutral Ortho-poos. nitrite, BOD, nitrate, silica, residues														
GA	Gen Chem/Acidic COD, TOC, ammonia, Kjel N, Tot Phos., Nitrate & Nitrite												H2SO4		
GG	Gen Chem/ Phenolics-Glass														
GB	Gen Chem/Basic Cyanide												10 N NaOH		
S	Sulfide												1 M ZnAC 10 N NaOH		
CA	Chlorophyll a												1% MgCO3		
GS	Gen Chem/sed-soils TP, Kjel-N, Phenolics, DOD														
MA	Metals/Total Acidic Cd,Cr,Cu,Ni, Pb,Zn,Fe,Co,Li,Mn,Al,Tl,V,Ba, Ag,Hg,As,Se,Sb,Ca,Mg,Na,K												1:1 HNO3		
MAD	Metals/Acidic Dissolved Same as MA, Field Filt.												1:1 HNO3		
MD	Metals/Dissolved Same as MA, Lab Filt.														
MN	Minerals/Neutral pH,Conduct.,Cr+6,Chloride,Sulfate ,Alk.Carbonate,Bicarbonate,														
MB	Metals/Minerals Brine,Na,K,Mg,Ca,Alk.Carbonate, Bicarb,Chloride,Sulfate,Bromide														
OG	Oil and Grease												H2SO4		
MS	Metals/Soil, Sed. Same as MA														
M	Metals/Tissue Same as MA														
MO	Metals/Oil Liq & Solid Waste Same as MA														
MX	Metals/EP Tox/TCLP Ba, Se, Ag, Cd, Cr, Pb, Cu, Zn, Hg, As (MI-10)														
PO-1	Purg. Halocarbons Scan 1												1:1 HCl		
PO-2	Purg. Aromatics Scan 2 (BTEX)												1:1 HCl		
POV	Purg Volatile/soil 8260														
OX	TCLP Volatiles														
ON	Org/Neutral Extract Scan 3												10 N NaOH 1:1 H2SO4		
OB	Org/Basic Extract GC/MS B/N														
OA	Org/Acidic Extractables Scan 6														
OS	Org/Soil, Sed, Sludge Scans 3 GC/MS, O&G														
OL	Org/Liquid and Solid Waste Scans 1, 2, 3, IR Scan, Flash pt.														
AR	Air Toxics														
TOTAL REQUESTED															
NUMBER PREPARED															

Other Requested Supplies:

Please arrange for air toxics supplies with the Lab

MESSAGE RECEIVED BY: _____ PREPARED BY: _____

APPENDIX 1.C.-9

ENVIRONMENTAL LABORATORY
RESULT REMARK CODES

A	value reported is the mean of two or more determinations.
C	value calculated from other independent parameters.
J	estimated value or value not accurate.
K	actual value is known to be less than the value given, i.e. substance, if present, is below detection limit.
L	actual value is known to be greater than the value given.
T	value reported is less than criteria of detection.
W	value observed is less than lowest value reportable under **"T"** code.
DL	sample analyzed using a dilution(s).
DM	dilution required due to matrix problems.
HT	recommended laboratory holding time was exceeded before analysis.
LH	Q. C. indicated possible low recovery. Actual level may be higher.
LL	Q. C. indicated possible high recovery. Actual level may be lower.
MM	analytical method or matrix is not within SOP of this laboratory.
NC	no confirmation by a second technique.
NH	non-homogeneous sample made analysis of a representative sample questionable.
PI	possible interference may have affected the accuracy of the laboratory result.
QC	quality control problems exists.
RB	Reagent Blank. The level of reagent blank contamination is reported in the comment column and may be subtracted from the analyte value by the user.
ST	recommended sample collection/preservation technique not used.
ACC	laboratory accident resulted in no obtainable value.
FCN	free cyanide was not analyzed due to low level of total cyanide.
INT	interference encountered during analysis resulted in no obtainable value.
IST	Improper sample collection/preservation. Sample not suitable for analysis.
NAV	requested analysis not available.
QNS	quantity not sufficient to perform requested analysis.
STR	settleable residue was not analyzed due to low suspended solids.

CHAPTER 2

LABORATORY PRIORITY AND SCHEDULING

Prepared by
State of Michigan
Department of Natural Resources
March 1994

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FIGURES

CHAPTER 2. LABORATORY PRIORITY AND SCHEDULING

2.A. INTRODUCTION

The Environmental Laboratory provides basic analytical services to all environmental programs in the department. In recent years the size and complexity of the analytical workload has grown significantly. Sample priority and scheduling procedures are necessary to maintain the Laboratory workload at manageable levels. The objectives of sample priority and scheduling are to:

- control the sample load submitted to the Laboratory;
- ensure that sample analyses are performed within EPA mandated sample holding times;
- optimize Laboratory efficiency by matching laboratory workload with capacity;
- improve communication between the Laboratory and Laboratory users;

  and

- allow a reasonable number of priority sample analyses consistent with general department priorities.

2.B. SAMPLE PRIORITIES

All samples received by the Environmental Laboratory are placed into one of three priority categories.

Priority I is for samples requiring faster than normal turnaround time. Turnaround time and the number of samples accepted as Priority I is based on user needs and Laboratory abilities. Priority I samples must be approved by the Chief of the Division paying for the analysis.

Priority II samples are all samples submitted to the Laboratory within daily or weekly sample processing capacity by Divisions that fund positions in the Laboratory. The Laboratory strives for a turnaround time of less than four weeks on these samples. Although the Laboratory prefers to be notified one week prior to sample submittal, unscheduled samples will be accepted as priority II if there is available capacity. If there is no available capacity for unscheduled samples, they will not be accepted. Therefore, accepted samples will be analyzed in four weeks or less.

Priority III is assigned to samples submitted to the Laboratory by Divisions which do not fund Laboratory positions or from funded divisions which have exhausted their funded allocation for the fiscal year. Priority III samples will be analyzed after Priority I and II samples as time permits. Analysis may not be attempted if samples are held beyond maximum holding time. There is no commitment on turnaround time for these samples.

2.B.1. SAMPLE PRIORITY PROCEDURES

Priority I analyses are requested through the laboratory management prior to or upon delivery of samples to the Laboratory. Priority I analyses also require approval from the appropriate Division Chief or designee (such as the Division Laboratory Coordinator) prior to analysis. The Priority I Analysis Request Form is provided in Figure 2.B.-1. Because

Priority I samples are frequently disruptive to efficient Laboratory operations and may displace other samples, the requesting division is interaccounted three times the normal rate for Priority I analysis. The consequence of the triple interaccounting is that annual Laboratory capacity for routine (Priority II) sample analysis is exhausted more rapidly. The use of contract laboratories is an alternative to Priority I analysis.

Priority II analyses are provided to divisions which provide positions to the Laboratory, and to other divisions when Laboratory capacity is available. Funded divisions are generally able to receive Priority II analyses at quantities commensurate with the number of positions supported at the Laboratory. Whenever a funded division exceeds its allotted capacity in any given fiscal year, all additional sample analyses beyond the funding level then become Priority III. Priority III samples may not be analyzed if lab capacities are full with Priority I and II samples.

2.C. SAMPLE SCHEDULING

Laboratory workload is controlled by advance scheduling of a few key parameters through the appropriate Division Laboratory Coordinator. These key parameters (at this writing) and their respective capacities are as follows:

Key Parameters	Capacity
WATER SAMPLES	
BOD (waste)/UBOD	40/week (combined)
Residues	135/week
Oil & Grease	16/week
EP Tox (schedule if more than 10/site)	20/week
TCLP (schedule if more than 10/site)	20/week
SPLC (schedule if more than 10/site)	20/week
Volatile 8260/Scan 1 & 2	100/week
Scan 3 PCB & Pesticides	30/week
Scan 8 Phenols	30/week
GC/MS B/N	30/week
SEDIMENT SAMPLES	
Volatile 8260	50/week
Scan 3 PCB and Base Neutral combination	45/week
TCLP Volatiles	10/week

Changes in key parameters and capacities will be announced as needed in the Laboratory Newsletter. Whenever planned sampling activities involve key parameters, notify your Division Laboratory Coordinator of your proposed sampling plan (location, key parameters, numbers of samples and arrival dates) at least 6 work days prior to the week when samples will arrive at the Laboratory. Scheduling request forms are no longer necessary. If a project comes up too late for scheduling, call the lab and inquire about walk-in capacity.

2.C.1. SAMPLE SCHEDULING PROCEDURES

By Monday morning of the week preceding the sampling week, Laboratory Coordinators will notify the Laboratory Organic or Inorganic Unit staff of key parameters to be sampled. Laboratory capacity will be allocated to funded divisions first (AQD, WMD, ERD, and SWQD). Remaining capacity will then be assigned to unfunded divisions and divisions which have exhausted their capacity. If scheduling conflicts exist, they will be worked out by Monday afternoon with the appropriate Division Laboratory

Coordinator(s). Field personnel will then have about a week to finalize sampling plans. After the first Monday of the week preceding the sampling week, field staff must contact the Laboratory directly to determine if vacancies exist for unscheduled samples.

If samples cannot be scheduled in advance, check with your Division Laboratory Coordinator to determine if unused capacity is available. Your Division Laboratory Coordinator may also decide to switch your samples with previously scheduled, but less urgent samples from your division.

The scheduling system is based on the assumptions that overall Laboratory workload can be controlled by controlling a few key parameters. These key parameters have been identified from past Laboratory use patterns. In order for this system to succeed, previous use patterns must remain approximately the same. If your Division Laboratory Coordinator informs you that your scheduling request cannot be accommodated (because certain key parameters are overbooked) then the entire request should be canceled; not just the key parameters. Once capacity for key parameters has been fully allocated, the Laboratory will not accept any more samples for those key parameters.

2.C.2. LABORATORY COORDINATORS

Each Division has appointed a Laboratory Coordinator to serve as a liaison between program divisions and the Laboratory. The Division Laboratory Coordinator is responsible for certain sample scheduling duties and other Laboratory issues, such as projecting future analytical needs, communicating division needs to the Laboratory, and serving as the division expert on Laboratory policies and procedures. Please keep this person informed of needs and problems related to Laboratory services. The following persons are presently serving as Laboratory Coordinators.

Name	Phone	Division
Karen Kajiya	335-4858	Air Quality Division
Carrie Monosmith	373-1874	Air Quality Division
George Jackson	373-3561	Environmental Response Division
Jan Sealock	373-4740	Waste Management Division
John Suppnick	335-4192	Surface Water Quality Division
or Karen Gates	335-4180	" " " "
Sue Koppelo	322-1320	Law Enforcement Division
Ralph Bednarz	335-4211	Land and Water Management
Cheryl Stanfield	322-6351	Geological Survey Division

Figure 2.B.-1

REQUEST
FOR
PRIORITY I LABORATORY ANALYSIS

Lab Log No.	Lab Sample Nos.	Expected Arrival Date	Actual Arrival Date

Requested By	Contact Person	Division	Section	Phone No.

Source or Location of Samples

Authorization of Division Chief (Signature)*

☐ Memo Approval ☐ Verbal Approval

Reasons For Priority Request:

Sample Matrix: ☐ Water ☐ Solid ☐ Oil ☐ Other (specify):

Parameters	Number of Samples	Date Results Requested	Check for Verbal Results	Completion Dates Agreed Upon By Lab. Supervisors**	Initial	Date Results Reported
Organic						
Inorganic						
General Chemistry						

* Priority I analyses are charged at three times the cost of routine analyses. Authorization must be made by the chief of the division to be charged for Priority I analyses.

** Completion dates must be authorized by the appropriate unit supervisor.

R 4422
Rev. 8/85

3/94

CHAPTER 3

SAMPLE PRESERVATION AND HANDLING

Prepared by
State of Michigan
Department of Natural Resources
September, 1994

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FIGURES

CHAPTER 3. SAMPLE PRESERVATION AND HANDLING

3.A INTRODUCTION

Analysis of all samples immediately after collection at the sampling site would be ideal from the standpoint of holding time. However, this is generally impractical and only occurs when immediate analysis is an absolute necessity. As an alternative, special sample preservation and handling techniques are used in an attempt to stabilize the constituents of interest until analyses can be practically performed.

Complete stabilization of every sample constituent is impossible to achieve. Preservation techniques are generally used to retard chemical, biological, or physical changes in a sample. Sample containers, preservation, handling, and holding times must be strictly controlled to maintain sample integrity.

3.B METHODS OF PRESERVATION

Preservation methods are generally limited to temperature control, pH control and chemical addition. These techniques are used to retard biological actions, slow hydrolysis of chemical complexes, and reduce the volatility of constituents.

3.B.1. TEMPERATURE CONTROL

Refrigeration or icing of samples is a common preservation technique used for many constituents. Refrigeration generally does not cause changes which will result in interference's with most analytical methods. Sample refrigeration is often the preferred preservation technique if it does stabilize the constituents of interest. Icing of samples is practical for most field work.

Freezing of water samples may be an effective long term preservation technique for some applications, but it is generally not recommended. Freezing and thawing of samples may cause changes in some sample components, particularly various residues. Freezing of fish tissue and other biological samples is often recommended, and becomes a necessity if analysis is delayed substantially.

3.B.2. pH CONTROL AND CHEMICAL ADDITION

pH control is often used to affect the solubility of a constituent or retard biological action. For example, nitric acid is added to samples to maintain metal ions in a dissolved state.

Other chemicals may be required for proper preservation of other constituents. For example, sulfide is readily oxidizable under aerobic conditions. Zinc acetate is added to cause precipitation of sulfide as zinc sulfide, which is relatively inactive.

Some precautions must be considered when chemicals are added to samples.

-- Chemical preservatives are generally intended for <u>water</u> samples. Violent reactions can occur if certain chemicals are added to some wastes. For example, acid preservation of a highly caustic (basic) sample could result in violent spattering and considerable heat generation. KNOW AS MUCH ABOUT YOUR SAMPLE SOURCE AS POSSIBLE AND USE COMMON SENSE. Proper safety precautions should be used as the situation dictates (i.e., safety glasses, goggles, face shield, apron, gloves, etc.). The laboratory should also be warned of potential problems.

-- Chemical preservatives should be used in the recommended dosage. If a little preservative is good, a lot is not necessarily better. An ideal chemical preservative should have no detrimental effects on any subsequent chemical analysis. However, this is not always the case. Many chemical reactions are particularly pH dependent. Samples with excess amounts of chemicals added may produce erroneous results.

-- Some recommended preservatives may also be required for the subsequent analysis to proceed properly. For example, the sulfuric acid preservation for total organic carbon is used to inhibit degradation. But it is also necessary to convert inorganic carbon present (carbonates and bicarbonates) to carbon dioxide, which is removed later. Lack of adequate acid preservation results in erroneously high results.

-- Chemical preservatives must be free from contaminants which will affect the validity of results. Only preservatives supplied and verified by the Environmental Laboratory should be used. It is the responsibility of field personnel to maintain the integrity of the chemicals in an assigned field preservative kit. If it is suspected that preservatives may have become contaminated, they should be returned to the laboratory and replaced. The laboratory can verify contamination if requested. All kits should be replenished periodically, with six months being the maximum time between replacements. Use of field blanks is discussed in Chapter 5, Field Quality Control Procedures.

3.B.2.a. Dechlorination of Samples

Chlorinated samples must be immediately dechlorinated upon collection to prevent possible oxidation of some compounds or other chemical reactions which may invalidate subsequent analyses. The best procedure is to measure the residual chlorine content of a sample and then add a slight excess of the appropriate dechlorinating agent. Large excesses of dechlorinating agents may result in additional analytical problems. If there is some doubt as to whether a sample is fully dechlorinated, the sample can be rechecked for residual chlorine after addition and mixing of the dechlorinating agent.

3.B.2.a.1. Cyanide and Thiocyanate Samples

Chlorine and other oxidizing agents decompose most of the cyanides and convert Thiocyanate to toxic cyanogen chloride. The "free" cyanide test (cyanides amenable to chlorination) is actually a quantification of the cyanides which are destroyed by chlorination. After the amount of residual chlorine has been measured, dechlorinate with 0.6 g/l ascorbic acid <u>before</u> preservation with sodium hydroxide to pH greater than 12.

3.B.2.a.2. Phenolics Samples

Phenolic compounds will be partially oxidized if chlorine and other oxidizing agents are not removed immediately after sample collection. After the amount of residual chlorine has been determined, dechlorination with ferrous ammonium sulfate (FAS) should occur before preservation with sulfuric acid to pH less than 2. On unchlorinated samples, the total recoverable phenolics analysis will be taken from the same sample container (GA bottle) as chemical oxygen demand (COD) and total organic carbon (TOC). A separate container for phenols is required for a dechlorinated sample (GP code) because the dechlorinating agent could invalidate COD and TOC results. One drop (0.05 ml) of 0.141 <u>N</u> Fe $(NH_4)_2$ $(SO_4)_2$ for each 250 ml sample will destroy 1 mg/l residual chlorine.

3.B.2.a.3. Organic samples

Because chlorine may oxidize some organic compounds, samples for acid extractables, base-neutral extractables, and purgeable organics should be dechlorinated with sodium thiosulfate upon collection. While $Na_2S_2O_3$ does not interfere with most organic analyses, a large excess should be avoided. One drop (0.05 ml) of 0.141 N $Na_2S_2O_3$ will destroy 1 mg/l residual chlorine in a 250 ml sample and 6 mg/l residual chlorine in a 40 ml sample.

3.B.3. PRESERVATION GUIDELINES

The preservation techniques recommended by the Environmental Laboratory are listed in Table 3.B.-1, "Collection and Preservation of Water, Sediment, Tissue, and Waste Samples". Most of these are in accordance with EPA recommended procedures specified for NPDES samples (Table II, Guidelines Establishing Test Procedures for Analysis of Pollutants Under the Clean Water Act, 40 CFR Part 136). A present discrepancy with the existing guidelines includes:

-- Dissolved metals, orthophosphate, and other dissolved constituents should be membrane filtered immediately after collection in the field. Because this is not always practical and can cause sample contamination if all necessary precautions are not taken, the lab will filter samples for dissolved constituents, however the sample to be filtered in the lab should be delivered to the lab within 24 hours and the filtration should take place at the lab immediately.

3.C. CONTAINERS

Sample containers and caps are supplied by the Environmental Laboratory. Only these containers are to be used for sample containment and transfer. Sample containers are recommended based upon the following factors:

-- lack of interference with constituents to be analyzed,
-- cost,
-- ability to be cleaned or sterilized,
-- durability,
-- availability,
-- size, and
-- weight.

As a general rule, glass containers are used for pesticides, oil and grease, other organics, and dissolved oxygen samples. Disposable plastic containers are used for most inorganic constituents, because of the time and cost involved in properly cleaning containers for reuse. The laboratory periodically checks containers for contamination. Proper use of field blanks also serves as a routine check on sample container contamination.

The construction of the cap and cap liner must be carefully considered also. Polyethylene caps are generally used unless the container requires a tight seal or organics are to be used. Then a bakelite cap with an appropriate liner is used. Liner material is generally either wax coated paper (do not use with organics), aluminum foil (may contaminate sample with some metals), or Teflon (inert but expensive). Because bakelite caps are made from a phenolic resin, special precautions must be followed if phenolics are to be analyzed.

Container construction must be considered for special samples. Wide

mouth containers are necessary for solid or semi-solid samples. Volatile hydrocarbon samples must be collected in a tightly sealed bottle to prevent loss of the constituents.

The sample containers that the Environmental Laboratory presently recommends and supplies are listed in Table 3.B.-1.

3.C.1. SAMPLE BOTTLE LABELING AND CODES

A Department of Natural Resources label and Law Enforcement Division Criminal Enforcement Label have been developed for labeling sample containers. The DNR label is white (Figure 3.C.-1) and is used for all routine sampling. The Law Enforcement Division uses a green label for all criminal investigations (Figure 3.C.-2). When the green labels are used, they must bear an investigation number assigned by the Law Enforcement Division. The use of sample bottle codes is recommended. All bottle codes are to be clearly marked in the designated area of the sample bottle label. The codes are used by field and laboratory personnel for identification and sorting of sample containers. They indirectly indicate if chemical preservation should have been added to a sample. The sample bottle codes are listed in Table 3.B.-1.

Each batch of samples gets a unique log number and the samples in the batch are assigned sample numbers sequentially by the lab computer.

3.D. HOLDING TIMES

The holding time for a sample is the time delay between when the sample is collected and when it reaches a critical stage in the analytical procedure. For example, many organic compounds have two holding times. One is from collection to the extraction step and the other is from the extraction step to quantification. For time composite samples, the holding time clock is started after sample compositing is completed. However, proper preservation must be followed during compositing if possible.

Each analytical constituent has a recommended maximum holding time. Depending upon its stability, the holding times range from immediate analysis (temperature) to 6 months (most trace metals). The holding times that the Environmental Laboratory presently follows are included in Table 3.B.-1. These generally follow the guidelines established by the EPA for NPDES compliance monitoring. Variance from these holding times require special studies and approval. Although it is impossible to state exactly how much time may elapse on a particular sample before it changes significantly, studies have shown the recommended holding time to be suitable for many environmental water samples.

It is a good practice to deliver the samples to the lab as early as possible. Field staff should as a goal plan their work so that samples will be recieved by the lab within 48 hours of collection. Except samples with 2 day holding times and samples needing lab filtration must be brought in within 24 hours and samples needing filtration should be filtered immediately.

Table 3.B-1 COLLECTION AND PRESERVATION OF WATER, TISSUE AND SEDIMENT SAMPLES

BOTTLE CODE	PARAMETER GROUP	NOTES	BOTTLE TYPE	SIZE/COMMENTS	COOL TO 4 C° X = YES	PRESERVATIVE	AMOUNT	MAXIMUM HOLDING TIME
	GENERAL CHEMISTRY							
O	DISSOLVED OXYGEN	1	GLASS	250 ML GLASS STOPPER	X	FIX ON SITE (WINKLER)		8 HR
GN	GEN CHM/NEUTRAL	2,3	PLASTIC	500 ML	X			2 DA, 7 DA, 28 DA
GA	GEN CHM/ACIDIC	3,4	PLASTIC	500 ML	X	H2SO4 TO pH < 2	10 DROPS/ 500 ML	28 DA
GG	GEN CHM/PHENOLICS	5	GLASS	250 ML SCREW CAP	X	H2SO4 TO pH<2	5 DROPS/ 250 ML	28 DA
GB	GEN CHM/BASIC	3,6,7,8	PLASTIC	250 ML OR 500 ML	X	10N NaOH TO pH=12	10 DROPS/ 250 ML	14 DA (24 HR)6
S	SULFIDE	1	PLASTIC	250 ML	X	1N ZnAC, 10N NaOH TO pH>9	10 DROPS 1 DROP/ 250 ML	7 DA
CA	CHLOROPHYLL A	9	PLASTIC	250 ML	X OR FREEZE	1% MgCO3	5 DROPS/ 250 ML	2 DA
HW	FLASH POINT		GLASS	250 ML	X			
GS	GEN CHM/SEDIMENT	16	GLASS	250 ML W.M.	X			
	INORGANIC							
MA	METALS/TOTAL ACIDIC	10	PLASTIC	500 ML		1:1 HNO3 TO pH<2	5 ML/ 500 ML	28 DA, 6 MO
MAD	METALS/ACIDIC FIELD DISSOLVED	10,11	PLASTIC	500 ML		FILTER ON SITE THEN ADD 1:1 HNO3 TO pH<2	5 ML/ 500ML	28 DA, 6 MO
MD	METALS/LAB DISSOLVED	11	PLASTIC	500 ML	X	LAB FILT. & PRES.		W/IN 24 HRS.
MN	MINERAL/NEUTRAL	12	PLASTIC	500 ML	X			W/IN 24 HRS, 2 DA, 14 DA, 28 DA
MB	METALS/MINERALS BRINE	12	PLASTIC	500 ML	X			14 DA,28 DA
MS	METALS/SOIL, SEDIMENT		GLASS	250 ML W.M.	X			
M	METALS/TISSUE		GLASS	250 ML W.M.	X OR FREEZE			
MO	METALS/OIL, WASTES (LIQUID/SOLID)		GLASS	250 ML W.M.	X			
MX	METALS/ TCLP/SPLP OR ASTM LEACHATE		GLASS	250 ML W.M.	X			
OG	OIL & GREASE		GLASS	2 x 250 ML W.M.	X	H2SO4 TO pH < 2	20 DROPS/ 500 ML	28 DA
	ORGANIC							
POV	PURGEABLE VOLATILES SCAN 1 & 2 , BTEX/MTBE 601/8010, 602/8020, 8260	13,14	GLASS	2-40 ML SEPTUM VIALS	X	1:1 HCl TO pH<2	5 DROPS/ VIAL	14 DA
OV	PURGEABLE VOLATILES/SOIL 8260 / BTEX/MTBE		GLASS	2-125 ml SEPTUM JARS	X			14 DA
ON	ORG./NEUTRAL EXT. 608/612 (SCAN 3)	14	GLASS	1000 ML AMBER FOIL-LINED CAP	X	CK AND ADJUST pH TO 5-9, NaOH or H2SO4		7 DA
OB	ORG/BASIC EXT. 625/8270 (B/N)	14	GLASS	1000 ML AMBER FOIL-LINED CAP	X			7 DA
OA	ORG./ACID EXTRACTABLES, 625 (SCAN 8)	14	GLASS	1000 ML AMBER FOIL-LINED CAP	X			7 DA
OS	ORG./SOIL, SEDIMENT 8081/8121 & 8270		GLASS	250 ML W.M.	X			14 DA
OL	ORG/WASTES OIL, (LIQ./SOLID)	15	GLASS	250 ML W.M.	X			
OX	TCLP VOLATILES		GLASS	250 ML SEPTUM JARS	X			14 DA
AR	ORG/AIR TOXICS (VOLATILE)		STAINLESS STEEL	CANNISTER				

NOTES

1 EXTRA CARE SHOULD BE TAKEN DURING COLLECTION SO THAT THE SAMPLE IS NOT AERATED BEFORE PRESERVATION.

2 GN, GEN CHM/NEUTRAL, INCLUDES THE FOLLOWING PARAMETERS WITH THEIR HOLDING TIMES: SETTLEABLE RESIDUE, NITRITE, ORTHOPHOSPHATE, BOD, AND TURBIDITY (2 DAYS); TOTAL, FILTERABLE, NONFILTERABLE AND VOLATILE RESIDUES (7 DAYS); SILICATES (28 DAYS).

3 ADD SUFFIX "D" TO BOTTLE CODE WHEN SAMPLE IS FIELD FILTERED.

4 EXCESS ACID PRESERVATIVE WILL CAUSE INTERFERENCE...COUNT DROPS CAREFULLY, CHECK pH, ADD MORE ACID IF NECESSARY (pH=2). GA INCLUDES CHEMICAL OXYGEN DEMAND (COD), TOTAL ORGANIC CARBON (TOC), NITRATE PLUS NITRITE, AMMONIA, KJELDAHL NITROGEN, AND PHOSPHORUS.

5 CHLORINATED SAMPLES FOR PHENOLS SHOULD BE COLLECTED IN A SEPARATE BOTTLE AND DECHLORINATED WITH .141N FAS (FERROUS AMMONIUM SULFATE, USUALLY ONE DROP) BEFORE PRESERVATION (USE BOTTLE CODE GP).

6 GB INCLUDES TOTAL CYANIDE, AND CYANIDE AMMENABLE TO CHLORINATION (FREE). HOLDING TIME IS 24 HOURS IF SULFIDES ARE PRESENT.

7 CHLORINATED SAMPLES FOR CYANIDES MUST BE DECHLORINATED WITH ASCORBIC ACID (0.6 G/L) IMMEDIATELY AFTER COLLECTION AND THEN PRESERVED WITH NaOH.

8 THE PROPER CONTAINER DEPENDS ON PARAMETERS REQUESTED. 250 ML FOR TOTAL ONLY, 500 ML FOR AMENABLE

9 IF SAMPLE IS FILTERED ON SITE AND THE MEMBRANE FILTER ADDED TO 90% ACETONE (SUPPLIED BY THE LAB) AND REFRIGERATED, OR IF UNFILTERED SAMPLE IS FIELD FROZEN, HOLDING TIME IS ONE MONTH.

10 RECOMMENDED MAXIMUM HOLDING TIME FOR MERCURY, SODIUM, POTASSIUM, MAGNESIUM, CALCIUM (28 DAYS); OTHER METALS (6 MONTHS).

11 IF FIELD FILTRATION IS NOT AVAILABLE, SEND UNFILTERED SAMPLE TO THE LAB AS SOON AS POSSIBLE (WITHIN 24 HOURS). DO NOT ADD ACID TO DISSOLVED METAL IF UNFILTERED.

12 MN, MINERALS/NEUTRAL INCLUDED THE FOLLOWING PARAMETERS WITH THEIR HOLDING TIMES: pH (ANALYSES SHOULD BE PERFORMED IMMEDIATELY ON SITE); HEXAVALENT CHROMIUM (24 HOURS); ALKALINITIES (CO3, HCO3, TOTAL ALK) (14 DAYS); SPECIFIC CONDUCTANCE, CHLORIDE, SULFATE (28 DAYS).

13 FILL BOTTLE COMPLETELY (NO AIR BUBBLES) AND MAKE SURE TEFLON SIDE OF SEPTUM FACES SAMPLES. DUPLICATE VIALS REQUIRED.

14 CHLORINATED WATER SAMPLES FOR ORGANIC COMPOUNDS SHOULD BE DECHLORINATED BY ADDING .141N Na2S2O3 (SODIUM THIOSULFATE) TO THE BOTTLE BEFORE FILLING WITH SAMPLE.

15 INCLUDES PETROLEUM HYDROCARBONS, SPILL IDENTIFICATIONS, METHANOL (RCRA) EXTRACTION FOR SCANS 1 AND 2.

16 GEN CHM/SEDIMENTS INCLUDES: TOTAL PHOSPHORUS, KJELDAHL-N, CYANIDE, PHENOLICS AND COD.

Collector's Initials	DEPT. OF NATURAL RESOURCES	Date
Field ID	Location	
Analysis or parameter code	Chemicals added	

Figure 3.C.-1 DNR Sample Bottle Label

ENVIRONMENTAL ENFORCEMENT DIVISION
INVESTIGATIVE SECTION

Date	Time	File No	File Class	Priority
Location (Corp — Stream — Landfill)				
Description of Evidence				
Lab ID Sticker				
Station	Officer			

R2801

Figure 3.C.-2 EED Sample Bottle Label
(Criminal Enforcement in green and Non-criminal Enforcement in white.)

Recommended holding times which are not met for many samples include analyses for pH and sulfite (analyze immediately), Winkler set dissolved oxygen (DO) (eight hours), hexavalent chromium (twenty-four hours), cyanides (24 hours when sulfides are present). Analysis for pH should be performed by an approved procedure in the field if compliance or litigation is involved. Winkler set DO samples should be titrated in the field if practical. Storing set DO samples in the dark at 4°C does appear to effectively prolong the holding time for non-effluent samples. A practical method of routinely setting bacti samples within the six hour holding time is not available from the Environmental Laboratory. Extended holding times for hexavalent chromium may result in oxidation of trivalent chromium or reduction of hexavalent chromium.

3.E. SAMPLE PACKAGING AND SHIPPING

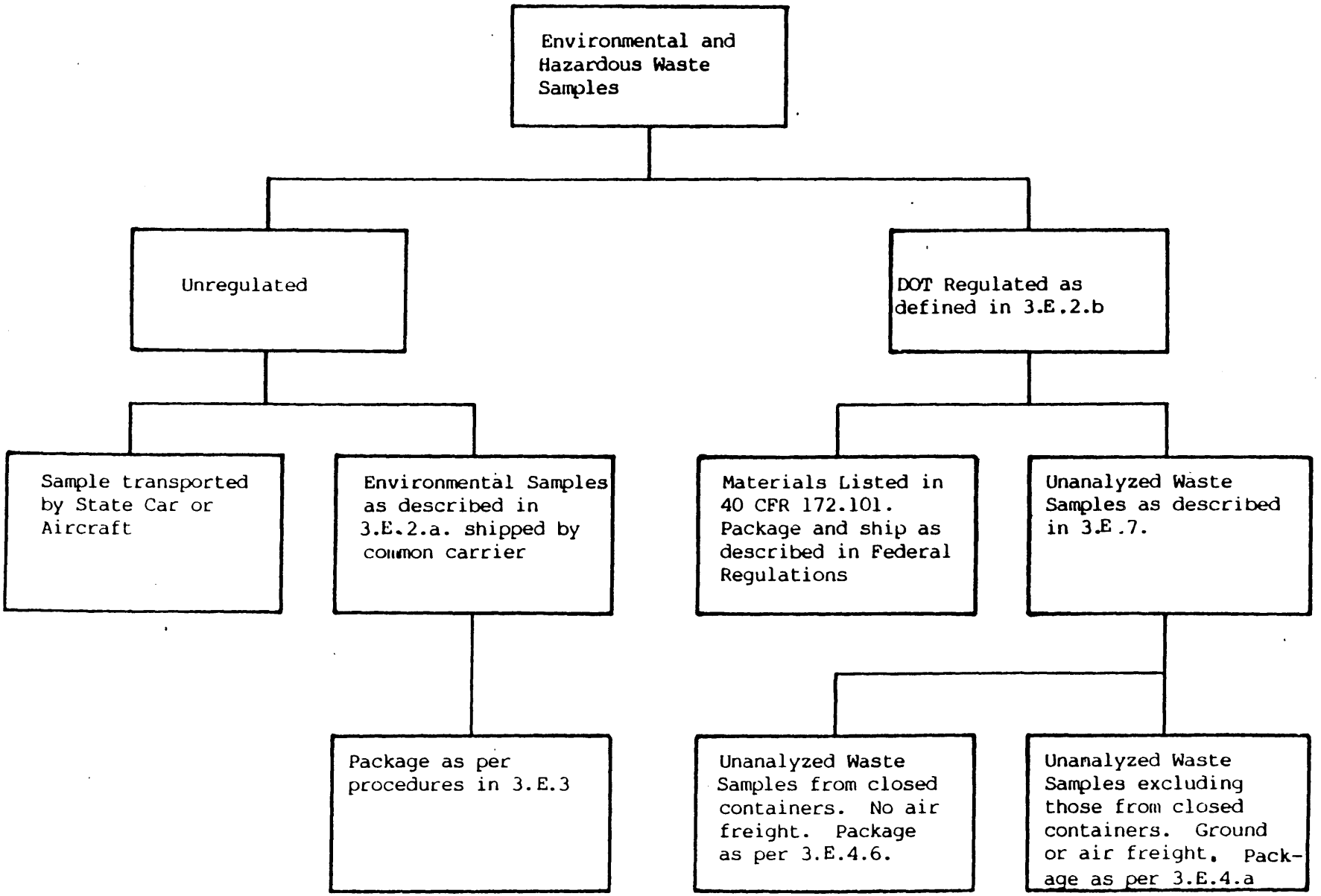
3.E.1. INTRODUCTION

The purpose of this Section is to review alternatives and provide guidance for transporting environmental and waste samples from field locations to the Laboratory or a commercial laboratory and to convey general information concerning transport services, packaging requirements and other considerations.

A schematic description of sample shipment requirements based on sample type is provided in Figure 3.E.-1. This guidance is necessary to help staff comply with Department of Transportation (DOT) regulations (49 CFR, Parts 171-179) covering transport of hazardous materials. DOT regulations place the burden on the shipper to determine if the sample meets the definition of a hazardous material. It is assumed that the shipper has some knowledge concerning the sample and based on that information is able to make a reasonable judgment whether or not the sample is likely to be classified as a hazardous material. When a reasonable doubt exists as to whether a sample is subject to DOT regulations, the shipper should either not ship the samples by common carrier or treat the samples as a DOT regulated material. The shipper is liable for compliance with these regulations. Civil penalties up to $10,000 and criminal penalties up to $25,000 and 5 years are prescribed.

49 CFR, Parts 171 to 179 consist of approximately 1300 pages of regulations concerning shipment of hazardous wastes. This chapter is not intended to cover all aspects of hazardous sample shipment but rather as an introduction to the regulations and to provide general guidance. Copies of the Code of Federal Regulations are available at Document Depository Libraries (In the Lansing area: State of Michigan Law Library and Michigan State University Library). Alternatively, the Code of Federal Regulations can be purchased from the Superintendent of Documents, U.S. Government Printing Office, Washington D.C. 20402. Parts 100-177 and Parts 178-199 are bound in two separate volumes and cost about $13 each. The Code of Federal Regulations is revised annually. Since Parts 178 and 179 refer to Shipping Container Specifications and Specifications for Tank Cars you may wish to purchase only Parts 100-177.

Figure 3.E -1 Packaging and Shipping Requirements for Laboratory Samples



3.E.2. SAMPLE TYPES

For the sake of interpreting applicable federal regulations, samples can be categorized as unregulated and DOT regulated. The DOT regulated category is further divided into Unanalyzed Waste Samples from closed containers, Unanalyzed Waste Samples from open containers and Listed Wastes. These categories are described as follows:

3.E.2.a. UNREGULATED SAMPLES

Unregulated samples include environmental samples such as preserved and unpreserved drinking water, groundwater, ambient water, lake and stream samples, treated municipal and industrial effluent, lake and stream sediments, fish samples, coal samples, and other fuels and uncontaminated or weakly contaminated soils. DOT Hazardous Materials Transportation Regulations do not apply to weak aqueous solutions of HCl, HNO_3, H_2SO_4 and NaOH (environmental samples preserved with the required quantities and concentrations of preservatives).

3.E.2.b. REGULATED SAMPLES

DOT regulated samples include untreated sewage, industrial process samples, spill investigation samples, sludge from industrial processes, and samples from hazardous waste sites which may pose an unreasonable risk to health, safety or property when transported by common carrier. DOT regulated samples are further divided into the following three categories:

- Unanalyzed Waste Samples from closed containers -

- Unanalyzed Waste Samples from open containers or from contaminated waste site soils or liquids.

- Listed Wastes - Samples containing wastes listed on the DOT Hazardous Materials Table, 40 CFR Section 172.101. (Sample content must be known prior to analysis.)

3.E.3. SAMPLE PACKAGING - UNREGULATED

The following procedure is recommended for shipment of unregulated samples:

1. All samples are to be placed inside a strong shipping container. This container should be able to withstand a 4 foot drop on solid concrete in the position most likely to cause damage. A metal picnic cooler lined with hard plastic meets this test. The cooler drainage hole should be secured to prevent the contents from escaping. The cooler should be marked, "This End Up" with arrows indicating the proper upward position. The cooler lid should also be taped shut to prevent leakage in the event that the cooler is overturned.

2. Screw type caps should be tightened before placement in the shipping container. Ground glass stoppers should be secured with nylon reinforced tape. Glass bottles should be separated in the shipping container by cushioning with styrofoam or an absorbent material to prevent breakage. Styrofoam sheets made to fit tightly in the cooler, with circular openings to accept sample bottles snugly are suitable for this purpose. Volatile organic samples (40 ml vials) can be placed inside a larger container and packed with absorbent or cushioning

material to prevent breakage or leakage. Glass sample containers should be packaged so as to survive the 4 foot drop test.

3. Ice should be placed in separate plastic bags and sealed or water should be frozen in plastic sample bottles to prevent melting ice from saturating the packing material or floating the sample bottles. Do not rely on loosely packed ice to cushion glass sample bottles. Sample bottles and packaged ice can also be placed together in a large sturdy plastic bag within the cooler to provide an additional waterproof lining.

3.E.4. SAMPLE PACKAGING REGULATED

The following procedures are required for samples such as untreated sewage, industrial process samples, spill investigation samples, sludge from industrial processes, drum samples, samples from unregulated hazardous waste sites and similar samples which in the judgment of the project leader cannot be considered unregulated samples. For purposes of sample transport and packaging under DOT Regulations, unanalyzed waste samples are divided into two primary categories: Unanalyzed Waste Samples (excluding those from closed containers) and Waste Samples from Closed Containers.

3.E.4.a. UNANALYZED WASTE SAMPLES, EXCLUDING THOSE FROM CLOSED CONTAINERS

This category includes samples which may contain concentrations of contaminants in excess of those normally encountered in preserved drinking water, ambient water, effluent, biological sediment and sludge samples. Waste samples include such samples as leachates, untreated process materials, samples from spill investigations, industrial sludges, and contaminated soils, groundwater and surface water from uncontrolled waste disposal sites.

Procedures for packaging, marking and labeling unanalyzed hazardous waste site samples, excluding those from closed containers are as follows:

1. Collect the sample in a suitable container for the parameters being analyzed. Leave approximately 10% of the container empty to allow for expansion of the sample.

2. Attach a properly completed DNR label (or equivalent) to the sample container.

3. Seal the sample container and place it in a 2 ml or thicker polyethylene bag.

4. Place the sealed bag inside a metal can with incombustible, absorbent cushioning material (e.g. vermiculite or earth) to prevent breakage; one bag per can. Pressure - close the can and use clips, tape or other fasteners to hold the lid securely.

5. Mark and label the metal can with the following information: laboratory name and address and "Flammable Liquid n.o.s." (or if not a liquid) "Flammable Solid n.o.s.".

6. Place one or more metal cans surrounded with incombustible packaging material in a strong outside container, such as a picnic cooler or fiberboard box.

7. Mark and label this outside container as in 5 above and mark the outside container with the words "Laboratory Samples" and "This Side Up" or "This End Up" on the top with upward pointing arrows on all four sides of the exterior container.

8. Complete the carrier provided bill of lading and sign the certification statement. If the carrier does not provide these documents, provide the following information in the order listed: "Flammable Liquid, n.o.s." (or "Flammable Solid, n.o.s.," as appropriate); "Cargo Aircraft Only"; "Limited Quantity" or "Ltd. Qty."; "Laboratory Samples"; "Net Weight _____" or "Net Volume _____" (of hazardous contents), by item, if more than one can is inside an exterior container. The net weight or net volume must be placed just before or just after the "Flammable Liquid, n.o.s." or "Flammable Solid, n.o.s." description.

3.E.4.b. WASTE SAMPLES FROM CLOSED CONTAINERS

Waste samples from closed containers include samples from drums, tanks and other similar containers. Such wastes have not been exposed to the environment, diluted or degraded by mechanisms such as volatilization, hydrolysis, absorption and photochemical and biochemical degradation and are, therefore, potentially more hazardous than exposed wastes.

The following packaging, marking, labeling, and shipping methods represent a worst-case procedure for wastes samples from closed containers by treating them as Poison A materials (49 CFR 173.328). In the absence of reliable data which excludes the possibility of the presence of Poison A chemicals or compounds, these procedures must be followed:

1. Collect the sample in a polyethylene or glass container which is of an outer diameter narrower than the valve hole on a DOT spec. 3A1800 or 3AA1800 metal cylinder. Fill sample container allowing sufficient ullage (approximately 10 percent by volume) so it will not be liquid-full at 130° F. Seal sample container.

2. Attach a properly completed sample label to the container.

3. Lower the container into a metal cylinder partially filled with incombustible, absorbent, loose packaging material (vermiculite or earth). Allow sufficient cushioning material between the bottom and sides of the container and the metal cylinder to prevent breakage. After the cylinder is filled with cushioning material, drop the ends of the string or wire into the cylinder valve hole. Only one sample container may be placed in each metal cylinder.

4. Replace valve, torque to 250 ft-lb (for 1-in opening) and replace valve protection on metal cylinder using Teflon tape.

5. Mark and label cylinder as described below.

6. One or more cylinders may be placed in a strong outside container.

7. Place the following information (either handprinted or on preprinted labels) on the side of the cylinder, or on a tag wired to the cylinder valve protector as well as on any outside packaging: "Poisonous Liquid or Gas, n.o.s." and the laboratory name and address. Place the label "Poisonous Gas" on the cylinder ("Poisonous Liquid" label not acceptable here, even if liquid).

8. Complete the shipper-provided bill of lading and sign the certifi-

cation statement. If the carrier does not provide these documents, provide the following information in the order listed and use abbreviations only as specified: "Poisonous Liquid, n.o.s."; "Limited Quantity" or "Ltd. Qty."; "Laboratory Samples"; "Net Weight _____" or "Net Volume _____" (of hazardous contents), by cylinder if more than one cylinder is packaged in an exterior container. The net weight or net volume must be placed just before or just after the "Poisonous Liquid, n.o.s. marking.

9. A chain-of-custody record form must also be properly executed and included in the container or with the cylinder.

10. A staff member should accompany the shipping containers to the transport carrier and open the outside containers for freight inspection if required.

3.E.5. CHAIN OF CUSTODY REQUIREMENTS

If there is a chance that sample results might be used as legal evidence, chain of custody should be maintained from sample collection until analysis. The use of locked metal picnic coolers during transport by a common carrier will enable the receiver to verify that the cooler has not been opened.

Some carriers offer special custody services which formally transfer custody from the shipper to the carrier and then to the laboratory. Such special custody services are not necessary provided that the shipper and the laboratory can document that the sample package was not opened during transit.

3.E.6. SAMPLE PRESERVATION AND HOLDING TIME

Parameter holding time and the amount of time required to ship samples to a laboratory can be an important consideration of sample shipment. Parameters with 2 to 8 hour holding times, such a pH, dissolved metals sulfite and dissolved oxygen cannot usually be transported to a laboratory within their holding times (via common carrier or state vehicle) and should be analyzed or filtered on site as appropriate. Parameters with 24-48 hour holding times include certain nutrients, chlorophyll a, hexavalent chromium, BOD and turbidity.Samples to be analyzed for these parameters and samples requiring refrigeration as a part of their preservation scheme must be collected and transported to the laboratory within this 24 to 48 hour time period. It is up to the field staff to select a delivery method that will meet the holding times in table 3.B-1. All parameters except metals (excluding hexavalent chromium and mercury should be packaged so as to maintain refrigeration during transport.

Unanalyzed hazardous waste samples should not be "fixed" with preservative or refrigerated with ice or dry ice. Moreover, there are no EPA promulgated holding times for samples such as soils, sludges, oils and wastes. It is generally assumed that decay of waste sample constituents is not significant compared to the levels present. Samples should always be collected, transported and analyzed as soon as conveniently possible.

3.E.7. SAMPLE SHIPMENT

Samples could be shipped from any location in the state to any

laboratory in the nation. The shipment could range from a single sample shipped via U.S. Mail to large sample lots packed in several ice chests for overnight delivery. Specific guidance for such diverse shipments is not practical. Consequently, each program manager should investigate the services, pick-up and delivery schedules, and rates of the major carriers from the point of departure to the laboratory. Commercial laboratories will also be able to recommend appropriate carriers.

Carriers such as Federal Express and other types of air freight provide rapid service. Other carriers such as United Parcel Service, U.S. Mail or Bus are slower and should not be used if sample holding time and sample refrigeration needs (if any) cannot be met.

Interdepartmental (I.D.) Mail makes daily pick-up at Grand Rapids, Saginaw, Plainwell, and Jackson. Check with your office manager for pick up times. Environmental samples can be transported to the MDNR laboratory by I.D. Mail provided that their packaged weight does not exceed 50 lbs. The advantages of I.D. Mail are cost and daily pick up from Region III district offices. I.D. Mail should be considered when holding times allow and when refrigeration (if required) can be maintained.

CHAPTER 4

FIELD COLLECTION AND FIELD ANALYSIS PROCEDURES

Prepared by
State of Michigan
Department of Natural Resources
Surface Water Quality Division
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TABLES

FIGURES

4.A. INTRODUCTION AND GENERAL PROCEDURES

4.A.1. INTRODUCTION

The objective of sampling is to collect a portion of material small enough in volume to be conveniently transported to and handled in the laboratory while still accurately representing the material being sampled. This implies, first, that the relative proportions or concentrations of all pertinent components must be the same in the sample as in the material being sampled, and second, that the sample must be handled in such a way that no significant changes in the composition occur before the tests are performed.

In carrying out an appropriate sample collection program, the following items should be considered:

-- Selection of parameters to be measured.

-- Selection of representative sampling sites.

-- Collection of sufficient volume of sample to perform the required analysis.

-- Selection and proper preparation of sample containers.

-- Preservation of samples to maintain the samples' integrity.

-- Identification for each sample by proper labeling of the containers.

-- Procedure to insure that recommended sample holding times are not exceeded.

-- Procedures for identifying and handling potentially hazardous samples.

-- Chain of custody procedures.

4.A.2. GENERAL SAMPLING CONSIDERATIONS

The wide variety of conditions existing at different sampling locations always requires that some judgment be made regarding the methodology and procedure for collection of representative samples. There are, however, basic rules and precautions generally applicable to sample collection. Some important considerations for obtaining a representative water sample are as follows:

-- The sample should be collected where the greatest mixing occurs. The sample should be collected near the center of the flow channel, where the turbulence is at a maximum. Skimming of the water surface or dragging the channel bottom should be avoided.

-- Before samples are collected from distribution systems, flush the lines sufficiently to insure that the sample is representative of the supply, taking into account the diameter and length of the pipe to be flushed and the velocity of flow.

-- The sampling of wastewater for immiscible liquids, such as oil and grease, requires special attention. Oil and grease may be present in wastewater as a surface film, an emulsion, in solution, or as a combination of these forms. As it is very difficult to collect a

representative oil and grease sample, the sampler must carefully evaluate the location of the sampling point. The most desirable sampling location is the point where greatest mixing is occurring. Quiescent areas should be avoided, if possible. Because losses of oil and grease will occur on sampling equipment, the collection of a composite sample is impractical. Individual portions collected at prescribed time intervals, must be analyzed separately to obtain the average concentrations over an extended period.

-- If manual compositing is employed, the individual sample bottles must be thoroughly mixed before pouring the individual aliquots into the composite containers.

4.A.3. TYPES OF SAMPLES

4.A.3.a. Grab Sample

A grab sample is defined as an individual sample collected over a period of time not exceeding 15 minutes but usually over just 1 or two minutes. Grab samples represent only the condition that exists at the time the sample is collected. The collection of a grab sample is appropriate when:

-- Characterization of the sample material is desired at a particular instance in time;

-- To provide information about minimum and maximum concentrations;

-- To comply with the NPDES Permit monitoring specifications; and

-- To corroborate with composite sample.

In addition, there are certain parameters, such as pH, temperature, residual chlorine, D.O., oil and grease, coliform bacteria, that must be evaluated in-situ or by using a grab sample because of biological, chemical or physical interactions which take place after the sample collection and affect the results.

4.A.3.b. Composite Sample

A composite sample is the aggregate of 2 or more sub samples that vary either spatially, in time or both.

4.A.4. SAMPLE PRESERVATION AND CONTAINERS

Sample Preservation - In most cases, the sample may contain one or more unstable pollutants that require immediate analysis or preservation. The rate of change of pollutant concentration is influenced by temperature, pH, bacterial action, concentration, and intermolecular reactions. Since treatment to fix one constituent may affect another, preservation is sometimes complicated, requiring the collection of multiple samples or the splitting of a single sample into multiple parts.

Immediate analysis is the most positive assurance against error from sample deterioration, but this is not always possible. It is, therefore, important that stabilization of the sample be provided as soon after sampling as possible. Procedures used to preserve samples include refrigeration, pH adjustment and chemical treatment. Refrigeration is the most common method of sample preservation. Temperature control near 4°C retards bacterial action and suppresses volatilization of most dissolved gases. The appropriate preservatives and sample containers are listed in table 3.B-1.

There are a variety of individual preservation techniques depending on the constituent to be analyzed. A detailed discussion is contained in the Chapter 3, Sample Preservation and Handling.

4.A.5. COMMON OR UNIVERSAL FIELD ANALYSES PROCEDURES

Unless specific procedures say otherwise, all field measurements should be replicated at a frequency of once per 20 samples. For field measurements that require calibration of an instrument, calibration checks should be performed at least daily unless specific procedures call for more frequent checks.

4.A.5.a. Temperature

-- Once each year, the thermometer should be standardized against a certified thermometer. This will be done by immersing the thermometer in an ice bath (0°C) and a warm water bath (50°C). Thermometers not reading within 1 C will be adjusted or discarded. New thermometers are not used until they have been standardized. Calibration curves will be maintained on file for each instrument.

-- Reading is made with calibrated thermometer immersed in water, flowing when possible, after a period of time sufficient to permit a constant reading (two to three minutes). Sample should cover at least half the thermometer stem or up to the immersion line on glass thermometer.

Temperature is recorded with a calibrated centigrade scale mercury thermometer, to the nearest 0.5° centigrade immediately following sample collection. Always, keep glass thermometers in an armored case to minimize breakage. Whenever possible the thermometer should be immersed directly in the stream. If sample is being obtained from a bridge with a sampling can use the following technique.

-- Measurement techniques with a sample can.

- Obtain a water sample in accordance with recommended procedures for use of sample can.

- Remove sample bottles inside of sample cans as soon as possible.

- Place a thermometer in the water remaining in the sample container, wait 2 to 3 minutes for thermometer to register, and read thermometer to the nearest 0.5° centigrade while the bulb remains submerged under water.

4.A.5.b. pH

Methods for the operation of the Sargent Welch model PBL and the Cole Parmer model 05996-80 are specified below. The manufacturer's procedures are used for the Orion model SA230 pH meter.

The following universal quality control procedures should be used for all pH meters:

1. When you are finished with measuring samples for the day (or after 10 measurements whichever is more frequent) recheck the calibration by remeasuring the pH of the two standard buffers you used to calibrate the meter. Record the readings in the log book. If the readings do not agree within ±0.1 su of the

calibration readings the data should not be used.

2. Measure a split sample or field replicate at least once a day or once per 20 samples. Record in the log book.
3. If there are two meters available, measure at least one sample with each meter. This information should be recorded in each log book.

4.A.5.b.1. Sargent Welch model PBL

-- Calibration and Operation

Set up instrument for line or battery operation (see Sections 2-4 of the Sargent-Welch instruction manual). In most cases, just check to see that the power switch is set on BATT.

Turn operation switch to STBY. No warm up time is necessary, but probe should be wet for 24 hours prior to use. Keep in KCl solution available from electronics technician.

Immerse the probe in pH 7.0 buffer and swirl.

Measure buffer temperature and set the temperature dial to correspond.

Turn the operation switch to READ.

To read the meter, line up the dial needle with its mirror image.

Use the standardization control to set the meter reading to exactly 7.0.

Return to STBY and rinse the probe with distilled water.

Immerse probe in pH 4 buffer and swirl. Check and adjust temperature dial if needed.

Turn to READ. Turn the buffer adjust control (phillips screw, rear top of meter) until the meter indicates the exact value of the buffer.

Return to STBY and rinse the probe. Repeat previous step with pH 10 buffer. A reading variance is greater than 10.0 $\pm$ 0.1 unit indicates meter problems that require repair or adjustment by the electronics technician.

If the reading is 10.0 $\pm$ 0.1, return to STBY, rinse the probe and record the calibration information in the pH log provided.

Collect a sample, measure the temperature and adjust the temperature dial. Immerse the probe in the sample and swirl.

Turn to READ and allow the meter reading a few seconds to stabilize. The reading will indicate the sample pH.

Return to STBY, rinse the probe and immerse in KCl until the next use.

Meter is to be left in STBY position during the survey. At survey completion, re-calibrate the meter as in previous

steps, (large deviations from the standards may indicate that meter repair is necessary). Turn to off. Record calibration data in log.

Notes

1. The bulb at the end of the glass electrode should be handled carefully to avoid scratching of the surface. Always keep electrodes immersed in KCl solution when not in use. If dismounted from holder, use a soft hand tissue in a beaker filled with KCI solution, for example, to prevent electrode from resting on the bottom of the beaker.

2. Store the electrode between periods of use by immersing the pH sensitive glass bulb in KCI solution. Storage in distilled water may result in a high resistance junction which may give the appearance of loss of electrode efficiency in use.

3. The electrode should be stored inside during periods of extreme cold weather.

4. Do not remove probe from any solutions when the meter is set to READ. This can and does cause the probe to short out.

5. The meter must be standardized to pH 7.0 buffer. Use of any others will result in slope errors.

6. For each calibration, immerse the probe in a small quantity of buffering solution (25-50 ml). After calibrating the meter, discard the used buffer solution. Replace each buffer solution with a fresh lot as it is consumed or at least every 3 months.

4.A.5.b.2. Cole-Parmer pH Meter

-Calibration:

A. Preparation

1. Check the expiration date of the buffers. Do not use outdated buffers.
2. Connect the probe (connection is on the right side of the meter).
3. Turn the **OFF-mV-pH-EXP** switch to pH.
3. Measure and record temperature of the standardization buffer in the log book. Adjust the temperature compensation dial to the proper temperature.

B. Calibrate the meter to two points

1. Remove the probe from the storage buffer, rinse well with distilled water and blot, **not wipe**, the excess moisture with a lint free tissue. **Note** - this step should be done each time before the probe is immersed in a different fluid. The bulb at the end of the glass electrode should be handled with great care. Avoid any situations which might cause scratches to the bulb.
2. Immerse the probe in pH 7.0 standard buffer and turn the operation switch to **READ**.
3. Swirl the buffer and wait 30 seconds for the probe to stabilize. At this point the needle dial should be stable. (If it is not consider using another meter.)

4. Adjust the **SET** control until the meter reads 7.0.
5. Remove the probe from pH 7.0 standard, rinse with distilled water and blot.
6. Measure the pH 10.0 standard buffer. If the reading is not exactly pH 10.0, adjust the **SLOPE** control until the meter reads 10.0.
7. Remeasure the pH 7.0 buffer, if necessary readjust the standardization control. If it is necessary to readjust the standardization control you must check the slope again. Repeat these steps as many times as necessary. (If it is not possible to adjust the meter to read the two points exactly do **not** use the meter.)

C. Check the meter

1. Measure the pH of the 4.0 standard buffer. Record the calibration information in the log book. If the reading is not within ±0.1 su do **not** use the meter.
2. After rinsing the probe return it to the storage buffer until you are ready to measure samples. Do not turn the meter off.

-Measuring the pH of a Sample:

1. Measure and record the sample temperature. If the temperature varies, from the temperature of the standardization buffer, by more than 2 °C readjust the temperature compensation dial.
2. Remove the probe from the storage buffer, rinse and blot.
3. Immerse in the sample and stir at a constant rate to provide homogenicity and suspension of solids. (Rate of stirring should minimize the air transfer at the air, water interface of the sample.)
4. Read and record the pH after one minute.
5. Repeat the measurement on successive volumes of the sample until the values differ by less than 0.1 su. Two or three changes are usually sufficient.
6. Report pH to the nearest 0.1 su and temperature to the nearest °C.

-Quality Control:

1. When you are finished with measuring samples for the day (or after 10 measurements whichever is more frequent) recheck the calibration by remeasuring the pH of the two standard buffers you used to calibrate the meter. Record the readings in the log book. If the readings do not agree within ±0.1 su of the calibration readings the data should not be used.
2. Measure a split sample or field replicate at least once a day or once per 20 samples. Record in the log book.
3. If there are two meters available, measure at least one sample with each meter. This information should be recorded in each log book.
4. Store the pH meter inside during cold weather.
5. If you have any reason to believe that you have contaminated a buffer: order replacement buffer and discard the old buffer.
6. When you are finished with the meter for the day turn the meter to **OFF** and immerse the probe in the storage buffer (1M KCl which has been adjusted to pH 4.0). (Extra KCl is provided in a labeled bottle in the pH kit.) **NOTE:** This storage buffer is not the same storage buffer used for the Sargent-Welch meter probes do not interchange these buffers.

4.a.5.B.3. Orion pH Model 250A

-- Calibration and Operation

A two buffer autocalibration must be performed using a automatic temperature compensating (ATC) electrode before pH is measured. A two buffer calibration using buffers that bracket the expected sample range is to be performed at the beginning of each day to determine if the electrode is working properly and determine the slope of the electrode.

Connect electrode to meter. Choose either 4.01 and 7.00, or 7.00 and 10.01 buffers, whichever will bracket your expected sample range.

Move the plastic band on the electrode down to uncover the electrolyte fill hole.

Press the **mode** key until the pH mode indicator is displayed.

Place electrode into either 4.01, 7.00, or 10.01 buffer.

Press **2nd cal** key. CALIBRATION is displayed above the main field and the time and date of the last calibration are displayed. After a few seconds P1 is displayed in the lower field. P1 indicates that the meter is ready for the first buffer and a value is stable, READY will be displayed and the temperature-corrected value for the buffer is displayed. Press the **Yes** key. The display will remain frozen for two seconds, then P2 will be displayed in the lower field indicating the meter is ready for the second buffer.

Rinse electrode and place in second buffer. Wait for a READY display and press **Yes**.

After the second buffer value has been entered the electrode slope will be displayed. SLP appears in the lower field with the actual electrode slope in percent in the main field. The slope should be between 92 and 102 % if not check the manual for instructions.

Rinse electrodes. Collect sample and place electrodes in sample. The meter will beep and READY will be displayed when the pH is stable. Record the pH from the main meter and if needed the temperature from the lower field.

References:

EPA: Methods for Chemical Analysis of Water and Wastes. (1979). Procedure 150.1
Clesceri, L.S. et al.
Standard Methods for the examination of Water and Wastewater.(1989) 17th edition. 4-94 - 4-102.

4.A.5.c. Conductivity

The following procedure is for the Beckman RC-19 Conductivity Bridge with a Beckman CEL-K-1 Cell.

4.A.5.c.1. Instrument Preparation

1. Connect to power source. Either 120 volts A.C. or battery. ☼If a battery is used do a battery check. Deflection to anywhere right of the red line indicates sufficient battery power.
2. Connect to red cell terminals , polarity not important
3. Set panel controls as follows:

Power	A.C. or battery
Frequency	100 H_2 for low conductance
Capacitance	100 H_2 for high conductance
Course	Zero
Fine	Min.
Balance switch	Res.
Multiplier	Desired capacitance range
Readout dial	5.00
Temp compensator	Solution temperature

4.A.5.c.2. Sample testing

1. Adjust the temperature compensator to correspond to the sample temperature.
2. Immerse the cell to at least 1/2" above air holes and at least 1/4" from bottom and sides of vessel. Agitate the sample to circulate through the cell and insure there are no air bubbles on the electrodes.
3. Rotate **multiplier dial** until meter passes through zero. Rotate **balancing knob** until meter reads zero. Clockwise rotation - deflection to right. Counterclockwise rotation - deflection to left.
   ☼If the meter does not pass through zero the cell may be defective, the reading was outside the range of the instrument, or the value falls within one of the end ranges.
4. When a zero reading is reached, change **balance switch** to **Cap.** If a reading of other than zero is obtained, adjust the meter to zero with the course and fine **capacitance controls.** Change the **balance switch** back to **Res** and adjust **balance knob** until the meter reads zero. Repeat these 2 steps until the meter reads zero for both **Res** and **Cap** modes.
5. Return the **balance switch** to the neutral position.
   ☼When cell is not immersed, leave **balance switch** in neutral position.
6. Record the conductance of the sample, turn the **balance switch** to the neutral position and rinse the cell with D.I.
7. Fill out the QA log after each use.

4.A.5.c.3. Trouble shooting

1. A gradual upward drift in conductance followed by an immediate drop when the cell is agitated indicates an incompletely cleaned cell.
2. Rotation of the multiplier dial may occasionally be necessary for conductance readings below 100 or above 1100. A multiplier dial reading of 100 is normally sufficient.Beckman RC-19 (Cell K-1) Conductivity Bridge

4.A.5.d. Dissolved Oxygen

4.A.5.d.1. Wet Winkler Analysis

-- Collect a sample in a 250 ml glass stoppered bottle using the 4-hole sample can or by allowing water to run gently down bottle side. Keep agitation to a minimum to prevent sample uptake (or loss) of oxygen. Stopper immediately.

-- Remove stopper, gently add 2 ml manganese sulfate solution (reagent I). Two ml is about ½ the neck volume.

-- Add sufficient alkali-iodide-ozide reagent II to fill the remaining volume of the bottle (2 ml).

-- Stopper carefully; avoid trapping air bubbles.

-- Mix by inverting bottle several (20) times.

-- When the precipitates settle leaving a clear supernatant above the floc, shake again.

-- When settling has produced at least 200 ml clear supernatant, carefully remove the stopper and immediately add 2 ml concentrated sulfuric acid. Allow the acid to run down the neck of the bottle. Restopper and mix by gentle inversion until dissolution is complete.

-- If the Environmental Lab is to complete the analysis, hold the sample at 4°C in the dark, and deliver to the lab.

-- To complete the analysis on-site, proceed as follows:

- Measure carefully 102 ml of the sample from the fixed sample into a 250 ml flask. A specially calibrated container is available from the Environmental Lab for this purpose.

- Titrate with 0.0250 N sodium thiosulfate ($Na_2S_2O_3$) to a light straw color.

- Add 1-2 ml starch solution, swirl to mix and continue titration to the first complete disappearance of the blue color.

- Mg/1 diss. oxygen = mls 0.0250 N $Na_2S_2O_3$ x 2.

Notes: One sample in 10 should be re-titrated to determine analyst precision. The second titration should not be greater than ± 0.1 ml different from the first. Results should be logged.

. Reagents I-III should be replaced at 6-month intervals or sooner if contamination is suspected. The starch should be kept in the dark, refrigerated and replaced when 2 ml fails to produce a strong blue color. The sodium thiosulfate should be standardized daily for greatest accuracy.

. D.O. results must be corrected for positive interference if chlorine was present in the sample. Actual D.O. = Wet Winkler D.O. - (Chlorine residual x 0.25).

4.A.5.d.2. Standardization of Sodium Thiosulfate

-- Dissolve approximately 1 g potassium iodide in about 100 ml distilled water in an erlenmeyer flask.

-- Carefully add about 0.5 ml (approx. 10 drops) conc. sulfuric acid swirl, and add 5.00 ml 0.025 N standard biniodate solution.

-- Titrate the liberated iodine with thiosulfate titrant, adding starch toward the end of the titration when a pale straw color is reached.

-- If the solutions are of equal strength, 5.00 ml of thiosulfate should be required.

$$N \text{ thiosulfate} - \frac{N \text{ biniodate} \times \text{ml biniodate}}{\text{ml thiosulfate}} = \frac{0.125}{\text{ml thiosulfate}}$$

Notes

1. The thiosulfate should be replaced when the titrant volume deviates more than 5.0 ± 0.1 mls in duplicate tests.

2. The laboratory requires 1-2 weeks notice to prepare the reagents.

4.A.5.d.3. Operation of YSI Model 54 Dissolved O_2 Meter

-Instrument preparation:

For best results the instrument should be left on overnight before calibration and use. When using meter in a lab, keep meter plugged into wall outlet when not in use. This keeps the batteries charged. May also be used while on A/C power. It is important that the instrument be placed in the intended operating position vertical, tilted or on its back before it is prepared for use and calibrated. Readjustment may be necessary when the instrument operating position is changed.

1. Before taking the instrument in the field, check the supplies for: O ring, membranes for probe, electrolyte for probe, D.O. saturation table and instrument QA log.
2. Attach probe and stirrer cable.
3. With switch in the **OFF** position, adjust the meter pointer to zero with the screw in the center of the meter panel. Readjustment may be necessary if the instrument position is changed.
4. Turn power on. Switch selector knob to **RED LINE** and adjust if necessary. If the meter will not redline it probably needs new batteries.
5. Switch to **ZERO** and adjust the zero point if necessary.

-Calibration:

1. If the probe has not been stored in a calibration bottle: place a moist piece of tissue paper in the bottom of the small plastic calibration bottle. (The calibration bottle is a small plastic bottle with the bottom cut out. The calibration bottle ensures 100% humidity during calibration). Fasten protective collar to probe and slide the probe into the calibration bottle. The probe membrane must be completely dry

but in a humid environment. The probe should also be placed where the temperature will not be changing rapidly.

2. Wait ten minutes for temperature stabilization.
3. Determine the O_2 saturation from the D.O. Saturation Table and adjust the O_2 Calib for the proper temperature and altitude. Record temperature and the dissolved oxygen concentration that you calibrated to, in the QA log.
4. Leave the meter on overnight to allow stabilization of the probe.
5. The instrument may also be calibrated to the results of a Winkler analysis of the water to be tested.

-Maintenance:

Replace the membrane if any of the following is observed:

- membrane is damaged or wrinkled
- bubbles have formed under the membrane
- erratic readings
- calibration is not stable or will not calibrate

Membrane will normally need to be replaced every 2-4 weeks. Always store the probe in a humid environment such as in a calibration bottle or plastic whirl-pac.

-Dissolved Oxygen Measurement:

1. With the instrument prepared for use and calibrated, remove protective collar from probe and thread probe onto stirrer. Be sure to record the calibration information in the QA log and in your field notes.
2. Measure and record the D.O. of river water that has been made anaerobic through the addition of excess sodium sulfite (1 gram/liter) and a trace of cobalt chloride.
3. Measure and record the D.O. of River water that has been saturated by pouring between two containers. Saturation should be verified by demonstrating that the meter reading does not increase after additional aeration of the sample. The measurement of D.O. by the probe should be $\pm$ 0.8 mg/l of the theoretical value.
4. If not, then <u>re-check all maintenance and calibration procedures</u>. If error is still greater than $\pm$0.8 mg/l replace membrane. If error is still greater than $\pm$0.8 mg/l replace probe. If error is still greater than $\pm$0.8 mg/l there may be interfering substances present in this case collect a Winkler.
5. Collect a Winkler sample.
   *This is a quality control procedure for comparison and should be done with the first and lost sample and every 10 samples in between.
6. Measure the stream temperature. Note the stream temperature on the lab analysis request form.
7. Place the probe in the stream, turn on stirrer and read and record the D.O. and the temperature in your field notes.
8. Measure and record the D.O. of River water that has been saturated by pouring between two containers at each station to check for interfering substances. At the end of the sampling run or after 10 stations check the calibration by drying the membrane and rechecking the calibration in saturated air as described above.

4.A.5.e. Secchi Disc Transparency

The Secchi disc is used to determine the clarity of the water. Clarity

is affected by many factors, including phytoplankton, suspended solids, natural water color, etc. Twice the Secchi disc depth is termed the euphotic zone. It is the depth that has sufficient light for the growth of aquatic plants. The disc readings should be taken, preferably, between 10:00 A.M. and 4:00 P.M. If possible, readings should not be taken during times of the day when the lake or river is rough or being used by a large number of motor-powered boats which may agitate the bottom sediments and reduce clarity.

Use the following steps when measuring transparency:

-- Take reading from a secure platform (dock) or anchor the boat before measuring the transparency to ensure that the Secchi disc is observed straight down instead of on an angle.

-- Attach a graduated line (one foot increments) to the disc.

-- Disc measurement should be obtained by lowering the disc into the water on the shaded side of the platform or boat. The observer should lean over the side of the boat so that he is directly over the disc as it is lowered. The depth at which the disc just disappears is noted. It is then raised slowly until it again becomes visible and that depth is noted. The point halfway between the two readings is the Secchi disc measurement. The disc should then be raised several feet and the procedure repeated and an average for the two values calculated. Record on field notes if Secchi disc is visible at the bottom, record with a > sign prefixing the depth.

4.B. POINT SOURCE TESTING

4.B.1. INTRODUCTION

Any meaningful discussion of point source monitoring should begin with a definition of the term "point source". Generally speaking, a point source is any confined discrete conveyance, such as a pipe, conduit, channel, well, etc. from which pollutants are or may be discharged. The point source discharges addressed in this manual are wastewater effluent from industrial, commercial and domestic sources. They include process effluent, non-contact and contact cooling waters and sewage.

Monitoring of these discharges is carried out for several reasons. The information may be used to:

-- Determine compliance with state and federal effluent limitations and water quality standards during a Compliance Sampling Inspection (CSI).
-- Determine the effectiveness of present effluent limitations.
-- Formulate new effluent limitations or revise the present ones.
-- Verify a facility's self-monitoring data.
-- Document the effectiveness of treatment technologies.
-- Characterize a wastewater and predict its impact on receiving waters.
-- Support enforcement action.
-- Identify potential problem areas.

Point source monitoring may be split into two broad categories. The first attempts to identify and quantify the various wastewater constituents. Effluent samples may be collected and analyzed for a variety of chemical and biological parameters (pH, metals, PCB's, fecal coliform bacteria, etc.). Physical characteristics such as flow and temperature may also be determined. The sample collection typically takes place over a 24-hour period and includes both composite and grab samples. Both concentration and mass loading data are derived from the samples.

4.B.2. SAMPLE COLLECTION

4.B.2.a. General Recommendations

The primary concern in point source monitoring is the collection of a representative sample of the wastewaters being discharged. Because each outfall or sampling point is unique, the details of exactly how and where the samples are collected must be worked out on a case-by-case basis. A few general rules do apply however to all sample collecting:

-- Samples should be collected at the locations given in the NPDES permit unless a more representative site exists.
-- Sample where wastewater velocities and mixing are sufficient to prevent any solids deposition. Generally samples should be taken at 0.4 - 0.6 x depth in mid channel, i.e. where the turbulence is at a maximum.
-- Avoid sampling areas where floating oils and greases have accumulated.
-- Hand sample facing upstream. Submerge the container mouth completely (exception: oil and grease samples - see special sampling notes).
-- The hours and days a facility operates, shift changes, day-to-day production patterns, seasonal variations, batch discharges, special cleaning times, etc. should be considered when planning for sample collection.

4.B.2.b. Grab Samples

An individual sample collected over a minimal period of time not exceeding fifteen minutes is considered a grab sample. Grab samples are collected for the following reasons:

-- To characterize the wastewater at a particular time.
-- To document the extremes of wastewater quality at various flows.
-- When wastewater discharge is of short duration or irregular (batch discharge).
-- For parameters that are unstable and must be analyzed in-situ such as, temperature, pH, chlorine residual and dissolved oxygen.
-- For parameters that cannot be composited without affecting the sample results such as volatile hydrocarbons, oil and grease, cyanide, phenol and bacteria.

Grab samples are generally collected by hand or by an extension of the hand such as a bottle holder or beaker on a long pole. Sampling cans, as described in the RIVER AND STREAM section of this Chapter are used occasionally to collect dissolved oxygen samples.

4.B.2.c. Composite Sampling

In point source monitoring, a composite sample collected over a period of time is most commonly used. The composite sample is the summation of several individual samples or a continuous sample, collected over a time period greater than fifteen minutes. The time period in point source monitoring is usually 24 hours or an operating day.

Composite samples are collected to establish the average waste characteristics of a discharge. They are also required for determining the mass loading from the discharge to the receiving water and for this reason are required in many NPDES permits.

Since sampling sites and wastewater characteristics vary greatly, a variety of sampling methods are needed. Three methods are currently in use by MDNR for point source monitoring. The automatic interval peristaltic pump-type samplers composite discrete samples. The submergible jug is automatic and composites continuously. The grab composite method is a manual summation of several equal volume samples. Table 4.B.-1, lists the recommended usage, limitations, installation and operating procedures for the various sampling methods.

On occasion, a "space" composite may be collected. In this case, samples are collected from several locations or depths and combined to create a single sample. A space composite might be used to characterize something like a wide discharge channel with several inputs that could not be adequately represented by a sample collected at one point.

Table 4.B.-1 Recommended Usage and Limitations - Composite Samplers

Type	Use When	Do Not Use When	Remarks
Peristaltic Interval Pump	1. Flow Proportional sample is required. (Most representative sampling method) 2. The waste stream is highly variable	1. Head over 20 feet. 2. Where there is a high potential for vandalism 3. Do not use at freezing temperatures	This is the preferred composite sampling method for all parameters except organics and sulfides
Submergible Glass Sampler	1. Background water samples are desired at intakes, rivers, lakes. 2. Waste characteristics do not vary appreciably	1. Jug may be battered against solid objects by high flow, wave action, ships.	Sampler collects 500 mls. at start then samples steadily at 325 ml/hr for 20 hrs. Rate decreases slowly to 200 ml/hr during last 4 hours.
Grab Composite	1. Collecting samples requiring immediate preservation (sulfides) or organic samples in conjunction with other samplers. 2. Sampling wastes with large solids (wwtp influents)		This method allows for immediate addition of chemical preservatives. This method is preferred for organic composite samples.

4.B.2.c.1. Automatic Interval Peristaltic Pump-Type Sampler

-- Install new medical grade silicon pump tubing (3/8 in. OD) in peristaltic pump of sampler.
-- Attach proper length of new medical grade polyethylene sample delivery tubing (1/4 or 3/8 in. OD) to the inlet end of the pump tubing using disposable plastic or stainless steel connectors.
-- Attach teflon/stainless steel strainer to the end of the delivery tubing.
-- Submerge the strainer in the wastewater stream in a location where a representative sample will be obtained. In some manner, secure the stainer in place. Do not allow the strainer to locate in an area where solids from the bottom or sides of the channel will be drawn into the sampler.
-- Connect sampler to 110 power source using invertor or connect battery to sampler.
-- Program the sampler using the users manual. Normally the sampler is programmed to collect one sample every fifteen minutes during the 24 hour inspection period for a total of 96 samples.
-- Determine the volume that will need to be collected for each sample and calibrate the sampler following the manual instructions. Normally calibration is done by operating the sampler manually and measuring the volume of sample delivered at the outlet end of the pump tubing with a graduated cylinder and adjusting the sampler accordingly.
-- Place the new or clean sample collection jug or bottles in the bottom of the sampler.
-- Connect a short length of new medical grade polyethylene tubing (3/8 in. OD) to the sample collection jug and to the outlet end of the pump tubing.
-- Place a sufficient amount of ice next to the sample collection jug in the bottom of the sampler to maintain the temperature at 4°C.
-- Manually operate the sampler to insure that the sample is being delivered to the collection jug.
-- Start the sampler following the manual directions.
-- Close the sampler and secure it with padlock and chain.
-- Periodically inspect the sampler to confirm proper operation and replace ice if needed.
-- At the end of the sampling period agitate sampling jug and pour sample into laboratory bottles. Preserve samples.
-- Deliver the excess sample to the permittee for replicate analysis.

Note
-- This sampler type is not recommended for collection of samples for organic analysis unless teflon lined tubing and collection bottles are used.

4.B.2.c.2. Submergible Sampler

-- Remove plastic bag from 4.5 or 9 liter sampler bottle. Replace bottle in cage and secure with safety chain.
-- Insert stopper (including sample intake and air outlet tubing) into bottle.
-- Cut a hole or notch in protective plastic sleeve covering hypodermic needle (hole or notch allows air to escape).
-- Position needle and protective sleeve on air-outlet tubing.
-- Secure appropriate length of rope to chain on sampler cage.
-- Carefully lower sampler into water until needle is just submerged.
-- Observe water in area of sampler for a slow steady stream of small air bubbles. If no air bubbles are present, if bubbling rapidly or if big bubbles keep rising, sampler is not working properly. If OK, lower to desired depth and secure.

-- After nine hours the sample from the 4.5 liter sampler must be poured off into sample bottles filling each bottle half full. The 9 liter jug is poured off at survey end. To pour off, retrieve the sampler, shake the jug to mix sample and pour off desired quantities into appropriate container for preservation. The jug should be shaken several times during pour-off of each parameter.

4.B.2.c.3. Grab Composite Samples

-- Collect 800-1000 ml minimum total sample (volume depends on analyses required).
-- Collect at least 4 equal portions per 24 hour sample period.
  - More portions may be collected with the appropriate reduction in portion volume.
  - Portions are 200-250 ml per grab usually depending on final desired volume and number of portions to be collected.
-- Samples to be split with the facility should be 4 times the size of other samples. Biosamples are also 4 times as large.
  - Ex. CN 4 grab composite = 1000 ml total 250 ml/portion. Facility split = 4000 ml total, 1000 ml/portion.
-- Samples may be preserved in two ways:
  - Since final sample volume is known, the total amount of preservative recommended may be added with the first sample portion.
  - Each portion may be individually preserved after it has been added to sample container.

Notes

When chlorine is found or suspected, each sample portion collected for CN or phenol, must be dechlorinated and preserved before adding it to the composite. See Chapter 3, Section 3.B.2.a. Dechlorination, for the appropriate dechlorinating and preserving agents.

The same sample bottle or graduated cylinder may be reused to collect each portion of the grab composite, provided it has been labeled with the outfall number being sampled. Bottles or graduates must not be interchanged between outfalls.

Glass must be used to collect the composite portions taken for hydrocarbon analyses.

4.B.2.d. Composite Sample Pour-Off Procedure

When a composite sample is collected with an automatic type composite sampler a standardized procedure will be followed for pouring samples from the collection bottle into the sample bottles if the collection bottle is insufficient in volume to hold the entire sample or if the sample collection bottle can not be kept cool. The procedure is as follows:

-- Set up an appropriate size container for each parameter group at the first pour off. A container should also be set up for the split sample and the biosample (if any).
-- Estimate, conservatively, the volume of sample in the collection bottle.
-- Compute how much water should go into each sample bottle to make each sample proportional to the total amount.
-- Shake the collection bottle vigorously each time before the contents are poured into the graduated cylinder.
-- Measure and pour the computed amount into each sample bottle set up. Swirl the graduated cylinder to insure complete mixing.

-- Pour the water remaining in the collection bottle into the graduated cylinder.
-- Divide the remaining volume of sample proportionally into the sample bottles.

There should not be more than a ten (10) hour interval between pour offs.

Label graduated cylinders with outfall numbers or identifying codes. Do not use a graduated cylinder for more than one outfall.

Always swirl the graduated cylinder before pouring into the sample bottles.

Add the appropriate amount and type of preservative (if required) after each pour-off and ice the sample. Chapter 3 lists the appropriate quantity and type of preservative.

4.B.2.e. Special Sampling Notes

The following is summarized from a variety of sources including field experience and memos. The information is intended to improve the chemical data collected and clarify the lab results (or the lack thereof) for some parameters.

4.B.2.e.1. BOD_5

Sample prior to chlorination or after dechlorination when possible.

Indicate if the samples are chlorinated or dechlorinated on lab sheets. Reseeding is needed in these cases to prevent abnormally low results.

4.B.2.e.2. COD

Chloride concentrations exceeding 2000 mg/1 interfere with the COD analysis. TOC analyses should be requested in this case and COD's estimated from TOC results.

4.B.2.e.3. Cyanide and Phenol

Any chlorine present in samples collected for cyanide or phenolics must be removed using the appropriate dechlorinating agent prior to preservation, see Chapter 3, Section 3.B.2.a. Dechlorination.

When total CN is less than 0.05 mg/1, the lab will not analyze for CN-A (A = amenable to chlorination) or free cyanide.

Sulfides and H_2S interfere with the CN and phenol analyses. Let laboratory personnel know if sulfides are suspected in samples. Collect a sulfides samples and/or ask for sulfides analysis to provide more information.

It is recommended that analysis for cyanide and phenol be done only on grab samples that were preserved immediately after collection.

4.B.2.e.4. Microbiological Samples

Do not fill more than 3/4 full.

Do not touch the bottle mouth or the inside of the cap. Do not use the bottle if it has been stored open. Do not rinse a bacti bottle.

4.B.2.e.5. Oil and Grease

Do not rinse an oil and grease bottle.

Do not allow the bottle to overflow.

Samples for quantitative analyses must be collected, without skimming, where mixing is greatest.

Only gravimetric results are comparable to NPDES permit limitations.

4.B.2.e.6. Field Blanks

Field blank results are not subtracted from the sample results by laboratory personnel. Interpretation of blank results is left up to the discretion of the investigator. The laboratory will try to indicate field blank values which are significantly different from background levels.

4.B.2.e.7. Settleable Solids

The lab will analyze for settleable solids only when suspended solids is greater than 20 mg/1.

4.B.2.e.8. Sulfides

The sample must be preserved immediately upon collection. Collect only as a grab or grab composite unless the preservative has been added to the collection container of an automatic sampler.

4.B.2.e.9. Volatile Hydrocarbons (purgeable organics)

Fill the bottle completely - leave no airspace.

The teflon (shiny-white or red) side of cap liner must touch the sample.

Add the dechlorinating agent (if required) and hydrochloric acid to the full bottle - there will be a slight overflow.

4.B.3. FIELD INSTRUMENTS AND ANALYSIS

The following are procedures for operation of field instruments and conducting analyses presently in use for point source monitoring. The procedures were written as a step-by-step guide to the accepted methodology. However, most require that the investigator be at least somewhat familiar with the equipment or test that he/she is using. Users are encouraged to refer to the manufacturers' instruction manuals when more specific information is required.

The procedures for conducting field Wet-Winkler dissolved oxygen analyses and procedures for calibration and operation of the, YSI Oxygen Meters, Sargent-Welch and Orion Model 250A pH Meters and bimetallic and glass thermometers are contained in the Introduction and General Procedures, Section 4.A. of this chapter.

4.B.3.a. Total Residual Chlorine

4.B.3.a.1. Amperometric Titration

Several different models of amperometric titrators are in use to determine total residual chlorine concentrations in the field. The following is a general description applicable to all models.

Equipment Set Up

-- Charging the battery:
Plug in titrator to 110 volt outlet overnight to fully charge the battery. Titrator can also be used when plugged in continuously. It cannot be overcharged.
-- Cleaning probe and sample jar:
Disconnect the probe from the unit by pulling it straight down. Clean the probe, agitator, and sample jar using a non-abrasive, chlorine-free household cleanser (Bon Ami or equivalent). Make sure to clean the ends of the electrodes also. Rinse the assembly with distilled water.
-- Filling the titrant pipet:

- Fill the plastic titrant container with phenylarsene oxide (PAO).
- Open the pinch valve or "refill" valve. Open the cap on the titrant container if needed.
- If the model has a micro-pump - place a finger over the opening at the top of the pipet. Rotate the pump clockwise until the titrant flows down the spout and enters the tubing to the tee. Close the pinch valve and remove the finger from the pipet opening. With the cap of the titrant container open, open the pinch valve slightly and observe the pipet filling because of the siphon action.
- Fill to the "0" mark. Close the pinch or "refill" valve.
- Rotate the pump or open the "refill" valve until all the air bubbles come out of the dispenser end and again re-zero the pipet. The titrator is now ready.

Forward Titration For Total Residual Chlorine

-- Fill the sample jar with 200 ml of tap or distilled water and allow the titrator to operate for 5-10 min. on the FREE position. This will stabilize the meter.
-- Thoroughly rinse the probe, sample jar, and agitator with distilled water.
-- Fill sample jar with 200 ml of sample.
-- Add 1 eyedropper (approx. 1 ml) of pH 4 buffer.
-- Add 1 eyedropper (approx. 1 ml) of 5% potassium iodide solution.
-- Place the sample jar on the titrator.
-- Place the switch in the TOTAL position. The meter cannot be damaged even if the indicator "pins" on the right or top.
-- Slowly rotate the Micro Pump (clockwise) or open the "titrate" valve to add titrant to the sample jar.
-- Add the titrant (PAO) slowly until one more drop of titrant does not cause the meters needle to deflect to the left or down. The "end point" has now been reached. For greatest accuracy the volume of the last drop added should be subtracted from the total volume of titrant used in the titration.
-- Immediately titrate a second sample from the wastestream to confirm reading.
-- The total volume of titrant used = the ppm (or mg/1) of total chlorine.

Quality Control and Standardization

-- Always maintain a 200 ml sample level within the sample jar. A lower level will allow the saturated electrolyte level to deplete from the electrodes.
-- Perform the titration within a 6-minute period.
-- The phenylarsene oxide solution should be standardized every month.

The laboratory will check the normality of the solution upon request.

-- Discard the 5% potassium iodide solution when it develops a yellow color.
-- Have the pH 4 acetate buffer checked at the lab every three months.
-- Store all solutions in covered brown glass bottles.
-- When possible check the results of the amperometric titrator with another method for total residual chlorine.

4.B.3.a.2. Specific Ion Meter

The Orion Model SA 270 Meter is used to determine total residual chlorine in the field.

-- Calibration and Operation

A two standard calibration must be performed before total residual chlorine concentration is measured. A two standard calibration using standards with concentrations that bracket the expected sample range is to be performed at the beginning of each day to determine if the electrode is working properly and determine the slope of the electrode. A one standard calibration check should be performed every two hours of operation to compensate for drift. The standards should be at the same temperature as the sample to be measured.

Consult electrode instruction manual for electrode preparation, required solutions and special requirements. Prepare two standards that differ in concentration by a factor of 10 and that bracket the expected sample concentration.

Add ionic strength adjustor or pH adjustor as recommended by the electrode manual.

Connect electrode to meter and slide mode switch to either **conc** or **expand**.

Place electrode in the less concentrated standard.

Press **cal**. The display will alternate between **.1.** and the measured concentration value of the standard indicating this is the first standard and a true value has not been entered.

Wait for a stable concentration value display. Scroll until the actual concentration of the standard is displayed and press **enter**. The display will freeze for 3 seconds then will advance to **.2.** indicating the meter is ready for the second standard.

Rinse electrode and place into the second, more concentrated, standard. After the display had stabilized scroll until the actual value of the standard is displayed and press enter.

After the second value has been entered **ISE** will be displayed. The meter is now calibrated and automatically advances to measure samples in the concentration units of the standards.

Rinse electrode and place into sample. Read and record the concentration of the sample directly from the meter display.

4.B.3.a.3. DPD Spectrophotometric Method

Field analysis of total residual chlorine can be determined with a field spectrophotometer using Hach DPD Total Chlorine Reagent Powder Pillows.

Following are the field procedures for the Hach "Pocket Colorimeter":

The Hach "Pocket Colorimeter" is a single parameter filter photometer permanently calibrated to measure total chlorine concentration in the range of 0 to 4.5 mg/l. The meter is set

to a wave length of 528 nm and is accurate to 0.02 mg/l. To measure "low range" (<0.02 to 2.00 mg/l) total residual chlorine:
Fill the 10 ml cell to the 10 ml line with sample.

Add the contents of one DPD Total Chlorine Powder Pillow to the sample cell. Cap the cell and gently shake for 20 seconds. Let the prepared sample sit for 3 minutes.

Fill a second 10 ml cell to the 10 ml line with sample. This cell will be the "blank". Cap the blank and shake for 20 seconds.

Remove the instrument cap and place the blank in the cell holder making sure the diamond mark on the cell is facing the front of the instrument. Cover the cell with the instrument cover making sure the cover fits tightly against the instrument.

Press **ZERO**. The instrument will on and the display will show "---" followed by "0.00". Remove the blank from the cell holder.

After the 3 minutes place the prepared sample in the cell holder and cover the sample cell with the instrument cover.

Press **READ**. The instrument will show "---" followed by the total residual chlorine concentration in the sample in mg/l. Record the concentration.

Depending on the accuracy needed it may be necessary to check the chlorine concentration with another method.

4.B.3.b. Dissolved Metals Sampling

-- Clean items to be used in sampling in accordance with Section 4.B.6., of this Chapter.
-- Set up filtration apparatus (vacuum pump and filter flask). Insert 0.45 um (micron) membrane filter between two parts of the glass filter holder and clamp together. Support filtration apparatus using ring stand.
-- Acidify a bottle of distilled water with 1:1 nitric acid (HNO_3). This will be used as a blank for quality assurance purposes for total metals.
-- Filter a bottle of distilled water through clean, dry apparatus. Acidify using 1:1 nitric acid to pH less than 2. Mark as "Filtered Distilled Water". This will also be used as a blank.
-- Insert new membrane filter into clean filter holder and filter flask.
-- Collect sample and allow short time for settling. Decant sample supernatant into filter holder. If sample contains floc that will not settle or floc that is easily carried over into the filter holder, use cellulose fiber prefilter or withdraw clear supernate using pipette.
-- For GRAB samples, filter approximately 500 ml of sample. For COMPOSITE samples, filter enough sample (50% if possible) each pour-off to insure proportionality with time and flow and so that lab has a total of approximately 500 ml of sample to analyze. Mark sample bottle and sample sheet with the bottle code "MD" to indicate analysis for dissolved metals and acid preservation. Additional volume is required for certain metals or for lower detection limits.

-- Remove filtrate (filtered sample) from filter flask and acidify to a pH less than 2.
-- Also, collect a total metals sample (unfiltered) and acidify.
-- Glassware should be field cleaned as follows:
  - Remove filter and suck 1:1 hydrochloric acid through apparatus by carefully squirting the acid around the inside of the filter holder with suction applied.
  - Rinse at least twice with distilled water.
  - Pour acid solution from filter flask and rinse with liberal amounts of tap water (if available) followed by distilled water.
  - Shake excess water from cleaned glassware.
  - Store in clean plastic bag or in dissolved metals carrying case.
-- After each survey, turn in vacuum pump for cleaning and oiling.

4.B.3.b.1. Equipment Checklist

Filter Holders (two parts each) w/rubber stoppers
Filter Holder clamps
Filter Flasks

Membrane Filters (0.45 micron)
Deionized distilled water (for rinsing)
Wash Bottle of 1:1 Hcl

Vacuum Pump
Rubber Tubing
Vacuum pump oil

Ring Stand and Clamp

Cellulose prefilters or Pipettes

Preservative (1:1 HNO_3)
Bottles of Deionized Distilled Water (for blank)
Sample Bottles

4.B.3.c. Sargent Welch Recorder Model XKR

4.B.3.c.1. Calibration and Operation

-- Rotate power switch to on.
-- Connect positive lead from the signal source to the red terminal, the negative lead to the black terminal, and the shield wire, if any to the ground terminal.
-- Select the span. The span switch selects 10, 20, 50 and 100 MV full scale on the chart. The variable span control is used in conjunction with the span switch to change the value of the span selected continuously from its nominal value down to 40 percent of that value.
-- Select chart speed.
-- Rotate power switch to pen. Press input switch to short and adjust zero control for desired pen zero.
-- Rotate power switch to record and release input switch.
-- The chart must be labeled for identification with: location of facility, outfall number, inclusive dates, and operator's initials.

Notes

A chart speed of .05 cm/min. and span of 100 mv are generally used when operating the recorder in conjunction with a Sargent-Welch pH meter for

longer studies. A pH of 7 is considered the zero point and is usually located in the center of the chart. Check this with pH probe in 7.0 buffer and readjust with zero control if needed. Then place probe in second buffer, set power switch to record and use the variable span control to adjust the pen to the corresponding value on chart.

4.B.4. FLOW MEASUREMENT

4.B.4.a. Introduction

Determining the volume of wastewater that a facility discharges is as important to point source monitoring as documenting the wastewater constituents. Accurate flow measurements are required to compute representative mass loadings which may be limited by permit. Most permitted point source dischargers have accurate flow monitoring devices installed and have them regularly calibrated as required by their discharge permit. On occasion flow measurements independent of the permittee's are needed to assess the accuracy of self monitoring data. Accurate flow records can indicate the presence and extent of shock loads or hydraulic overloads which may have an environmental impact on receiving waters. Determination of dilution rates and times is also very dependent on high quality flow measurements. The methods currently being used to measure wastewater flows are outlined in the following section. The procedures deal primarily with open channel flow measurements.

When needed, a continuously recorded flow measurement is made which can be used to calculate mass loading/unit time. Generation of a continuous flow record requires the use of both primary and secondary flow devices. Primary devices are structures with predictable hydraulic responses related to the flow rate of water. Examples are venturi, orifice, ultrasonic meters that measure both depth and velocity and magnetic flow meters as well as weirs and flumes. Secondary devices are sensors which measure, transmit, and record (usually) the hydraulic response of the primary device. Examples are floats, scows, bubble gages, ultrasonic meters that measure depth only, sonic meters and electromagnetic cells.

Because of their accuracy and relative ease of installation, staff-installed devices are usually ultrasonic meters. If the point source has a reliable primary device bubbler gages or Stevens Type F Level Recorders are installed. If needed staff can install weirs.

The following measurement systems (primary + secondary devices) are ranked in order of their preferred use for generating accurate and independent (if needed) measurements.

1. Existing properly installed primary and secondary device where calibration is recorded and maintenance is adequate. (i.e.) Company Parshall flume + Company installed sonic meter.

2. Existing primary device and staff installed secondary device. (i.e.) Company weir + staff bubble gage.

3. Existing flow configuration and staff-installed secondary device. (i.e.) Cement trough with known configuration + staff-installed ultrasonic meter (Q-Logger).

4. Existing primary and secondary device with verification of flow by independent, instantaneous methods. (i.e.) Submerged orifice plate with ultrasonic sensor checked by dye studies.

5. Facility flow estimate derived from known water usage, metered incoming water, etc. with verification by independent instantaneous methods if possible. (i.e.) Bucket and stopwatch, dye studies.

Where flow cannot be measured continuously, instantaneous measurements may be possible. These measurements only represent the flow at a given time but several measurements over a 24-hour period can provide a rough estimate of daily flow.

The following miscellaneous methods are presently in use for point source monitoring. The choice of method is dependent on the quantity of flow and the conduit or channel characteristics.

-- Head Stick

-- Bucket and stopwatch.

-- Gurley or Electromagnetic velocity meter. Methods outlined in Section 4.D. River and Stream Sampling.

-- Fluorometry - Dye dilution technique.

-- Vessel volume X number of batches.

-- Pump capacity X time of pumping.

4.B.4.b. Use of Existing Primary Flow Devices (Weirs & Flumes)

The six checklists that follow are for evaluation of flow structures already in place. How closely the criteria are met will determine whether or not the structure provides an accurate measurement and may be used to determine flow. Deviations from the list should be noted in a field log. If excessive, it may be necessary to repair the device, replace it or use an alternative flow measuring method. These same criteria also apply to field installed devices.

4.B.4.b.1. Parshall Flume

The general conditions listed below should be met whenever using a Parshall flume, to insure accurate flow measurements.

-- The flume should have a straight approach channel, free of bends.

-- The flow velocity should be uniform at the entrance to the flume and without surges, waves, turbulence.

-- The crest should have smooth definite edges.

-- If installed in a sewer, the incoming pipe should be far enough from the throat to allow even flow distribution across the entrance width.

-- The crest floor should be level in all directions.

-- The dimensions should be correct for the flume size. See Department of Interior (1967) for details.

-- The head measurements should be taken at the proper location - see the (Figure 4.B.-1).

-- The zero head measurement should match up with the flume crest.

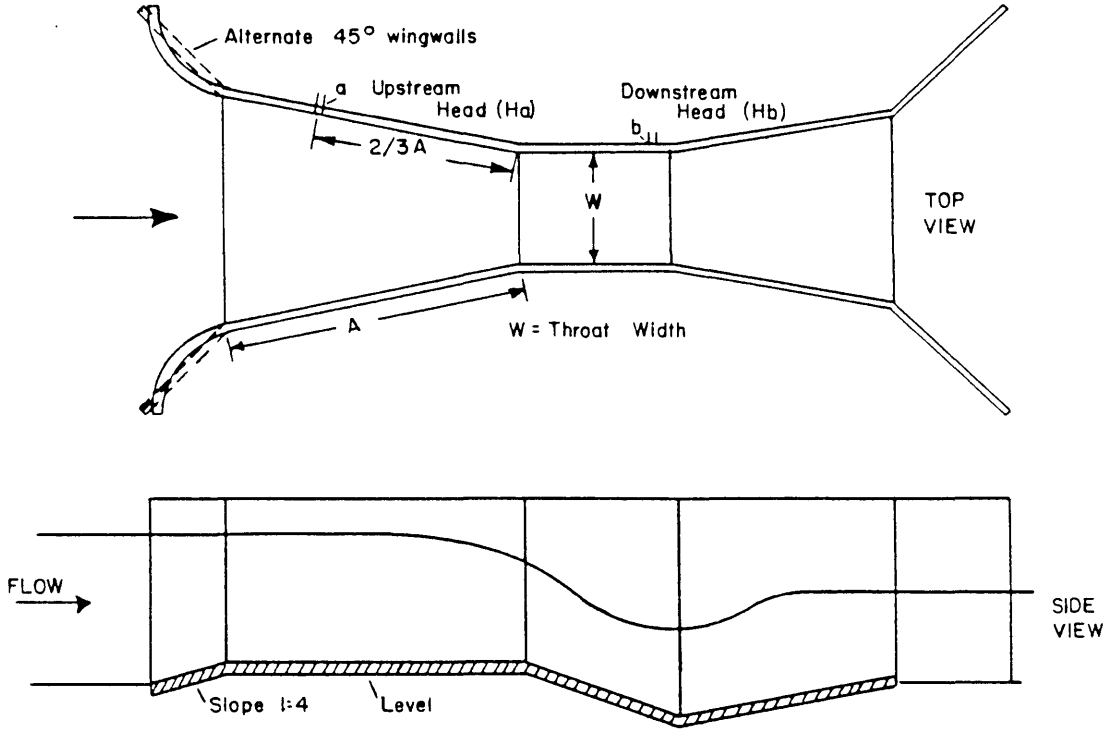


FIGURE 4.2.-1 Typical Parshall Flume

(adapted from Dept. of Commerce, 1975)

-- The flume throat should be clean and free of debris.

-- The flume should be operating without submergence unless proper steps are taken to compensate the flow measurements for the submergence rate. The flume is submerged when the ratio of the downstream head Hb to the upstream head Ha exceeds the limits given below.

Throat Width	Hb/Ha
Less than 3"	0.5
3" - 9"	0.6
1' - 8'	0.7
10' - 50	0.8

4.B.4.b.2. Sharp Crested Weirs (see Figure 4.B. - 2)

The conditions listed below are for ideal sharp crested weirs to insure the accuracy of the flow measurement. Special conditions relating to specific weir types are included under individual headings. Practical experience indicates that significant deviations can be made from these criteria while maintaining accuracy within an acceptable range. Variations from the criteria are allowed provided that it can be demonstrated that deviation does not cause a significant error or when the use of the weir equation and C values have been verified with other flow measuring means.

-- The upstream face of the bulkhead should be smooth and vertical.

-- The weir axis should be perpendicular to the axes of the channel (checked with line and carpenter square).

-- The thickness of the crest should not exceed 0.03 - 0.08 inches (1-2 mm).

-- The downstream edges of the weir opening should be chamfered at an angle of 45° or greater.

-- The distance from the crest to the bottom of the approach channel should be 2 times the head over the crest or a minimum of 1 foot.

-- The overflow sheet (nape) should touch only the upstream edge of the crest and sides. The nape should spring free and there should be freefall.

-- A zero head reading should match up with the crest level.

-- The water surface measurement should be taken at a point upstream 4 times the maximum head over the crest to avoid drawdown.

-- The cross-sectional area of the approach channel should be 8 times that of the overflow sheet.

-- The cross-sectional area of the approach channel should prevail upstream for a distance of 15 times the depth of the overflow sheet.

-- The minimum head to be measured is 0.2 feet.

4.B.4.b.3. Contracted Rectangular Weirs

-- The maximum measurable head should not exceed 1/2 the crest length.

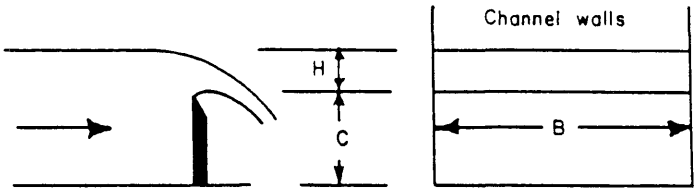
-- The crest should be level.

-- The upstream corners of the crest should be sharp and perpendicular to the upstream face.

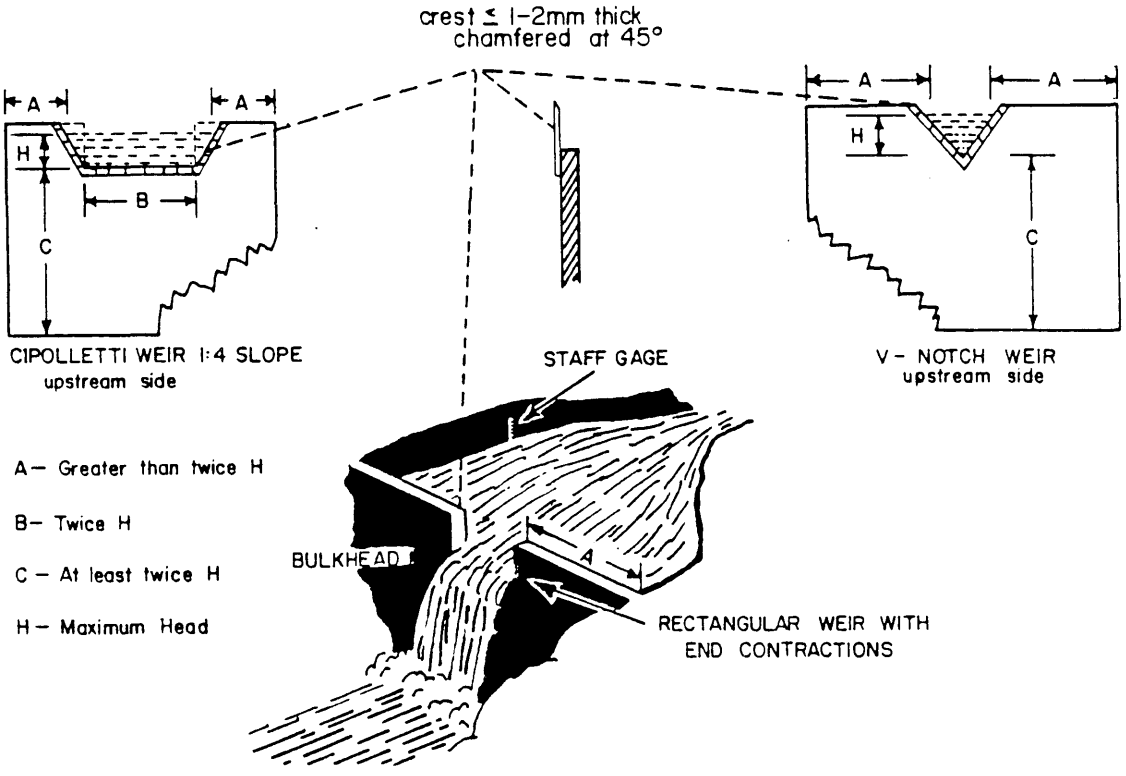
-- The distance from the sides of the weir to the sides of the approach channel should be twice the depth of the water over the crest, or a minimum of 1 foot.

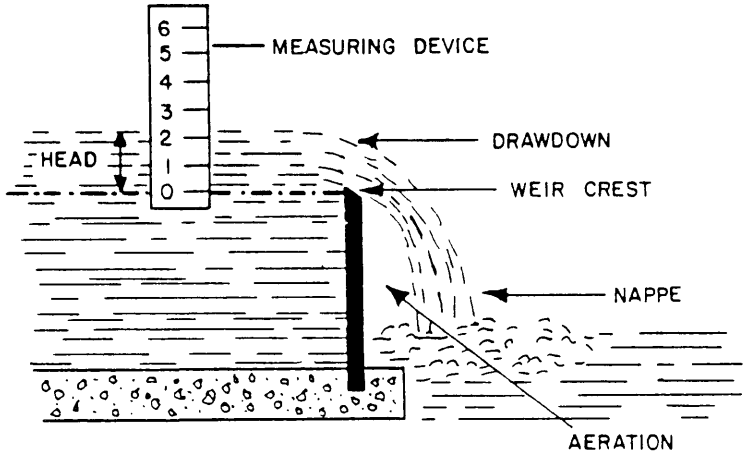
Figure 4.B.-2

Typical Sharp Crested Weirs and some General Conditions Pertaining to Them



Suppressed Rectangular Weir. (full channel)





SHARP CRESTED WEIR

(adapted from Leupold and Stevens, 1978; Dept. of Commerce, 1975)

4.B.4.b.4. Cipoletti Weirs

-- The first four items under contracted rectangular weirs apply.

-- The sides of the weir opening should have 1 horizontal: 4 vertical outward slopes.

4.B.4.b.5. Suppressed Rectangular (Full Channel) Weirs

-- The first three items under contracted rectangular weirs apply.

-- The nape should be vented on both sides.

-- The sides of the approach channel should be coincident with the sides of the weir, vertical and extend beyond the crest far enough to prevent lateral expansion of the nape.

4.B.4.b.6. V-Notch Weirs

-- The top of the weir plate should be level.

-- The upstream corners of the crest should be sharp and perpendicular to the upstream face.

-- The distance from the edge of the notch to the side of the approach channel should be twice the head on the weir, measured at the point of intersection of the maximum water surface with the weir. One foot is the minimum distance.

4.B.4.c. Field Installed Primary Devices

In the rare instance where a primary device is not available for flow measurement, an ultrasonic meter that measures both depth and velocity can be installed. Staff currently uses a Q-Logger manufactured by Montedoro-Whitney. The Q-Logger can be installed in a pipe or in an open channel if the characteristics of the channel are known. The Q-Logger probe is placed in the wastestream using springs or blocks and the data logger is programmed using the instruction manual to the specifics of the installation using a lap-top computer.

If necessary a primary device may be constructed and installed. Weirs are presently the only field-constructed primary devices used. Materials required include 3/4 inch plywood, 2 x 4's, burlap bags, nails, a source of sealing material (mud, clay, sand) and the appropriate hand and power tools. Flow velocity, the volume of water carried in the channel and channel size are important factors to consider in determining if a field installation is practical or even possible. The effects of backing up a flow should be known beforehand to prevent adverse conditions or damage within the facility being monitored.

4.B.4.c.1. Procedures For Installing Weirs

-- Select location of weir. The plate should be:

- Perpendicular to flow.

- Where good approach velocity can be achieved.

-- Determine size of weir

- Estimate flow based on observation, DMR data, etc.

- Weir selection - use only 90° v-notch or rectangular weir. Head over weir of 0.2' - 0.4' is desired. See Levpold and Stevens (1978) for weir sizes corresponding to estimated flows.

-- Cutting out weir.

- After weir size has been determined, lay weir out on good side of plywood. "A" should be greater than twice the maximum head (1 foot minimum), B should be at least twice the maximum head, C should be twice the maximum head (1 foot minimum), D must be 9-1/2 if the scoop type sampler is to be used with the weir, Figure 4.B.-3.

- Cut weir opening out with saber saw on a 45 degree angle, leaving pencil line. The sharp crest should be on the upstream (good) side of weir plate (Figure 4.B. - 4).

- Using carpenter square and rasp, true opening if needed.

- Cut a 2 x 4 the length of weir plate and nail it to upstream side (good side) of the plate for additional support and to hold the sampling equipment. The top of the 2 x 4 must be exactly 9-1/2 inches above the weir crest for proper operation of the scoop type sampler (Figure 4.B. - 5).

-- Weir installation

- Fill all sand bags first.

- Drive 2 stakes vertically into the channel bottom to rest the plate against. When the channel has solid (i.e. concrete) sidewalls, wedge two 2 x 4's across it and allow the plate to rest against them.

- Set the weir plate in place by resting it on the channel bottom. Do not drive the plate into bottom sediments if they are sandy.

- Sandbag the face of the plate (upstream side) first.

- Sandbag the ends next.

- Seal any leaks that develop with more sandbags, or loose sand, clay, dirt, or even burlap.

-- Install sampling and flow measuring equipment. Allow adequate head development and for the water to return to its discharge state before activating the equipment.

FIGURE 4.B-3

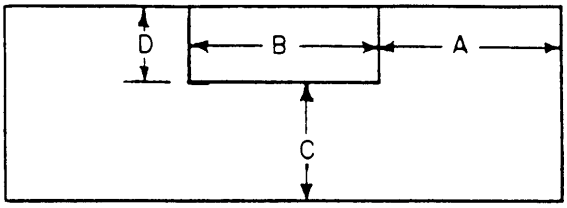


FIGURE 4.B-4

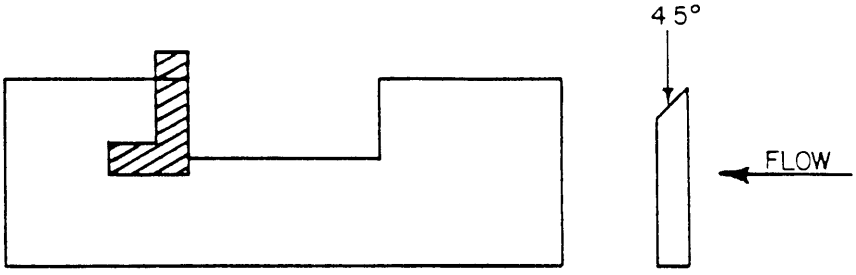
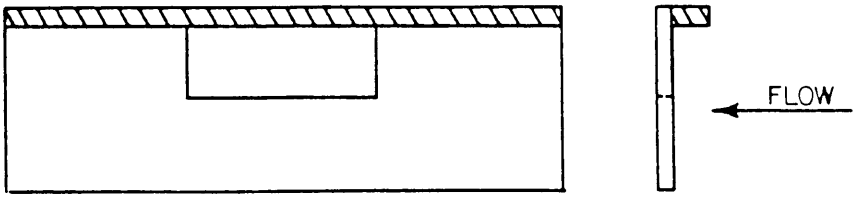


FIGURE 4.B-5



Notes

Staff constructed and installed primary devices have been tested under laboratory conditions with the following conclusions:

1. 60° and 22-1/2° V-notch weirs should not be field installed.

2. 90° V-notch weirs are accurate when head levels range between 0.3' - 0.5'.

3. Full channel weirs are accurate when head levels range between 0.3' - 0.6'.

4. Rectangular weir with end contractions are accurate where:

   a. Head levels range between 0.2' - 0.4' for small weirs (4 inch weir tested).

   b. Head levels range between 0.2' - 0.5' for larger weirs (12 inch weir tested).

4.B.4.d. Using Existing Weir Configuration

When conditions prohibit the construction of a weir and one does not exist, an existing configuration may be used to determine the flow. These will normally resemble rectangular or full channel weirs. These may consist of a wall at the end of a chamber or some other similar situation. If the configuration is broadcrested the crest width must be noted on the flow chart so it can be incorporated into the flow calculation.

4.B.4.e. Company Flow

When none of the previous methods are available, the company flow must be used. Before the company flow is used, the company's technique and calibration procedures must be reviewed.

4.B.4.f. Secondary Flow Devices

4.B.4.f.1. Bubbler Gage

The ISCO Model 2870 Flow Meter is currently used by staff. The meter uses a bubbler system to measure depth or head. The bubbler can be used with a flume or a weir to record flow. The meter must be installed and programmed using the manufacturer's instruction manual and flow tables.

4.B.4.f.2. Stevens Water Level Recorder

The Stevens Type F water level recorders are occasionally used for continuously recording the flow. The recorder may be used with a variety of staff installed and existing primary devices to obtain an accurate, independent flow measurement at a facility. The instrument operates in the following manner: A float is suspended from a chart cylinder which rotates over a distance proportional to the change in water level (head) in the primary device. The chart cylinder is set initially, to correspond to the instantaneous head measured with a head stick, with zero representing the weir or flume crest.

A pen, attached to a timing device, traces the pattern of up-and-down movement while moving across the chart. The result is a line which represents the head level over a period of time (usually 24 hours) which can then be converted into a flow volume. An example of a Stevens Chart

is given in Figure 4.B.-6.

Procedures

-- Fill in necessary information on chart (See Figure 4.B.-6)

-- Wind both springs and start clock.

-- Remove pen and fill ink pen reservoir. Be sure that ink will flow from the tip.

-- Attach float and counter-weight to pulley cable.

Figure 4.B.-6

Stevens, Inc.
0.3
0.5
0.6
0.7
0.8
start 09:30:63
510024 (001) S
NAME P.C.A.
LOCATION Filer City
DATE & TIME STARTED 6-10-80 0930
DATE & TIME ENDED 6-11-80 0930
RECORDER No. 73534 INITIAL HEAD
NUMBER SAMPLER
STARTING 0
ENDING 125
LENGTH OF WEIR 19'8" full chann
SURVEYED BY Kelly Broone
COMPUTED BY
ACTUAL FLOW
PROJECT FLOW MGD
Stevens Water Level Recorder — Type F
10/88

-- Place recorder platform at least 4 times the maximum head height from' weir. For Parshall flumes center the float (boat) 2/3 the length of the converging section upstream of the flume throat. The pulley cable attached to the boat top should be vertical. Attach a long string to the boat bow and secure it upstream at the maximum practical angle from vertical to steady the boat in the flow and allow for the unrestricted rise and fall of the boat.

-- Place cable on pulley so that float is on clock side of recorder. Do not let counter-weight touch water surface.

-- Take head reading with head stick and adjust chart cylinder so that chart corresponds to head reading.

-- Free pen assembly so that pen contacts chart.

-- Record head reading and time of start on chart.

-- Periodic head checks w/head stick should be recorded on chart. DO NOT READJUST CHART CYLINDER.

-- At the end of survey, remove chart and perform routine maintenance as follows. Install new chart, replace cover and secure unit for transport.

Care and Maintenance for Stevens Type F Level Recorder

-- After each use

- Clean chart drum w/dry cloth.
- Oil bearings on each end of chart drum.
- Clean centering pins and oil.
- Wipe carriage rods and oil.
- Check carriage drive cable.
- Clean and oil carriage drive pulleys.
- Rinse pen and reservoir w/distilled water and blow dry.
- Check for slop in drum/pulley gears and adjust if needed.
- Wipe down complete unit with clean rag.

-- Once Yearly

- Send clock in for cleaning and adjustment.
- Disassemble unit, clean, replace worn parts, oil and reassemble.

Note

If the recorder is submerged or damaged in any manner, follow once year schedule immediately.

4.B.4.f.3. Stevens Flow Charts-Altek Model AC72 Data Digitizer

After the recorder chart is completed, the pen tracing must be converted from' raw head levels to a flow volume/unit time. The chart is digitized following the procedure given below, then interpreted by computer. The output includes flows in M^3/day and MGD as well as the primary device type, size and monitoring period. An example of the output follows the digitizing procedure (Figure 4.B. - 7).

Procedures

-- Clean tape drive (w/tape path cleaner)
-- Mount tape
-- Push "BOT"
-- Push "IRG" - 2 times
-- Affix flow chart to table
-- Enter:
  Station Name,
  Date,
  Time (begin),
  Time (end),
  Weir type,
  Weir size,
  1. Width (inches or degrees)
  2. Breadth (inches) (Broadcrest)
  - Selector switch on "Point"
  - Enter: 0-Head @ 0 hours
  0-Head @ 24 hours
  0.5 Head @ 24 hours
-- Type in "Start"
-- Selector on "Continuous
-- Digitize (trace) pen line on chart.
-- Type in "End," to continue with another chart-enter-station name etc., as shown above.
-- To continue, type in comma, go to II.A.
-- Push "Fill"
-- Push "EOF" 3 times

Commas are required to separate the data being entered, as shown above. The flow computations should be spot checked for accuracy. An easy method involves comparing computer results for maximum and minimum flows with hand calculations made using the maximum and minimum head readings.

PCA

BEGIN 06/10/80 @ 10:00, END 06/11/80 @ 10:00

19.88 INCH FULL CHANNEL WIER WITHOUT END CONTRACTIONS

TOTAL FLOW MONITORED	1,378,450	GALLONS		
FLOW RATE	1.3785	MGD		
	5,224.3264	CMD		
PERIOD MONITORED	24.00	HOURS		
HIGHEST FLOW RATE	1.8945	MGD	ON	06/11/80
	7,180.2134	CMD		@ 9:59
LOWEST FLOW RATE	0.8931	MGD	ON	06/11/80
	3,384.9500	CMD		@ 6:23

FIGURE 4.B.-7

4.B.4.f.4. Head Stick

The head stick is a simple device used to determine instantaneous head levels which are unaffected by weir draw-down. The horizontal arm and level gage on the vertical arm make it possible to read the head at the appropriate distance upstream from the weir crest.

-- Rest bottom edge of horizontal arm on crest of the weir. Vertical arm should be upstream from weir plate a distance of at least 4 times head height to avoid draw down.

-- Level the stick with level gage and be sure stick is true vertically (not leaning left or right).

-- Read to the nearest .01 feet and record on data sheets and on flow chart.

-- Check quarterly for levelness with records being kept for each check. If damaged, repair immediately.

Note:

A head stick may be used to determine the head in a Parshall flume. Drawdown does not exist in a flume so the vertical arm should be placed 2/3 the wingwall length upstream from the crest.

4.B.4.g. Fluorometric Flow Measurement

Accurate instantaneous flow measurements can be made using fluorometry The techniques given below is particularly well suited to waste streams with high volume and velocity that are difficult or impossible to assess by other means.

4.B.4.g.1. Set-up

The fluorometer should be set up on fairly level and stable ground. Submerge the intake pump in the center of flow of water for which the test is being run. Tie the rope from the pump securely to a fixed object. Start the generator before turning on the fluorometer or pump, as changes in the current feeding the instrument may burn up the instrument's transformer. After the generator has been started and the current is steady, the fluorometer may be started by the switch marked "power" To turn the ultraviolet light on, the switch marked "start" may have to be used. The fluorometer should be allowed to run for about 20 minutes before any calibrating is started. Use the switch on the fluorometer marked "sample" to start instruments that are equipped with a continuous recorder. This may be used at times of extended surveys.

4.B.4.g.2. Dye Injection

The Manostat varistaltic pump is used to inject the dye from the 100% stock (A) solution reservoir into the stream to be measured. Remove the plastic guard from the face of the pump and the tubing retainer bar to fit the desired size tubing to the pump. Tubing sizes can range from 1/8" to 3/8" inside diameter with a maximum wall thickness of 1X8". Trials may be necessary to determine the optimum tubing size and pump speed for individual measurements. A soft, clear polyvinyl or surgical latex rubber tubing should be used in the pump. Avoid tubing materials that may adhere or adsorb the dye, such as rubber, so as not to reduce the dye concentration in solution. It is especially important to use a soft, pliable tubing material as the rotating tube rollers seal the

tubing against the side of the pump head creating the pressure necessary to deliver the dye fluid. Tubing that is too rigid will damage the pump. Tygon or Managon brands work well during mild weather. The latex is very pliable even during cool winter periods.

Plug the pump into a suitable 110V AC power source. After the power has been turned on, determine the direction of rotor travel required, turn on the pump and adjust for the approximate rotation rate. Periodically during the injection period the pump should be checked to ensure that the tubing has not "crept" out of position as a result of the rotor working against the tubing.

Pump calibration can be performed using either of two methods. The first technique is to measure the discharge from the pump by collecting dye into a clean graduate cylinder for a measured time span and converting to ml per minute. The second method is to measure the amount of liquid removed from a graduate cylinder over a known time span and convert to ml per minute. The latter method is very useful for calibration when dye must be injected into a submerged orifice. For either technique, the calibration test should be checked at least three times before a flow determination and at least once following to ensure the injection flow rates have not changed. During the calibration procedure, spent dye should be collected and discarded in an area safe from contamination during a flow determination.

Knowing the exact time of passage for dye from the injector to the fluorometer is not necessary, but may be of help if fluorescence is detected earlier than expected. By rechecking, it may be determined that an additional fluorescent material had been discharged into the water supply by a outside source.

Care should be taken to assure that the entire dye stream is getting into the flow of water. An ideal method is to submerge the injection tube into the stream flow. Submergent injection also provides for a more uniform mix between the dye and the stream to be measured.

4.B.4.g.3. Preparation of Dye Dilutions

Make a solution of dye by adding a known number of ml of dye to a known number of ml of distilled water as follows:

254 ml 20% Rhodamine WT + 20,800 ml distilled water = A

190 ml 20% Rhodamine WT dye + 15,600 mls distilled water = A (smaller quantity)

Assume the "A" solution to be your 100% solution which will be used in the injection apparatus. From solution "A" make dilutions as follows:

10 ml A + 990 ml (background water) = B

10 ml B + 990 ml (background water) = C

Assume solution "C" to the stock solution. Using "C" make further.

Dilutions with background water as follows:

50 ml C + 450 ml (background water) = D

10 ml A + 990 ml (background water) = B

40 ml C + 460 ml (background water) = E

30 ml C + 470 ml (background water) = F

20 ml C + 480 ml (background water) = G

10 ml C + 490 ml (background water) = H

5 ml C + 495 ml (background water) = I

After each dilution above, clean the glassware used by rinsing out with distilled H_2O and then rinsing with water similar to that used in the dilution. Each dilution should be stored in a clean container, until ready for use. Place the container of dye solutions in the overflow tub with the discharge hose from the fluorometer running background water into the tub. The purpose of this is to maintain the dye solutions at the same temperature as the background water, since temperature variations will yield faulty results.

4.B.4.g.4. Calibration of Fluorometer

Place a piece of carbon paper between the glass plate and the light source with the scale selector on the 30X scale. If the dial reading is not on zero, but above or below, make the dial read zero by use of the lock nut on top of the instrument. With the instrument zeroed remove the carbon paper and allow undyed background water to flow past the lens. Take dial readings on each of the scales, 30X 1OX 3X 1X to determine the natural background fluorescence of the water or the blank. Next take the weakest solution, I, and pour it into the tube connected to the lens, making sure the water level is to the top of the lens. Take dial readings on each of the 4 scales, making sure that the door is closed tight. Next hook the tube back to the pump and run background water past the lens until the dial reading on the 30X scale has returned to the blank dial reading. Rinse the lens out with the second weakest solution, H, then fill the area behind the lens with the "H" solution and with the fluorometer set on the four scales take dial readings again. Continue in this manner until you have calibrated through the "D" solution. Now simply leave the pump running so that water will flow through the instrument and take dial readings when the dye comes through. Continue taking readings until the dial has held a fairly constant reading on one scale. The dye that is being injected into the water will have to be held at a constant injection rate that is known in ml per minute. Variations in injection rate will yield faulty results.

The main problems encountered in the procedure arise from errors in calibration. The instrument is so sensitive that any residual of dye solution will alter the results.

4.B.4.g.5. Percentage Determinations

The percentage of dye from the 100% solution that is contained in each diluted solution is determined as follows:

$$\text{Concentration final \%} = \frac{\text{Concentration initial (\%) X volume initial ml}}{\text{Volume final (ml)}}$$

Concentration A = 100%

$$\text{Concentration B} = \frac{100 \text{ X } 10}{1000} = 1\%$$

Concentration C = $\frac{1 \times 10}{1000}$ = .01% (stock solution)

Concentration D = $\frac{.01 \times 50}{500}$ = .001%

Concentration E = $\frac{.01 \times 40}{500}$ = .0008%

Concentration F = $\frac{.01 \times 30}{500}$ = .0006%

Concentration G = $\frac{.01 \times 20}{500}$ = .0004%

Concentration H = $\frac{.01 \times 10}{500}$ = .0002%

Concentration I = $\frac{.01 \times 5}{500}$ = .0001%

4.B.4.g.6. Calibration Curve

In order to use a certain scale for flow determination, during the calibration of the instrument the dial reading for at least three of the dye solutions must have values between 0 and 100 for an individual scale. Preferable values are between 20 and 80. For plotting the calibration curve take the dial value obtained for the individual dye solutions for the scale used and plot a dial reading vs. percent concentration on graph paper. Drawing a straight line through the 3 points the extension for the line should pass through the abscissa at the reading that is obtained from the blank for the scale being used. With the line drawn, find the percent concentration corresponding to dial reading for dye concentration in the flowing water. See (Figures 4.B.- 8 and 4.B.- 9).

4.B.4.g.7. Flow Determination

The formula for determining flow in cubic feet per second (cfs) is as follows:

formula 1-1 $q \times C = (Q + q)c1$

q = flow rate of dye from injector in $ft^3/sec.$
C = Concentration of dye in injector (%)

c^1 = Concentration of dye in flowing water (%) (determined from graph)

Q = flow rate of unknown

Which reduces to:

formula 1-1a

$$Q\ (cfs) = \left(\left(\frac{C}{c^1}\right) - 1\right) c$$

Since "q" is in units of ml/min the following formula will convert "q" to the proper units for use in formula 1-1.

formula 1-2

$$q\ [ml/min] \times \left(\frac{in^3}{16.38\ ml}\right) \times \left(\frac{min}{60\ sec}\right) \times \left(\frac{ft^3}{1728\ in^3}\right) = q\ [ft^3/sec]$$

formula 1-2 reduces to

formula 1-3 $q(ml/min) \times (5.88 \times 10^{-7}) = q\ (ft^3/sec)$

Using this value for "q" in formula 1-1a yields Q in cfs, multiplying Q in cfs by 0.646 yields Q in mgd.

4.B.4.g.8. General Information

The fluorometer is an instrument that gives a relative measure of the intensity of light emitted by a sample containing a fluorescent substance; the intensity of fluorescent light is directly proportional to the amount of fluorescent substance present. A fluorometer reading by itself is meaningless until compared with readings for samples of known concentrations on the same fluorometer under similar instrumental and environmental conditions. The Turner Model III fluorometer has the ability to measure dye concentration at concentrations near 1 part/billion. The following formula applying the ideas of sensitivity and proportionality yields the volume of flow.

$q \times C = (Q + q)\ c$

C = concentration of dye in injector

c^1 = concentration of dye

Q = flow rate of unknown

which reduces to formula 1-1a

The fluorometer can be used to determine the volume of flow under certain conditions where:

-- The temperature of flow is fairly constant.

-- The composition of the flow is relatively constant.

-- A point can be found where a fluorescent dye can be introduced and become uniformly mixed with the wastewater by the time it reaches the fluorometer.

The storage of the dye solutions in background water eliminates a source of error due to temperature variation at calibration, therefore no temperature corrections need be made, if this procedure is followed. Trouble will arise if hot and cold surges occur in the background water.

Dye tests should be performed in a section of flow' where there are no pockets or drastic changes in direction of flow which could cause the dye to be retained.

Avoid dye tests in chlorinated water supplies.

Rhodamine WT dye has a tendency to adhere to suspended and bed materials, aquatic materials and the like or to be absorbed by such materials.

For this reason all materials that come in contact with the dye must be of such a consistence as to not reduce the dye concentration in solution. Glass, tygon tubing, PVC pipe and metal are materials that may

be used with little loss of dye concentration. Rubber is an example of a poor material.

Any tubing connected to the lens area of the fluorometer must be opaque or masked with opaque tape to eliminate all outside light.

4

FIGURE 4.B.-8

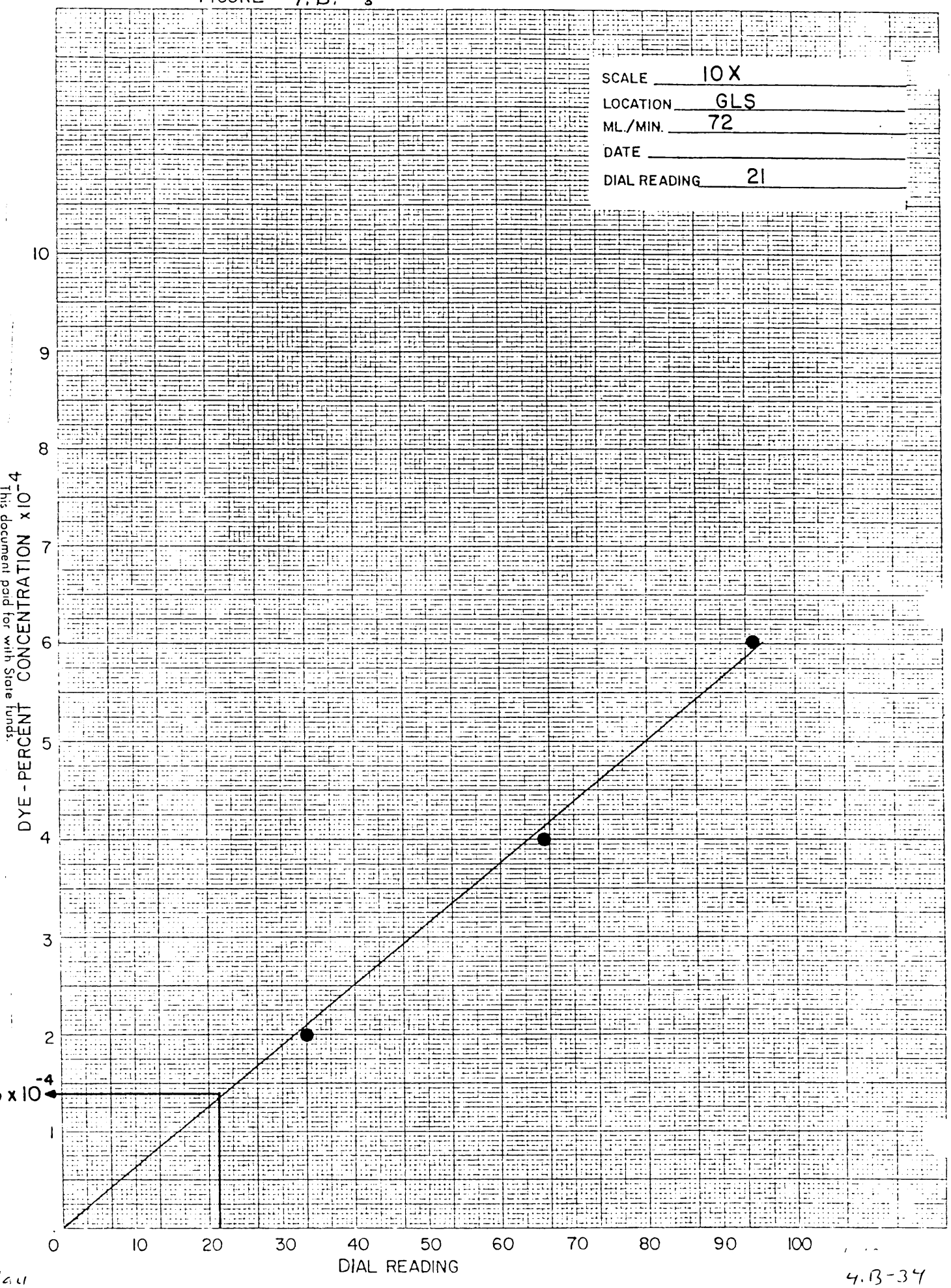


FIGURE 4.B.9 GREAT LAKES STEEL

Scale	Conc.	Dial		Scale	Time	Dial
	Blank			10x	1046	8
30x		6.5			1047	20
10x		2			1048	21
3x		1			1049	18
1x		0.5			1050	20.5
	H				1051	22
30x		100+			1052	20
10x		35			1053	19
3x		13			1054	20
1x		9.5			1055	24
	G					
30x		100+			Avg.	≈ 21
10x		70				
3x		24				
1x		9.5				
	F					
30x		100+				
10x		96				
3x		32				
1x		12				
	E					
30x		100+				
10x		100+				
3x		47				
1x		16.5				
	D					
30x		100+				
10x		100+				
3x		52				
1x		18				

Equivalent to 1.3×10^{-4} percent dye. See Figure 4.C. - 8.

Fluorescent substances are defined as those which absorb light at one wave-length and emit light at a longer wavelength. In the fluorometer, the light source consists of an ultraviolet lamp. This lamp emits light at a very restricted wavelength that is to be absorbed by the fluorescent material. Since the fluorescent material will emit the light at an increased wavelength, a selected filter may be used which will restrict light of wavelength other than that near the known fluorescent material wavelength. This combination of filter and light source eliminates the possibility that the sensing device is detecting other than the fluorescent materials as long as no outside light gets in or no extra fluorescent materials is picked up in the system. The sensing device is equipped with a sensitivity shutter. The shutter positions are listed as the 30X, 10X, 3X, 1X scales. The shutter positions simply indicate the size of the opening that the emitted wavelengths must pass through in order to be detected by the sensing device. The 30X scale would have the shutter open to a maximum which would increase the detecting area allowing the sensing device to detect more wavelengths. This increase in area can be compared to looking at a woods through a pinhole in a paper and then viewing the same woods through a large nail hole in the paper. A much greater number of trees can be counted since a larger area is visible.

Example

Two types of flow determinations will be discussed with an example worked for each.

The first determination arises when the approximate flow rate is not known and trial dye injection rates must be made until a dial reading can be obtained that falls within the range of dial readings on one of the graphs, (Figures 4.B. - 11, 4.B. - 12, and 4.B. - 13).

First the (Figure 4.B.-10) fluorometer was calibrated with the dye solutions that were prepared. The dial readings are then plotted on a graph of "dial reading" vs. "percent dye concentration" for a particular scale as in Figures 4B-11 through 4B-13. The values used for "percent dye concentration" were determined in Section 4.6.4.g.5. and were used since the dye solutions were prepared as described. From Figure 4B-11 it was noted that a dial reading above 25 on the 1X scale could not be used, unless the graph is extended. Similarly, from Fig 4B-12., a dial reading above 78 on the 3X scale could not be used. From observation of the graphs the 3X scale appeared to be the most accurate, therefore a dial reading between 10 and 75 on the 3X scale was desired.

The first injection rate was 45 ml/min which gave a dial reading of 83 on the 3X scale and 45 on the 1X scale. The dye concentration being too great, the second injection rate was 33 ml/min which gave a dial reading of 63 on the 3X scale which was permissible. Using formula 1-3 the injection rate in ml/min was converted to cubic feet per second (cfs) as follows:

q = dye injection rate

$$q\ (cfs) = (ml/min)\ 5.88x10^{-7}$$

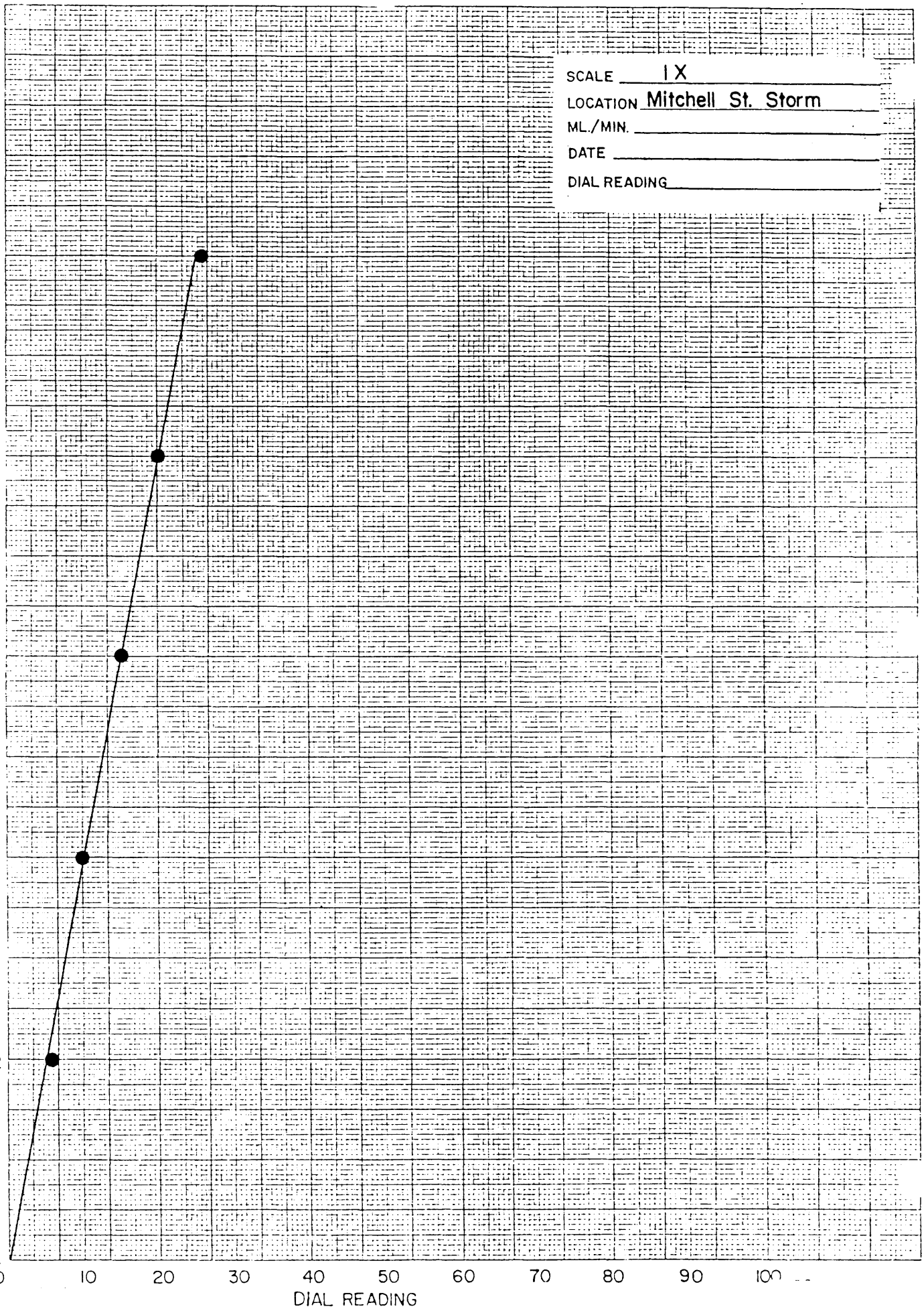
$$q\ (cfs) = q\ (33)(5.88x10^{-7})$$

$$q\ (cfs) = 1.94x10^{-5}$$

FIGURE 4.B.-10 MITCHELL STREET STORM SEWER

ml of Sol. C	Conc.	Scale	Dial
0	Blank		
		30x	4
		10x	1
		3x	0
		1x	0
5	1×10^{-4}		
	I	30x	100+
		10x	28
		3x	10
		1x	3
10	2×10^{-4}		
	H	30x	100+
		10x	48
		3x	17.5
		1x	5.5
20	4×10^{-4}		
	G	30x	100+
		10x	85
		3x	32
		1x	10
30	6×10^{-4}		
	F	30x	100+
		10x	100+
		3x	47
		1x	15
40	8×10^{-4}		
	E	30x	100+
		10x	100+
		3x	62
		1x	20
50	10×10^{-4}		
	D	30x	100+
		10x	100+
		3x	78
		1x	26

FIGURE 4.B.-11



2/94

FIGURE 4.B.-12

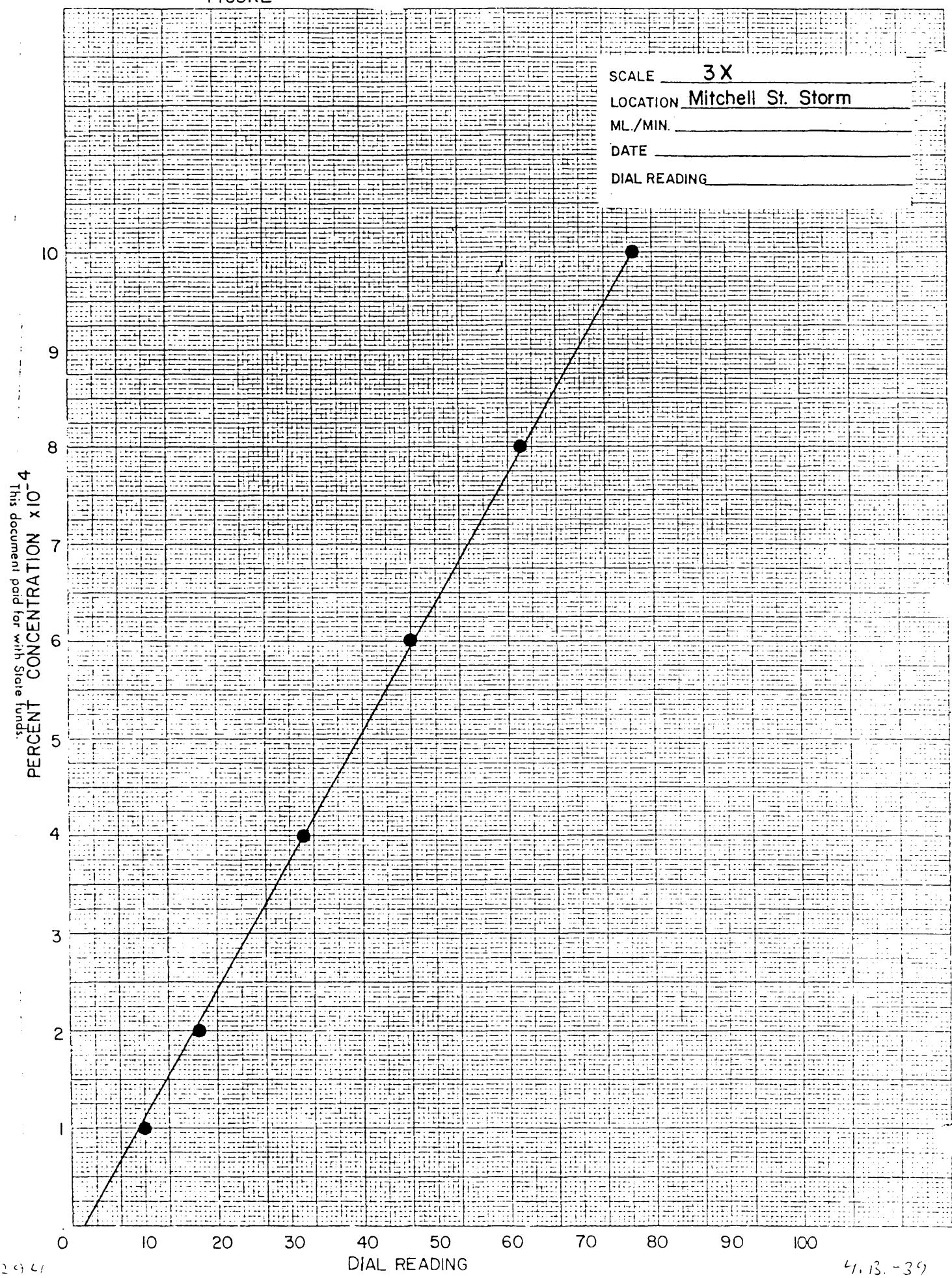
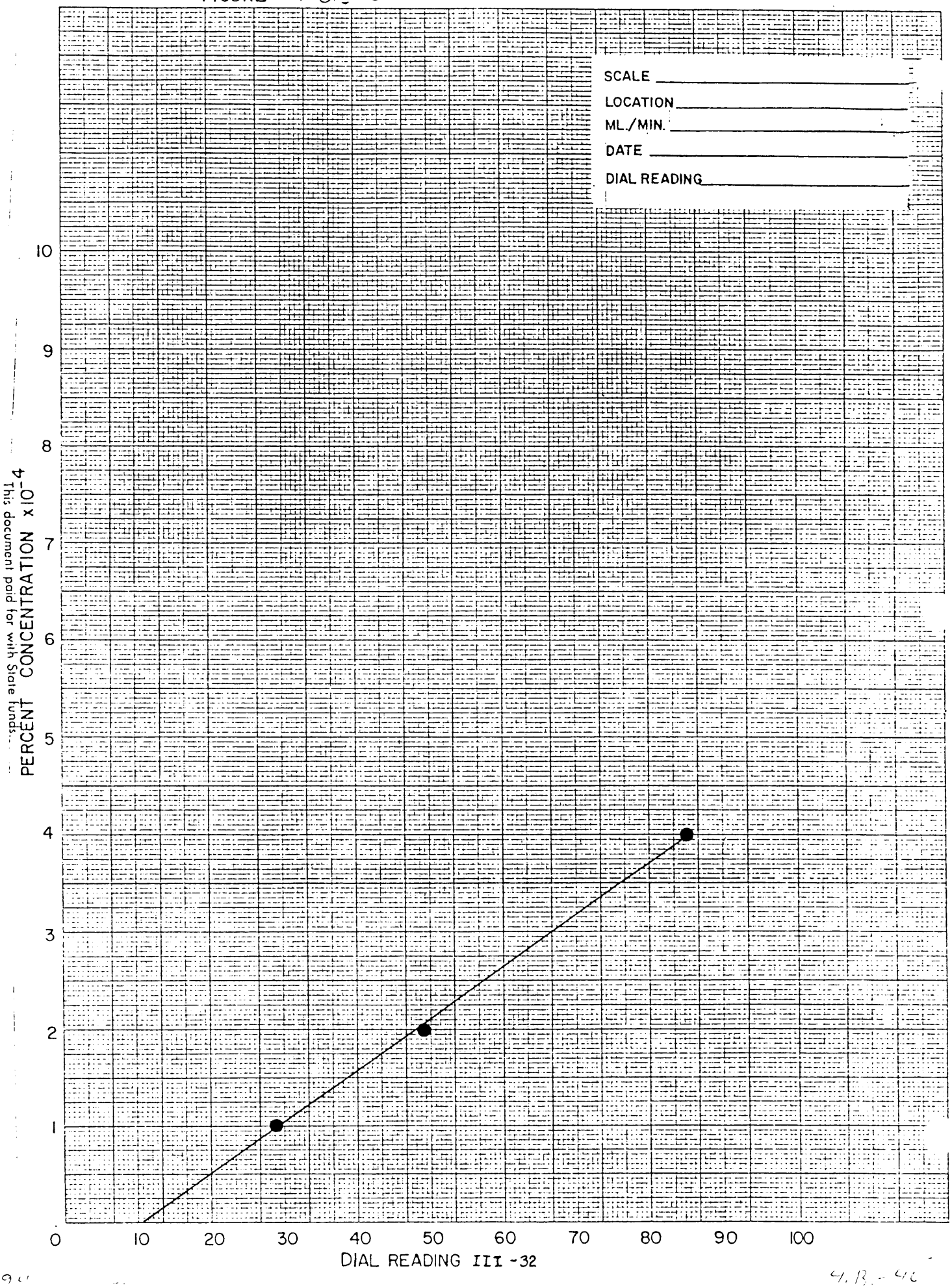


FIGURE 4.B-13



Using q(cfs) in formula 1-1a gave the exact flow, Q, in cfs. The dye concentration equivalent to the dial reading of 63 on the 3X scale was 8×10^{-4} as determined from figure 4.B. -12. Q in cfs was determined as follows:

C = concentration of injected dye = 100%

C_1 = concentration of dye in flow = $8x^{-4}$%

q = flow form dye injector in cfs = 1.94×10^{-5}

Q = actual flow in cfs

Q(cfs) = 2.43

Multiplying Q in cfs by .646 yields Q in MGD as follows:

Qmgd = Qcfs (.646)

Qmgd = (2.43)(.646)

Qmgd = 1.57

The second situation that may arise is when an approximate flow is known and it is required to obtain a dial reading in a specific range for a specific scale.

The flow at the survey point was known to be in the area of 1.5 MGD. Knowing this the injection rate of dye was determined that would yield a dial reading of about 40 on the 3X scale was 5.05×10^{-4}. from (Figure 4.B.-12). The injection rate was determined from formula 1-1a as follows:

$$Q\ (cfs) = \left(\left(\frac{C}{C^1}\right) - 1\right) c$$

Q = assume flow rate = 1.5 MGD = 2.32 cfs

C = concentration of injected dye = 100%

C_1 = concentration of dye equivalent to a dial reading of 40 on the 3X scale = 5.05×10^{-4}

q = injection rate in cfs

$$2.32 = \left(\left(\frac{100}{5.05 \times 10^{-4}}\right) - 1\right) \times q$$

To change q in cfs to q in ml/min formula 1-3 was used as follows:

$q(cfs) = 5.88 \times 10^{-7}\ q\ (ml/min)$

$q\ (ml/min) = 1.17 \times 10^{-5}$

q (ml/min) = 19.9

Injecting dye at 20 ml/min should yield a dial reading in the area of 40 on the 3X scale. The dial reading obtained on the 3X scale was 34 which is equivalent to a dye concentration of 4.25×10^{-4} percent.

The flow rate of dye in cfs for 20 ml/min was determined from formula 1-3 as follows:

$q\ (cfs) = 5.88 \times 10^{-7}(20)$

$q\ (cfs) = 1.18 \times 10^{-5}$

With the aid of formula 1-1a the actual flow was determined as follows:

$$Q\ (cfs) = \left(\left(\frac{C}{c^1}\right) - 1\right) c$$

C = concentration of injected dye = 100%

c_1 = concentration of dye in flow = 4.25×10^{-4} percent

q = injection rate of dye in cfs = 1.18×10^{-5}

Q = actual flow

$$Q\ (cfs) = \left(\left(\frac{100}{4.25 \times 10^{-4}}\right) - 1\right) \times 1.18 \times 10^{-5}$$

The flow in MGD was determined as follows:

Qmgd = Qcfs (.646)
Qmgd = (2.78) (.646)
Qmgd = 1.79

4.B.4.g.9. Check List for Fluorometer Use

Fluorometer

Varistaltic Pump

Intake Pump

100% Dye Bottle & Tubing

Generator & Gas Can

Hose

Tarp (to block out sunlight which interferes with meter reading)

Equipment Carrier (Flasks & Pipettes)

Circuit Guard

Soap

Pig Tails

Extension Cords

Notebook

Extra Fuses

Calculator

2-1/2 Gal. Distilled Water

Concentrated Dye Solution

Overflow Tub

Carbon Paper

Squirt bottle (H_2O)

4.B.4.h. Manual Flow Measurements

4.B.4.h.1. Bucket and Stopwatch

This method provides instantaneous flow measurements. The number of individual measurements required to characterize the flow over a 24-hour period must be determined on a case by case basis.

-- Use a vessel which will hold a measured volume of water such as a graduated cylinder, graduated bucket, etc.

-- Using a stopwatch, determine the length of time required to fill the vessel to the desired volume.

-- Repeat three times and average the results. Convert to flow/unit time desired (m^3/day, GPM) and record.

4.B.4.h.2. Time Period Flow Measurements

The two following methods may be used to determine the total flow volume discharged over a specific period of time. Unlike the Stevens recorder neither method provides a continuous recording of flow variations.

Tank Volume X No. of Batches

-- Compute tank volume (length x width x water height) or obtain from facility management.

-- Determine number of batches discharged during the survey period.

-- Multiply tank volume times number of batches discharged to yield total volume discharged during survey period.

Pump Capacity X Pumping Time

-- Determine pump capacity by one of the following methods.

- Obtain from pump identification plate. Verify this with facility management. Ask if pump capacity has been calibrated. Ask how calibration compared to rating. If necessary adjust pump capacity to company's data. If possible use following methods to improve on this.

- Further refine capacity by considering pumping cycles. If access to a wet well is available and an influent flow rate can be determined for the wet well, adjust the capacity as follows:

$$Qp = \frac{Vw + Q^{I} \times t_1}{t_1}$$

where Qp = Pump Capacity
Vw = wet well volume that is pumped
Q_I = influent flow rate to wet well during observed cycle
t_1 = time of pump cycle

If access to wet well is available but influent flow rate is not, calculate pump capacity as follows:

$$Qp = \frac{Vw}{t_2} + \frac{Vw}{t_1}$$

where T_2 = time between pump cycles

-- Determine time of pumping by

- Reading pump totalizer at beginning and end of survey period.
- Attach an Amprobe to pump. This will record both the time of pumping and the time between pump cycles. Instructions for using the Amprobe are inside the cover of the carrying case.

-- Multiply pump capacity times the period of pumping during the survey to yield total volume discharged during the survey period.

4.B.5. AQUATIC TOXICITY TESTING

4.B.5.a. ON-SITE AQUATIC TOXICITY TEST PROCEDURE

See Procedure number 46 of the Great Lakes and Environmental Assessment Section

4.B.5.b. Static and Static-Renewal Acute Effluent Toxicity Evaluations

See GLEAS Procedure 42

4.B.5.c. Invertebrates Static Acute Toxicity Screening Test

See Procedure # 24 of the Great Lakes and Environmental Assessment Section

4.B.5.d. Fathead Minnow Hatchery Procedure

See GLEAS Procedure #41 REVISED MARCH, 1992

4.B.5.e. Daphnia Care And Maintenance

See GLEAS Procedures #44 and #37

4.B.5.f. Fathead Minnow Larval Survival and Growth Test

See GLEAS Procedure #38

4.B.5.g. Ceriodaphnia dubia Survival and Reproduction Test

See GLEAS Procedure #54

4.B.5.h. Algal Culturing Method

See GLEAS Procedure #40

4.B.5.i. Laboratory Glassware Cleaning Procedure For Toxicity Lab

See GLEAS Procedure #25

4.B.6. REFERENCE DOCUMENTS

-- Leupold and Stevens. 1978. Stevens Water Resources Data Book. Beaverton, Oregon, 1978. 154 p.

-- Peltier, W. 1978. Methods For Measuring the Acute Toxicity of Effluents to Aquatic Organisms. Environmental Monitoring and Support Laboratory, U.S. EPA. Cincinnati, Ohio, 1978. 51 p.

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4.C. RIVER AND STREAM SAMPLING

4.C.1. INTRODUCTION AND GENERAL PROCEDURES

When conducting stream and river sampling, one must be observant and take note of unusual conditions or activities impacting water quality. Field notes should include a record of all such occurrences. These notes may prove to be critical to data interpretation. As a minimum, always take note of the following:

-- Floating material, oil, grease, debris, untreated sewage materials, dead fish and/or animals.

-- Unusual water color, color of bottom, and odors.

-- Algae blooms and/or plant die-off.

-- Sewer overflows or other direct discharges.

-- Unusually high amounts of particulate matter in the water.

-- Upstream conditions which may disturb and resuspend bottom sediments such as bathers, fishermen, boats, livestock, dredging activities, mining activities, and construction.

-- Backwater effects (reversal of stream current) which may occur when sampling river mouths near a lake, large impoundment or confluent with other streams.

-- Weather conditions at the sampling site and upstream.

4.C.2. SAMPLING TECHNIQUES

There are several standard techniques for obtaining river samples which may be classified in the following general categories:

-- Grab or surface grab samples.

-- Vertical depth sampling, and

-- Depth integrated sampling

There are also combinations and variations to these techniques which may be appropriate depending on the requirements of the sampling program such as composite equal transect grab sampling. The choice of which technique to be used is left to the program manager. The decision should be based on the objectives and specific data requirements of the sampling Program, with considerations given to resource demands and technical capabilities. Almost without exception, all river and stream sampling now conducted utilizes surface grab sampling techniques.

4.C.2.a. Surface Grab Sampling

Surface grab sample is defined as a single discrete sample obtained from a depth of approximately one foot below the water surface over a time period of less than 15 minutes. These samples may be taken from a bridge, river bank (wading), or from a boat. They should be collected with a sampling device (water sampler), but may be hand dipped if samplers cannot be used.

There are two grab sampling devices which are available for use; 1) sampling can; and 2) wire frame sampler. It is always preferable to use samplers in lieu of hand dipped where conditions allow. Samplers cannot be used when liquid preservation reagents are applied before collection.

4.C.2.a.1. Sampling Can

The sampling can is a weighted cylindrical container made of polyvinyl chloride (PVC) which can be used to collect multiple water samples (Figure 4.C.-1). Its primary use is to collect samples for physical, chemical, microbiological and metals analysis, all during one operation.

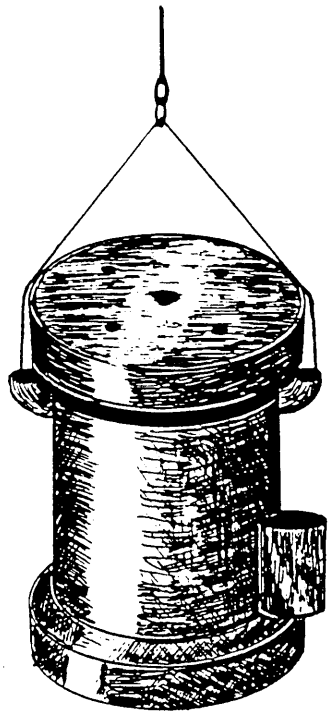


Figure 4.C.-1 Sampling Gun

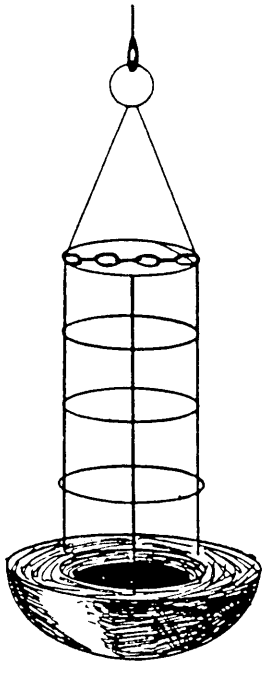


Figure 4.C.-2 Wire Frame Sampler

-- Important Features:

- Accommodates up to four 250-500 ml plastic or glass bottles internally and one 125 ml bacteriological bottle attached to the outside.
- It is weighted for sampling in flowing waters.
- Rinses bottles placed internally during collection by use of a flexible Tygon tubing inserted to each bottle.
- Attachable line for use on elevated sampling platforms (bridges, boats, etc.).
- Cannot be used for hydrocarbon samples.

-- General Instructions for Use:

- Place the desired number and type of clean sample bottles inside the sample can. Bottles must be clean inside and out to prevent cross contamination during rinsing process.
- Replace lid, making sure the flexible tubing extends into each bottle and seal around lid is tight.
- Place bacteriological bottle in outside holder and remove cap just prior to collection.
- Lower into water to a depth of one foot below the surface.
- Keep submerged until sampler is filled completely (bubbles stop emitting from top).
- Lift out of water, remove the bacteriological bottle and pour off to 3/4 full, cap immediately.
- Carefully remove remaining bottles from inside the sampler and preserve in accordance with the recommended procedures outlined in Chapter 3, Sample Preservation and Handling, of this manual.

4.C.2.a.2. Wire Frame Sampler

The wire frame sampler is a weighted coarse wire container used to collect a single water sample (Figure 4.C.-2). Its primary use is for collecting samples for organic contaminant analysis.

-- Important Features:

- Accommodates one 500-1000 ml glass or plastic bottle.
- Weighted for use in flowing water.
- Attachable to a line for use on elevated sampling platforms.
- May not be used for metals or dissolved oxygen analysis.

-- General Instructions for Use:

- Place the desired type of sample bottle in wire frame.
- Secure bottle tightly with use of chain link strap.

- Remove bottle cap and lower sampler into water to a depth of one foot below the surface and fill completely.

- Retrieve from water and preserve sample according to recommended procedures.

4.C.2.a.3. Selection of Sampler

The sample can device is used when collecting samples for analysis of the following parameters: dissolved oxygen, BOD, nutrients, solids, COD, TOC, cyanides, phenols, metals, chlorophyll a, and bacteriological samples. It is not to be used for collecting organic samples of any type.

The wire frame sampler is used when analyzing for BOD, nutrients, solids, COD, TOC, cyanides, phenols, chlorophyll a, and hydrocarbon samples. It is not to be used when sampling for metals, dissolved oxygen, volatile hydrocarbons and other parameters which may be affected by the entrainment of air during collection.

4.C.2.a.4. Grab Sampling from a Bridge

Bridge sampling is an efficient method for collecting most surface grab samples. It can be utilized with accuracy for most sampling applications. Recommended procedures for this operation are as follows:

-- Location of sampling point

- Collect samples from the downstream side of the bridge whenever possible. The sampling device will drift way from bridge and should be kept in full view during collection. Collection from upstream side of bridge may result in the sampler being swept under the bridge. Under these circumstances, take special precautions to avoid contamination which may occur by the line scrapping along the bridge structure during retrieval.

- Select a point on a river transect that represents the greatest stream flow. Avoid low flow and stagnant areas. Survey upstream before collection so as to avoid water which has been disturbed.

- Do not sample in areas which may be affected by water, or debris falling from' bridge. This is especially pertinent during sampling in wet weather when storm water and road salts may be flowing through bridge drains.

- When stream flow is low and sampler makes contact with stream bed discontinue use and collect sample by wading and hand dipping.

-- Use of sample can or wire frame sampler from a bridge

- Lower sampler down into water on a clean line. Do not allow line to contact any part of the bridge structure as debris may be knocked off and fall into the sampler. If line becomes contaminated with use, replace or rinse thoroughly to clean before continued use.

- Let out enough line to allow sampler to sink to a depth of approximately one foot below the surface. In cases where

stream velocity is very high, the sampler may not sink. Under these conditions, allow the current to carry the sampler a few yards downstream, then quickly pull the sampler out of the water and allow it to swing upstream in a pendulum motion. Drop immediately back into the water at the end of the upstream swing. Sampler will sink with the force of being dropped and begin to fill. Repeat this procedure until the sampler either stays submerged or fills completely after a number of trials

- When sampler is full, retrieve at a slow steady pace, using the current to position the sampler directly below the bridge. Lift out of the water in a manner which avoids collisions with the bridge structures.

- At all times throughout the sample collection process, take care not to knock or kick debris off the bridge or allow line to scrape the bridge structure.

4.C.2.a.5. Grab Sampling From a River Bank

Bank sampling or wading out into the watercourse to sample is a less desirable method of collection. The likelihood of contamination due to increase contact with the water is greater with this technique. As such, special care is required to prevent and minimize sampling error.

-- Select a point along the river bank where the current flow is pronounced. This will most often occur at the outside bend in the stream. Do not sample in stagnant water or in areas which may be affected by direct upstream runoff.

-- A sampling device (sample can or wire frame) should be used whenever conditions allow. Follow the procedures outlined in the preceding sections for basic use of samplers. The samplers are designed to be lowered into and retrieved from the water at a 90 degree angle to the water surface. Under <u>no</u> circumstances are samplers to be thrown into the water course from the river bank or shallow water.

-- In situations such as low water level or ice cover, it is appropriate to collect samples by hand. The collection techniques vary from parameter to parameter. The following is a description of specific procedures for hand collection.

- Dissolved oxygen samples - fill bottle by allowing water to flow down the neck of the bottle in a smooth flow without turbulence or entrainment of air. When full, tap the side of the bottle to dislodge any bubbles which may be present and cap.

- Bacteriological samples - plunge sample bottle upside down into the water to a depth of 1 foot. Turn upright and fill 3/4 full. Lift out of water and cap immediately. Do not rinse the bottle.

- Volatile hydrocarbon samples - fill sample bottles without entrainment of air. Replace septum cap underwater to insure all entrapped air is emitted. The Teflon side of septum should be face down in contact with the water sample.

- Oil and grease samples - skim surface of water to fill bottle 90% full. Do not rinse bottle during this process. This

Procedure will provide qualitative results only.

- Chemical parameters (emission of air not critical), -Plunge sample bottle upside down to a depth of 1 foot. While submerged, turn over and fill. Add chemical preservatives and cap.

-- When sampling by hand either by wading or from the bank, always face upstream during the collection. If bottom is soft and stream is slow moving, stand quietly to allow current to sweep away disturbed sediments or move slowly upstream during collection. Hold bottle in such a manner as to avoid water from passing over samplers hand before collection.

4.d.2.a.6. Grab Sample Collection From a Boat

Sampling from a boat is conducted when bridge and bank sampling techniques cannot be effectively utilized. It is recommended that this technique only be used when it is found to be superior in terms of meeting program objectives. Whenever possible, collect samples from a boat with the use of samplers. In all cases, follow procedure outlined in preceding sections regarding the use of sampling devices and proper hand collection methods. Additionally, note the following:

-- Always travel upstream while collecting samples.

-- Collect samples from forward portion of boat.

-- Do not operate and sample in water shallow enough to have bottom sediments riled by the boat.

-- Try to position the boat into the wind so that the exhaust from engines do not drift toward sampling operations.

-- Avoid sampling in wake, turbulence, oil or gasoline which may be present.

4.C.2.b. Vertical Depth Sampling

Vertical depth sampling is defined as a discrete sample obtained from a known, predetermined vertical depth from the surface. Samples must be taken from a stable platform such as a bridge or boat. Vertical sampling from a river bank is not recommended. Depth or vertical sampling equipment such Kemmerers and Van Dorn bottles are required.

There are a number of sampling devices available which are capable of obtaining a vertical depth water sample. This document shall discuss the use of Kemmerer and Van Dorn bottles. When other equipment is used, obtain instructions for use from the manufacturers.

4.C.2.b.1. Kemmerer and Van Dorn Samplers

The Kemmerer and Van Dorn samplers are cylindrical containers constructed of either metallic or plastic (PVC) materials, with openings at both ends and mechanisms for remote closure (Figure 4.C.-3).

-- Important Features:

- Variable sample volumes from 1 to 12 liter capacities.

- Both ends are open to allow free passage of water as sampler

is lowered to desired depth.

- Messenger is dropped from sampling platform to trigger entrapment of water sample at desired depth.

- Water samples are poured off into individual bottles after the sampling device has been raised out of the water.

-- Both the Kemmerer and the Van Dorn may be used for collection of common physical and chemical water parameters such as BOD, nutrients, solids, and chlorophyll a. Sampling for metals and organics is dependent on the type of material used in construction of equipment. A metal container may not be used for obtaining metal samples. Likewise, a device constructed of plastic or PVC materials may not be used for water samples to be analyzed for organics. Bacteriological samples cannot be collected from either of these two devices.

Sample Collection

With the use of proper equipment, the vertical sample may be obtained from any stable platform, including bridges, boats or docks. The procedures for use of standard equipment are as follows:

-- Mark rope or line at one foot intervals with alternating colors of water proof paint, ink, nail polish or tape.

-- Open both ends of sampler.

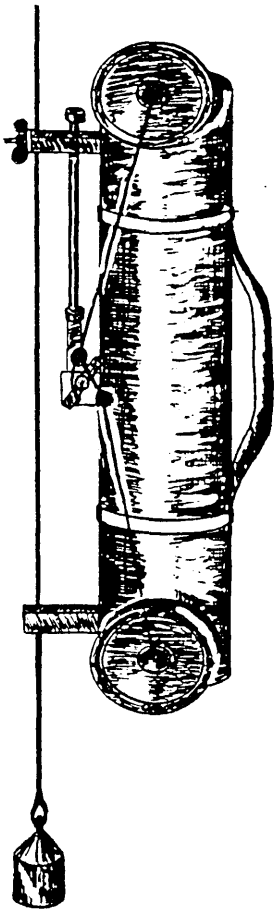
-- Lower to desired depth, being careful not to touch the bottom and disturb sediments.

-- Drop messenger down to trigger closure at desired depth.

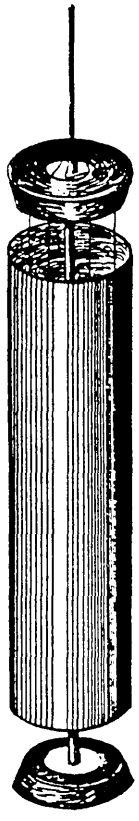
-- Retrieve and fill individual sample bottles from sampler. Note - Do not allow entrainment of air when filling dissolved oxygen and volatile hydrocarbon bottles from sampling device.

-- Preserve all samples in accordance with procedures recommended in Chapter 3, Sample Preservation and Handling.

-- Record sample depths on data sheets and/or field notes.



VAN DORN BOTTLE



KEMMERER BOTTLE

FIGURE 4.C.-3 Vertical Depth Sampling Equipment

4.C.3. STREAM GAGING PROCEDURES

4.C.3.a. Introduction

During the course of dye studies and selected water sampling surveys, stream flow measurements are required. Flow measurements by Surface Water Quality Division staff are made only when Water Management Division or U.S. Geological Survey personnel are unable to make the measurement. The procedure used for the measurement of stream flow is adapted from the publication: Techniques of Water Resources Investigations of the United States Geological Survey, Book 3, chapter A8, discharge measurements at gaging stations. Briefly, the procedure consists of dividing a stream cross section into partial sections, determining the velocity in each partial section and then summing the products of the partial section areas and their respective average velocities.

Required equipment includes; stop watch, head set, tag line, wading rod, meter, fins, clip board, measurement notes, pencil, and screw driver.

4.C.3.b. Equipment preparation

Note: this should be done before going into the field

	Pygmy Meter	**AA Meter**
Stream depth:*	0.75-1.5 feet%	>1.5 feet and/or the majority of the velocities are >2.5 feet/second.
Preparation:	Exchange the storage pivot pin for the operation pivot pin.	Loosen the thumb screw.
Spin test: (spin the bucket by hand)	Should spin for ≥30 seconds.@	Should spin for ≥90 seconds.@
Attach the meter to the wading rod and fasten the set screw. Connect the head set to the appropriate lead and check the number of clicks/revolution.	There should be 1 click/ revolution.	Attach the fins to the wading rod and tighten the set screw. Should be 1 click/revolution with lead wire attached to the top connector and 1 click/5 revolutions with the lead wire connected to the bottom connector.
General maintenance	Repeat the spin test to verify that the meter was working properly. **Dry meter and oil all moving parts** before storage.	

%Measurements may be made at depths less then 0.75 feet but the accuracy may be affected.
*Neither instrument is recommended at velocities <0.2 feet per second. It is not necessary to change the meter for a few measurements outside of the recommended range.
@If the meter fails this test, do not use the meter. Return it for service.

4.C.3.c. Measuring the Section

1. Set staff gage or reference point.
2. Cross section selections should be determined by the personnel of Land & Water Management Division or of the U.S. Geological Survey. If this is not possible see Appendix A.
3. Read and record the staff gage measurement or permanent reference point to determine the flow stability during the measurement.
3. Stretch the tag line across the section perpendicular to the flow, secure and determine the width. Divide the cross section into ≥20 partial sections. Using guidelines from Appendix B.
4. Determine the appropriate method of measurement.
   Stream depth <2.5 feet: measure at 0.6 of the depth.
   Stream depth >2.5 feet: measure at 0.2 and 0.8 of the depth.
5. Assemble the proper equipment. (See Appendix C.)
6. Starting at the initial point on either the left or right bank (facing downstream), measure and record the distance to the edge of the water. (The edge is the first vertical and the center of your first partial section.)
   ✡Stand so that you will least affect the velocity of the water passing the meter. If the stream is small enough stand on a plank or other support over the water. If you must stand in the water, stand downstream of the tag line and the meter with the flow hitting the side of your leg. The rod should be 1 to 3 inches downstream of the tag line. You should be 18 inches or more downstream of the meter rod. Keep the rod in a vertical position with the meter parallel to the direction of the flow.
7. Measure and record the depth.
8. Set the meter to the desired depth and allow a few seconds for the meter to become adjusted to the current.
9. Time the number of revolutions by the rotor for a period of 40-70 seconds. End the count with a convenient number of revolutions. **The number of revolutions must be within the limits of the meter rating table.** Record the time interval (to the nearest second), and the number of revolutions.
   ✡Start the stop watch simultaneously with the first click counting 0. Stop the watch on the desired count.
10. Repeat steps 6-9 for each partial section. Record the distance from the initial point, stream depth, meter position, revolutions and time interval until the cross section has been traversed.
11. Read and record the staff gage or permanent point.

4.C.3.d. Calculations

Determining the velocity in each partial section and summing the products of the partial section and their respective average velocities.

The flow in each partial section is determined by the following equation:

$$Q_x = V_x * \frac{b_{(x+1)} - b_{(x-1)}}{2} * d_x$$

Where:

Q_x = discharge through partial section x
V_x = mean velocity at x

$b_{(x+1)}$ = distance from location x to the next location
$b_{(x-1)}$ = distance from location x to the preceding location
d_x = depth of water at location x

1. Determine the velocity at each point using the number of revolutions and the time interval, from the rating table for your meter. **Match the number on the rating table with the number stamped on the meter.**
2. For an end partial section: the boundary is a vertical line at the edge of the water. The depth is not 0 and the velocity may or may not be 0. It is usually necessary to estimate the velocity as some percentage of the adjacent section. Accurate measurement with the meter is frequently impossible this close to a boundary.
3. Sum the flows in the partial sections to determine the total discharge in the stream at this location.

References: *Techniques of Water Resources Investigations of the United States Geological Survey.* Book 3. Chapter A8.

4.C.3.e. Selecting a cross section

Select a cross section from a reach which satisfies as many as possible of the following criteria.

1. A straight reach where the threads of velocity are parallel to each other.
2. A stream bed which:
   - is stable
   - has a flat profile (eliminates vertical velocity components)
   - is free of obstructions which create turbulence i.e. rocks, weeds, protruding obstructions

*You may modify the section by removing obstructions which create turbulence and/or construct dikes to cut off dead water or shallow flows. Allow the flow to stabilize.

4.C.3.f. Partial Sectioning

It is not necessary that each partial section be of equal width.

1. Section the stream using the following criteria:
   - No more than 10% of the flow in any one section and preferable no more than 5% of the flow in any one section.
   - The width of each section decreases as the depth and velocity increases
2. Any flow which is not perpendicular to the tag line must be measured with the meter parallel with the flow in the subsection and the angle coefficient between the tag line and flow line carefully recorded. The coefficients are along the right edge of the USGS note sheets. The angle coefficient is measured by holding the edge of the paper parallel to stream flow and placing the point of origin on the left side of the paper at the tag line and reading the angle coefficient opposite the tag line on the right side of the paper. The coefficient is recorded in the appropriate column on the note sheet. The "adjusted for horizontal angle velocity" is computed by multiplying the "mean in Vertical Velocity" by the recorded coefficient and placed in the appropriate column.

Equipment List

meter	measurement notes	wading rod
fins (if necessary)	pencil	head set
meter rating table		

4.C.4. PROCEDURES FOR DETERMINING TIME OF WATER TRAVEL

4.C.4.a. Preparations

1. Well in advance of the release obtain permission from the District Office of the area where the release will be made.
2. No less than 5 days prior to the dye release notify:

   The MDNR District Supervisor
   The ERD PEAS Coordinator
   The MDNR Regional Director
   SWQD, Division Chiefs for Fisheries, Land and Water Management, Wildlife
   MDPH Water Supply
   Any industrial or other river water users that may be affected

3. Estimate the volume of dye you will need using the following formula.

$$V_s = 3.4 \times 10^{-4} \left(\frac{Q_m L}{v}\right)^{0.94} C_p$$

Where:

V_s = volume of stock Rhodamine WT 20% dye in liters
Q_m = maximum stream discharge at the downstream site in cfs
L = distance to downstream site in miles
v = velocity of stream in the reach in ft/sec
C_p = peak concentration desired at downstream sample site ug/l. This is usually 5-15 ug/l for time of travel studies, depending on the sensitivity of the Fluorometer you are using.

*If a public drinking water supply is downstream, follow USGS guidelines which call for less than 10 ppb dye at the intake.

4.C.4.b. Releasing the dye

1. **Be sure to handle dye with gloves and eye protection. Always work with and transport dye using double containment.**
2. A dye study consists of introducing a quantity of fluorescent Rhodamine WT dye into a stream and then monitoring the slug at a downstream location to determine the time of travel. The objective of the dump is to have a dye as evenly distributed as possible vertically and across the river at the moment of injection. For most streams, this is easily accomplished by pouring the dye into the point of greatest flow and allowing the stream to do the mixing. A more elaborate injection procedure should be considered for very sluggish or poorly mixed streams.
3. **Thoroughly** rinse the dye container and anything else which has been in contact with the dye, with stream water after the dump.

4. To determine the stream flow, see the procedure for stream gaging.

4.C.4.c. Sampling for Dye

1. Collect samples in 50 ml screw cap vials. Protect the samples from light, store at room temperature.
   Hand collection: rinse the sample bottle twice with river water and fill to top. Automatic collection: Either the dye boat or an automatic sampler such as the ISCO may be used.
2. After collection transfer the sample to screw cap vials. ☼Record the date, time and location on the sample bottles or use a coding system which corresponds to the date, time and location on the field data sheet.
3. Determine the time increment between samples. It should be short enough so that at least 20 samples are collected to define the passing dye slug. This time increment will be determined by the survey chief.
4. A fluorometer can be used in the field to monitor the arrival and passing of dye slug. (See fluorometer procedure.) Do not discard any samples after field analysis, even if no dye is detected. Discard samples only at the direction of the survey chief.

References:

Techniques of Water Resources Investigations of the United States Geological Survey. Chapter A9. *Measurements of Time of Travel and Dispersion by Dye Tracing*. F. A. Kilpatrick.

4.C.5. WINTER SAMPLING

River sampling during winter months is a routine part of the ambient water monitoring programs. Due to ice coverage and freezing weather conditions it is more difficult to effectively collect a representative sample. The sampler's first priority when working on river ice, as it is with all other sampling, is safety. Learn to identify unsafe ice conditions and obey all ice safety precautions. Safety policy requires a minimum crew of two when sampling in winter months. The following special procedures are recommended for winter sample collection.

4.C.5.a. Required Equipment

-- Life vest
-- Life line
-- Ice auger
-- Ice spud
-- Torpedo (large weight attached to a line used for breaking ice from bridges)
-- Ice scoop (type used by ice fishermen to scoop ice from hole after spudding)
-- Bucket or box for carrying sample bottles
-- Rubber or latex gloves
-- Warm Clothing

4.C.5.b. Selection of Sample Site

When sampling at routine sampling stations during ice free periods,

envision the location in times of ice coverage. Make written field notes at what point in the cross section the greatest flow occurs. Note the depth and velocity of the cross-section. Note any large rocks or obstructions which may alter the current. Often river bed configuration influences ice thickness.

When arriving at a station with ice coverage, look for openings in the ice. At times bridge supports, rocks, logs or other obstructions will halt the current so there is an opening through the ice. If the opening exists and appears to have good flow through it, use sample can to collect a sample at that point.

If ice coverage is total with no openings, look for spots which may be thin or weak. Try to punch hole in these spots by dropping torpedo from bridge or bank. Make hole large enough to use sample can, if possible. If the torpedo is allowed to hit the bottom, the sediments will most likely be disturbed. Allow time for current to clear the area before sampling. NOTE: improper use of torpedoes can be ineffective and dangerous. Always tie free end of retrieval line to bridge post or tree before use. Keep hands and feet clear of line at all times.

If the hole cannot be made with the torpedo, the ice is usually thick enough to walk on and obtain a sample. However, remain observant and continuously monitor ice color and thickness while proceeding to sampling site.

Select a site which most likely has a representative flow. Noting the bends upstream and down, observing the obstructions, etc. will aid in picking the best location.

Avoid locations where road salt or other debris has fallen off bridges or the bank into the ice. Either keep completely away from bridge and bank or sample under the bridge where the ice is protected. Avoid locations where the ice appears dirty. Try to find clean, clear ice to sample through. Avoid locations where snow melt or other water is laying on top of the ice, and locations where ice is layered with columns of water between the layers. If sample must be taken in such conditions, make a hole through all layers. Allow time for thorough circulation within the hole before collecting a sample.

It may be necessary at times to make several test holes at one location to find the adequate flow.

4.C.5.c. Cutting a Sample Hole

-- Cutting a hole with a spud.

- Inspect the spud for dirt and oil. Clean thoroughly before use.
- Clear all snow from site.
- Chop a hole of sufficient size for all sample bottles.
- During this process, stop frequently to remove ice chips from hole. The less ice in the hole when breaking through to the water, the less chance of contamination from ice.
- Inspect the ice as you bore through. Watch for slushy ice, water running into the hole from' ice, layers of dirt in the ice, oil, etc. Spud new hole if necessary.

- Allow current to circulate in the hole and flush out any possible contamination before sampling. If there is not sufficient current to do this, new hole must be made.

- Avoid riling the bottom with a spud when spud breaks through the ice. When hole is made, skim slush and ice with an ice scoop, making sure the scoop is clean before using.

- Avoid kicking or dropping ice, snow or other materials in the hole after it is made and during collection.

-- Drilling a hole with an ice auger.

- Observe all safety and contamination precautions mentioned above for spudding the hole through the ice.

- Two persons must securely hold a power during operation to ensure adequate and safe operation of the machine

- Inspect auger blade for dirt and oil and clean if necessary. Clear snow away from sampling site.

- If using rubber gloves to collect sample, do not wear the same pair during operation of auger. Oil, gas or other contaminants may accumulate on gloves from the auger.

- Start auger, observe to make sure no materials from exhaust fall on the ice or near the sampling hole. Select a new site if contamination occurs.

- Avoid getting exhaust on hands or clothing.

- Make sure that the sample bottles are clear away from auger exhaust.

- When auger blade cuts through the water, allow as little of the blade as possible to contact water.

- Avoid riling the bottom sediments with the blade. If this is done, a new hole will need to be drilled.

- Do not shut auger off immediately as it cuts through into the water. As auger is still running, pull blade out, and the rotation of the blade will clear most debris out of the hole before it has a chance to fall into the water. Total control of the auger is required when performing this function. Avoid being cut by the blade. Shut motor off immediately when finished.

- Do not lay auger on side when completed. Gas and oil will leak from tanks creating a possible contamination source for future sampling holes.

- Use a scoop to skim out remaining ice debris.

- Inspect and allow water circulation before sample collection.

4.C.5.d. Sampling Through Thin Ice Cover

-- If flow is sufficient near shore, break ice with spud and take bank sample.

-- If flow is insufficient near shore, sample from deeper waters by breaking ice and wading into the river. This operation may be dangerous, again, safety is the first priority. Recommendations for this procedure are as follows:

  - Locate a point on the river where the bottom is sound and footing is firm.

  - While proceeding into water have bottom in sight at all times. Wear life jacket.

  - Have life line attached to you and a partner on shore.

  - When current becomes swift, stop at that point and collect sample. Never proceed into a strong current which is capable of sweeping an individual under ice.

  - Allow current to clear sediments before starting sample collection.

4.C.5.e. Sample Collection Through Ice

Bottles need to be clean inside and out to avoid contamination in the restricted area of the sample hole.

Collect samples with bare hands if conditions allow to assure proper handling of containers. If latex gloves are used, clean and rinse beforehand.

Follow bottle filling techniques recommended in the preceding Section 4.C.2.a.5. Grab Sampling From a River Bank. The order in which samples are collected through ice may affect analysis results. Fill in accordance with the following order:

-- (1) Oil and grease samples - collected at surface.

-- (2) Volatile hydrocarbons - collected at surface.

-- (3) Bacteriological samples - collected one foot below surface.

-- (4) Dissolved oxygen - collected at surface.

-- (5) Organics and pesticides - collected one foot below surface.

-- (6) General chemistry - collected one foot below surface.

If at any time during collection the hole becomes contaminated beyond what the current flow can flush out, cut new hole and continue sample collection at new site.

Glass bottles may break immediately in extreme cold. Keep all glass inside clothing while transporting outdoors.

4.C.5.f. Winter Sample Storage

When sampling during extreme cold, take precautions to avoid freezing samples during the transportation to the laboratory. Freezing samples may cause breakage of glass sample containers or seriously alter analysis results for certain parameters. When operating from a camper type monitoring unit, keep camper furnace set at a temperature slightly greater than 4° C. Store samples indoors during overnight sample collection surveys.

4.C.6. OPERATION OF ISCO AUTOMATIC SAMPLER

This procedure is for the stage activated - non-uniform time increment mode of operation. For other modes of operation consult the manufacturer's manual.

4.C.6.a. Pre-program Set Up

Location: must meet the following criteria.

1. Less than 20 feet of suction head.
2. There is an intake tube limit of 25 feet.
3. Sampler located well above high water mark.
4. A representative sample collection area.
5. Should be a secure location (near tree or other fixed object).

Set-Up:

1. Set up the security box on the above location and place the sampler in the box.
   ✡For long term deployment feed the strainer and the activator through the opening in the security box and then through a pvc pipe. The pipe can then be buried to increase security.
2. Pound a metal fence post into the stream bottom at the desired intake point.
3. Wire the **sample intake strainer** to the fence post.
   ✡The strainer should be ≈midway between the surface and the stream bottom for sampling in a stable flow situation.
   ✡For event sampling where the flow will increase the strainer may be placed at or above the water surface to avoid having the strainer pick up material travelling as bedload.
4. The **stage activator** may be mounted on the same fence post or secured at the edge of the stream; positioned at a higher level than the strainer to insure that the strainer is completely submerged when the program is activated.
   ✡It should be positioned with the stainless steel pin pointed down to prevent activation by rain. Check to be sure the inside is clean and the vent hole is unobstructed. The vent hole must be above the upper electrical contact.
5. Connect the sample intake strainer and the stage activator to the sampler.

4.C.6.b. Programming the Sampler

The following is a description of programming for the non-uniform time mode. Consult the manufacturer's manual for programming instructions for other modes.

1. Connect a charged battery to the sampler. Turn the sampler on.
   ✡The sampler is now in the standby mode. The liquid crystal display (LCD) will alternately display the bottle number where the distributor is positioned and "---".
2. Reset the **stage activator switch** by moving it to reset and then to latch.
3. Press **program/step program** and then enter the mode - **variable time increment.**
4. Press **program/step program** and then enter the desired time interval which will be the amount of time you wish to elapse between the activation of the program and the first sample.
   ✡At this point the sampler will be displaying 00 (sample number) but the distributor will be positioned over bottle

number one.

5. Enter the time interval. Continue to program in the desired time intervals for the rest of the samples. Program the first two intervals for 1 minute each. Program the last interval (23) at 9000; this will allow you to determine the real time (as opposed to the programmed time) at which the samples were collected. **Enter this data on the field sheet.**
6. Set the sample volume, type of suction line and suction head. The sampler is now in **standby** mode.
   *Selecting the non-uniform time mode eliminates the following steps: delay to first/next sample, multiplex mode, multiplex number, number of composite samples.
7. Program the **stage activator:** press the **enter value** key five times in succession. (The **mode** and **interval between samples** indicator lights are now lit.) The mode of the **stage activator** previously programmed is now shown on the LCD. Enter the number one if necessary. (The **enter value** and **clear entry** keys work as in the normal program state.) Press the **program/step program** key to return the sampler to the standby mode.
8. Reset the **stage activator** by flipping the toggle to **reset** and back to **latch.**
9. Push the **start program/reset distributor key** to initiate the program. (If necessary the sampler will now reposition the distributor over sample bottle number one.) The LCD will flash 01 (the sample number) and the time interval you programmed for 00. The sampler is now in a dormant mode waiting for the signal to initiate the program.
10. Review the program. For a sampler in the run state, the programmed values may be reviewed without interrupting the program by pressing the **program/step program** key five times in succession. This places the sampler into an **automatic program scan** mode, whereby the sampler automatically scans through the indicator lights at approximately a 2 second interval, showing on the LCD the value of the program quantity whose light is on. After the last light has been scanned, the sampler will return to the normal run state.

4.C.6.c. Post-program Set Up

1. Submerge the activator briefly (10 seconds) to initiate the program. Observe the time interval until the first sample is collected. Let the sampler collect two to three samples. Press the **halt program key.**
2. Determine if the sample volume is sufficient and that the correct bottles were filled. If not reprogram the volume. Empty the filled sample bottles and rinse thoroughly with tap or distilled water. Replace the bottles.
3. Fill the 24^{th} bottle with distilled water to use as a field blank. Fill the reservoir in the **bottle case** with ice (one bag) and replace the programmer/distributor over the bottle case. (The ice will last 24-48 hours under summer conditions.)
4. Reset the activator by flipping the toggle switch to **reset** and then back to **latch.** Press the **start program/reset distributor key.** Wait the interval of your first sample (1 minute if programmed as above) to insure the program is not immediately initiated. The LCD should be alternating between 01 (the bottle number) and the first time increment you programmed. Place the cover over the programmer/distributor.
5. Stuff any holes etc. in the security box with steel wool to