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Research and Development



Drinking Water Laboratory Certification for Chemistry

Course Manual



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DRINKING WATER CHEMICAL LABORATORY CERTIFICATION

This manual was developed by the Environmental Protection Agency, Environmental Monitoring and Support Laboratory-Cincinnati with the Technical Support Division in response to a request from the Office of Drinking Water

U. S. ENVIRONMENTAL PROTECTION AGENCY
Office of Research and Development
Environmental Monitoring and Support Laboratory-Cincinnati

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DRINKING WATER CHEMICAL LABORATORY CERTIFICATION

INTRODUCTION

Course Instructional Objectives:

This course is designed to meet the needs for training those persons whose responsibilities include the evaluation of laboratories which analyze potable water for chemical parameters. The course can be used by either State or Federal personnel.

Persons desiring to attend this course should be appointed Certification Officers by their supervisors or be responsible for certification and be experienced professionals and hold at least a bachelor's degree in their respective discipline.

Persons attending this course will receive sufficient instruction to be qualified to carry out a chemical laboratory certification inspection according to the current Criteria and Procedures Manuals. The person will be able to carry out the inspection which will include:

1. Laboratory facilities
2. Laboratory equipment and instrument specifications
3. Sample collecting, handling and preservation
4. Methodology, including free chlorine residual, and turbidity
5. Quality control
6. Data handling
7. General laboratory practices
8. Personnel

In addition, the following topics will be presented to prepare the Certifying Officer to deal with the personnel operating the laboratory.

1. Implementation of the laboratory certification program
2. The pre-evaluation work-up
3. The post-evaluation conference
4. Report writing

Method of Instruction:

Instruction in the course will consist of material presented in the lecture format combined with applied laboratory evaluation in a laboratory set up to perform chemical analysis for potable water contaminants as specified in the Primary Drinking Water Regulations.

The present edition of this handbook has been written from the 1982 edition of the Manual for the Certification of Laboratories Analyzing Drinking Water: Criteria and Procedures, Quality Assurance, EPA 570/4-82-002 (hereafter called "Criteria and Procedures" manual). As that document changes and eventually becomes finalized, this manual will need up-dating.

When this manual is used by a State to train its evaluation team(s), the manual must be looked at to make it fit the State's certification program.

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Unit 1

IMPLEMENTATION OF CERTIFICATION PROGRAM

I. CERTIFICATION OF REGIONAL LABORATORIES AND PROGRAMS

The Environmental Monitoring and Support Laboratory - Cincinnati (EMSL-CI) is responsible for certifying the regional laboratory, if one exists, for microbiological and chemical analyses, and for approving the regional program for certifying other laboratories for these parameters. EMSL-Las Vegas (EMSL-LV) has similar responsibilities for a region having radiochemistry capability. The regional certification program must be approved before a region can exercise its authority to certify other laboratories.

A. Certification of Laboratories

Regional laboratories analyzing potable water samples under the Safe Drinking Water Act must meet the minimum criteria specified in the "Criteria and Procedures" manual, pass an on-site inspection at least once every three years, and satisfactorily analyze an annual set of PE samples. For those regions certified for radiochemistry, satisfactory performance on two cross check samples per year is also necessary.

B. Individual(s) Responsible for Certification Program

The USEPA Region must designate the individual(s) to coordinate drinking water certification activities. This individual(s) must be experienced in quality assurance; hold an advanced degree or have equivalent experience in microbiology, chemistry, or radiochemistry; and have sufficient administrative and technical stature to be considered a peer of the director of the principal State laboratory.

C. On-Site Evaluation Team

One or more teams must be established by the region to evaluate a laboratory in microbiology and chemistry. Team members must be experienced professionals, holding at least a bachelor's degree (or equivalent education and experience) in the specific discipline being evaluated. Team members must participate in training activities as specified by EMSL-CI.

D. Development of Regional Plans for Certifying Local Laboratories in Non-Primacy States

Regions are required to develop plans for certifying local drinking water laboratories in non-primacy states. Written plans should include the following:

1. Certification official;
2. Types and numbers of laboratories;
3. Analyses to be examined;
4. Schedule for on-site evaluations; and
5. Plans for providing technical assistance to laboratories in need of upgrading.

II. CERTIFICATION OF STATE LABORATORIES

The principal State laboratory system must have the capability to analyze every parameter included in the drinking water regulations (40 CFR 142.10(b)(4)); however, an individual laboratory which is part of a principal State laboratory system may be certified for only one, several, or all the cited analyses. If a principal State laboratory contracts with another laboratory, including a laboratory outside the State, to assume the lead role in analyzing a regulated parameter (e.g., radiochemical contaminants), that contract laboratory will, for the purposes of this manual, be considered part of the principal State laboratory system. In this case, the contract laboratory must be certified either by USEPA or by the State in which the laboratory is located for the contaminants of interest. In the latter case, the State must have primacy.

The certification process for a principal State laboratory or a local laboratory in a non-primacy State will begin when the laboratory director makes a formal request to the region. This application may result from the following:

- A request for first-time certification for microbiology, chemistry and/or radiochemistry;
- A request for certification to analyze additional or newly regulated parameters;
- A request to renew a laboratory's certification status after three years; and
- A request to reapply for certification after correction of deficiencies which resulted in the downgrading/revocation of certification status.

The Region should respond to a formal application for any of the requests within 30 days, and a mutually agreeable date and time should be set for the on-site laboratory evaluation. The recommended protocol for conducting these evaluations is given in Appendix B of the "Criteria and Procedures" manual. For certification, a laboratory must pass an on-site inspection and satisfactorily analyze performance evaluation samples for those parameters for which it requests certification.

After the on-site visit and the review of PE sample results, the Region can classify the laboratory for each type of analysis according to the following ranking scheme:

- o Certified – a laboratory that meets the minimum requirements of the "Criteria and Procedures" manual. The certification shall be valid for up to three years.
- o Provisionally Certified – a laboratory which has deficiencies but can still produce valid data.
- o Not Certified – a laboratory possessing major deficiencies which in the opinion of the Regional Administrator, cannot consistently produce valid data.

In the case of laboratories classified as Provisionally Certified, up to one year will be permitted for correction of the deficiencies. A one-time extension of no more than six months may be considered by the Region as long as the laboratory is making "good faith" progress in the resolution of its deficiencies and the continued provisional status does not impact the generation of valid data. A Provisionally Certified laboratory may analyze drinking water samples for compliance purposes. In no case should provisional certification be given if the evaluation team believes that the laboratory lacks the capability of performing the analysis within

specified limits. Once deficiencies have been corrected to the Regional Administrator's satisfaction, the latter should upgrade the laboratory to Certified status.

For laboratories requesting first-time certification or certification to analyze additional or newly regulated parameters, the Region, at its discretion, may administratively grant a laboratory Provisionally Certified status, pending an on-site evaluation. It is granted only when the Region judges that the laboratory has both the appropriate instrumentation and trained personnel to perform the analyses, and the laboratory has satisfactorily analyzed PE samples for the contaminants in question.

For those regions lacking the expertise required to certify laboratories in radiochemistry, EMSL-LV will conduct on-site inspections.

III. CERTIFICATION OF LOCAL LABORATORIES

For the purpose of this document, local laboratories include any State, county, municipal, utility, Federal, or commercial laboratory, but excludes principal State laboratories and USEPA Regional laboratories. In non-primacy States, the Regions will certify local laboratories, using the criteria and policies in the "Criteria and Procedures" manual.

Only primacy States where not all drinking water analyses are conducted at State-operated laboratories are required to establish a certification program for local laboratories (see 40 CFR 142.10(b)). All states, however,

are encouraged to develop such programs. Certification must be based upon criteria contained in the "Criteria and Procedures" manual or State-developed equivalents which are at least as stringent. Those States required by regulation to develop a certification program must appoint a laboratory certification officer(s) who is certified by the Region as the official(s) responsible for the State program.

The principal State laboratory system must have the technical capability to analyze for all regulated contaminants. If the principal State laboratory has the resources to perform 100% of the analyses for one contaminant (e.g., lead), but does not have adequate resources to perform 100% of the analyses for another contaminant (e.g., can only analyze 20% of all total coliform samples), then the State certification program need only include certification criteria for contaminants for which the State will not be analyzing 100% of the samples.

Federal facilities must comply with all Federal, State and local requirements with respect to the Safe Drinking Water Act. For the purpose of certification, Federal laboratories in which routine monitoring of public drinking water supplies is conducted are to be considered local laboratories. The agency with primary enforcement authority, either the State or the Region, will be responsible for carrying out certification activities. If requested by the State, the Region may conduct on-site evaluations of Federal laboratories in that State. USEPA will have primary enforcement authority over any facilities on Federal Indian lands.

IV. OTHER CONSIDERATIONS FOR LABORATORY CERTIFICATION

A. Quality Assurance Plan

It is essential that all laboratories analyzing drinking water compliance samples adhere to defined quality assurance procedures. This is to insure that routinely generated analytical data are scientifically valid and defensible and are of known and acceptable precision and accuracy. To accomplish these goals, each laboratory should prepare a written description of its quality assurance activities (a QA Plan). The following items should be addressed in each QA plan:

1. Sampling procedures.
2. Sample handling procedures.
 - specify procedures used to maintain integrity of all samples, i.e., tracking samples from receipt by laboratory through analysis to disposal.
 - samples likely to be the basis for an enforcement action may require special safeguards (see Chain-of-Custody procedures).

3. Instrument or equipment calibration procedures and frequency of their use.
4. Analytical procedures.
5. Data reduction, validation, and reporting.
 - data reduction: conversion of raw data to $\mu\text{g/L}$, picocuries/L, coliforms/100 mL, etc.
 - validation: includes insuring accuracy of data transcription and calculations.
 - reporting: includes procedures and format for reporting data to utilities, State officials, and USEPA.
6. Types of internal quality control (QC) checks and frequency of their use.
 - may include preparation of calibration curves, instrument calibrations, replicate analyses, use of EMSL-CI provided QC samples or calibration standards and use of QC charts.*

* QC chart for chemistry is explained in Handbook for Analytical Quality Control in Water and Wastewater Laboratories, EPA-600/4-79-019, March 1979. QC chart for radiochemistry is explained in Handbook for Analytical Quality Control in Radioanalytical Laboratories, EPA-600/7-77-088, August 1977.

7. Preventive maintenance procedures and schedules.

8. Specific routine procedures used to determine data precision and accuracy for each contaminant measured.

- precision is based on the results of replicate analyses.
- accuracy is normally determined by comparison of results with "known" concentrations in reagent water standards and by analyses of water matrix samples before and after adding a known contaminant "spike."

9. Corrective action contingencies.

- response to obtaining unacceptable results from analysis of PE samples and from internal QC checks.

The QA plan may consist of already available standard operating procedures (SOP's) which are approved by the laboratory director and which address the listed items, or may be a separately prepared QA document. Documentation for many of the listed QA plan items can be by reference to appropriate sections of the "Criteria and Procedures" manual, the laboratory's SOPs or to other literature (e.g., "Standard Methods for the Examination of Water and Wastewater").

If a particular listed item is not relevant, the QA plan should state this and provide a brief explanation (e.g., some laboratories never collect samples and thus have no need to describe sampling procedures). A laboratory QA plan should be concise but responsive to the above-listed items (a maximum of five pages is suggested). Minimizing paperwork while improving dependability and quality of data are the intended goals.

B. Chain-of-Custody Procedures

Certified laboratories which may be requested to process a sample for possible legal action against a supplier must have a chain-of-custody procedure available.

V. REQUIREMENTS FOR MAINTAINING CERTIFICATION STATUS

A. Periodic Performance Evaluation (PE) Samples

Certified drinking water laboratories must satisfactorily analyze PE samples on an annual basis for each chemical, radiochemical, or microbiological parameter (when available) for which certification has been granted. Results must be within the acceptance limits established by USEPA for each analysis. To maintain certification in radiochemistry, the laboratory must satisfactorily analyze two cross-check samples per year in addition to the annual set of PE samples.

B. Methodology

Laboratories must use methodologies sanctioned by the National Interim Primary Drinking Water Regulations (40 CFR 141.21 – 141.25) or otherwise approved by USEPA for compliance with the Safe Drinking Water Act.

C. Notification of Certifying Authority (CA) for Major Changes

Laboratories must notify the appropriate CA (Regional Administrator or the appropriate EMSL), in writing, within 30 days of major changes in personnel, equipment, or laboratory location which might impair analytical capability. A major change in personnel is defined as the loss or replacement of the laboratory supervisor or a situation in which a trained and experienced analyst is no longer available to analyze a particular parameter for which certification has been granted. The CA will discuss the situation with the laboratory supervisor and establish a schedule for the laboratory to rectify deficiencies.

D. On-Site Evaluation

The CA must be satisfied that a laboratory is maintaining the required standard of quality for certification. Normally, this will be based upon a recommendation resulting from a USEPA on-site evaluation conducted at least every three years.

VI. CRITERIA AND PROCEDURES FOR DOWNGRADING/REVOKING CERTIFICATION STATUS

A. Criteria for Downgrading Certification Status

A laboratory may be downgraded to a Provisionally Certified status for a particular contaminant analysis for any of the following reasons:

1. Failure to analyze a PE sample (or an EMSL-LV cross-check sample) within the acceptance limits established by USEPA. If more than one concentration of a particular contaminant is provided, the laboratory must satisfactorily analyze all concentrations, except where otherwise stated. After downgrading to a provisionally certified status, a laboratory may request that USEPA provide QC samples (standard solution samples for radiochemical contaminants) and technical assistance to help identify and resolve the problem. Provisionally Certified status will continue until the laboratory's analysis of a follow-up PE sample (or EMSL-LV cross-check sample) produces data within the acceptance limits established by USEPA.
2. Failure of a certified laboratory to notify the CA within 30 days of major changes in personnel, equipment, or laboratory location which might impair analytical capability.

3. Failure to satisfy the CA that the laboratory is maintaining the required standard of quality, based upon an USEPA on-site evaluation.

During the provisional status period, which may last for up to one year with a possible six month extension, the laboratory may continue to analyze samples for compliance purposes until it resolves its difficulties. It must, however, notify its clients of its downgraded status.

B. Criteria for Revoking Certification Status

A laboratory may be downgraded from Certified or Provisionally Certified status to a Not Certified classification for a particular contaminant analysis for the following reasons:

1. Failure to analyze an initial and follow-up PE sample (or EMSL-LV cross-check sample) for a particular contaminant within the acceptance limits established by USEPA.
2. Failure to correct identified deviations (including continued use of unapproved methods and equipment) by the time specified by the CA.
3. Submission of a PE sample to another laboratory for analysis and reporting data as its own.

4. Falsification of data or other deceptive practices.

C. Procedures for Revocation

The CA will notify the laboratory in writing (registered or certified mail) of the intent to revoke certification. If the laboratory wishes to challenge this decision, a notice of appeal must be submitted in writing to the CA within 30 days of receipt of the notice of intent to revoke certification. If no notice of appeal is so filed, certification will be revoked.

The notice of appeal must be supported with an explanation of the reasons for the challenge and must be signed by a responsible official from the laboratory such as the president/owner for a commercial laboratory, or the laboratory supervisor in the case of a municipal laboratory.

Within 60 days of receipt of the appeal, the CA will make a decision and notify the laboratory in writing. Denial of the appeal results in immediate revocation of the laboratory's certification. The CA will request the laboratory to notify its clients of its status in writing, and to submit verification that this has been accomplished. Once certification is revoked, a laboratory may not analyze drinking water samples for compliance purposes until its certification has been reinstated.

If the appeal is determined to be valid, the CA will take appropriate measures to reevaluate the facility and to issue to the laboratory within 60 days a written decision on its certification status.

D. Reinstatement of Certification

Certification will be reinstated when and if the laboratory can demonstrate to the CA's satisfaction that the deficiencies which produced Provisionally Certified status or revocation have been corrected. This may include an on-site evaluation, a successful analysis of samples on the next regularly scheduled EMSL water supply performance evaluation study, or any other measure the CA deems appropriate.

VII. RECIPROCITY

Reciprocity, which is defined as mutually acceptable certification among Regions and States, is endorsed by USEPA as a highly desirable element in the certification program for drinking water laboratories. States are encouraged to adopt provisions in their laws and regulations to permit it. States may request USEPA to arbitrate disputes involving reciprocity. Data from USEPA certified laboratories will be acceptable under the Safe Drinking Water Act in jurisdictions where USEPA has primary enforcement responsibility.

VIII. TRAINING

Training is an integral part of the laboratory certification process for: a) personnel responsible for certifying laboratories either on behalf of the Regional office or a primacy State; b) the laboratory analysts responsible for microbiological, chemical, and radiochemical measurements. Mechanisms for providing adequate training should be examined by primacy agencies or other groups.

IX. TECHNICAL SERVICES

A. Reference Samples

There are four types of EMSL reference samples: calibration standards, quality control (QC), performance evaluation (PE), and intercomparison cross-check samples. EMSL-CI provides QC and PE samples for all regulated chemical and microbiological contaminants and residual chlorine, and in addition, provides calibration standards for trace organic chemicals. As part of the QC/PE sample packages, contaminant concentrations are furnished along with detailed user instructions. EMSL-LV provides calibration standards, PE samples, and intercomparison cross-check samples for all regulated radiochemical contaminants.

QC samples and standards are provided on request as part of a laboratory's own quality assurance activities. They serve as independent checks on reagents, instruments, and analytical techniques; as an aid for testing or training analysts; or for determining intralaboratory precision and accuracy. Although no certification or other formal USEPA evaluation functions result from using these samples, their routine use is considered fundamental to a proper laboratory QA plan.

EMSL-CI and EMSL-LV conduct periodic water supply performance evaluation studies using PE samples as a requirement for certification. In contrast to QC samples and calibration standards, contaminant concentrations are not furnished before analysis. Laboratories should request PE samples through the appropriate Regional office for chemistry and microbiology, or EMSL-LV for radiochemistry.*

At the conclusion of each study, the EMSLs prepare individual reports for each laboratory and provide them to the participants. The certifying authority reviews unacceptable data with the laboratory to identify and resolve problems. QC samples and calibration standards are useful for this purpose. Once problems are corrected, the laboratory must analyze a second series of PE samples for problem parameters during a follow-up EMSL study.

*EMSL-LV address is USEPA/EMSL, P.O. Box 15027, Las Vegas, Nevada 89114

In addition to the annual PE sample requirement, EMSL-LV also requires satisfactory performance in two intercomparison cross-check studies per year. Intercomparison cross-check samples differ from PE samples in that the former contain only one or two radionuclides (e.g., radium-226 and radium-228), while PE samples for radiochemistry are complex mixtures of alpha, beta, and photon-emitting radionuclides. In neither case are contaminant concentrations furnished to the laboratory until after completion of the study.

X. ALTERNATE ANALYTICAL TECHNIQUES

Section 141.27 of the National Interim Primary Drinking Water Regulations permits approval of alternate analytical techniques. Such a technique, also known as an alternate test procedure

(ATP), shall be accepted "...only if it is substantially equivalent to the prescribed test in both precision and accuracy as it relates to the determination of compliance with any maximum contaminant level."

EMSL-CI, through its Equivalency Staff, is responsible for and provides coordination of a program to determine the acceptability of proposed techniques, and makes recommendations for approval or denial to the appropriate authority. Applications for approval of an ATP may be made on a limited or a nationwide basis. Requests for limited use approvals

are submitted to the appropriate Regional Administrator or designee who, after receiving recommendations from the Director of EMSL-CI and the Director of Office of Drinking Water, has the final authority to approve requests. Requests for nationwide use approvals should be forwarded directly to the Director of EMSL-CI, who, after review by the Equivalency Staff, will provide recommendations to the Director of Office of Drinking Water, with whom final authority for approval rests.

Applicants who propose an ATP need to provide a step-by-step procedure, applicable literature citations or other references, and any available comparability data between the proposed ATP and the USEPA-approved test procedure for the same contaminant.

In the case of new techniques where precision and accuracy data may not be available to support an application, the applicant for a limited use ATP will be asked to provide comparability data from the analysis of samples collected from one to five water supply systems most representative of those routinely analyzed. From each of these systems, three samples, in which the concentrations range from the limit of detection (LD) to the maximum contaminant level (MCL), should be collected and each sample analyzed eight times, four times each, by the proposed technique and the USEPA-approved test procedure. Samples can be spiked as necessary to cover the concentration range between the LD and MCL. Applicants for a nationwide ATP may also be asked to provide comparability data. For each of a minimum of five sources, six samples should be collected and analyzed eight times, four times by each

technique. The water supply sources selected must be dispersed geographically throughout the United States. Samples may also be spiked as necessary to cover the concentration range between the LD and the MCL.

The EMSL-CI Equivalency Staff will apply a series of proven statistical techniques to the data submitted with all applications to determine equivalency between the proposed and the approved techniques, and submit recommendations to approval authorities.

Unit 2

PLANNING A LABORATORY CERTIFICATION

Before actually mentioning the steps involved in preparing for a certification visit, a few words of introduction are needed. It is important that the Certification Officer have the proper attitude when carrying out a survey. He is attempting to help the laboratory, by offering a form of technical assistance and training combined. He is to aid the laboratory in correcting problems that exist and offer suggestions for improvement.

I. PURPOSE

The object of reviewing a laboratory's analyses of drinking water samples is to increase the quality of those analyses so that the water consumer or recreational user's health is given the greatest possible protection. It is better for the evaluator to consider the survey as a conference on methods and procedures with emphasis on the acceptance of an approved methods approach as verification of data reliability. This attitude yields much better results with the majority of the laboratories than does having the Certification Officer emphasize the regulatory aspects of his visit. Certainly endorsement of the laboratory as a certified laboratory by the State or Federal government does bring significant prestige, while the discussion with recognized experts in drinking water analysis does afford the opportunity for increased technical knowledge.

II. THE EVALUATION

The frequency of evaluation and certification of a laboratory has been set at once every three years. Past experience has shown that more frequent evaluations yield little additional value to either the staff or the program. However, where there are major difficulties or where there are large turn-overs of laboratory personnel, evaluations should be performed at more frequent intervals.

A. Requesting an Evaluation

Certification should be initiated by a formal request from the laboratory to the appropriate certification authority. This request should include a statement stating which type of analysis or tests for which the laboratory is seeking certification and the name, address, and telephone number of the laboratory's contact person. A laboratory may be certified for one, several, or all analyses included in the National Interim Primary Drinking Water Regulations revised as published in the Federal Register* of August 27, 1980 (chemical and bacteriological). A timely response to the request for the laboratory evaluation should be given (preferably within 30 days).

B. Scheduling an Evaluation

In order to set a mutually agreeable date and time for the evaluation, the person designated to schedule laboratory evaluations should contact the laboratory director. The date selected should be agreed upon by all members of the certification team and should allow sufficient time to conduct the evaluation without being rushed. This pre-evaluation conference with the laboratory director should establish an evaluation schedule that would have a minimum impact on the laboratory activities.

As a guide to help establish scheduling of laboratory certifications, a minimum of one week should be allowed for each laboratory to be certified. This allows approximately one and a half to two days for the evaluation and about three days for the report to be written. The on-site evaluation time assumes that the chemical and bacteriological evaluations are carried out simultaneously by different individuals during the same visit.

The guidelines do not consider travel time. Travel time can be minimized if laboratories to be evaluated within a given year are grouped into a defined geographical area so that the team can visit several laboratories before returning to their office.

C. Data Reviews

If the information is available, the chemical Certification Officer should review the results of the annual unknown performance sample analyzed by the laboratory. If the laboratory has participated in any performance studies or has analyzed any known performance samples, these results should also be evaluated. This data evaluation could indicate to the Certification Officer which analysis he might wish to schedule for operation during his visit.

If the laboratory has previously been evaluated by an on-site visit, the Certification Officer should review this pertinent data, particularly if the previous on-site visit was conducted by someone other than himself. He should note any unacceptable areas to assure himself they have been corrected properly. This should also include any equipment needs which were suggested during the previous visit.

A few words on the use of the survey forms might be appropriate here. Remember the intent of the survey form is to serve as a guideline for complete coverage of the laboratory's activities, not as a grading sheet for answers supplied by the laboratory staff. It is from this basic information that the Certification Officer formulates his oral report in a wrap-up conference held at the conclusion of the visit and from which a formal report is prepared with specific comments and recommendations.

Each deviation observed during the laboratory evaluation should be discussed at the time it is observed. The discussion should include the deviation, its effect on validity of results, remedial action, and reasons justifying the change in procedures. The final hour of the laboratory evaluation visit has traditionally been devoted to an informal presentation of the material to be covered in the report. Generally, the wrap-up conference is made to the laboratory director, chemist in charge of the water program, and a representative of the water supply engineering staff. If the laboratory is a principal State laboratory, the presence of Regional engineering staff members from the federal water program should be encouraged whenever the evaluation involves public water supplies.

Unit 3
ANALYTICAL METHODOLOGY

I. INTRODUCTION

The analytical methods section of the Criteria and Procedures manual is one section that is to be considered mandatory. This is due to the inclusion of the methods in the Federal Register issuance of the National Interim Primary Drinking Water Regulations of December 24, 1975, as well as additions made in the National Interim Primary Drinking Water Amendments published on August 27, 1980, and the Trihalomethane regulations published November 29, 1979. These promulgations determine the methods that all laboratories will use for analyzing potable water supplies.

Until the National Interim Drinking Water Regulations are revised or additional alternate methods are approved, the methods and the references shown in Table I and III are to be used.

This unit will separate the methods into inorganic and organic types of analysis in order to facilitate the coverage. The inorganic category will be further broken down into metal and nonmetal techniques. However, the methods will not be covered in detail in this unit because it is assumed that the trainee in this course has knowledge of all the methods.

When the Certifying Officer visits a laboratory there is very little possibility of evaluating the technique of all the methods. Rather, the

individual should consult the results of the unknown performance sample the laboratory has analyzed. The records of the laboratory should contain results of the analysis of internal laboratory check samples run as part of the laboratory's quality control program. These data should indicate to the Certifying Officer any trouble spots which exist in the methodology. It is at this point where this outline will be of value, to point out spots where trouble could most likely occur.

II. THE NONMETAL METHODS

The contaminants covered in this section are nitrate, fluoride, sodium, and the corrosivity parameters. Nitrate and fluoride have established MCL's. Sodium has a set monitoring frequency and a reporting requirement but no MCL. Corrosivity must be determined and calculated, and in order to do this the alkalinity, temperature, total dissolved residue, and calcium must be determined. All methodology for inorganics that must be carried out in a approved laboratory are listed in Table I.

A. Nitrate

1. Manual Cadmium Reduction Method

The Cadmium Reduction method reduces all nitrate to nitrite by passing the sample through a column containing copperized cadmium. The colorimetric step diazotizes the nitrite with sulfanilamide and couples with N(1 naphthyl)-ethylenediamine to form a highly colored azo dye which is measured. In order to get

Table I
Approved Methodology for Inorganic Contaminants
to be done in Approved Laboratories

Contaminant	Methodology	EPA ¹	ASTM ²	SM ³	USGC ⁴
Alkalinity	Methylorange titrimetric or potentiometric	310.1	D1067-70B	403	
Arsenic	Atomic Abs; Furnace	206.2			
	Atomic Abs; gaseous hydride	206.3	D2972-78B	301A-VII	I-1062-78 ⁴
	Spectrophote; silver diethyldithiocarbamate	206.4	D2972-78A	404A after B(4)	
Barium	Atomic Abs; direct aspiration	208.1		301A-IV	
	Atomic Abs; furnace	208.2			
Cadmium	Atomic Abs; direct aspiration	213.1	D3557-78A or B	301A-11 or 111	
	Atomic Abs; furnace	213.2			
Calcium	Atomic Abs; direct aspiration	215.1	D2576-780	301A-11	
	EDTA; titrimetric	215.2	D1126-67B	306C	
Chromium	Atomic Abs; direct aspiration	218.1	D1687-77D	301A-11 or 111	
	Atomic Abs; furnace	218.2			
Corrosivity	Langelier Index			203	
	Agressive Index				C400-77 ⁵

Table 1 (continued)

Contaminant	Methodology	EPA ¹	ASTM ²	SM ³	Other
Fluoride	Colorimetric; SPADNS with distillation	340.1	D1179-72A	414A and C	
	Potentionmetric; ion selective electrode	340.2	D1179-72B	414B	
	Automated Alizarin blue; with distillation	340.3		603	129-71W ⁶
	Zirconium eriochrome cyanine R with distillation				I-3325-78 ⁴ 380-75WF ⁷
	Automated ion selective electrode				
Lead	Atomic Abs; direct aspiration	239.1	D3559-78A or B	301A-11 or 111	
	Atomic Abs; furnace	239.2			
Mercury	Manual cold vapor	245.1	D3223-79	301A-VI	
	Automated cold vapor	245.2			
Nitrate	Colorimetric; brucine	352.1	D992-71	419D	
	Spectrophotometric; cadmium reduction	353.3	D3867-79B	419C	
	Automated hydrozine reduction	353.1			
	Automated cadmium reduction	353.2	D3867-79A	605	
	Ion selective electrode				93MM-79 ⁸
	Ion Chromatography	300.0			
Selenium	Atomic Abs; furnace	270.2			
	Atomic Abs; gaseous hydride	270.3	D3859-79	301	
Silver	Atomic Abs; direct aspiration	272.1		301A-11	
	Atomic Abs; furnace	272.2			
Sodium	Atomic Abs; direct aspiration	273.1			
	Atomic Abs; furnace	273.2			
	Flame photometric		D1428-64A	320A	
Total filterable residue	Gravimetric	160.1		208B	

1. "Methods of Chemical Analysis of Water and Wastes" EPA Environmental Monitoring and Support Laboratory, Cincinnati, Ohio 45268 (EPA-600/4-79-020) March 1979. Available from ORD Publications, CERL, EPA, Cincinnati, Ohio 45268. For approved analytical procedures for metals; the technique applicable to total metals must be used.
2. Annual Book of ASTM Standards, Part 31 Water, American Society for Testing Materials, 1916 Race Street, Philadelphia, Pennsylvania 19108.
3. "Standard Methods for the Examination of Water and Wastewater", 14th Edition, American Public Health Association, American Water Works Association, Water Pollution Control Federation, 1975.
4. Techniques of Water Resources Investigation of the United States Geological Survey, Chapter A-1 "Methods for Determination of Inorganic Substances in Water and Fluvial Sediments," Book 5 (1979, Stock #024-001-03177-9). Available from Superintendent of Documents, U.S. Government Printing Office, Washington, D.C. 20402.
5. "AWWA Standard for Asbestos-Cement Pipe, 4 in. through 24 in. for Water and Other Liquids" AWWA C400-77, Revision of C400-75, AWWA, Denver, Colorado.
6. "Fluoride in Water and Wastewater, Industrial Method #129-71W". Technicon Industrial Systems, Tarrytown, New York 10591, December 1972.
7. "Fluoride in Water and Wastewater", Technicon Industrial Systems, Tarrytown, New York, February 1976.
8. "Methods Manual-93 Series Electrodes" Form 93 MM/9790, pp 3-6, 1970. Orion Research Incorporated, Cambridge, Massachusetts.

a single answer for nitrate alone the sample would have to be run with and without passing the sample through the column, obtaining two values for nitrite only and for nitrate plus nitrite present in the sample. The nitrate concentration is found by difference between the reduced and nonreduced values.

The sample should be filtered through a glass fiber filter or a 0.45 μ membrane filter before passage through the column. Build-up of suspended matter in the reduction column will restrict sample flow. Highly turbid samples may be pretreated with zinc sulfate before filtration to remove the bulk of particulate matter present in the sample. Other possibilities for interferences are the presences of high concentrations of iron, copper or other metals. EDTA is added to the sample to eliminate this interference.

Care must be taken when preparing the reduction column. If the column is not properly prepared, the column efficiency for converting nitrate will be low. This column efficiency should be calculated for all newly prepared columns and each time the column is used. For the primary determination of the column's efficiency, a series of nitrite standards should be compared to reduced nitrate standards of the same concentrations to check the column efficiency. Then, each time the column is used, at least one nitrite standard should be compared to a reduced nitrate standard of the same concentration. Efficiency should range from 96 to 104%.

The Certifying Officer should also be aware of the toxicity of cadmium so he can caution the analyst about proper techniques for handling the cadmium during column preparation and in the proper disposal of column washings which might contain some of the metal.

The cadmium should not be allowed to dry out; it should be stored when not in use by addition of the ammonium chloride-EDTA solution to the column assuring that it covers the cadmium. Also, after the sample has been reduced the colorimetric procedure should be carried out as soon as possible and in no case should the reduced sample be allowed to stand longer than 15 minutes before color development is begun. Finally, the flow rate from the column is critical and should be kept between the specified rate of 7-10 mL per minute.

2. Automated Cadmium Reduction Method

The procedure involved is the same as that of the manual method. Care must be taken to be assured that air is not trapped in the reduction column. In order to minimize entrapment of air the straight column is inclined at a 20° angle and the U shaped column should be packed wet. The column flow characteristics must not be impaired; by sample turbidity or formation of colloidal copper. The operator should not run a distilled water wash, rather, he should use ammonium chloride while the column is in the system.

3. Automated Hydrazine Reduction

This method utilizes the Auto Analyzer, which can run about 20 samples per hour. The apparatus included in the system must contain a heating bath as well as a continuous filter to remove the precipitate produced in the reaction. Time should be allowed between peaks for complete washout of the sample, i.e. the recorder should return to near baseline before the next peak.

The Hydrazine sulfate reagent is toxic and the analyst should be aware of this. The color developing reagent is stable for about one month and should be kept in a dark bottle in the refrigerator.

Standards should be run about every 20 samples to assure that the standard curve is still correct. The curve is produced by plotting known concentration of standards against peak heights.

4. Brucine Method

The Brucine method analyzes for nitrate itself so two runs are not necessary as in the Cadmium Reduction method. The reaction between nitrate and Brucine produces a yellow color which can be used for the colorimetric determination of nitrate. The main drawback of this method is the need for reproducibility of technique and reaction conditions. Consequently, it is recommended that at least two standards for each batch of samples are analyzed as a check.

All strong oxidizing or reducing agents interfere. The presence of oxidizing agents may be determined by adding orthotolidine reagent, as in the measurement of residual chlorine. The interference by residual chlorine may be eliminated by adding sodium arsenite, provided that the residual chlorine does not exceed 5 mg/liter. A slight excess of sodium arsenite will not affect the determination. Ferrous, ferric iron, and quadrivalent manganese give slight positive interferences, but in concentrations less than 1 mg/liter these are negligible. An interference due to nitrite of up to 0.5 mg $\text{NO}_2\text{-N/liter}$ is eliminated by the use of sulfanilic acid. Chloride interference is masked by addition of excess NaCl.

As mentioned previously, the duplication of reaction conditions is a prime concern in the Brucine procedure. Consequently, cautions are given about spacing the reaction tubes in racks with each tube being surrounded by empty spaces. Mixing the sample thoroughly and not using "vortex" type mixers are also items where caution is prescribed.

The method calls for the light path of the spectrophotometer to be at least 2.5 cm (1 inch) long and recommends using reaction tubes approximately 2.5 x 15 cm in conjunction with the spectrophotometer to determine transmittance while avoiding the necessity of transfer following the reaction. In addition,

using a stirred water bath with a gabled top is recommended in order to maintain a temperature of at least 95°C when cooled samples are introduced.

Again, the reagents Brucine sulfate and sodium arsenite are toxic and precautions should be taken in the laboratory so that these reagents are not ingested.

Of the two manual methods, the Brucine method is probably best used in larger laboratories where large numbers of samples are analyzed in batches. The procedure of the Brucine method would be at its best under these circumstances. Having the same analyst using the method as often as possible would also enhance its performance, as good technique is often generated by constant repetition. Smaller laboratories would not need the stirred water bath and special tubes if the Cadmium Reduction method were used. Since the column can be stored, provided it is not allowed to dry out, small numbers of samples are best carried out via this procedure.

5. Electrode Method

This procedure is based on the use of a nitrate electrode and the measurement of a potential developed across the membrane when the latter is immersed in a sample or standard. A pH

meter with an expanded millivolt scale or a selective ion meter must be used with the electrode. In addition, a double junction reference electrode is needed.

The electrode must be given time to stabilize after being introduced into the sample. One to two minutes, with constant stirring, is usually sufficient.

There are a number of materials and circumstances that can cause difficulties in obtaining the true potential reading. However, the procedure calls for the use of a buffer which was developed for use with the nitrate electrode. When added in equal proportions with the sample, this buffer alleviates most difficulties.

The certifier should be aware that the calibration curve is not linear; therefore, the analyst must have enough standards to cover the working range. Standards should be run every ten samples to ensure that the calibration curve is still valid. The curve is produced by plotting known concentration values of standards against the obtained millivolt readings.

B. Fluoride

The NIPDWR's maximum contaminant level for fluoride varies with the annual average of the maximum daily air temperature. The basis for

this is the increased consumption of water in higher temperature locations. The values are listed in Table II.

1. SPADNS Method

The SPADNS method is a colorimetric method based on the loss of color resulting from the reaction of fluoride with the zirconyl-SPADNS dye. Several of the interfering substances in the SPADNS procedure are materials found in use in water treatment plants. For example, aluminum and hexametaphosphates are two materials which cause considerable interference. Both these materials are added to some types of waters as part of the treatment. Consequently, distillation is specified in the Federal Register as a preliminary step to the use of the SPADNS procedure.

The preliminary distillation step separates the fluoride from other constituents in water by distilling the fluoride as fluorosilic (or hydrofluoric) acid from a solution of the sample, in an acid with a higher boiling point. The procedure uses a diluted sulfuric acid mixture which is conditioned by heating it to the same end temperature (180°C) as the sample will be heated. Precautions in the distillation procedure include complete mixing of the heavy sulfuric acid and the aqueous sample. Failure to do this could result in the entire mixture splattering out of the distilling flask and injuring the analyst and/or the equipment.

TABLE II

<u>Annual Average of Maximum Daily Air Temperatures</u>		<u>Maximum Fluoride Level-mg/liter</u>
Degrees F	Degrees C	
53.7 and below	12.0 and below	2.4
53.8 and 58.3	12.1 to 14.6	2.2
58.4 to 63.8	14.7 to 17.6	2.0
63.9 to 70.6	17.7 to 21.4	1.8
70.7 to 79.2	21.5 to 26.2	1.6
79.3 to 90.5	26.3 to 32.5	1.4

Heating the distillation flask should be stopped immediately upon reaching the end temperature of 180°C. Proceeding beyond this point will allow sulfates to be carried over. Sulfates are another positive interference. In this same case, the flame under the distillation flask must never touch the sides of the flask above the liquid level. Superheating of the vapor may result in high sulfate carryover.

When high-fluoride samples are distilled, repeat the distillation using 30 mL of distilled water. An analysis of the distillate will indicate completeness of the fluoride recovery. If substantial amounts of fluoride appear in the second distillate, add this quantity to that obtained initially and flush again. Quantities of less than 0.03 mg/300 mL may be disregarded.

Because of the simplicity of apparatus and procedure, the distillation procedure can be readily automated. However, the final heating temperature and sample volumes should be adhered to. Some manufacturers utilize different temperatures and

volumes for their automated stills for fluoride; however, unless the automated still uses the approved temperatures and volumes of both sample and reagents, it cannot be used as an accepted procedure. Automatic stills are generally designed for samples whose fluoride content is within a narrow range from day to day. Should this range be surpassed the results of the distillation could be in error.

The actual colorimetric procedure is simple and requires only minor precautions. The most important of these is that the amount of reagent (10 mL) be very carefully added, since the fluoride concentration is measured as a difference of the absorbance in the blank and the sample, and a small error in the reagent addition is the most prominent source of error. After the reagent has been added, mix thoroughly to assure a homogeneous mixture.

Since almost all methods covered in this unit prior to this point have been colorimetric in nature, some points on good techniques should be pointed out for the certification officers benefit. When standard curves are utilized it is wise to check two points of the curve with each batch of samples to assure that the standard curve is still valid. Also check for use of matched cells. Proper maintenance of the equipment is another point that will indicate to the Certification Officer that proper technique is being followed.

2. Electrode Method

The procedure is based on the use of a lanthanum fluoride crystal and the measurement of a potential developed across this crystal by fluoride ions. There are a number of materials and circumstances that can interfere with the measurement of this potential. However, the procedure calls for a special buffer developed for use with the electrode. When added in equal proportions with the sample, this buffer deletes most of these interferences and eliminates the need for distilling the potable water sample.

The electrode must be given time to stabilize after being introduced into the sample. Usually a three minute time with constant stirring is sufficient. However, at concentrations under 0.5 mg/liter F^- , up to five minutes may be needed to achieve a stable meter reading; higher concentrations stabilize more quickly.

A pH meter with an expanded mv scale or a selective ion meter must be used with a selective ion electrode. In addition, a single junction sleeve type reference electrode, is needed. A magnetic stirrer and stirring bar is a good piece of equipment to have since the sample must have constant agitation while the electrode is immersed.

3. Zirconium Eriochrome Cyanine R

This procedure, like the SPADNS method, requires an initial manual distillation procedure. See pages 3-9 to 3-12 for the procedure and comments.

Since the quality of Eriochrome Cyanine R. varies with the source, it is necessary to test the reagent each time it is prepared. The individual absorbance curves show corresponding differences, and the sensitivity of fluoride between reagents may differ by 20 percent.

As many interferences are the same as with the SPADNS reagent, up to 10mg/L of Aluminum can be tolerated by allowing the solution to stand for two hours before reading. Sulfate interference is more drastic and special care must be taken with the distillation procedure so as not to have sulfate carry-over. If particularly high concentrations of sulfate are present, precipitation as barium sulfate may be necessary.

The procedure shows a salt effect when dissolved solids are present at concentrations of 10,000 mg/L or greater. Sensitivity may be depressed by as much as 5-10 percent. Distillation should prevent this.

4. Automated Alizarin Blue (Complexone)

These procedures require the use of automated equipment such as the Technicon AutoAnalyzer or equivalent. This equipment will usually only be found in the larger laboratories because of cost. A fair degree of operator skill and knowledge together with adequate instructions, are required for successful automated analysis.

When produced during the reaction, sample color and turbidity can escape detection of the analyst consequently causing interference. Therefore, some sample knowledge and regular use of standards should be recommended.

5. Automated Electrode Method

When run at forty samples per hour the equilibration time for the electrode may be surpassed. Consequently an error of 1.5% of full scale may be expected when a low sample succeeds a high sample and an error of 3% of scale may be expected when a high sample succeeds a low sample. A slower rate of analysis will produce less error. This procedure utilizes the electrode and an "AutoAnalyzer" or its equivalent.

C. Corrosivity

On August 27, 1980, the National Interim Primary Drinking Water Regulations were revised and paragraph 141.42 was added to require special monitoring for corrosivity characteristics. The monitoring and reporting requirement is limited to one year. The purpose was to identify those public water systems which were distributing corrosive waters.

The Langelier Index and the Aggressive Index are used to indicate the corrosive tendencies of a water. In order to calculate these values, the temperature, calcium, alkalinity, and total filterable residue values must be known.

The methods for measuring alkalinity and total filterable residue are covered in this section. Only the EDTA titration procedure for calcium will be covered here; the atomic absorption procedure will be covered in the metals section.

1. Total Alkalinity: Methyl Orange Titrimetric or Potentiometric Method.

This procedure involves titration of the sample with 0.02 N sulfuric acid to an end pH of 4.5 as determined by a color change of methyl orange indicator or by use of a pH meter.

The sample should not be filtered or altered in any way, including by dilution or preservation. The sample may be cooled to 4°C for preservation.

Color and turbidity in the sample can cause error by making it difficult to detect the proper end point color. It is also important that the same volume of methyl orange indicator be added to each sample.

Soaps, oily matter, suspended solids, and precipitates may interfere. These materials may have an effect on the color change or cause a sluggish response of the electrode.

The pH meter should be standardized at pH 4.0 to 4.6 with buffers. Frequent standardization checks should be made and care taken to insure that the electrodes are in good condition.

For both procedures, laboratory control samples should be analyzed before each run to assure proper operation. The sulfuric acid should be standardized frequently, preferably before each use.

2. Total Filterable Residue: (Total dissolved solids)

This method is utilized to determine the corrosivity value for drinking waters. When evaluating this method it should be

determined that the laboratory has a copy of an approved method reference and the proper equipment. Ideally one person should be assigned to carry out this method, since the best values are due to technique, and repeated use of the method would lead to the best values.

Equipment needed for this method would include a good four-place analytical balance. It should be determined if the laboratory has a service contract on the balance and a set of class S weights to check calibration of the balance. Some type of documentation, such as a notebook, should be available to show routine checks of the balance calibration. In addition, a good drying oven and desiccator should be available.

When reviewing the data from this method there should be an indication that the analyst is weighing until a constant weight is achieved. This will indicate that no water is left in the sample.

Laboratory quality control samples should be analyzed each time the method is used to indicate the method is in control.

3. Calcium – EDTA Titrimetric

This procedure involves the titration of calcium with EDTA at a pH of between 11 or 12. The main indicator for this procedure

is Murexide, however, for some the end point is very difficult to detect. Therefore, other indicators specifically designed for calcium are used.

Magnesium is the major interference, but at a pH above 11 magnesium is precipitated as the hydroxide. For samples with high hardness, a small sample (less than 50 mL) should be analyzed to prevent the pH from changing during the titration. For samples that are preserved with acid, more NaOH may be needed to ensure that pH is 11 to 12.

Laboratory control samples containing magnesium and calcium should be used to determine the efficiency of the indicator.

III. METHODS FOR METAL ANALYSIS

This grouping will cover the following 14 contaminants.

	MCL, mg/L
1. Arsenic (As)	0.05
2. Barium (Ba)	1
3. Cadmium (Cd)	0.010
4. Chromium (Cr)	0.05
5. Lead (Pb)	0.05
6. Mercury (Hg)	0.002

	MCL, mg/L
7. Selenium (Se)	0.01
8. Silver (Ag)	0.05
9. Sodium (Na)	—
10. Calcium (Ca)	—
11. Copper (Cu)	1
12. Iron (Fe)	0.3
13. Manganese (Mn)	0.05
14. Zinc (Zn)	5

The first eight elements are primary contaminants. For safeguarding public health, they are required to be monitored in community water supplies. Each has an MCL which is expressed in concentration and should not be exceeded. Sodium must also be monitored to protect public health, but it does not have an established MCL. Calcium is monitored as a parameter in the measurement of corrosivity while the remaining four elements are secondary contaminants and are monitored for aesthetic qualities. The secondary contaminants also have MCL's, and although not enforceable, it is recommended that they be analyzed at the same interval as the primary contaminants.

A total element measurement is required for the analysis of these contaminants. Except for the arsenic colorimetric method and the calcium EDTA titrimetric method, all other methods are atomic spectrometric procedures. To better understand the analytical approach and use of these spectrometric methods, they will be discussed according to technique.

The different techniques can be grouped into two categories: 1) techniques (like colorimetric methods) that always require a chemical reaction or pretreatment sample digestion step prior to analysis and, 2) those considered to be total element techniques that are of sufficient energy to vaporize the analyte into an atomic state for either atomic absorption or atomic emission. Included in the first category are atomic absorption techniques like flameless cold vapor (CV), chelation-extraction (CE), and gaseous hydride (GH) methods. The second category consists of direct flame aspiration atomic absorption (FLAA), graphite furnace atomic absorption (GFAA) and inductively coupled plasma atomic emission spectroscopy (ICP). The following sections provide a general discussion of the techniques, sample preparation, and specific requirements particular to the individual contaminants.

A. Labware Cleaning, Reagents and Standards

The analysis of trace elements in drinking water necessitates the labware be kept free from contamination. Care should be taken to ensure that labware, whether glass, plastic or Teflon has been thoroughly washed with detergent and tap water; rinsed with 1:1 nitric acid, tap water 1:1 hydrochloric acid, tap water and finally deionized distilled water in that order.

Deionized distilled water equivalent to or of better quality than ASTM Type II reagent water should be used in the preparation of all reagents, calibration standards, and as dilution water. All acids should be analyzed to ensure no contaminants are present. The use of redistilled acid or acids of ultra-high purity grade are preferred.

The directions for preparing stock standards and calibration standards are given in each method. When different starting materials are available, the preferred order of selection is high quality pure metals, oxides and stable salts. Compounds which are hygroscopic or can vary in waters of hydration should be avoided when possible. Purchased standard solution may also be used, but in all cases, whether purchased or prepared, the concentration of the calibration standard should be verified with a standard obtained from an independent outside source (Quality Assurance Branch, Environmental Monitoring and Support Laboratory - Cincinnati).

B. Sample Preparation for Total Element Analysis Techniques

Irrespective of the valence state or chemical species, the term "total" refers to the sum of the elemental concentration in the dissolved and suspended fractions of a sample. The sample is not filtered, but immediately preserved at the time of collection with nitric acid to a pH of less than 2. When suspended material is not

present, as in most finished drinking water, the contaminant concentration in solution or the dissolved fraction of an acid preserved sample will equal a "total" element determination.

Under these circumstances, a direct analysis without acid digestion using a total element technique will provide a "total" element analysis. The technique most frequently used for this analysis is GFAA. Although pretreatment may be omitted, compliance with the other analytical steps, as noted in each GFAA method, is still required.

The same situation would not be true for gaseous hydride methods, atomic absorption chelation-extraction, colorimetric methods, or the cold vapor technique because the "total" element concentration must be chemically converted to a particular species before the analysis can be completed. In each of these cases, the sample preparation procedure is either given or referenced in the method.

While GFAA is recognized as being the most sensitive technique, an improved sensitivity can be achieved for FLAA and ICP if the sample is concentrated by evaporation prior to analysis. This is usually accomplished during sample preparation using an approved procedure with concern given to the amount of dissolved solids in the analysis solution. For FLAA, dissolved solids should be limited to 5000 mg/L and the analysis completed using a high solids burner. In ICP, the calcium concentration of the analysis solution should be limited to 400 mg/L, or analysis by method of standard additions may be required.

If a sample contains suspended or particulate matter, a pretreatment acid dissolution step is required prior to analysis. The purpose of the acid dissolution step is to solublize that portion of the contaminant that may be occluded or adhering to the suspended material. Included in the FLAA methods are two acceptable sample preparation procedures. One is a vigorous nitric acid digestion,^(1,2) while the other is a total recoverable acid solubilization procedure using a mixture of nitric and hydrochloric acids.^(3,4) The total recoverable procedure is preferred for drinking water analysis because there is less chance of losses from volatilization, the formation of insoluble oxides or occlusion in precipitated silicates. The EPA atomic absorption procedures also describe sample preparation procedures for GFAA where only nitric acid is used and the hydrochloric acid is omitted.^(1,3) Certain elements (arsenic & selenium) have specific preparation procedures for GFAA and these are described under the individual element method.⁽⁵⁾

To determine if an acid dissolution step is needed for GFAA, an aliquot of a well mixed acidified sample should be transferred to a Griffin beaker and visually examined. If the solution is free of suspended or particulate matter, the acid pretreatment step for GFAA analyses is not needed.

If drinking water is to be analyzed by ICP using the Appendix to EPA Method 200.7,^(6,7) the following modified "total" recoverable acid solubilization procedure must be used for the preparation of all samples.

Sample Preparation Procedure for ICP Analysis of Drinking Water

From a well mixed acid preserved sample, transfer of 200 mL aliquot to a Griffin beaker. Add 1.0 mL of (1+1) HNO_3 and 5.0 mL (1+1) HCL to the sample and heat on a steam bath or hot plate until the volume has been reduced to near 20 mL making certain the sample does not boil. Allow the sample to cool, transfer to a 50 mL volumetric flask, dilute to the mark with deionized-distilled water and mix. The sample is now ready for analysis. (Note: If after preparation the sample contains particulate material, an aliquot should be centrifuged or the sample allowed to settle by gravity before aspiration.)

It is important to note, irrespective of the method or technique, that once the sample is ready for analysis the calibration standards should be prepared using the same type of acid or acids, and at the same concentrations as will result in the sample to be analyzed either directly or after processing.

C. Atomic Absorption Techniques

The following techniques can differ in sensitivity and length of analysis time, but each offers a particular advantage depending on the chemistry of the contaminant and the concentration required to be measured. Some contaminants can be analyzed by more than one technique. Those circumstances along with a preferential ranking of acceptable methods are addressed in the discussions of each individual contaminant.

1. Description of Instrumental Needs

Although the design of the atomic absorption spectrophotometer (whether single or double beam) is not specified, the instrument should be properly optimized prior to the analysis of any samples. If the instrument is converted to different set-ups, for example graphite furnace determinations, the optimization can be especially important. The burner or atomizer should be properly aligned, the lamp properly positioned, the wavelength peaked and the proper slit width used.

There are two pieces of accessory equipment important for use with the atomic absorption. First, a recorder is recommended. This will provide a graphic record of each

sample analyzed. Should any questions arise on the results of the runs, the QC samples will give proof of proper technique when their peaks on the recorder chart are examined.

Secondly, the atomic absorption should have a vent installed about 15 to 30 cm (6 to 12 inches) above the burner compartment to remove fumes and vapors from the flame or graphite atomizer. This protects the laboratory personnel from toxic vapors and protects the instrument from corrosive vapors.

Except for the cold vapor analysis of mercury, gases are used in all other atomic absorption techniques as either a flame or an inert atmosphere for GFAA. For FLAA two gases are needed in addition to a supply of dry filtered air. They are acetylene and nitrous oxide (which is used exclusively for barium analysis). For GFAA analyses, argon is recommended because it provides greater sensitivity than nitrogen and can be used for the analysis of all elements. However, nitrogen is slightly less expensive, but should not be used in the analysis of chromium because of possible cyanogen band interference. For gaseous hydride analyses, an argon-hydrogen or nitrogen-hydrogen flame is used.

The two light sources used in atomic absorption are hollow cathode and electrodeless discharge lamps. The hollow cathode lamps may be purchased as a single or multi-element lamp. The single element lamp is preferred because of its greater emission intensity and improved signal to noise ratio. As hollow cathode lamps age they may become noisy or weak. A noisy lamp will give imprecise data, while a weak lamp will require more gain on the photomultiplier tube and have a smaller linear concentration range. Electrodeless discharge lamps provide greater output energy and are longer lasting than hollow cathode lamps. Their main disadvantages are a separate power supply is needed and they have a longer warm-up time. Electrodeless discharge lamps are highly recommended for arsenic and selenium analyses.

When GFAA techniques are employed the instrument should be equipped with a background correction device. Its purpose is to correct for additive non-specific absorption interferences. If a deuterium source or a tungsten halide lamp is employed it should be properly aligned and its output energy should be set equal to the output energy of the hollow cathode lamp. The use of the Zeeman and Smith-Hieftje background correction techniques is also acceptable and does not require application for a method variance.

The use of an automatic sampler for GFAA is strongly encouraged. They are more reliable in providing an accurate furnace aliquot which improves both precision and accuracy. Either direct injection samplers or aerosol spray units are acceptable. However, if an automatic sampler is not available all pipet tips should be washed to remove any possible contamination. This is usually done by soaking in 1:5 HNO_3 .

For GFAA analyses either pyrolytic or both pyrolytic and nonpyrolytic graphite tubes must be available. Only pyrolytic graphite can be used for the analysis of barium while all other contaminants can be analyzed using either type of graphite. Although the pyrolytic tube is longer lasting and usually produces a signal with greater sensitivity, the optimum analytical concentration range is less than with nonpyrolytic graphite. Because of the increased sensitivity samples may require dilution before analysis and a multi-standard second order regression plot may be necessary to provide an adequate calibration curve.

When pyrolytic graphite first became available, contamination and erratic data presented real problems. The coating process has since improved and although nonpyrolytic graphite is recommended for analysis of many elements, the choice of graphite remains at the discretion of the analyst.

In GFAA the only restriction on the type of atomizer used is that it must be graphite. At least one instrument manufacturer offers a platform insert for the furnace. The sample is volatilized from the surface of the platform into an isothermal inert atmosphere that has already reached atomization temperature. The slight momentary delay in the vaporization of the analyte results in reduced matrix effects. A method variance is not required for the use of the platform.

For the cold vapor analysis of mercury special accessories for the atomic absorption spectrophotometer are required. The accessories for a closed system consist of a absorption cell, air pump, pump tubing, bubbler, detector, and scrubber. If an open system is used or the vapor is not collected in a scrubber, it must be vented to an exhaust hood. The absorption cell, which is transparent to UV radiation, is carefully strapped to a burner head and placed in the hollow cathode light path. The bubbler is inserted into a BOD bottle to aerate the reduced mercury from solution into the atomic vapor state for absorption in the cell. Dedicated instruments designed specifically for the measurement of mercury may be substituted for the atomic absorption spectrophotometer.

In the gaseous hydride technique, the hydride of arsenic or selenium is formed in a special glass reaction vessel. After formation, the hydride, using argon, is swept directly from

the vessel into either an argon-hydrogen flame or a heated quartz cell for disassociation and absorption. Each method specifies the appropriate equipment needed. Commercially available hydride systems can be used if they can be operated using the same procedures and chemistry as given in the approved methodology.

Finally, when using chelation-extraction methods, it is important for precise and accurate data that the extraction process be well controlled. When possible, the extraction should be done using the same volume of liquid in separatory funnels of the same size. The use of a platform or wrist shaker is highly recommended for controlling the critical parameter of shaking rate and length of extraction time. Although separatory funnels are common to most laboratories, a mechanical shaker may be considered special equipment. However, if many extractions are performed its use becomes a necessity.

2. Direct Flame Atomic Absorption (FLAA)

Although this technique is the easiest and most convenient to use, it usually lacks the required sensitivity for drinking water analysis. Of the primary and secondary contaminants three elements, arsenic, mercury and selenium, are not

analyzed by this technique. Of the remaining nine, only barium, copper, iron and zinc have MCL's at a concentration that do not require concentrating the sample prior to analysis.

For the analysis of cadmium, chromium, lead, silver and manganese it is recommended that the sample be concentrated ($\leq 10X$) by evaporation using a combination acid solubilization procedure.^(3,4) In concentrating by evaporation, attention must be given to the amount of dissolved solids (<5000 mg/L) in the analysis solution. Concentrated samples should be analyzed using scale expansion (10X) and a high solids (boiling) burner. Background correction should be used unless it can be verified that nonatomic absorption is not occurring from the matrix.

The opposite condition is true for the analysis of sodium and calcium. For these two elements dilution is usually required. The linear range of FLAA analysis of these elements is limited and the burner head is normally rotated 45° from the hollow cathode line of light.

When the use of FLAA is possible, the air-acetylene flame is used except for the analysis of barium. For barium, the nitrous oxide-acetylene flame is used which requires a special burner head.

The EPA method for chromium specifies the nitrous oxide flame with the optional use of the more sensitive air-acetylene flame for concentrations below 200 $\mu\text{g/L}$. Even with concentrating the sample, the added sensitivity of the air-acetylene flame is needed for the analysis of chromium in drinking water. However, concentrating the sample will increase the calcium and magnesium concentration, which can cause a possible matrix interference which does not occur in the nitrous oxide-acetylene. To eliminate that possibility and the different absorption response of the two chromium valence states, samples and standards should be prepared to contain 1% ammonium bifluoride (NH_4HF_2) and 0.2% sodium sulfate (Na_2SO_4).

Unlike chromium, concentrating the sample does not cause a noticeable chemical matrix effect in the analysis of silver, cadmium, manganese and lead. The sensitivity of the lead analysis can be improved while maintaining accuracy if an electrodeless discharge lamp is available and the more sensitive 217.0 nm wavelength is used.

To control ionization in both barium and sodium analyses, potassium chloride (1000 $\mu\text{g/L}$) is added to each sample aliquot, calibration standard and reagent blank. To control anion interferences in the calcium analysis, lanthanum

chloride is added to each sample aliquot and calibration standard alike. If the concentrations of the acids in the samples and standards are well controlled, the necessity for the addition of lanthanum is minimized.

Silver in tap water is most probably present as silver chloride. Acidification with nitric acid to pH 2 will not solubilize nor prevent the precipitation of silver chloride. It also will not desorb silver from the walls of the sample container. However, low concentrations of silver chloride near the MCL will remain soluble in tap water after the sample has been acid preserved. In samples where a measurable quantity of silver is detected, the sample should be made basic with the addition of ammonium hydroxide prior to treatment with cyanogen iodide to solubilize the precipitated silver chloride. Of course this is not done until after all other analyses have been completed, and the remaining volume of the sample is measured. The sample container should also be rinsed and treated in a similar manner to desorb silver from the walls of the container. The sample concentration reported from the combined determinations must be based on the original sample volume collected.

Of the 11 contaminants which can be analyzed using FLAA methods, FLAA is the preferred atomic absorption technique for the analysis of calcium, copper, iron, manganese, sodium, and

zinc. Although the analysis of manganese will probably require scale expansion or concentration by evaporation, it is included with the FLAA group because of the limited analytical concentration range of the GFAA method and the poor stability of the manganese chelate. Barium also can be analyzed by FLAA, but the GFAA method is preferred because of normally occurring low concentrations. The preferred atomic absorption technique for the other four contaminants (silver, cadmium, chromium and lead) is GFAA methodology. If a graphite atomizer is not available, it is more convenient and accurate to concentrate the sample by evaporation and compensate for possible matrix interferences and nonspecific absorption than complete the analysis using the chelaton-extraction technique.

3. Graphite Furnace Atomic Absorption (GFAA)

The GFAA technique is two to three orders of magnitude more sensitive than FLAA. This added sensitivity plus being a total element technique make GFAA the preferred technique for the analysis of most primary drinking water contaminants.

As with FLAA methods, when visible particulate or suspended material are present in the sample, an acceptable digestion or solubilization procedure must be used. In GFAA analyses, the addition of hydrochloric acid should be avoided in the

solubilization procedures. (See Section B-Sample Preparation for Total Element Analysis Techniques.)

When doing GFAA analyses, method of standard addition (MSA) must be followed unless it can be verified it is not required. Verification is usually accomplished by determining the percent recovery of a single spike at the MCL or the midpoint of the calibration curve. MSA is not required if recovery is within either ± 10 percent or three standard deviations of the mean value of the spike, whichever is the smaller. Verification is required on every new and unusual sample matrix. Further, when the sample analyte concentration as determined from the calibration curve is within 10 percent of the MCL or above, the concentration should be confirmed by reanalyzing the sample by MSA.

In GFAA analyses it is important that the standards and samples be matrix matched. This not only includes any matrix modifier that is added, but also the type of acid and its concentration. For most analyses, only nitric acid is used at a concentration between 0.5 percent and 1 percent (v/v). When MSA is used, the matching requirement is satisfied because the standards are diluted in the sample matrix. When it is verified with spiking that MSA is not required and the sample concentration is read from the calibration curve, standard operating procedures, along with records of reagent additions and sample dilutions, will serve as evidence of matrix matching.

Once standards and samples have been prepared and matrix matched, the same size volume of aliquot should be used for all furnace injections. If a sample requires dilutions or concentrating, it should not be done by changing the volume of the aliquot injected. The recommended aliquot volume is 20 microliters, with the maximum not to exceed 50 microliters.

The composition of the sample matrix and its effect is the main reason why samples must be analyzed by MSA. Matrix effects can be reduced and sometimes eliminated with the use of matrix modifiers. An example is the addition of ammonium nitrate to a sodium chloride matrix to form both ammonium chloride and sodium nitrate during the drying cycle. These compounds are then volatilized during the relatively low temperature char cycle and thereby eliminating the sodium chloride interference before atomization.

The individual graphite furnace methods describe procedures for matrix modification for some of the known interferences. The recommended matrix modifier used in a given procedure may not necessarily be applicable to all presently known interferences. Since the publication of the USEPA methods, more information on interferences and the use of other acceptable matrix modifiers has been gained. Although the approved method should be followed when possible, it is not intended to restrict the analyst to the use of only certain

modifiers. The most appropriate modifier should be used for the type of interference encountered.

The use of a different matrix modifier does not require a variance, but the analyst should document the purpose of the modifier and the full range of its effects. An example is the addition nickel nitrate to arsenic and selenium analyses to prevent loss during charring, to enhance the signal with the use of higher atomization temperatures, and in the case of selenium, lessen sulfate interference.

The use of some matrix modifiers prevent losses during the char cycle, but this may not be true in all cases. The analyst should verify that the instrumental settings or temperature used are below the critical point where the analyte could be lost. Also, when relatively low atomization temperatures are used ($< 2000^{\circ}\text{C}$), it is advisable to sometimes use a high temperature burn (2700°C) with continuous purge gas flow to clean the furnace following atomization. The need for such a step will depend on the sample matrix and modifier used, and must be experimentally determined by the analyst.

Two types of graphite are available, pyrolytic and non-pyrolytic. The user should be aware of the advantages and disadvantages of each type before using them. (See Section 1 - Description of Instrumental Needs).

A new graphite tube usually needs conditioning before use. This is especially true for pyrolytic tubes. This can be accomplished by injecting an acid blank, drying the liquid, charring at 500°C for five seconds and atomizing at 1000°C for three to five seconds. This procedure is successively repeated five times while advancing the atomization temperature upward in increments of 300°C. A properly conditioned tube will result in more precise and accurate data.

Tube life will depend on the atomization temperature required and the acid concentration of the solution injected. As the tube ages, a second calibration may be required, but in any event, either type of tube should last well over 100 burns.

The absorbance response in GFAA is a transient signal and is usually read and recorded as a peak height response. If the sample matrix or volatilization characteristics of the analyte broaden the signal response time, a peak area measurement would be more appropriate. Either means of reading the signal is acceptable and selection is left to the discretion of the analyst.

On some graphite atomizers, the operating conditions can be changed to increase sensitivity and lower the limit of detection. Two of these operating parameters are internal gas flow interrupt and maximum power heating. With gas interrupt, the internal flow is stopped immediately prior to

atomization. This still allows the matrix volatilized during the char cycle to be swept from the absorption path but the atomized analyte will remain in the chamber for a longer period of time, giving a higher absorbance reading. The second option of maximum power heating brings the furnace to atomization temperature in a shorter time period than the normal atomization mode. The rapid heating rate is controlled by a sensing circuit to prevent atomizer from exceeding the preselected temperature. When these two operating parameters are used in conjunction with the platform furnace technique, matrix effects are reduced resulting in more accurate and precise data. The instrumental settings of these parameters are at the discretion of the analysts and a variance for their use is not required.

For GFAA analysis, the use of a background correcting device for nonatomic absorption is highly recommended. If the instrument is not equipped with a background corrector, a nonabsorbing wavelength must be used. Normally the deuterium source is only usable up to 350 nm. Above that wavelength, a tungsten halide lamp, a nonabsorbing wavelength, the Zeeman or Smith-Hieftje background correction technique is used. Of the contaminants listed, only the wavelength for barium and sodium are distinctively above the 350 nm deuterium source cutoff point.

Of the contaminants listed, only calcium and mercury do not have GFAA methods. Although GFAA methods are provided for sodium and zinc, the ubiquitous nature of these elements and their sensitivity make these methods very difficult to use. Therefore, for the analysis of sodium and zinc along with the analyses of calcium, copper, iron, and manganese FLAA methods should be used. For the remaining seven elements, GFAA is the preferred atomic absorption method of analysis with barium most probably requiring sample dilution prior to analysis.

The following comments particular to individual elements will be of help in understanding the GFAA methods and evaluating laboratory practice.

Arsenic and Selenium

Hydrogen peroxide (30 percent) is added to acid digestion to ensure complete oxidation. A side benefit is that it enhances the selenium signal and for this reason, it is added to samples not requiring digestion. The peroxide used should not be stabilized with tin.

Nickel nitrate is added for the formation nickel arsenide or selenide during the dry cycle and prevents loss during the high temperature char. The concentration of the nickel nitrate affects

the absorbance signal and the slope of the calibration curve. A 0.1 percent nickel nitrate gives adequate enhancement while serving as a matrix modifier for drinking water. If the sulfate concentration exceeds 200 mg/L, the nickel nitrate in the selenium analysis should be increased or the sample should be analyzed by MSA.

Argon gas and internal gas flow interrupt should be used for both arsenic and selenium analyses. Past research has shown that nonpyrolytic graphite gives a higher absorbance than pyrolytic graphite. It is now reported this phenomenon will vary with the quality of the pyrolytic coating. In any event, the use of nonpyrolytic graphite is recommended.

Electrodeless discharge lamps should be used for arsenic and selenium analyses. These lamps provide a more stable signal, higher intensity, and improved sensitivity over hollow cathode lamps.

When a 20 microliter injection is used for the selenium analyses, the MCL is near the low end of the calibration curve. The absorbance signal can be increased for improved concentration resolution if a 50 microliter injection is used instead.

Barium

Pyrolytic graphite must be used to reduce the formation of barium carbide. Maximum purge gas flow should be used for minimum memory

effects. Argon is preferred to nitrogen to avoid chemical interferences in the formation of nitrides. Even with the use of a 20 microliter injection, dilution will probably be required to keep the sample within the optimum concentration range.

Cadmium

Ammonium phosphate $(\text{NH}_4)_2\text{HPO}_4$ is added to form cadmium phosphate upon drying and to prevent the loss of cadmium during the 500°C char cycle. Nonpyrolytic graphite should be used with continuous internal gas flow to achieve the maximum optimum concentration range. Even using these conditions, cadmium is only linear to near 7 microgram/liter. In the past, pyrolytic graphite gave erratic results and high blank values. Pipet tips that are yellow in color contain cadmium sulfide and should not be used.

Chromium

Trivalent and hexavalent chromium have slightly different absorbances for the same concentration. Hydrogen peroxide is added to the acidified samples and standards to reduce all chromium to the trivalent state.

Calcium has a suppressive effect on chromium, which increases with increasing Ca concentration from a 10% suppression at 10 mg/L Ca to a constant suppression of approximately 20% between 50 mg/L and

100 mg/L. The effect remains constant from 200 up to 1000 mg/L Ca. Therefore, calcium is added to both samples and standards to a level above 200 mg/L.

Nonpyrolytic graphite is preferred for Cr analysis. Using a nonpyrolytic tube the Cr MCL concentration is near the midpoint of the calibration curve for the optimum concentration range.

Nitrogen should not be used as a purge gas because of possible cyanogen band interference.

Lead

Lanthanum nitrate is added to suppress the sulfate interference. 50 mg La added to a 10 mL aliquot of sample will counteract up to 1500 mg/L sulfate interference. It is suggested by other researchers that magnesium nitrate and ammonium phosphate be used instead of lanthanum nitrate for both sulfate and alkali/alkaline-earth chloride interferences. (Atomic Spectroscopy Vol. 4, page 69, May-June 1983.)

Silver

Silver chloride is formed in tap water that contains both silver and chloride ions. Preserving the sample by acidifying to pH 2 with nitric acid does not completely solubilize silver chloride, nor does it prevent its precipitation, nor will it desorb silver

from the walls of the sample container. If a preliminary analyses indicates silver to be present, for an accurate silver analysis, the sample and container must be made basic using ammonium hydroxide and treated with cyanogen iodide solution to solubilize the silver. The cyanogen iodide does not interfere with the GFAA analysis of silver.

4. Chelation/Extraction, Atomic Absorption (CE)

Two CE procedures are approved for the analysis of silver, cadmium, copper, iron, manganese, lead, zinc, and chromium⁺⁶ in drinking water. Both procedures use the diethyldithiocarbamate chelating reagent but each is a different chemical form. To use either of the CE procedures the sample must first be taken through a vigorous sample digestion procedure to ensure the contaminant is available for chelation. This must be done even for samples that do not contain particulate or suspended material. Since trivalent chromium does not react with the chelating reagent for a total chromium analysis, all chromium must be converted to the hexavalent state. This is accomplished using an acid permanganate digestion.

In the "Standard Methods" procedure, the salt form (ammonium 1-pyrrolidine carbodithioate, CAS Registry No. 5108-96-3)

commonly called ammonium pyrrolidine dithiocarbamate (APDC) is added to an aqueous sample at pH 3 and mixed for chelation of the trace elements. Methyl isobutyl ketone (MIBK) is then added, followed by 30 seconds of vigorous shaking. The organic aqueous mixture is allowed to separate and the lower aqueous layer is drained and discarded. The remaining MIBK layer is centrifuged to remove entrained water and then aspirated into an air-acetylene flame for analysis. The same instrument conditions are used as given in the FLAA methods, except the nebulizer O-ring is replaced with a cork gasket and the flame fuel-oxidant ratio is adjusted to compensate for the added fuel from the organic ketone solvent. MIBK must be used as the wash solvent between samples.

This procedure not only offers the advantage of concentrating the analyte for the analysis of lower concentrations, but also separates the analyte from the major alkali alkaline-earth ions. Also, the lower surface tension of the organic solvent results in a higher rate of aspiration which increases absorption sensitivity.

Although the procedure is useful, it has certain disadvantages. Of the two procedures, the shaking rate and time in APDC system is most critical. If the extraction is prolonged beyond one minute, the extraction efficiency of

cadmium is reduced, whereas three minutes of vigorous shaking is required for the complete extraction of hexavalent chromium. Also, the chelates of silver and manganese are not stable and should be analyzed soon after extraction. The small volume of organic layer limits the number of analyses that can be completed using a single extraction and standards must be extracted at the time of analysis for the preparation of the calibration curve.

The second chelation extraction procedure is an EPA method which also is included in ASTM D-19 methods. This procedure uses the acid form of the chelate (1-pyrrolidine carbodithioic acid, CAS Registry No. 25769-03-3), commonly called pyrrolidine, dithiocarbamic acid (PDCA). In this procedure, the chelating reagent is formed directly in chloroform by adding small aliquots of carbon disulfide to the already dissolved pyrrolidine. This reagent is very stable and can be used for months if stored in a brown bottle in a refrigerator. To extract the analytes, the chelating reagent in the chloroform is added to the aqueous sample which has been adjusted to pH 2.3. The aqueous organic mixture is vigorously shaken for two minutes after which the denser chloroform layer is drained into a Griffin beaker. (Although probably not required multiple extractions the same procedure is repeated and the chloroform extracts are combined.) The chloroform is evaporated and the chelates are destroyed using a nitric acid

digestion. The digested residue in nitric acid is diluted to a predetermined volume and analyzed using FLAA methods. The concentration of the diluted extract is read from the calibration curve. A check standard which is extracted along with the samples is used to determine the percent extraction efficiency and used in calculating the final sample concentration.

The PDCA extraction has some distinct advantages over the APDC extraction. First, there is better separation between the organic and aqueous layers and lower water entrainment in the organic solvent. Second, chloroform being more dense is the bottom layer in the separatory funnel and more convenient to collect. Third, samples do not have to be analyzed the same day they are extracted, but can be held in dilute nitric acid solution. Finally, since a FLAA aqueous calibration curve is used, the volume of the standards is not limited and instrument changes to accommodate the organic solvent are not required.

For the analysis of chromium, an acid permanganate digestion step also must be included.

5. Gaseous Hydride Atomic Absorption (GH)

There are two acceptable methods that use the GH technique for the analysis of arsenic and selenium in drinking water.

Organic forms of arsenic and selenium must be converted to inorganic compounds and organic matter must be oxidized before beginning the analysis. Certain metals may cause interferences with these methods but their concentrations in potable water are not normally high enough to cause interferences. The working range of these methods is 2 to 20 $\mu\text{g/L}$.

The first method which is described in all four reference texts is commonly referred to as the zinc hydride method. In this method for the analysis of arsenic the sample is subjected to vigorous nitric-sulfuric acid digestion which is taken to fumes of sulfur trioxide. After cooling, the sample is reduced to arsenic⁺³ in hydrochloric with the additions of potassium iodide and stannous chloride and diluted to a predetermined volume. Zinc metal is added to the sample to generate arsine which is swept into a heated quartz cell or low temperature argon-hydrogen flame for dissociation and absorption.

It should be noted that the digestion procedure given in Standard Methods differs from the EPA, ASTM, and USGS

digestion procedures in that a perchloric acid digestion step is included. It is recommended that unless the laboratory is equipped with a perchloric acid hood the perchloric step should be eliminated for reasons of safety.

The second GH method for arsenic is similar to the zinc hydride method except sodium borohydride is used in place of zinc to generate the arsine. Of the approved references, only the ASTM text describes this optional procedure. Sodium borohydride methods are listed in other sources, but only the ASTM method is approved. This method is preferred to the zinc hydride method because the sodium borohydride is chemically a cleaner reagent, easier to handle as an additive and results in more precise and accurate data.

The zinc hydride method also can be used for selenium analysis, but methods are given in only two of the texts, Standard Methods and the EPA manual. The described methods are the same as that for arsenic except the addition of potassium iodide is omitted.

The USGS hydride method for selenium differs from the zinc hydride method in the type of digestion, reduction and hydride generation procedure that is used. In the USGS method the sample is made acid with the addition of hydrochloric acid.

Calcium chloride and potassium permanganate are then added and the sample is heated to boiling while maintaining a purple tint. After the selenium has been oxidized to the hexavalent state with boiling permanganate, the sample is cooled, made basic with sodium hydroxide and evaporate to dryness. The formation of calcium selenate prevents the loss of selenium during evaporation. The residue is redissolved in hydrochloric acid and ammonium chloride, the selenium⁺⁶ is reduced to selenium⁺⁴ and the solution diluted to a predetermined volume. Stannous chloride is added for final reduction and the hydride is swept from the solution with nitrogen into the hydrogen-nitrogen flame or heated quartz absorption cell for analysis.

The ASTM selenium hydride method is a combination of the USGS digestion procedure and sodium borohydride reduction. Although the addition of sodium borohydride requires a well controlled and reproducible technique, it provides a faster response time and higher absorbances than the stannous chloride reduction. The result is data with improved precision and accuracy which makes the ASTM selenium method, the hydride method choice.

6. COLD VAPOR ATOMIC ABSORPTION (CV)

The determination of mercury is carried out by reducing the various forms of mercury in the sample to the elemental state through a chemical reaction. The mercury vapor formed is then aerated from solution through a cell positioned in the light path of an instrument which will measure the absorption. The method does not utilize the flame of the atomic absorption instrument and, consequently, is referred to as the cold vapor technique. (See Section 1 - Description of Instrumental Needs)

In order to assure complete conversion of all forms of mercury, including methylmercuric chloride care should be taken to follow the procedure in the Methods for Chemical Analysis of Water and Waste EPA-600/4-79-020. This procedure has included extra steps, including a two-hour permanganate/persulfate digestion which is carried out in a water bath at 95° C.

It is recommended that whatever type instrument is used, a conventional atomic absorption or an instrument specifically designed for mercury, that a recorder be attached to it. A good quality 10 mV recorder with high sensitivity and fast response time is needed to record the peaks resulting from the determination of mercury.

The flow system which precedes the instrument may be used in either an open or closed mode. The closed mode allows the mercury vapor to continuously pass through the flow system until the operator traps or vents the vapor. The open system allows one pass through the cell and then the vapor is trapped or vented. Two points should be made here: First, that the calibration of the instrument is dependent on the volume of the flow system and should be done only after the system has been configured and assembled in the same manner that will be used in the analysis of samples. Second, mercury vapor is extremely toxic and safety precautions should be practiced to protect the operator.

Certain volatile organic materials may interfere in the determination of mercury. If this is expected to occur, the sample should be analyzed by the regular procedure and again under nonreducing conditions, that is, without the addition of stannous chloride. The true mercury concentration can then be obtained by subtracting the two values.

D. Inductively Coupled Plasma Atomic Emission Spectroscopy (ICP)

Like FLAA and GFAA, ICP is also a total element technique. It operates on the principle of atomic emission which is the exact opposite of atomic absorption. In atomic emission, excited atoms

returning to lower energy levels or the ground atomic state emit characteristic energy which can be measured at discrete wavelengths particular to each element. The amount of energy emitted is directly proportional to the concentration of the element.

To produce the emitted energy the atoms must first be excited. In ICP this is accomplished by generating a high temperature plasma of metastable argon atoms that collide with the analyte atoms, transfer energy, and raise the analyte atoms to a higher level of energy or to the ionic state. Power to generate and sustain the plasma comes from a radio frequency (R.F.) generator which is usually operated at a frequency of 27.1 megahertz and at a power output between 0.9 to 1.2 kilowatts (equivalent to a small radio station). The power is transferred to the plasma through an induction or work coil which serves as the antenna of R.F. generator. Inside the coil is a quartz tube assembly called the torch. The plasma is formed when the argon gas flowing through the torch is seeded with electrons from a Tesla coil and becomes conductive in the magnetic field that surrounds the coil.

The sample reaches the plasma as small aerosol droplets from the nebulizer. As the aerosol enters the bottom of the plasma it passes through a central channel where it is desolvated, dissociated and made available for excitation.

To record the energy emitted, the characteristic radiation from the plasma is focused on the entrance slit of the spectrometer. As the light passes through the slit it assumes the image of the slit and strikes the diffraction grating. The imaged radiation is diffracted into line spectra of characteristic wavelengths and dispersed onto either a single photomultiplier tube (PMT) or series of tubes placed on the focal curve of the spectrometer. An exit slit is placed in front of the PMT to define the bandpass of energy that strikes the PMT. Photocurrents from the PMT are processed and controlled by a computer system and translated into concentration.

In addition to the major components of the system (R.F. generator, spectrometer, and dedicated computer) there are other hardware and environmental requirements. Since acid and toxic fumes exhaust with the plasma, the plasma compartment must be vented similar to FLAA. This is especially important to those instruments where front surface optics are exposed to these vapors.

The optical train and electronics are sensitive to both temperature and humidity. Therefore, the environment in which the instrument is placed should be well controlled, with constant temperature and humidity, to ensure accurate determinations.

Argon gas for the plasma may be supplied from a high pressure cylinder containing dry argon or as a vapor from a tank of liquid argon. The liquid argon supply is preferred to dry argon because a tank will last up to three weeks, while a cylinder of dry argon will last less than eight hours.

The nebulizer used to generate the analyte aerosol should be rugged, not subject to clogging from dissolved solids, easy to clean, and if adjustable, easy to align and give reproducible aspiration.

A peristaltic pump should be used to deliver the sample solution to the nebulizer. The pump rate should be set equal to or slightly less than the aspiration rate of the nebulizer.

Spare parts which should be kept on hand are: a power tube for the RF generator, a quartz torch, pump tubing, PMT's that cover the full wavelength range, and computer disks and paper.

The phenomenon of atomic emission provides certain advantages over atomic absorption.

1. Instruments can be designed and configured as either a sequential or simultaneous system for multielement analyses.
2. ICP has similar or better detection limits than FLAA while providing a linear analytical range equal to four orders of

magnitude. This is attributed to the excellent signal to noise ratio of the ICP, and the signal transparency of the sheathing argon gas that surrounds the central analytical channel of the plasma and cools the quartz torch. Self absorption is greatly reduced, increasing linearity, because the analyte atoms for the most part are confined to the central channel. Although the extended linearity is not needed for the analysis of the primary and secondary contaminants in drinking water, it is useful in the analysis of the major constituents (calcium, magnesium, sodium, and potassium) for determining water quality.

3. The high temperature of plasma 6000°C to 8000°C makes it almost totally free of chemical interferences. Although chemical interferences are not severe in drinking water analysis, as noted in earlier discussions, they are present in some FLAA and GFAA methods.

4. If the total dissolved solids do not exceed 1500 mg/L, physical interferences are not usually a problem in ICP analysis of drinking water. The use of a peristaltic pump in the sample introduction system can eliminate fluctuations in aspiration, can be used to regulate the solution flow uptake rate, and provide a uniform sample delivery to the nebulizer. If more sample is pumped to the nebulizer than is needed, excess sample is drained

to waste. The pump rate is usually set to slightly starve the nebulizer to achieve the optimum conditions of maximum precision with adequate intensities.

An operational disadvantage of ICP can be spectral interference. Many elements are spectrally rich and emit energy at many different wavelengths. Many of these wavelengths are far less intense and not used for analytical purposes, but may overlap and additively interfere with the more sensitive wavelengths used for analysis. The separation between wavelengths and how well they are resolved is a function of the grating and the design of the optical system. The intensity of an interfering wavelength is a function of the interfering element concentration. Fortunately, in drinking water analysis spectral overlap interference is not usually a problem. The analytes are of low concentration and the major constituents (calcium, magnesium, sodium and potassium) have relatively few lines and most are of low intensity.

A second type of spectral interference that can occur is when the sample matrix causes a shift in background intensity. Correction for this type of interference is accomplished by alternately measuring the background intensity adjacent to the wavelength peak during analysis. For this type of correction to be valid the location selected for reading the background intensity must change in the same manner and degree as the background intensity under the wavelength peak.

For operating the ICP instrument, the manufacturer's instructions should be followed. Prior to calibration allow sufficient warmup time (30 minutes) for the instrument to become thermally stable. If the system is a simultaneous instrument, the entrance slit should be optically profiled before calibration. On simultaneous instruments the exist slits also must be profiled, but this is only done at the time of installation and then usually verified every three months. If an exit slit is found to be out of profile, it is reprofiled and then checked daily until verified with certainty that the exit slit profile is correct and stable.

It has been determined that a well controlled and steady plasma will greatly reduce calibration drift and improve precision. The use of mass flow controllers on the argon gas supplied to the plasma has been found to be an excellent means to regulate and maintain an even, steady gas flow. Although not required, the purchase of mass flow controllers is greatly encouraged. A successful routine for reproducing plasma conditions on a day-to-day basis has been to use a mass flow controllers to adjust the argon flow rate of the central channel so as to match the copper/manganese emission intensity ratio to an experimentally predetermined value. If interelement correction factors are used to correct spectral interferences, it becomes of particular importance that the plasma condition be reproducible for the factors to remain valid.

Other important instrumental parameters that affect plasma reproducibility and the intensity of the analyte signal are the R.F. incident power, proper adjustment of the torch in the work coil, the height above the work coil where the plasma is observed and the sample flow rate to the nebulizer. It is interesting to note most instruments are operated using similar instrumental conditions. Power is set at or near 1.1 kilowatts with a plasma observation height of 15 to 16 mm above the work coil. Alignment of the torch in the coil is a straightforward procedure and the sample peristaltic pump rate is usually set at 1.2 to 1.4 ml/min. or just below the normal draw of the nebulizer. Once the operating conditions have been experimentally determined, they should be maintained and fine adjustment of the plasma be accomplished using the mass flow controller.

The most critical parameter of the plasma is the sample argon flow rate which carries the analyte through the central channel of the plasma. The concentration of the excited atoms is increased as the analyte resident time in the analytical zone of the plasma is increased. The lower the flow rate, the more intense the signal of the ion wavelengths. The sample argon flow also affects the penetration and size of the central channel in the plasma. The final flow rate selected is always a compromise between the desired intensities of atom and ion lines, but once selected must be maintained.

If it becomes necessary to replace the torch and the replacement is not a close replica of the previous torch the emission intensities will be different. The change in intensities will not be uniform across the spectrum and will demand the determination and calculation of new interelement correction factors.

Standard calibration curves for each element are stored in the computer and used in determining concentration. These curves are either verified or a new calibration is performed at the start of each analysis run. During the analysis, sample data is usually stored in a computer file for printout of a hardcopy report at the end of the analysis run. Also, included in most instrumental software programs are routines for performing some statistical analysis of the data and other routines such as wavelength scanning used for determining the presence or absence of spectral interference.

The recognized ICP method for the analysis of water and wastes is USEPA Method 200.7.⁽⁶⁾ This method has been amended with an Appendix⁽⁷⁾ which is specific to the analysis of drinking water. The Appendix is applicable to all listed elemental contaminants except mercury and selenium. Mercury could not be included in the Appendix because it is not a listed analyte in Method 200.7. Also, the ICP detection limit for both elements is above its respective established MCL's.

Included in the Appendix is a required sample preparation procedure for drinking water analyses. This procedure is described in Section B - Sample Preparation for Total Element Analysis Techniques. Incorporated in the procedure is a provision for concentrating the sample 4X before analysis. The purpose of concentrating the sample is to raise the concentration of the analyte so that the precision about the measurement will allow the analyst to determine if the contaminant is in-or-out of compliance with a 95 percent level of certainty. This provision allows the contaminants to be determined by ICP analysis with a precision and accuracy similar to GFAA.

It has been reported that large concentrations of the major cations (Ca, Mg, and Na) can affect the distribution of the analyte in the different size aerosol droplets that are formed during nebulization. This matrix effect is called "aerosol ionic redistribution" (AIR). Only small droplets enter the plasma (while large droplets drain to waste), any change in their analyte concentration so that they no longer reflect the concentration of the bulk solution being aspirated will result in a biased analysis. A 5 percent reduction in the cadmium intensity for a concentration 4X the MCL has been observed when the concentration of calcium exceeds 400 mg/L. This suppression increases with increasing Ca concentration. The matrix effect can be corrected using method of standard addition (MSA). It is recommended when the concentration of a primary

contaminant is determined to be within 10 percent of its MCL or above, and the calcium concentration in the analysis solution exceeds 400 mg/L, that the absence of AIR be verified by spiking or the sample be analyzed by MSA.

Included in Method 200.7 are recommended wavelengths, preparation procedures for calibration standards, expanded definitions of the type of interferences, a procedure for MSA, and instrumental quality control requirements. Included in the Appendix is a discussion on the requirements of drinking water analysis, tests and criteria for determining the presence of spectral and matrix interferences, typical instrumental operating conditions, mandatory quality control and data reporting requirements.

Although the initial purchase price of an ICP system is 3 to 6 times that of atomic absorption instrumentation, it can provide cost savings because less time is required to complete the analysis. Using the Appendix to Method 200.7 the ICP cost for the analysis of 12 analytes in 20 samples is 1/6 that of GFAA analysis. For this reason and the other advantages listed earlier, ICP analysis is the most preferred method of analysis for all elemental contaminants except mercury and selenium.

IV. ORGANIC METHODS

Techniques for the determination of organics are relatively new to most water supplies. Until the passage of the Safe Drinking Water Act, there were no regulations concerning specific compounds unless the supply had decided to analyze for these parameters. Analysis for organic compounds which utilize gas chromatography requires a good deal of experience to obtain reproducible qualification and quantitation. The methods for the organochlorine pesticides, the chlorinated phenoxy acid herbicides and the trihalomethanes are recommended for use only by experienced analysts or under close supervision of such qualified persons.

The methods to be used, including extraction and clean-up procedures, are not included in either of the usual references. However, they are available from the U. S. Environmental Protection Agency, Environmental Monitoring and Support Laboratory, Cincinnati, Ohio 45268.

Additional analysis for organics has been required with the publication of the final trihalomethane regulations on November 29, 1979. These are well as the pesticide and herbicide information is listed in Table III.

A. Organochlorine Pesticides

The compounds as listed in the National Interim Primary Drinking Water Regulations may be determined by the methods referenced in the accompanying table. However, special precautions must be taken to measure the toxaphene peaks. Interferences are experienced when contamination or other compounds such as polychlorinated biphenyls, phthalate esters and some organophosphorus pesticides are present. The referenced methods covers clean-up and concentration techniques to be used when interferences can not be tolerated. The method is recommended for use only by experienced pesticide analysts or under close supervision of such qualified persons.

Care should be taken to check such things as the state of activation of the florisil and the amount of florisil being used. Trial runs are recommended using standard mixtures of the pesticides to be analyzed. The gas chromatographic operating conditions should also be checked, via an included procedure, to determine if acceptable conditions exist. Standards should be

Table III:
Approved Methodology for Organic Contaminants

Contaminant	Methodology	EPA ¹	ASTM ²	SM ³	USGC ⁴
Chlorinated hydrocarbons	Solvent extraction, gas chromatography	pp 1-19	D3086-79	509A	pp 24-39
endrin					
lindane					
methoxychor					
toxaphene					
Chlorophenoxys	Solvent extraction, derivatization gas chromatography	pp 20-35	D3478-79	509B	pp 24-39
2,4-D					
2,4,5-TP					
Total Trihalomethanes	Purge and trap-gas chromatography	(5)			
	Solvent extraction, gas chromatography	(6)			
	Gas chromatography - mass spectrometry	(7) and (8)			

1. "Methods for Organochlorine Pesticides and Chlorophenoxy Acid Herbicides in Drinking Water and Raw Source Water"*
2. Annual Book of ASTM Standards, Part 31 Water, American Society for Testing and Materials, 1916 Race Street, Philadelphia, Pennsylvania 19103
3. "Standard Methods for the Examination of Water and Wastewater", 14th Ed. American Public Health Association, American Water Works Association, Water Pollution Control Federation, 1975.
4. Techniques of Water-Resources Investigation of the United States Geological Survey, Chapter A-3, "Methods for Analysis of Organic Substances in Water", Book 5, 1972. Available from Superintendent of Documents, U.S. Government Printing Office, Washington, D.C. 20402

5. "The Analysis of Trihalomethanes in Finished Waters by the Purge and Trap Method", Method 501.1 EMSL, EPA, Cincinnati, Ohio 45268.*
6. "The Analysis of Trihalomethanes in Drinking Water by Liquid/Liquid Extraction", Method 501.2, EMSL, EPA, Cincinnati, Ohio 45268.*
7. "Measurement of Trihalomethanes in Drinking Water by Gas Chromatography/Mass Spectrometry and Selected Ion Monitoring", Method 501.3, EMSL, EPA, Cincinnati, Ohio 45268.*
8. "Measurement of Purgable Organic Compounds in Drinking Water by Gas Chromatography/Mass Spectrometry", Method 524, EMSL, EPA, Cincinnati, Ohio 45268

*Available from ORD Publications, CERL, EPA, Cincinnati, Ohio 45268

Table IV
Approved Methodology for Measurements not Required to be Done in Approved Laboratories

Contaminant	Methodology	EPA ¹	ASTM ²	SM ³	Other
Free Chlorine Residual	Colorimetric or titrimetric DPD			409E or F	
	Colorimetric syringaldazine				408G ⁴
pH	Potentionmetric	150.1	D1293-78A or B	424	
Temperature	Thermometric			212	
Turbidity	Nephelometric	180.1		214A	

1. "Methods of Chemical Analysis of Water and Wastes," EPA Environmental Monitoring and Support Laboratory, Cincinnati, Ohio 45268 (EPA 600/4-79-020), March 1979. Available from ORD Publications, CERL, EPA, Cincinnati, Ohio 45268
2. Annual Book of ASTM Standards, Part 31 Water, American Society for Testing Materials, 1916 Race Street, Philadelphia, Pennsylvania 19103
3. "Standard Methods for the Examination of Water and Wastewater," 14th Ed, American Public Health Association, American Water Works Association, Water Pollution Control Federation, 1975.
4. "Standard Methods for the Examination of Water and Wastewater", 15th Edition, American Public Health Association, American Water Works Association, Water Pollution Control Federation, 1980.

injected frequently as a check on the stability of the operating conditions. Care should also be taken to assure good technique both in the cleaning of glassware and use of the chromatograph are observed.

B. Herbicides

Phenoxy acid herbicides are used extensively for weed control. These materials could enter the source supply by run offs and be taken into the water supply system. These chlorinated phenoxy acids and their esters are extracted from acidified water samples with ethyl ether. The esters are hydrolyzed to acids and extraneous organic material is removed by a solvent wash. The acids are converted to methyl esters which are extracted from the aqueous phase. The extract is cleaned up by passing it through a micro-absorption column. Identification of the esters is made by selective gas chromatography. Again, the identification should be corroborated through the use of two or more unlike columns.

Organic acids, especially chlorinated acids, cause the most direct interferences with the determination. Phenols, including chlorophenols, will also interfere. Solvents, reagents, glassware and other sample processing material may cause problems. All these should be checked to prove they are free from interferences.

Some of the reagents are toxic while others can present hazardous circumstances if improperly handled. Consequently, care must be exercised when using these materials. This method is recommended for use only by experienced pesticide analysts or under the close supervision of such qualified persons.

Quality control is another area that should be carried out with regularity. This topic will be covered in another instructional unit.

C. Trihalomethanes

Of the two procedures the liquid - liquid extraction method is the simplest to carry out and the least expensive. However the sample must be relatively free from interferences and is applicable only to the determination of the four trihalomethanes. For compounds other than these four, confirmation by GC/MS must be provided.

If analysis of raw source water is carried out, the purge and trap technique must be performed to characterize each raw source water if peaks appear as interferences.

Confirmatory evidence is obtained using dissimilar columns and temperature programming. If concentrations are high enough (> 50 µg/L) halogen specific detectors may be employed for improved specificity.

Although the purge and trap procedure is applicable to many more compounds it is more difficult to carry out and is much more expensive. The halogen specific detector is used to ensure specificity. This technique should be carried out only by persons experienced in gas chromatography or under the supervision of an experienced person.

In both procedures frequent analysis of standards should be carried out. Quality control is written into the methodology available from EPA. Traps should be placed in the line before instrumentation to assure gases do not contribute peaks and the traps should be changed regularly. These changes should be recorded as part of the instrument maintenance procedure.

V. Operator Tests

It was the intent of the National Interim Primary Drinking Water Regulations that all analysis be performed in approved laboratories. There were two exceptions in the original regulations, the revisions in 1980 added several more. These tests may be carried out by "any person acceptable to the state". The list of these methods now includes turbidity, free chlorine residual, temperature and pH. It is felt that Certification Officers should be aware of these methods. The approved methodology is listed in Table IV.

A. Residual Chlorine

1. DPD. This method was originally specified on the basis of the improved accuracy and sensitivity, particularly when compared with the o-tolidine procedure in common use. The o-tolidine was popular because of its simplicity and availability of field test kits. There are now available test kits designed around the DPD procedure. There should be no sample preservation; analyses must be made as soon as possible, or within one hour. The sample may be taken in either plastic or glass. Test kits are available from many sources, e.g., Hach Chemical Co. and LaMotte Chemical Company.
2. Syringaldazine. According to Standard Methods, this method has been shown to be the most specific colorimetric test for measuring free available chlorine. The accuracy and precision are comparable to the DPD method. One manufacturer of this type kit is Ames Division of Miles Laboratory Inc. in Elkhart, Indiana.

B. Turbidity

The method is based upon a comparison of the intensity of light scattered by the sample under defined conditions compared with the intensity of light scattered by a standard reference suspension.

Readings in NTU's are made in a nephelometer designed according to specified specifications. A standard suspension of Formazin, prepared under closely defined conditions is used to calibrate the instrument.

The presence of floating debris and coarse sediments which settle out rapidly will give low readings. Finely divided air bubbles will affect the results in a positive manner. The instruments should detect differences of 0.02 units in waters having

turbidities of less than one unit. The instrument should read from 0 to 40 units. Scales above 40 units are generally not used except for dilution purposes.

The sample tubes to be used must be of clear, colorless glass. They should be kept scrupulously clean, both inside and out, and discarded when they become scratched or etched.

The use of a prepared turbidity standard of styrene divinylbenzene polymer was permitted in the March 3, 1982 Federal Register Vol. 47, No. 42, Page 8997. This standard was permitted and formazin standard retained to allow the choice by the analyst. The new standard may be purchased from Amco Standards International.

C. Temperature

Temperature measurements may be made with any good grade of mercury filled Celsius thermometer. As a minimum, the thermometer should have a scale marked for every 1.0°C or finer. Markings should be etched on glass. The thermometer should have a minimal thermal capacity to permit rapid equilibration. It should be checked against a precision thermometer certified by the National Bureau of Standards. For field use it is a good idea to provide a metal case to prevent breakage.

D. pH (electrometric)

The certifier should be assured that the meter and electrodes are in working order and a sufficient supply and range of buffers are on hand. It would be good to see if the instrument manufacturers manual with operating instructions are available. The accepted equipment specifications are listed in the outline on Instrument and Equipment Needs.

VI. SUMMARY

Due to the number of chemical methods that a laboratory will be using, the laboratory Certification Officer cannot evaluate each one during his on-site inspection. The results of the required performance sample, as well

as the information available in the records of the daily quality control, will indicate problem areas in the methodology. At this point the certification person can offer assistance in guiding the laboratory toward correction of the problem.

The inspector will be expected to answer questions from technicians on the methods and to point out any deviations that may be detected. The inspector can supply information on equipment and instruct laboratories on methods should the laboratory decide to utilize a procedure different from that procedure currently in use.

It is suggested that the inspector schedule ahead of his visit those tests he may wish to observe. These can be tests which indicate problems, any test added since a previous visit, or an arbitrary analysis performed from a specific method.

REFERENCES

1. Part 4.1.3 of the Atomic Absorption Methods Section, "Methods for Chemical Analysis of Water and Wastes," U.S. Environmental Protection Agency, Environmental Monitoring and Support Laboratory, Cincinnati, Ohio, 45268 (EPA-600/4-79-020), March 1979.
2. Part 301A-I.1 "Standard Methods for the Examination of Water and Wastewater," 14th Edition, American Public Health Association, American Water Works Association, Water Pollution Control Federation, 1975.
3. Part 4.1.4 of the Atomic Absorption Method Section "Methods of Chemical Analysis of Water and Wastes," U.S. Environmental Protection Agency, Environmental Monitoring and Support Laboratory, Cincinnati, Ohio, 45268 (EPA-600/4-79-020), March 1979.
4. Methods, D3557-78A (Cd), D1687-77D (Cr), D3559-784 (Pb), and D3859-79 (Ag), "Annual Book of ASTM Standards", Part 31 Water, American Society for Testing and Materials, 1916 Race Street, Philadelphia, Pennsylvania, 19103.
5. Methods 206.2 (As) and 270.2 (Se), "Methods of Chemical Analysis of Water and Wastes" EPA Environmental Monitoring and Support Laboratory, Cincinnati, Ohio, 45268 (EPA-600/4-79-020), March 1979.
6. "Inductively Coupled Plasma Atomic Emission Spectrometric Method for Trace Element Analysis of Water and Wastes," Method 200.7, from "Methods for Chemical Analysis of Water and Wastes, EPA 600/4-79-020", U.S. Environmental Protection Agency, Environmental Monitoring and Support Laboratory, Cincinnati, Ohio 45268, December 1982.
7. "Inductively Coupled Plasma Atomic Emission Analysis of Drinking Water," Appendix to Method 200.7, U.S. Environmental Protection Agency, Environmental Monitoring and Support Laboratory, Cincinnati, Ohio 45268, January 1985.

Unit 4

SAMPLING

I. INTRODUCTION

Since the intent of the Safe Drinking Water Act is to insure proper drinking water quality, meaningful analysis of the water is imperative in order to know if the water meets the standards. This analysis can only be meaningful if it is performed on a sample that is representative of the water that the consumer will drink. Consequently, the proper sampling technique, use of proper containers, proper preservation and adherence to the set frequency of sampling must be carefully observed.

In many instances the laboratories themselves will not be responsible for sampling. However, it is necessary that all laboratories be aware of what constitutes a representative, properly collected sample. It is the responsibility of all laboratories sampling for parameters under the Safe Drinking Water Act to call for a resample if the initial one does not meet proper sampling procedures. To analyze a sample which has been collected dubiously is to present data which is dubious in meaning. If the laboratory is responsible for collecting the samples, it is doubly important that the persons in the laboratory be aware of proper techniques.

The Critical Elements portion of Chapter IV of the "Criteria and Procedures" Manual spells out the requirements that must be adhered to for the drinking water sampling. It is attached here for student reference.

When the laboratory has been delegated responsibility for sample collection, handling, and preservation, there needs to be strict adherence to correct sampling procedures, complete identification of the sample, and prompt transfer of the sample to the laboratory.

The collector should be trained in sampling procedures and approved by the State regulatory authority or its delegated representative. The sample must be representative of the potable water system. The water tap must be sampled after maintaining a steady flow for two to three minutes to clear the service line. The tap must be free of aerator, strainer, hose attachment, or water purification devices.

The sample report form should be completed immediately after collection with location, date and time of collection, collector's name and any special remarks concerning the sample.

A. Inorganic Contaminants

The type of sample container and the required preservative for each inorganic chemical contaminant are listed in Table 4-1.

It is essential that all samples be analyzed within the maximum holding times listed in Table 4-1. Where maximum holding times cannot be met, the sample is to be discarded and resampling requested.

B. Organic Contaminants

The type of sample container and the required preservative for the organic chemical contaminants are listed in Table 4-1.

When sampling chlorinated waters for TTHM analysis, sodium thiosulfate or sodium sulfite should be added to the empty sample bottles prior to shipping to the sampling site.

The TTHM bottles need to be filled in such a manner that no air bubbles pass through the sample as the bottle is filled. The bottle is to be sealed so that no air bubbles are entrapped. The hermetic seal on the sample bottle needs to be maintained until analysis.

It is essential that all samples be analyzed within the maximum holding times listed in Table 4-1. Where maximum holding times cannot be met, the sample is to be discarded and resampling requested.

A footnote to Tables IV-4 and IV-5 of the "Criteria and Procedures" manual which deals with sampling cautions that, if a laboratory has no control over sample collection, handling, and preservation, then it is critical that a laboratory director rejects any samples not meeting the criteria in the tables and so notify the authority requesting the analyses.

II. MONITORING REQUIREMENTS

A. Inorganic

1. Analyses for all community water systems utilizing surface water sources shall be completed within one year following June 1977. These analyses shall be repeated at yearly intervals.
2. Analyses for all community water systems utilizing only groundwater sources shall be completed within two years of June 1977. These analyses shall be repeated at three-year intervals.
3. For noncommunity water systems, whether supplied by surface or groundwater sources, analysis for nitrate shall be completed by December 24, 1980. These analyses shall be repeated at intervals determined by the State.
4. When the maximum contaminant level is surpassed, the frequency of resample shall be designated by the state and shall continue until the maximum contaminant level has not been exceeded in two successive samples or until a monitoring schedule as a condition to a variance, exemption or enforcement action shall become effective.

B. Organic, Other than TTHM's

1. For all community water systems utilizing surface water sources, analyses shall be completed within one year of June 1977. Samples analyzed shall be collected during the period of the year designated by the State as the time when contamination by pesticides is most likely to occur. These analyses shall be repeated at intervals specified by the State, but in no less frequency than at three year intervals.
2. For community water systems utilizing only groundwater sources, analysis shall be completed by those systems specified by the State.
3. If the results of an analysis indicate that the level of any contaminant exceeds the maximum contaminant level, the supplier of water shall report to the State within seven days and initiate three additional analyses within one month.
4. When the average of four analyses exceeds the maximum contaminant level the supplier of water shall report to the State. Monitoring after public notification shall be at a frequency designated by the State and shall continue until the maximum contaminant level has not been exceeded in two successive samples or until a monitoring schedule as a condition to a variance, exemption or enforcement action shall become effective.

C. TTHM's

All community water systems serving a population of more than 10,000 that adds a disinfectant to the water shall analyze for TTHM's. The minimum number of samples required to be taken shall be based on the number of treatment plants used by the system.

1. For supplies using surface water as well as those using groundwaters that have not been determined by the State to qualify for reduced monitoring frequencies, the sampling frequency is at least four samples per quarter per treatment plant. At least 25 percent of the samples shall be taken at locations within the distribution system reflecting the longest residence time in the system. The other 75 percent shall be taken at representative locations in the distribution system.
2. The State has the authority to reduce this monitoring frequency to a minimum of one sample analyzed for TTHM's per quarter taken at a point in the distribution system reflecting the maximum residence time of the water in the distribution system.
3. Water supplies using only groundwaters may request permission from the State to reduce monitoring to one sample analyzed for maximum trihalomethanes potential per year for each treatment

Table 4-1

Contaminant	Preservative ²	Container ³	Maximum Holding Time ⁴
Arsenic, Barium, Cadmium, Chromium, Lead, Selenium, Silver	Conc. HNO ₃ to pH<2	P or G	6 months
Fluoride	None	P or G	1 month
Mercury	Conc. HNO ₃ to pH<2	G P	38 days 14 days
Nitrate			
Chlorinated Supplies	Cool to 4°C	P or G	28 days
Nonchlorinated Supplies	Conc. H ₂ SO ₄ to pH<2	P or G	14 days
Sodium-Calcium	Conc. HNO ₃ to pH<2	P or G	6 months
Alkalinity	Cool to 4°C	P or G	14 days
Total filterable residue	Cool to 4°C	P or G	7 days
Chlorinated Hydrocarbons	Cool to 4°C as soon as possible after collection	Glass; with foil or Teflon-lined cap	14 days ⁵
Chlorophenoxys	Cool to 4°C as soon as possible after collection	Glass; with foil or Teflon-lined cap	7 days ⁵
TTHM	Sodium thiosulfate or sodium sulfite	Glass; with Teflon-lined septum ⁶	28 days

Table 4-1 (Cont'd)

1. If a laboratory has no control over these factors it is critical that the laboratory director reject any samples not meeting these criteria and so notify the authority requesting the analysis.
2. If HNO_3 is to be used and cannot be used because of shipping restrictions the sample may be initially preserved by icing and immediately shipping it to the laboratory. Upon receipt in the laboratory, the sample must be acidified with conc. HNO_3 to $\text{pH} < 2$. At the time of analysis, the sample container should be thoroughly rinsed with 1:1 HNO_3 ; washings should be added to the sample.
3. P = Plastic, hard or soft; G = Glass, hard or soft
4. In all cases, samples, should be analyzed as soon after collection as possible.
5. Well stoppered and refrigerated extracts can be held up to 30 days.
6. All samples are collected in duplicate.

plant used by the system. This sample should be taken at a point in the system reflecting the maximum residence time of the water in the system.

D. Unregulated

1. Sodium

With the publication of the amendment to the National Interim Primary Drinking Water Regulations, special requirements were set down for monitoring of sodium and corrosivity. Sampling is required at the rate of one sample per plant at the entry point to the distribution system. Samples should be taken annually for systems using surface waters, and at least every three years for systems using only groundwaters.

No maximum level has been set for sodium. The monitoring was required to provide data for the medical community when requiring low sodium intake for individuals.

Allowance is made for States to increase the monitoring frequency if needed. The supplier must notify the State or EPA of the concentration found. The goal set was 20 mg/L. This concentration is a goal and is not enforceable.

2. Corrosivity

Suppliers of water for community public water systems are required to collect samples from a representative entry point to the distribution systems. The frequency is two samples per plant, one sample during mid-winter and one during mid-summer. Supplies using only groundwater are required to sample only once per year. Again the State has the authority to set the frequency of sampling.

The intent of monitoring for corrosion characteristics is to ascertain the potential of harmful material entering the water due to the aggressive nature of the water on the pipes and or the joint material. These materials could be lead, copper, and asbestos.

The corrosivity is determined by calculation of the Langelier Index or the Aggressive Index. In order to carry out this calculation, the content in the water of Total Filterable Residue, Calcium, Alkalinity, and Temperature are required. Consequently the laboratories must be able to determine these parameters.

III. SAMPLE CONTAINERS

Types

Generally two types of containers are acceptable: these are glass and plastic. Plastic is the more convenient from a shipping standpoint; however, plastic may not be used for the organic parameters. The glass containers should preferably be made from a hard borosilicate glass (Kimax or Pyrex; however, other forms may be used).

All these various materials have certain advantages and disadvantages. The hard glass is inert to most materials. Conventional polyethylene is to be used when plastic is acceptable because of reasonable cost and less adsorption. Disposable type plastic containers, such as the molded polyethylene "Cubitainer" are convenient to use.

Usually, a wide mouth container is preferred. This allows easy sample removal and easier cleaning.

The sample containers for the total trihalomethanes should be a 25-mL capacity or larger screw cap vial sealed with Teflon faced silicone septa. These TTHM bottles should be the equivalent to the Pierce No. 13075 bottle and the septa equivalent to the Pierce No. 12722.

The pesticide containers should be a wide mouth container of 1-liter or 1-quart capacity with a screw cap lined with Teflon. If the Teflon liner is not available, aluminum foil may be used. Amber bottles are recommended, but if not available the sample should be protected from light. The same type container should be used to collect the sample for the chlorophenoxy herbicides.

Depending on the State or Regional requirements, the following is an estimate of the number and types of containers needed for a surface supply excluding those needed for resample.

Inorganics:

One 1 gal - plastic - with HNO_3 - all metals including sodium, calcium

One 1 gal - plastic - cooled 4°C - Nitrate, Alkalinity, Total Filterable Residue, Fluoride.

One 1 qt - plastic - with H_2SO_4 - Nitrate (nonchlorinated supplies)

One 1 qt - glass - with HNO_3 - Mercury (for longer holding time)

Organics

One 1 qt - glass (Teflon or foil lined cap) - cooled 4°C - pesticides

One 1 qt - glass (Teflon or foil lined cap) - cooled 4°C - herbicides

Thirty-two - ≥ 25 mL screw cap bottles with Teflon faced silicone septa - sodium thiosulfate or sodium sulfite added - for TTHM's

Additional containers would be needed for resampling, blanks and duplicates. A noncommunity supply would need one - 1-quart plastic container per year unless resampling is to be carried out.

In addition to the sample containers, some type of shipping containers must be provided for each sample. For those samples which require cooling a type of ice chest or other insulated container must be provided.

B. Container preparation and preservation:

A laboratory may have the responsibility for providing sample containers; consequently the Laboratory Certification Officer must be able to inspect the capability of the laboratory to provide the correct materials. This responsibility to provide, maintain, and clean containers is dependent on how the State has elected to carry out the certification program. The laboratory or the authority could purchase in large lots and make available sets of containers to each supply or the State may elect to require the supply to provide their own containers. Generally speaking, the plastic containers should not be reused for any trace analyses, that is the metals. The glass containers for organics analyses samples should follow the suggested cleaning procedure, including muffling at 400°C for about 15 minutes. Once cleaned, these containers should be stored and shipped in such a manner as to prevent recontamination.

Should the decision to reuse plastic containers be made, they should be cleaned carefully before reuse. There are several cleaning methods available. Choosing the best method involves careful consideration of the nature of the sample and of the constituent(s) to be determined.

1. Traces of dichromate cleaning solution will interfere with metal analyses. Use 1:1 nitric acid wash.
2. Traces of nitric acid may interfere with the nitrate analysis.
Use detergent with thorough rinses with tap and distilled water.

Shipping the containers to the sampling locations should take into consideration the numbers to be shipped and eliminate any contamination chances. The shipping containers to be used in transporting the sample itself to the laboratory must be provided either as a container for the empty sample container or in bulk form.

One item that must be given consideration is the preservative. Postal regulations will not permit mailing of acids, particularly nitric acid. Consequently, these materials must be purchased locally or shipped by truck or other common carrier. If the materials are to be purchased locally, the purity must be rigidly controlled to assure no contaminants are present to affect results.

Even when the preservative nitric acid has been added and diluted by the sample, postal restrictions may preclude the use of the mails. Therefore, a special footnote has been added to the certification procedures allowing an alternate icing followed by acidification upon receipt of the sample in the laboratory.

When shipping the sample to the laboratory for analysis, sufficient time should be allowed to assure that the holding times are not surpassed. Alternate forms of transportation should be checked out beforehand to allow use if needed. The sample container must be protected from physical damage in shipment and sufficient coolant added to the ice chest or other form of insulated container to last through the duration of shipment. Caps should be checked when the sample is taken to assure that they will not leak. Upon receipt in the laboratory, any deviation from the mandatory sampling requirements, i.e., preservative, holding times, should be noted and, if necessary, a resample ordered immediately.

IV. SAMPLE COLLECTING

When the laboratory has been delegated the responsibility for sample collection, handling, and preservation, there needs to be strict adherence to correct sampling procedures, complete identification of the sample and prompt transfer of the sample to the laboratory.

The collector should be trained in sampling procedures and approved by the State regulatory authority or its delegated representative.

According to the National Interim Primary Drinking Water Regulations, Section 141.2(c), the sampling location is the "free-flowing outlet of

the ultimate consumer." Since this represents a minimal effort, one sample can be taken at any point in the distribution system and fulfill the regulation. Some States may require more frequent samples at random locations, or a single composite sample taken at various locations.

The exception to this sampling location is the turbidity sample which must be taken at the point of entry of the water into the distribution system.

When collecting the sample, the tap should be run to assure that the water collected is from the distribution system and not from the private service connection. The tap should be allowed to run at a steady flow for two or three minutes before sampling. The sampler should be sure that the tap is free of aerator, strainer, hose attachment or water purification device. The sample container should be flushed two or three times before the actual sample is taken unless directed not to by the analytical method. The container should not be filled completely to allow extra volume for effects of temperature during transit. The preservative, if any, should be carefully added to the container, the container capped and the sample shaken.

If the sample is to be cooled during shipment, the sample container should be placed in an insulated container and sufficient coolant added to last during shipment.

The sample should be labeled to identify it during future analyses.

The information should include:

- A. Date, place and time of sampling; name of person collecting the sample.
- B. Identification of the sample as to whether it is a routine distribution system sample, check sample, raw or process water sample, or other special purpose sample.
- C. Analysis to be run on the sample as well as preservative added and what amount has been added.
- D. Any other remarks that the sampler thinks are necessary.

This information should be affixed to the sample container in such a way as to assure that it will not become separated in later handlings.

The "Criteria and Procedures" manual states that chain of custody procedures must be carried out on all samples taken for potential enforcement actions only. The exact procedure and directions on this procedure should be obtained from the appropriate certification authority.

V. FIELD MEASUREMENTS

As set down in the SDWA, there are two types of analysis which may be carried out in other than certified laboratories. These are the analysis for residual chlorine and turbidity. These measurements may be carried out in the field. In addition, should any other information about the sample be required, such as pH, temperature, etc., these should also be carried out in the field. It is not the scope of this outline to discuss the procedures involved in these analyses.

State regulations may require additional procedures to be carried out by the person taking the sample. The Interim Primary Drinking Water Regulations do not.

VI. SUMMARY

The importance of proper sampling is the foundation of meaningful analytical results. Consequently, a laboratory should know what constitutes a meaningful sample in order to judge when a resample is necessary due to improper sampling, preservation or handling techniques.

The preservative to be added, the type of container and the holding times are spelled out in the "Criteria and Procedures" manual in a mandatory section.

The Laboratory Certification Officer must evaluate whether or not the laboratory is conducting a proper sample receipt procedure and, if it has the responsibility, a proper sampling of the water supplies.

Unit 5

PERSONNEL

I. INTRODUCTION

The Safe Drinking Water Act, PL 93-523, has as its main intent to provide good quality drinking water to all individuals and to insure the continuation of this supply of high quality water. To do this a series of MCL's and a schedule for all water supplies to follow in monitoring for these chemical and bacteriological contaminants was established. In an effort to continue in this intent, the National Interim Primary Drinking Water Regulations, Section 141.28, requires that for compliance purposes "samples will be considered only if they have been analyzed by a laboratory approved by the state except that measurement for turbidity and free chlorine residual may be performed by any person acceptable to the state".

The present "Criteria and Procedures" manual has recommendations which attempt to indicate the type of persons and experience necessary to carry out the analysis of these contaminants.

This instructional unit will consider the personnel needs of a laboratory doing analysis for water supplies in order to adequately carry out the analysis of chemical contaminants. The guidelines set down in the "Criteria and Procedures" manual are for a minimal program. This does not in any way hinder a state from adopting guidelines or regulations more stringent than those listed in the Federal guidelines.

II. GUIDELINES FOR POSITIONS AND EXPERIENCE

Again, it should be stressed that this section is a recommendation and not a requirement. The "Criteria and Procedures" manual has addressed considerable thought to this section, listing the various personnel that can be expected to be needed in a laboratory and the minimum of academic training and experience required. The appropriate statements for each position from the "Criteria and Procedures" manual have been included for your reference.

A. Chemical Personnel Guidelines

1. Analyst for inorganic contaminants—that is, all chemical measurements other than organic chemicals.
 - a. Academic Training: Minimum of high school diploma or its equivalent (state certification or licensing may be considered).
 - b. Experience
 - 1) Minimum of six months of on-the-job training, under the direct supervision of a qualified analyst, in measurements being considered for approval.

- 2) After six months, the analyst must demonstrate acceptable skills through the successful participation in the analysis of applicable performance evaluation samples.

This individual would be responsible for all chemical measurements other than organic chemicals. These would include all atomic absorption techniques including the extraction portions as well as the methods for nitrate and fluoride. Looking at the minimal conditions a person who had graduated from high school would receive six months, training before being considered a qualified analyst. The section on "under the direct supervision of a qualified analyst," could be a person who has the above mentioned qualifications himself. The measurements carried out by this individual during this training period would be acceptable for compliance with National Interim Primary Drinking Water Regulations.

The acceptability of his results would be based on the criteria mentioned above being a guideline. The only mandatory stipulations would be 1) that he use approved methods, i.e., those referenced in the Federal Register; 2) that the sample have been properly preserved; and 3) that the laboratory meets the quality control regulations.

2. Analyst for organic chemicals

- a. Academic Training: Minimum of a bachelor's degree in chemistry or its equivalent (state certification or licensing may be considered).
- b. Experience: Minimum of six months of experience in measurements being considered for certification and two years of experience in organic analysis. Each year of college level training in related scientific fields or demonstrated equivalency shall be considered equal to one year of work experience. Such a substitution should not exceed one-half of the required experience.
- c. Supervision: Supervision by an analyst (also eligible to analyze for organic chemicals) who has 1) a professional degree or its equivalent with one year of course work in organic chemistry; and 2) one year of experience in measurement of organic chemicals; by gas chromatography.

This individual will be responsible for the operation of the gas chromatograph and its use in determining the chlorinated hydrocarbons, the chlorophenoxys, and the TTHM's. Some indication has been given that if any changes in the National Interim Primary Drinking Water Regulations are made the most probable area would be the organics. The Regulations might be expanded to include

more extensive organic monitoring. It would be the area this individual would be responsible for, so it might be well to know this when this individual is being considered.

Here, too, the results generated by this individual would be immediately acceptable with the same provisions as listed under the inorganic section.

3. GC/MS Operator: In addition to the organic analyst requirements above, the following are recommended minimum standards for the GC/MS operator, if this technique is used.

- a. Training: Satisfactory completion of a minimum one week course in GC/MS offered by an equipment manufacturer, professional organization, university, or other qualified operators.
- b. Experience: Minimum of one year experience in the operation of a GC/MS instrument.

4. Supervisor¹

- a. Academic Training: Minimum of bachelor's degree in chemistry or its equivalent.

¹ These positions should be optional in smaller laboratories.

- b. Experience: Minimum of two years of experience in measurements being considered for certification.

With the equalization of a year of college-level training to a year of experience this individual would only need his bachelor's degree in chemistry to qualify for the position.

4. Laboratory Director¹

- a. Academic Training: Minimum of a bachelor of science degree or its equivalent.
- b. Experience: Minimum of five years' experience.

Larger laboratories would probably have a necessity for this type individual to oversee the entire operation of the laboratory. The following section on staffing will give some consideration as to when administrative type individuals are required.

III. LABORATORY STAFFING NEEDS

The fact that this section is not mentioned in the "Criteria and Procedures" manual would indicate its lack of importance. However, it would seem that an evaluator of a laboratory should have some ideas on the subject. If individual analysts try to carry out too many analyses in a

given time, their quality and analytical precision can suffer. Laboratory directors will have interest in this subject in order to predict future needs should additional workloads materialize.

If the Certifying Officer has knowledge of some of the figures and knowledge of what assumptions must be made to manipulate these numbers, he can offer additional technical assistance to the laboratory he is inspecting for certification.

One of the first pieces of data required in order to estimate staffing requirements is an indication of the number of analyses a single individual can carry out. All data of this nature are extremely variable. The accompanying table gives some estimates of the rate of analysis for an analyst. These data represent the number of a particular type analysis that a single individual can run in one man-day. For example, 60 arsenic determinations can be done in one man-day.

Several thoughts should be considered when contemplating these figures. While it might be possible to run 150 samples/day when utilizing an atomic absorption technique without any preliminary treatment, switching from one technique to another would consume time. For example, to convert the atomic absorption from its direct aspiration set-up to a gaseous hydride configuration or to a flameless set-up would consume time.

The instrument would also need to be optimized after each conversion. There is the possibility that more than one instrument would be available to

be used, i.e., one for direct aspiration use, one for gaseous hydride and/or one for the flameless determination of mercury.

Some consideration must also be given to how samples can be expected to be received. Unless a laboratory can set dates for the samples to be taken, the sampling would be at the discretion of the water treatment plant operator. Consequently, there could presumably be times when no samples are received in a laboratory and times when the volume of samples on hand to be analyzed are beyond the capability of the personnel of the laboratory.

One possibility to relieve this peaking would be position sharing. A single analyst could be working in both water pollution and water supply and as peaks occur could be switched from one batch of samples to another. Since the same parameters as determined under the NPDES program, the analyst would have the same needs for expertise in both programs.

Of course, the individuality of analysts would dictate that all individuals would not run the same number of samples in a given time. Perhaps an analyst could be kept on one type of analysis, say atomic absorption, and other on the wet analysis of nitrates or fluorides. However, this would be possible only in a laboratory where the staffing level would be high enough to make this feasible.

Automation of the methods will increase the number of samples that are capable of being run in a given time, but this would increase the instrument

investment considerably. Again, this would be a choice for a larger laboratory which would have the capital. A number of possibilities exist as to who would be doing the analysis. The size range of laboratories can vary from small laboratories doing only selected analysis, larger commercial laboratories doing all analysis, large state laboratories, and even combined state laboratories doing analysis for air, water, water supply and others. Consequently, these extremes of possibilities make it even more difficult to predict staffing unless more specific information is obtained.

The number of pieces of equipment available to the laboratory is another factor. Duplication could cut the time down, but will drive the costs up. All these items must be considered by a laboratory when determining the manpower requirements. The figures given here are meant to convey the simplest form, that is, one piece of equipment for each type needed and utilization of automatic sample reading which could mean use of equipment at night after the analyst has prepared the samples.

Once a rate of analysis has been chosen, the second number which must be established is the workload that the laboratory can expect. Some assistance in deciding this workload can be obtained from the sampling frequency set down in the National Interim Primary Drinking Water Regulations. Then if the laboratory knows how many water supplies it will have to be responsible for, the workload can be estimated.

Here again, some additional thought will be needed. Quality control will be recommended both from the "Criteria and Procedures" manual and from normal operating procedures in a laboratory. This level of quality control will place an additional workload on the laboratory by requiring check samples to be run in addition to the normal load. Resampling will also add to the workload. Resampling can occur from improper initial sample taking and also to validate or disprove results not meeting the maximum contaminant level. Those states having primacy could require additional sampling above the Federal requirements; this would also raise the workload of the laboratory. All these thoughts will need consideration before the total workload of a laboratory can be determined.

Another demand on the laboratory personnel time other than analysis will be a continued form of training. This could be in both providing training to new employees, and upgrading of existing laboratory personnel and, also being trained themselves to keep up their technical expertise and learning new techniques.

IV. SUMMARY

The indicated recommendations in the "Criteria and Procedures" manual for the Certification of Water Supply Laboratories lists four positions which might be used in a laboratory. The document also lists what minimum academic training and experience would seem to be needed to carry out the

NUMBER OF ANALYSIS THAT CAN BE RUN PER MAN-DAY PER ANALYST

CHEMICAL

Parameter	1 man year = 220 man days		
	Model St. Prog.* ¹	ERCO ²	EPA ³
	No./Day	No./Day	No./Day
Arsenic	60	60	70
Barium	60	30	150
Cadmium	20	10	70
Chromium	20	30	70
Lead	20	10	70
Mercury	20	20	70
Nitrate	85 (Auto-mated)	30	45
Selenium	60	20	70
Silver	60	30	150
Fluoride (probe)	100	30	113
Chlorinated Hyc.	2	1	3
Chlorophenoxy	2	1	3

One additional piece of data, the National Sanitation Foundation in its report estimated 4 man-days/year/system for laboratory support. However, this also included bacteriology.

* Excluding administrative overhead, chain of custody procedures, report writing, etc.

¹ Model State Water Monitoring Program, U.S. E.P.A. Office of Water and Hazardous Materials, Monitoring and Data Support Division

² ERCO, Energy Resources Co., Inc. Study for EPA.

³ Handbook for Analytical Quality Control in Water and Wastewater Laboratories EPA Analytical Quality Control Laboratory.

functions necessary. Two of the four positions would seem to be needed to carry out the functions necessary. Two of the four positions would be considered optional depending on the size of the laboratory, i.e., the Supervisor and laboratory director. However, in this case, it is suggested that some type of outside consultant be retained to give the laboratory some professional backup.

This unit tried to address the problem to how many persons a laboratory will need. The attempt was to develop some thought on the part of the Certifying Officer about the subject. It was felt that this type of information could be valuable in assessing the needs of a laboratory if it is operating above its capability or it needs to expand.

All laboratories, including those that exceed the recommendations outlined herein, are urged to maintain and continually improve their personnel, facilities, equipment, instrumentation, and quality control procedures. To ensure continued production of scientifically and legally defensible data, an ongoing training program should be an integral part of a laboratory's program.

UNIT 6

GENERAL LABORATORY PRACTICES

I. INTRODUCTION

This outline will consider general laboratory practices and services that are fundamental in the operation and management of any analytical laboratory. Sufficient information is offered for consideration by a certification official to evaluate laboratory facilities, services, and procedural details related in this outline. Although the material considered here serves as a guide for the certification official only and places no mandatory requirement on the part of a participating laboratory, deviations can be observed reflecting the need for updating and replacement of equipment and supplies, inadequate laboratory facilities, and the lack of attention given to procedural details for the care and maintenance of laboratory and service equipment.

II. LABORATORY FACILITIES (GUIDELINE)

A. Space

The quality of the analytical analyses and the production of reliable data can be adversely affected because of inadequate laboratory facilities. Laboratory space is of concern in that

space should be adequate to handle peak work loads. A laboratory that must continually program limited work space and time for various analyses operates under adverse conditions. As a guideline, there should be approximately 150 to 200 square feet/person, regardless of test, and approximately 15 linear feet of usable bench space. Working space requirement should include sufficient work bench space for processing samples; storage space for chemicals, glassware and portable instrumentation; open floor space for large equipment such as refrigeration, oven, water still, washing and hood facilities, etc.

Considering the above space figures and taking into account the many variables, a more practical estimate of space requirement can be derived from observing operating conditions in any given laboratory.

There are other variables affecting space requirements for any individual laboratory operation. A laboratory performing routine analyses for a small water plant may easily be housed in one room. However, such space may be inadequate for a laboratory engaged in more sophisticated analytical analyses or in laboratories doing research. Multidiscipline laboratories may require separate laboratory work area and support functions to facilitate timely processing of water and other samples throughout the course of a work day.

B. Utilities – Water and Electric

Laboratory services and services equipment available for use in laboratory operations can affect the quality of the laboratory output. Every laboratory should have hot and cold running water with a number of sinks depending on the size and workload of the laboratory.

Electrical service first of all should conform to local, state or national electrical codes. The adequacy of the electrical system can best be judged by the system capacity to meet or exceed the requirements of the laboratory operation. Consideration must be given to a proper laboratory lighting system, operation of delicate and sensitive laboratory instrumentation, and functioning of high current demand equipment. Sufficient 120- and 220- volt circuits must be located in specified areas and throughout the laboratory allowing for better flexibility and sufficient capacity to handle varying types of work. Independent circuits may be necessary for operation of some instrumentation.

C. Exhaust Hoods

The handling of toxic and/or hazardous chemicals, solvents, and gases may require the use of an exhaust ("fume") hood.

Methodologies that include in the the analytical scheme such steps as evaporation, extraction, distillation or digestion may also require the use of an exhaust hood. The performance of a fume hood is controlled by its designed hood face velocity, regulation of flow over the face opening and control of outfall of fumes from the hood face. Minimum face velocity at any point on the operating opening should not be less than eighty percent of the average design face velocity, which is the total air passage across the hood face divided by the hood face area. The following table gives average and minimum design face velocities in relation to the nature of materials handled.

Laboratory Hood Design Face Velocities

<u>Nature of Materials Handled</u>	<u>Gases Vapors</u>	<u>Dusts, Fumes, Mists</u>	<u>Mineral Dusts</u>	<u>Average^a</u>	<u>Minimum^b</u>
High Toxic	Less than 0.1	Less than 0.1 mg/cu meter	—	150	125
Moderately Toxic	0.1 to 100 ppm	0.1 to 15 mg/cu meter	To 5 mppcf	100	80
General Laboratory Use Non-Toxic	Above 100 ppm	Above 15 mg/cu meter	Above 5 mmpcf	60	50

^a Total hood cfm divided by total face area.

^b Lowest maintained velocity at any point across the hood face.

Hood efficiency is affected by velocity gradients over the hood face because of a hood's air distribution characteristics, inadequate maintenance, and wear factors such as dirty vent ducts, worn or loose fan belts, corrosion and deterioration. Exhaust hoods should at least meet minimum safety standards as prescribed in many states under labor codes.

Specifications should be such that the design constitutes a balanced system taking mainly into account adequate air movement and proper venting. Room temperature should not be affected while in the operating mode. Utilities should be available with water, cup sink, lights and electrical outlets being the more important.

III. GENERAL LABORATORY PRACTICES

A. Glassware and Plasticware

Quality of laboratory data can be compromised both in test sensitivity and reproducibility by improper choice, use, and cleaning of laboratory glassware and plasticware. Of the many types of glassware available, the best suited for all-round analytical laboratory use is made from borosilicate glass manufactured under the trade name "Pyrex" or "Kimble" brand. This glassware is not completely inert, but is satisfactory for all

analyses included in EPA's methods manual. Where required other brands are available for special purpose use possessing properties such as resistance to heat, light, shock, and alkali.

The use of plasticware made from Teflon, polyethylene, polystyrene, and polypropylene has supplemented or replaced many glassware items in the laboratory. The specific qualities of these plastics and their relative chemical resistance must be taken into account in regard to their use. Some points to consider in evaluating the appropriate choice of glassware and/or plasticware are:

1. Borosilicate glassware is not completely inert, especially to alkalies. Standard alkaline solutions and solutions of alkali metals are best stored in plastic bottles.
2. Selection of plasticware should be predicated on the basis of its specific properties, chemical resistance and intended use.
3. Plastic bottles and containers may be used for storage of reagents and standard solutions where no effect from the contents and container is encountered. Strong mineral acids and organic solvents will attack polyethylene and should be avoided.
4. Disposable glassware is generally made of soft glass.

5. Disposable glassware and plasticware should be discarded after initial use.
6. Cracked, chipped or etched glassware should be discarded.
7. Plastic sample containers are not satisfactory for samples collected for organic analyses.

B. Volumetric Glassware

Every laboratory should have a set of Class A volumetric glassware for precise measurements of liquid volume. The ware includes the usual burets, volumetric flasks and volumetric pipets. Class A volumetric glassware so designated meet the Federal Specifications as set by the National Bureau of Standards. Also one must be aware of the designation of volumetric apparatus calibrated either to delivery ("TD") or to contain ("TC") a definite volume of liquid. Less accurate types of glassware including graduated cylinders, serological, and measuring pipets, should never be used for precise measurement of volume of solution. The graduated markings of such glassware as Erlenmeyer flasks and beakers should be considered as mere approximation of actual volume marked and probably should not be relied upon as a volumetric measurement in any case.

C. Cleaning of Glassware

The cleaning procedure adopted must be amenable to producing chemically clean glassware and other items for reuse in the laboratory. For most analytical needs it would be sufficient to wash the items in a warm detergent solution followed by tap water rinse and then with distilled water. However, it would be good practice on the part of the analyst or whoever does the cleaning to be aware of special cleaning requirements pertaining to certain determinations and items of glassware. One may maintain separate sets of glassware for certain procedures to avoid cross contamination. Special cleaning requirements may be required for volumetric glassware, especially burets and pipets. Absorption cells used in spectrophotometers must be free of any film residues and scratches.

Certain determinations, especially for trace metals require 1:1 nitric acid-water rinse after cleaning followed by repetitive tap and distilled water rinses. Detergents containing phosphates should not be used to clean glassware for phosphate determinations. Ammonia-free water must be used to rinse glassware for ammonia and Kjeldahl determinations.

All glassware used in sample collection and organic residue analyses should be free of organic and other contaminants. Glassware should be thoroughly cleaned soon after use with detergent solution, rinsed with tap water, distilled water, redistilled acetone and a final rinse with high quality hexane. Glassware should be allowed to dry, any mouth opening covered with foil and ignited at 400°C for one hour. Volumetric ware, caps and Teflon liners are not ignited. Glassware, unless cleaned for immediate use, should be protected from environmental contamination and stored in a closed contaminant free area. Caps and liners should be stored in sealed containers. It has been found advantageous to maintain a separate set of glassware (suitably prepared) for the nitrate, mercury and lead procedures due to the potentiality for contamination from the laboratory environment.

IV. REAGENTS, SOLVENTS AND GASES

It is intended that only the best quality chemical reagents, solvents, and gases be employed in lieu of any particular method requirement. The minimum purity of reagents and chemicals should be analytical reagent grade. Organic solvents and gases should be compatible with whatever analytical operation is to be performed. Analytical standards should be reference grade, when available.

Factors such as the parameter being measured and sensitivity and specificity of a detection system will determine the purity of the reagents required. The quality of reagents and solvents may vary from lot to lot, even within a given lot; therefore, a laboratory should check each new container put to use. Proper storage is essential to prevent degradation. All reagents, solvents and gases when purchased should be dated and recorded to monitor shelf life. Subsequently, prepared reagents and standard solutions should be monitored for changes in concentration or deterioration. It would be expeditious to properly label these as to compound, concentration, solvent used, name of preparer and date.

In the interest of safety, personnel should be aware that many chemical reagents, both in their original state and prepared solutions, are hazardous and should be handled with discretion to prevent their inhalation, ingestion, absorption or contact through the lungs, mouth or skin.

V. DISTILLED AND/OR DEIONIZED WATER

The purity of distilled water and/or deionized water a laboratory normally uses should be evaluated rather closely whether it is produced in-house or purchased from a vendor.

Laboratory water should be free of substances that interfere with sensitive chemical measurement with the degree of water purity being

consistent with the needs for any particular analysis in question. Ordinary distilled water is usually not pure and may contain minute traces of impurities which could interfere with many colorimetric procedures. However, for many analyses the distilled water is used without further purification. Certain analysis may require a specific type of treatment, namely ammonia free, carbon dioxide free or ion free water. When determining trace organics the distilled water must be of sufficiently low organic background. This may require further treatment of the distilled water to eliminate this problem. To assure minimum contamination one must make careful selection of the distillation apparatus including the still, storage facility and any associated piping. Installation and maintenance should be of prime concern.

Demineralized water made by passing tap water through a mixed bed ion exchanger is applicable for many procedures. Very high purity water, less than 0.1 micromho/cm conductance, can be produced by passing distilled water instead of tap water through the same type filter.

Factors affecting suitability and quality of distilled and/or deionized water:

- A. Best distilled water system utilizes stainless-steel construction.
- B. Other systems utilized in order of preference are quartz, vicor, or Pyrex glass.

- C. Tin-lined systems are subject to corrosion exposing base metal to contact with distilled water.
- D. In order of preference, all connecting plumbing should be stainless steel, Pyrex or special plastic made of polytetrafluoroethylene (PTFE) material. Polyvinyl chloride (PVC) pipe should not be used for connecting plumbing.
- E. Storage tanks, in order of preference, should be stainless steel, fiberglass, or (PTFE) plastic. Tanks should be sealed and fitted with vented air filtering devices.
- F. Ordinary distillation of water will not remove ammonia or carbon dioxide. Volatile organics may distill over from the feed water and nonvolatile impurities at times may come over in the steam in the form of spray.
- G. Pretreatment of the input source water to a still by the use of any combination of water softening, deionizing and/or a carbon filtration will improve the quality of the distillate.
- H. Post-treatment of the distillate using a deionizing column and a carbon filter will produce very high purity water.

- I. A laboratory must monitor at scheduled intervals its distilled or deionized water supply. One essential laboratory water quality measure is conductivity. Supplemented with periodic checks for various physical and chemical parameters will insure a continued supply of high-quality laboratory water.
- J. Maintenance of distillation equipment, including replacement or recharging of any treatment columns should be performed on a scheduled basis.
- K. A laboratory must judge for itself the suitability of its laboratory water supply. If the quality of the water does not suffice, action must be taken along the lines of equipment update, more frequent monitoring and maintenance.

VI. ANALYTICAL BALANCES

A. Proper Care and Use of Balances

It has been stated that the most important piece of equipment in any analytical laboratory is the analytical balance, yet the care of the analytical balance is frequently overlooked.

Most laboratories today are equipped with the single-beam, one-pan balance. The controls and dials vary among different manufacturers. This balance permits very rapid determinations to be made by a substitution type weighing on a single beam with only two knife edges.

Some laboratories are still equipped with one of the two types of double beam analytical balances, one known as the rider and graduated-beam type and the other called the chain type, both types employing the use of analytical weights.

Deviations from the following observable precautions for the proper care and use of an analytical balance can have a cumulative effect on the critical weighing operation.

1. Any balance should be operated according to the manufacturer's instructions.
2. The balance should be mounted on a shock-proof table and located away from the laboratory traffic. Area subject to drafts, humidity changes and temperature changes should be avoided.

3. While using the balance, the balance level should be checked frequently and adjustments made when necessary.
4. The control knob which releases the beam support should be handled gently, so one does not jar the balance.
5. The beam should always be supported (not free-swinging) when adding or removing any object or weight from the pan or when adjusting a rider.
6. Never put chemicals directly on the balance pan, avoid spillage on the pan and inside the balance case.
7. Never weigh an object while it is hot or even warm.
8. For the double beam balances, handle analytical weights only with forceps; never use hands.
9. The balance case should be closed when taking final readings. When through weighing, the beam should be raised from the knife edges, weights returned to the beams or removed from the pan, objects removed from the pan and the door closed.

10. Balance accuracy and performance should be checked periodically with the use of standardized Class "S" weights. This may be performed in-house, however, lacking Class "S" weights or if adjustments or repair are required, the service of a company service man or balance consultant would be in-order.

VII. PREPACKAGED KITS-CALIBRATION INTERVALS

As stated in the implementation strategy document for certification of water supply laboratories, all kit procedures, other than the N, N-diethyl-p-phenylenediamine (DPD) Colorimetric Test Kit and the 3,5-dimethoxy-4-hydroxy-benzaldazine (Syringaldazine), are considered alternative techniques.

Visual comparison devices, whether color wheels, sealed ampules or other visual standards utilized in these test kits, should be calibrated at least every six months. These calibrations should be documented.

Unit 7

PRE- AND POST-CONFERENCES

I. INTRODUCTION

The on-site evaluation will begin and end with conferences involving the laboratory personnel. The Certification Officers will use the pre-conference to gain information about the laboratory, its personnel and the analytical methodology. After the inspection, they will meet with the laboratory personnel and discuss the results of the evaluation. They will indicate where improvements are necessary and, in general, assist the laboratory in improving its analytical capabilities. These meetings should leave the laboratory director or chief chemist with the impression of having been assisted by the certification team.

Another important aspect of an on-site visit is the ability of the certification team to offer technical assistance to the laboratory. The "Criteria and Procedures" manual points out that the Regional Plans for certifying local labs should contain plans for providing technical assistance to laboratories in need of upgrading. Again, in discussing the review of the on-site evaluation, the "Criteria and Procedures" manual points out that the certification team should discuss possible assistance the Region can provide the laboratory.

II. PRE-EVALUATION CONFERENCE

In attendance at this conference should be at least the laboratory's chief chemist, chief microbiologist and the laboratory director. This will enable the evaluation team to be assured of having someone available to answer questions about the various portions of the laboratory. This above list should not imply that only these individuals may be present. Any additional individuals whom the laboratory chiefs feel should be present should attend.

Some information will already be in the hands of the certification team, including which methods the laboratory has requested to be certified. In the pre-conference, the Certification Officer can begin filling out the evaluation forms by covering the personnel section, parts of the methodology, sampling, quality control, and data reporting sections.

The background of the laboratory personnel with regard to their formal education, training, experience, and responsibilities can be obtained by questioning the chief chemist or laboratory director. The number of personnel and the number of samples received by the laboratory per month can allow the evaluator to assess the staffing of the laboratory.

The laboratory director can indicate which methods of analysis are being used by the laboratory for each contaminant that is currently being analyzed and cite the reference work used to describe the method. Knowing the frequency of operation of each method gives the Certification Officer an

idea of how much quality control will be necessary for the laboratory to be carrying out to fulfill the certification mandate.

Information on sample handling such as the types of containers used, what preservation techniques are used for each type analysis, delivery times, and the policies on holding times can be obtained in the conference. The Certification Officer can observe during the laboratory walk-through, actual sample containers. He can then see if the sample containers are new or if they are in good condition and are they proper, that is, do the organic sample containers have Teflon cap liners and are they of acceptable materials. He will want to see an example of actual data report forms to be assured that it contains the required information. He could also check the sampling date to assure himself that the proper holding times are not being ignored.

The Certification Officer can also determine during the conference the types of instruments the laboratory has available. He can look at any performance data the laboratory might have on known reference samples and on unknowns, if he does not have this information already. He can also determine during the conference if the laboratory is having any problems in the analysis and can then spend more time during the actual evaluation on the trouble areas.

The Certification Officer should fill out as much of the check sheet as possible then do the actual evaluation and double check some items such as equipment repair and specifications.

III. POST-CONFERENCE

Before this conference is held, the certification team should review their evaluations and prepare themselves for the meeting. This will help identify forgotten items and allow the laboratory to offer explanations for any deviations. If done with a sincere effort, this preparation will minimize any new or undiscussed material in the actual report and keep down any misunderstanding between the laboratory and Certification Officers.

During the post evaluation conference, the laboratory director and chief chemist, should be in attendance. Any of the laboratory staff that might be involved in the discussion should be in attendance also. For example, if any deviations have been detected, the persons who are responsible for that area should be invited to be present at the conference and to participate in the discussions.

The actual discussions should center around any deviations in methodology, instrumentation, sampling, preservation, holding times, quality control, or any other subjects in which the evaluator has uncovered potential problem areas. The Certification Officer should consider this an oral report to the laboratory covering his evaluation. The topics in the post conference should not be limited and the certification team should allow sufficient time so as not to appear to be pressed for time. The laboratory officials should be encouraged to discuss all topics which they feel should be covered. As the certification document states, the post conference should end with a discussion of how the certification authority can aid the laboratory.

IV. SUMMARY

These conferences are extremely important. The pre-conference will provide considerable information to the certification team and also allow them to become acquainted with individuals in the laboratory whom they have not previously met. The post-conference is the concluding conference and should attempt to convey the idea of a technical assistance visit rather than any enforcement endeavor. If the entire evaluation is handled properly, a good working relationship can be established which can prevail through all future contacts with the laboratory and will provide more cooperation between the two parties.

Unit 8

RECORDS AND REPORTS

I. INTRODUCTION

Production of reliable analytical data is the prime effort of a laboratory. However, an addition to this responsibility, is the keeping of records and report writing. Records of the chemical analysis, sample information and quality control are all examples of information that must be stored. The return of the analytical data to the concerned treatment plant is an example of the reports a laboratory must produce. Records of chemical analysis should be kept by the laboratory for not less than three years. This includes all raw data, calculations and quality control data. The laboratory Certification Officer will have to review these data in order to properly certify the laboratory. This outline will list the records and reports that should concern the evaluation officer for chemical parameters.

The form of data and report storage may vary from laboratory to laboratory. Some larger laboratories may store the data in some automatic data processing system while others will have hard copy storage. If the Certification Officer knows exactly what is needed to satisfy his needs, he can request the laboratory to gather such records together for his visit.

II. ANALYTICAL QUALITY CONTROL DATA

When a Certification Officer certifies a laboratory, he will need to

evaluate the existence and significance of the laboratory's analytical quality control data. This will include as a critical element the following materials for all chemical parameters for which certification is sought.

A. Results of the Annual Performance Sample

The Certification Officer may have this data available at his own office if the appropriate regional or state principal laboratory has forwarded this information to him.

B. Standard Calibration Curves for Each Chemical Parameter for which the Laboratory is to be Certified

This should also include the verification of these curves daily or once each time the curve is used, depending on the frequency of analysis in the laboratory. If the frequency of use for a particular analysis exceeds 20 samples per day, the data should include proof of verification after every 20 samples.

C. The existence of a written Quality Assurance Plan

In order to assure that the laboratory data is of known and acceptable there should be a written QA plan. This plan should address the following, sampling procedures, sample handling, equipment calibration, methodology, data reduction, internal QC, preventative maintenance, routine for determining data accuracy and precision and corrective action contingencies.

- D. That blanks, reagent water and WC standards are run as necessary to assure good data

Reagent, field blanks and duplicates should be run to assure no contamination in samples. The proper number of laboratory quality control standards should be run to assure proper maintenance of precision.

Although listed as recommended the Certification Officer should ask to see if available, and encourage compliance with, the following:

1. Current service contract on all balances; which could include the use of class S weights to check accuracy of the balances.
2. A schedule and color standards for checking the wavelength of the spectrophotometers.
3. Availability of a thermometer certified by the National Bureau of Standards or one of equivalent accuracy.
4. Chemical should be dated before being placed on the shelf and replaced as needed or as shelf life has been exceeded.

The last set of guideline information that the Certification Officer should look for is only for those laboratories analyzing samples other than its own. This data would include results of the laboratory's performance on a known reference

sample. This should be carried out quarterly. These performance evaluation samples will be made available to all principal laboratories by EPA. The principal laboratories may then utilize these samples for the local laboratories being evaluated by the State.

Additional records should be available showing verification of precision and accuracy for each method. That is, duplicate samples every ten samples, or with each set of samples and calculations of standard deviations and use of quality control charts.

III. SAMPLING RECORDS

The laboratory may or may not be responsible for the actual taking of the samples. However, it is the responsibility of the laboratory to assure itself that the sample is meaningful and that the mandatory handling and preservation techniques have been carried out.

The actual sampling records retained by the laboratory will need to be evaluated by the entire evaluation team, provided that the laboratory is being evaluated for all the parameters. The chemical and bacteriological evaluators will have need to see these records. The data is required to be kept by the laboratory for at least three years.

The Certification Officers should satisfy themselves that sufficient data is being kept by the laboratory. They should review the records for

compliance with the required sampling frequency, check sampling program, sample transit time and resampling notices, if appropriate. The suggested data on each sample should include at least the following information:

- A. Date, place and time of sampling; name of the persons who collected the sample.
- B. Identification of the sample as to whether it is a routine distribution system sample, check sample, raw or process water sample, or other special purpose sample.
- C. Date of receipt of sample and analysis.
- D. Laboratory and persons responsible for performing analysis.
- E. Analytical technique/method used.
- F. Results of Analysis.

The Certification Officer might wish to make laboratories aware of some of the following points. If a laboratory has been contracted with by a public water supply to provide analytical services that laboratory might wish to set up a meeting with that supply. The laboratory can then assure that the proper information and sample frequencies are to be provided and what the laboratory will do when there is doubt of the veracity of the sample. State principal laboratories might wish to retain data on the turbidity and residual chlorine determinations and sampling to be assured

that these analysis are correct in analytical results, frequency and location of sampling.

IV. DATA RETENTION AND REPORTS

If a person compares the Data Reporting section of the "Criteria and Procedures" and Section 141.33 of the National Interim Primary Drinking Water Regulations, it should be remembered that the documents are referring to two different responsible parties. The National Interim Primary Drinking Water Regulations are referring to the Public Water System and requiring data retention for ten years. The "Criteria and Procedures" manual is referring to a laboratory which performed the analysis for that public water supply. There will be cases where the laboratory is part of the water supply. In this case the data will have to be kept for the longer periods to comply with the requirements for the public supply.

The laboratory should have the records of their personnel's training and experience available for inspection by the Certification Officer. However, since this area is a guideline, this information would be obtained from the laboratory director during the pre-evaluation discussion.

The Certification Officer might wish to see the reports from the laboratory to the water supply giving the results of the analysis. This would indicate whether sufficient data is being transmitted by the laboratory to fulfill the needs of the water supply.

Critical Element

Recommended

I. QUALITY CONTROL

A. Lab doing own analysis only

1. General
 - a. Written QA Plans
 - b. Annual performance sample
 - c. Available methods manual
 - d. Calibration of pH meter with each use
2. Inorganic
 - a. Standard curve for each parameter
 - b. Verification of standard curve daily or every 20 samples
3. Organic
 - a. Daily method blank for pesticides & herbicides
 - b. Stds. daily to show linearity
 - c. QC standard run quarterly
 - d. Filled blank for TTHM with each set of samples
 - e. 10% of samples should be duplicates for TTHM's
 - f. Daily TTHM lab control std.
 - g. Proven precision of TTHM equipment
 - h. Raw water blanks for Liq/Liq ext. of TTHM's
 - i. Prove performance of GC/MS by using BFB

1. Service contract on balances
2. Records showing calibration of instruments

Critical Element

Recommended

B. Lab doing other
than its own
samples

1. All of the above

1. Quarterly analysis of known sample
2. One duplicate sample every 10 samples – or with each set of samples
3. Calculate standard deviation
4. Daily use of quality control charts or tabulation of mean and standard deviation

II. SAMPLING DATA

1. Retention of data for not less than one year

Enforcement data for three years

2. Retained data to include
 - a. Date of sampling
 - b. Place of sampling
 - c. Time of sampling
 - d. Name of sample collector
 - e. Identification of sample
 - Distribution sample
 - Check sample
 - Raw sample
 - Processed sample
 - Special sample
 - f. Date of receipt of sample
 - g. Date of analysis of sample
 - h. Name of lab
 - i. Name of analyst
 - j. Method use for analysis
 - k. Result

III. DATA RETENTION AND REPORTS

1. Evaluate personnel background (education and experience)
2. Approval of plan for turbidity and residual chlorine
3. Retention times of dat

If the laboratory is a principal State laboratory, the records should be available to the Certification Officer showing the provisions the State has made to approve turbidity analysis and chlorine residual analysis if substitution is to be allowed by the State.

V. SUMMARY

An important part of the on-site visit is the evaluation of the records and reports of the laboratory. The Certification Officer will evaluate critical element quality control materials as well as the recommended data of the quality control and data reporting sections of the "Criteria and Procedures" manual.

The effort the laboratory has put forth to document the approval of the turbidity and residual chlorine determinations should be evaluated in the State principal laboratories. Also the time the data is kept and in what manner it is kept should be evaluated.

This section can indicate to the Certification Officer the reliability of the data (from the quality control materials) as well as the accuracy of the sampling techniques, handling and preservation, and documentation of the sampling program.

Unit 9
STATISTICS FOR CHEMISTS

I. INTRODUCTION

Statistics may be defined, for our purpose, as a collection of mathematical methods which have been developed for handling numerical data pertaining to samples or portions of entire populations.

The statistical methods with which we will concern ourselves deal with the presentation and analysis of numerical data from samples.

II. FREQUENCY

A. Definitions

1. Frequency – indicates how many times a particular, individual datum value occurs in a collection of data.
2. Frequency table – a tabular arrangement of data, ranged in ascending or descending order of magnitude, together with the corresponding frequencies (See Table I).

3. Frequency histogram – a set of rectangles having bases (lower & upper class boundaries) on a horizontal axis (abscissa) with centers at the given data values and heights equal to the corresponding frequencies depicted on the vertical axis (ordinate). NOTE: class boundaries should not coincide with any values in your data set (See Figure 1).
4. Frequency polygon – a line graph of frequencies plotted against data values. This graph can be constructed by connecting midpoints of tops of rectangles in the frequency histogram (See Figure 1).

B. Application

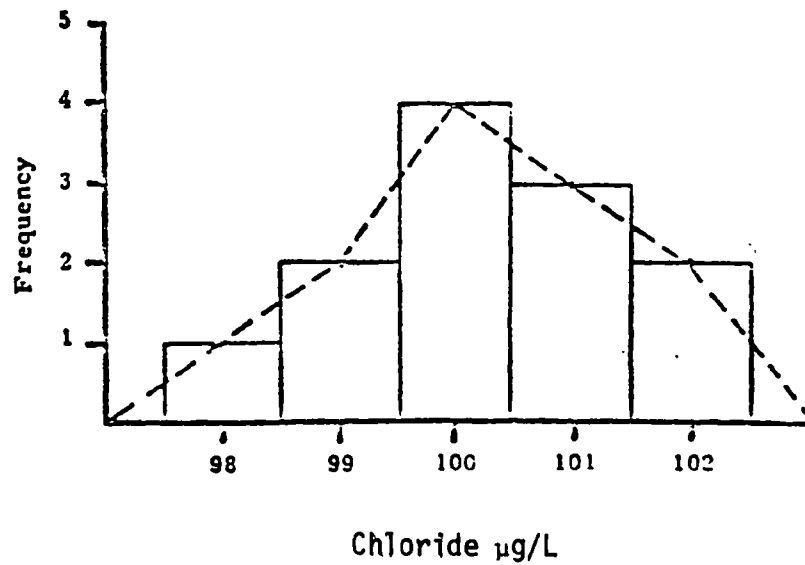
Consider the application of the above definitions to the following set of data, obtained from 12 determinations for chloride in water.

<u>Results ($\mu\text{g/L}$)</u>		
100	101	99
101	100	100
99	102	100
98	101	102

Table I
Frequency Table

<u>Chloride ($\mu\text{g/L}$)</u>	<u>Frequency</u>	<u>Lower Class Boundary</u>	<u>Upper Class Boundary</u>
98	1	97.5	98.5
99	2	98.5	99.5
100	4	99.5	100.5
101	3	100.5	101.5
102	2	101.5	102.5

Figure 1
Frequency Histogram & Frequency Polygon



III. MEASURES OF CENTRAL TENDENCY

A. Definitions

Central tendency – the tendency of values to cluster about a particular value in the distribution.

1. Mean – arithmetic average of all the values in the sample distribution, denoted by \bar{X} . The formula for calculating the sample mean is

$$\bar{X} = \frac{x_1 + x_2 + x_3 + \dots + x_n}{n} = \bar{X} = \frac{\sum_{i=1}^n x_i}{n}$$

where there are n numbers of values.

2. Mode – that value which occurs most frequently
3. Median – midpoint of an array (arranged in order of magnitude) of individual data values. It is the middle value or the arithmetic mean of the two middle values. If there are an odd number of observations, n, the median is

$$\frac{x_{\frac{n}{2} + 1}}{2} \quad \text{where} \quad \frac{x_{\frac{n}{2} + 1}}{2} \quad \text{represents the}$$

$$\frac{n+1}{2}$$

value in the frequency distribution. If there are an even number of observations the median is:

$$\frac{x_{\frac{n}{2}} + x_{\frac{n}{2} + 1}}{2}$$

the average of the middle two data values.

4. Geometric Mean: The n^{th} root of the product of the data points.

$$\bar{x}_g = \sqrt[n]{(x_1)(x_2)\dots(x_n)} = \sqrt[n]{\prod_{i=1}^n x_i}$$

This is what we get when we transform the data to logarithms, then take the anti-log of the arithmetic mean of the transformed data.

$$\bar{x}_g = \text{antilog} \left[\frac{\log(x_1) + \log(x_2) \dots + \log(x_n)}{n} \right]$$

B. Application

Consider the application of the above definitions to the previously mentioned set of data, obtained from twelve determinations for chloride in water, shown in Table I.

$$1. \text{ Mean} = \sum_{i=1}^n \frac{x_i}{n}$$

$$= \frac{98 + 2(99) + 4(100) + 3(101) + 2(102)}{12} = 100.25 \text{ } \mu\text{g/L}$$

2. Mode = 100 $\mu\text{g/L}$

$$3. \text{Median} = \frac{\frac{x_n}{2} + \frac{x_n}{2} + 1}{2} = \frac{x_6 + x_7}{2}$$

$$= \frac{100 + 100}{2} = 100 \mu\text{g/L}$$

$$4. \text{Geometric Mean} = \bar{X}_g = \sqrt[12]{1.03 \times 10^{24}} = 100.24 \mu\text{g/L}$$

$$\text{or } X_g = \text{antilog} \left[\frac{(\log (98) + 2 \log (99) + 4 \log (100) + 3 \log (101) + 2 \log (102))}{12} \right] = 100.24 \mu\text{g/L}$$

IV. MEASURES OF DISPERSION

A. Definitions

1. Dispersion – spread or variability of observations in a distribution.

2. Range – the difference between the highest value in the data set and the lowest value in the data set.

$$R = \text{max} - \text{min}$$

3. Variance – the sum of the squares of the deviations of the individual data values from their mean divided by the total number of data values(n) minus 1.

The definition of the variance can be expressed by the following formula:

$$s^2 = \frac{\sum_{i=1}^n (x_i - \bar{X})^2}{n - 1}$$

4. Standard deviation – the square root of the variance.

The definition of the standard deviation can be expressed by the following formula:

$$s = \sqrt{\frac{\sum_{i=1}^n (x_i - \bar{X})^2}{n - 1}}$$

However, the formula commonly used because of its adaptability to the hand calculator is the following:

$$s = \sqrt{\frac{\sum_{i=1}^n x_i^2 - \frac{\left(\sum_{i=1}^n x_i\right)^2}{n}}{n - 1}}$$

where there are n number of values.

5. Standard deviation – derived from the range statistic. For small data sets ($n < 10$), the range statistic is often used to

estimate standard deviation:

$$\frac{R}{d_n} \cong s$$

The value for d_n is obtained from Table II.

Table II

<u>Size of sample(n)</u>	<u>d_n</u>
2	1.128
3	1.693
4	2.059
5	2.326
6	2.534
7	2.704
8	2.847
9	2.970
10	3.078
12	3.258
16	3.532

6. Standard deviation of the mean ($s_{\bar{x}}$) – the standard deviation of individual data items(s) divided by the square root of the number of data items(n).

The definition of the standard deviation of the mean can be expressed by the formula:

$$s_{\bar{x}} = \frac{s}{\sqrt{n}}$$

7. Relative standard deviation – the standard deviation(s) expressed as a fraction of the mean:

$$RSD = \frac{S}{\bar{X}}$$

The relative standard deviation is often expressed as a percent. It is then referred to as percent relative standard deviation:

$$\% RSD = \frac{S}{\bar{X}} \cdot 100$$

The relative standard deviation is particularly helpful when comparing the precision of a number of determination on a given substance at different levels of concentration.

8. Relative range – the range (R) expressed as a fraction of the mean:

$$RR = \frac{R}{\bar{X}}$$

The relative range can also be expressed as a percent. It is then referred to as percent relative range:

$$\% \text{ RR} = \frac{R}{\bar{X}} \bullet 100$$

B. Application

Consider the application of the above definitions to the previously mentioned set of data, obtained from twelve determinations for chloride in water.

$$1. \text{ Range} = 102 - 98 = 4 \text{ } \mu\text{g/L}$$

$$2. \text{ Variance: } s^2 = \frac{\sum_{i=1}^n (x_i - \bar{X})^2}{n-1}$$

<u>f</u>	<u>x_i</u>	<u>x_i - \bar{X}</u>	<u>(x_i - \bar{X})²</u>	<u>f(x_i - \bar{X})²</u>
1	98	-2.25	5.06	5.06
2	99	-1.25	1.56	3.12
4	100	-.25	.06	.24
3	101	+.75	.56	1.68
2	102	+1.75	3.06	6.12
				<u>16.22</u>

$$s^2 = \frac{\sum_{i=1}^n (x_i - \bar{X})^2}{n-1} = \frac{16.22}{11} = 1.47$$

3. Standard deviation - square root of the variance

$$s = \sqrt{\frac{\sum_{i=1}^n x_i^2 - \frac{\left(\sum_{i=1}^n x_i\right)^2}{n}}{n-1}}$$

f	x_i	fx_i	x_i^2	fx_i^2
1	98	98	9604	9604
2	99	198	9801	19602
4	100	400	10000	40000
3	101	303	10201	30603
2	102	204	10404	20808
		<u>1203</u>		<u>120617</u>

$$s = \frac{120617 - \frac{1203^2}{12}}{11} = \frac{120617 - 120601}{11} = \sqrt{\frac{16}{11}} = 1.21 \mu\text{g/L}$$

4. Standard deviation - derived from the range statistic

$$s = \frac{R}{d_n} = \frac{4}{3.258} = 1.23 \mu\text{g/L}$$

5. Standard deviation of the mean:

$$S_{\bar{X}} = \frac{s}{\sqrt{n}} = \frac{1.21}{\sqrt{12}} = 0.35 \mu\text{g/L}$$

6. Relative Standard Deviation:

$$RSD = \frac{s}{\bar{X}} = \frac{1.21}{100.25} = 0.0121$$

or percent relative standard deviation

$$\% \text{ RSD} = \frac{s}{\bar{X}} \cdot 100 = \frac{1.21}{100.25} \cdot 100 = 1.21\%$$

7. Relative range:

$$\text{RR} = \frac{R}{\bar{X}} = \frac{4}{100.25} = 0.0399$$

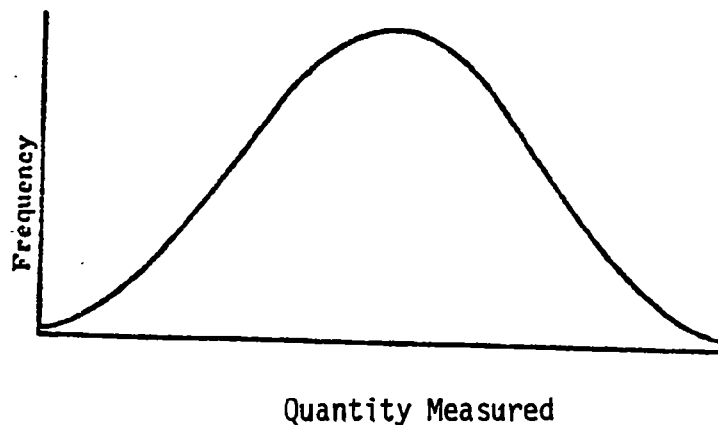
or percent relative range

$$\% \text{RR} = \frac{R}{\bar{X}} \cdot 100 = \frac{4}{100.25} \cdot 100 = 3.99\%$$

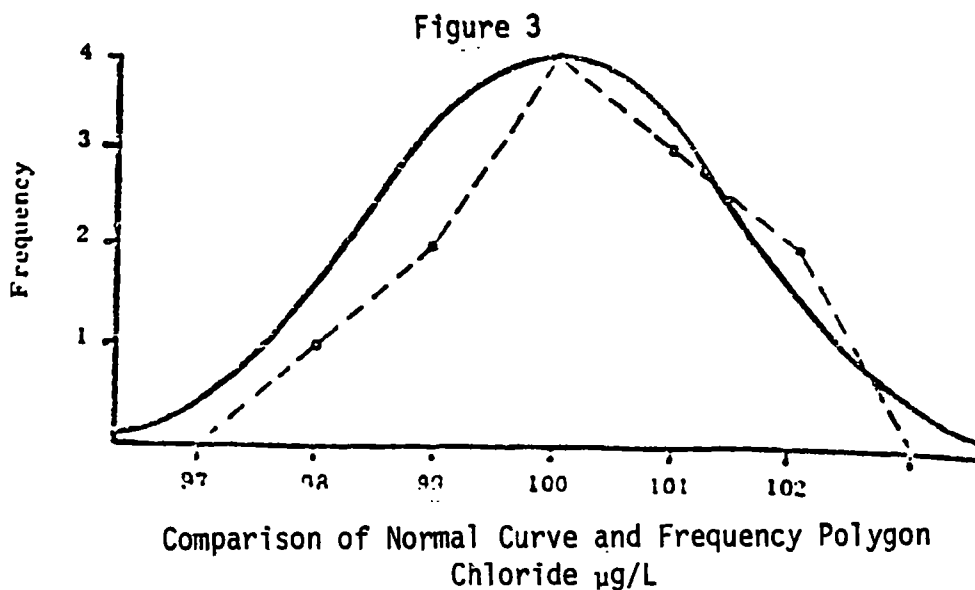
V. INTRODUCTION TO NORMAL DISTRIBUTION CURVE

A. Statistics deal with theoretical curves which are smoother than the frequency polygons, that are obtained from experiments in real life. However, frequency distributions or frequency polygons of experimental data often approximate a mathematical function called the "normal" distribution curve. (See Figure 2)

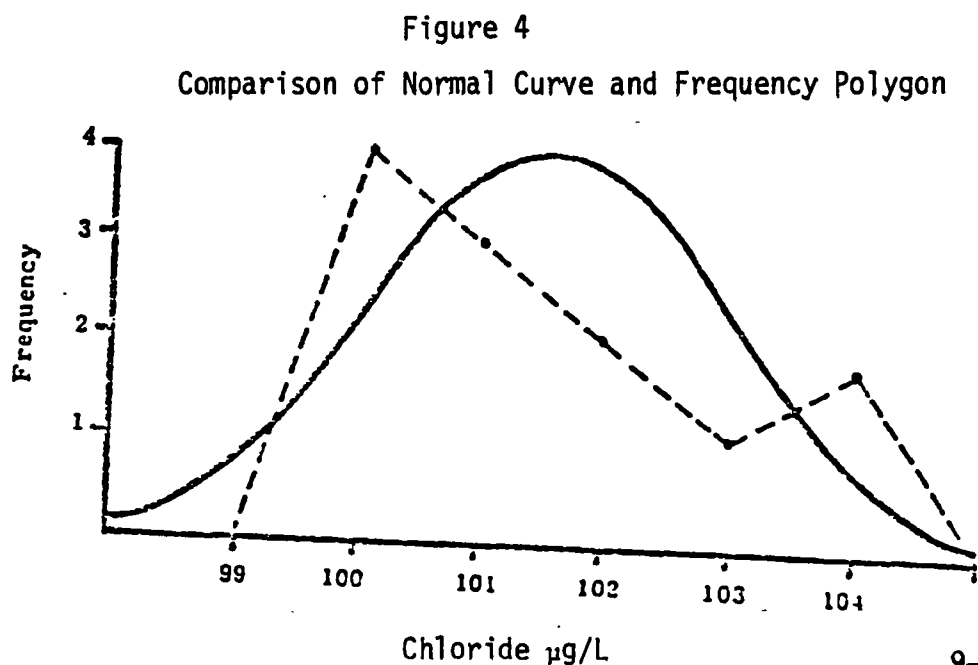
Figure 2
Normal Distribution Curve



As shown in Figure 3, the frequency polygon for the 12 determinations for chloride in water is a fairly good approximation of the normal curve.



If, however, in the chloride determinations we had obtained 103 $\mu\text{g/L}$ instead of 98 $\mu\text{g/L}$ and 104 $\mu\text{g/L}$ instead of 99 $\mu\text{g/L}$ this distribution would not have been a good approximation of the normal curve, as is shown by the frequency polygon in Figure 4.



- B. If a frequency distribution is a good approximation of the normal curve, we can use some facts about the normal curve to give us information about the frequency distribution.

The normal curve has the following equation:

$$Y = \frac{1}{\sigma \sqrt{2\pi}} e^{-(x_i - \mu)^2 / 2\sigma^2}$$

where $\pi = 3.1416$

$e = 2.7183$

x_i = corresponds to point on the abscissa

Y = corresponds to point on the ordinate

σ^2 = variance

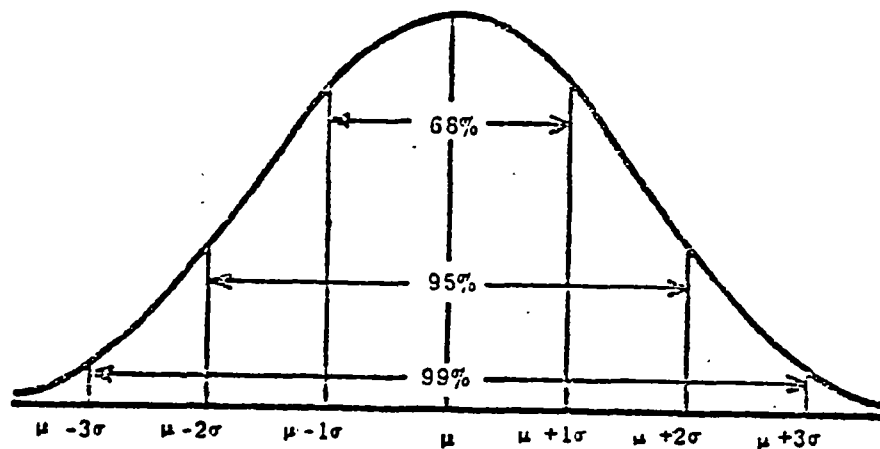
σ = standard deviation

μ = mean

The normal curve can be completely specified by σ , the standard deviation of the population of numbers represented by the curve, and by μ , the mean of the population of numbers. A population consists of a group of items or individuals.

Figure 5 shows the normal distribution in terms of the population mean, and the standard deviation of the population σ , and gives the percent of area under the curve between certain points.

Figure 5
Normal Distribution Curve



We may check the distribution of sample data to see if it is a "normal" distribution in the following manner. Substitute the value of the sample mean (\bar{X}) for the value of the midline and

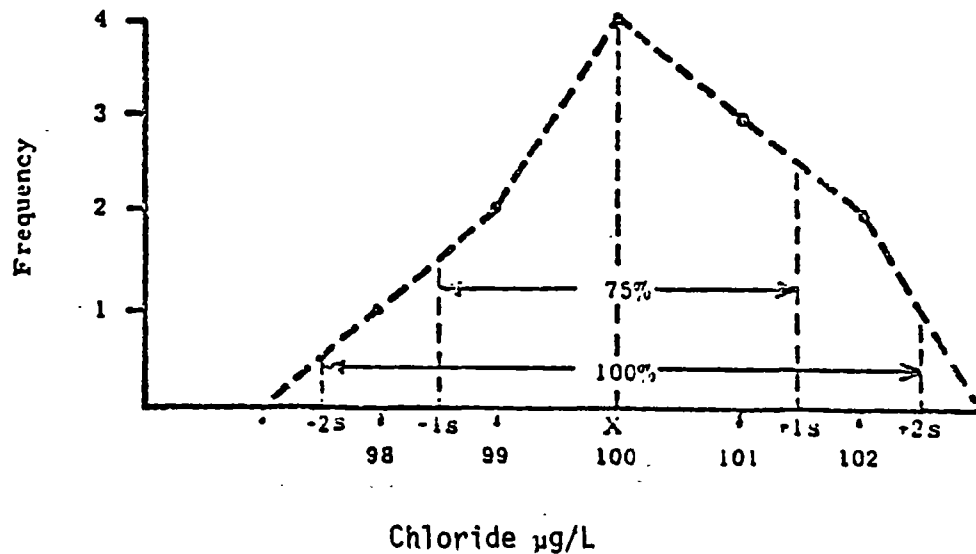
substitute the value of the sample standard deviation (s) for the limits of the value spans where we might expect certain percentages of the data items to occur. Then we can check the number of data items which actually do occur within these values spans.

Figure 6 demonstrates this application using the chloride data values from Table 1. The data values are marked on the horizontal line and the frequency of the occurrence of each value is marked on the vertical. The midline of the distribution is marked at the value of the sample mean ($\bar{X} = 100.25$, See III B 1). The value of the sample standard deviation ($s = 1.21$, See IV B 3) is used to mark value areas under the curve where different percentages of data values will probably occur. Thus, for the area $\bar{X} \pm 1s$, $\bar{X} - 1s = 99.04$ and $\bar{X} + 1s = 101.46$. Therefore, according to the normal distribution curve shown in Figure 5, we might expect about 68% of the data items to have values between 99 and 101. (The values are rounded to whole numbers since the data values are thus recorded).

Consulting Table 1, we find that 75% or 9 of the 12 data items have values in this range. This percentage is shown in Figure 6 by the frequency polygon for the data shown earlier in Figure 3.

Likewise assuming a normal distribution, we would expect 95% of the observations to lie within $\pm 2 \sigma$'s from the population mean. In fact, 100% of the observations were within $\pm 2 s$'s from the sample mean.

Figure 6
Frequency Distribution Polygon



The observed percentages of occurrences in Figure 6 are reasonably close to the percentages expected for normal distributions. A quick and dirty check for normality is to see if the mean, the mode and the median are all approximately equal. In a normal distribution, mean = mode = median. In our example mean = 100.25 µg/L, mode = 100 µg/L, and median = 100 µg/L.

It is also possible to check whether a series of measurements are normally distributed via a graphical technique using probability plot paper.

Probability paper allows one to check graphically whether or not data are normally distributed. It has the property of representing as a straight line, the plot of cumulative relative frequencies versus data, when those data were derived from a normally distributed population.

The procedure is as follows:

1. Find the upper class boundaries (see frequency histogram II A 3).
2. Calculate the cumulative relative frequencies as percentages using the formula:

$$P = 100(i-0.5)/n$$

where: P = cumulative relative frequency as a percentage

i = cumulative frequency

n = total number of data points

3. Plot the upper class boundaries (abscissa) versus P (ordinate).
4. Draw the line of best fit.
5. Using the pair of dots, located next to the vertical axes, locate the point where a horizontal line will intersect the line of best fit.
6. Project these intersections upward to where they intersect the proper line in the upper grid.

7. Construct the distribution curve.

Application: Consider the application of the above procedure to the previously mentioned set of data, obtained from twelve determinations for chloride in water, shown in Table I.

<u>Chloride ($\mu\text{g/L}$)</u>	<u>Frequency</u>	<u>Frequency Cumulative</u>	<u>P</u>	<u>Upper Class Boundary</u>
98	1	1	4.2%	98.5
99	2	3	20.8%	99.5
100	4	7	54.2%	100.5
101	3	10	79.2%	101.5
102	2	12	95.8%	102.5

Figure 7 depicts this data plotted on normal probability paper. The dashed lines show how one uses the pair of dots, located next to the vertical axes, to construct the distribution curve (steps 5, 6, and 7 of the procedure). From this plot the mean (\bar{X}) and the standard deviation (S) can be estimated. The mean is found by reading the value of the abscissa where the line intersects the cumulative frequency percent of 50 – (In our example \bar{X} is approximately equal to 100.5 $\mu\text{g/L}$). The standard deviation may be estimated by extrapolating the line until it intersects the top and bottom of the graph paper. These two points of intersection represents approximately 99.87% of the data, or $\bar{X} \pm 3S$. (In our example $\bar{X} \pm 3s$ is approximately equal to 104.6 – 96.9 = 7.7; s is approximately equal to 7.7 divided by 6 or 1.28 $\mu\text{g/L}$).

NORMAL PROBABILITY PLOT

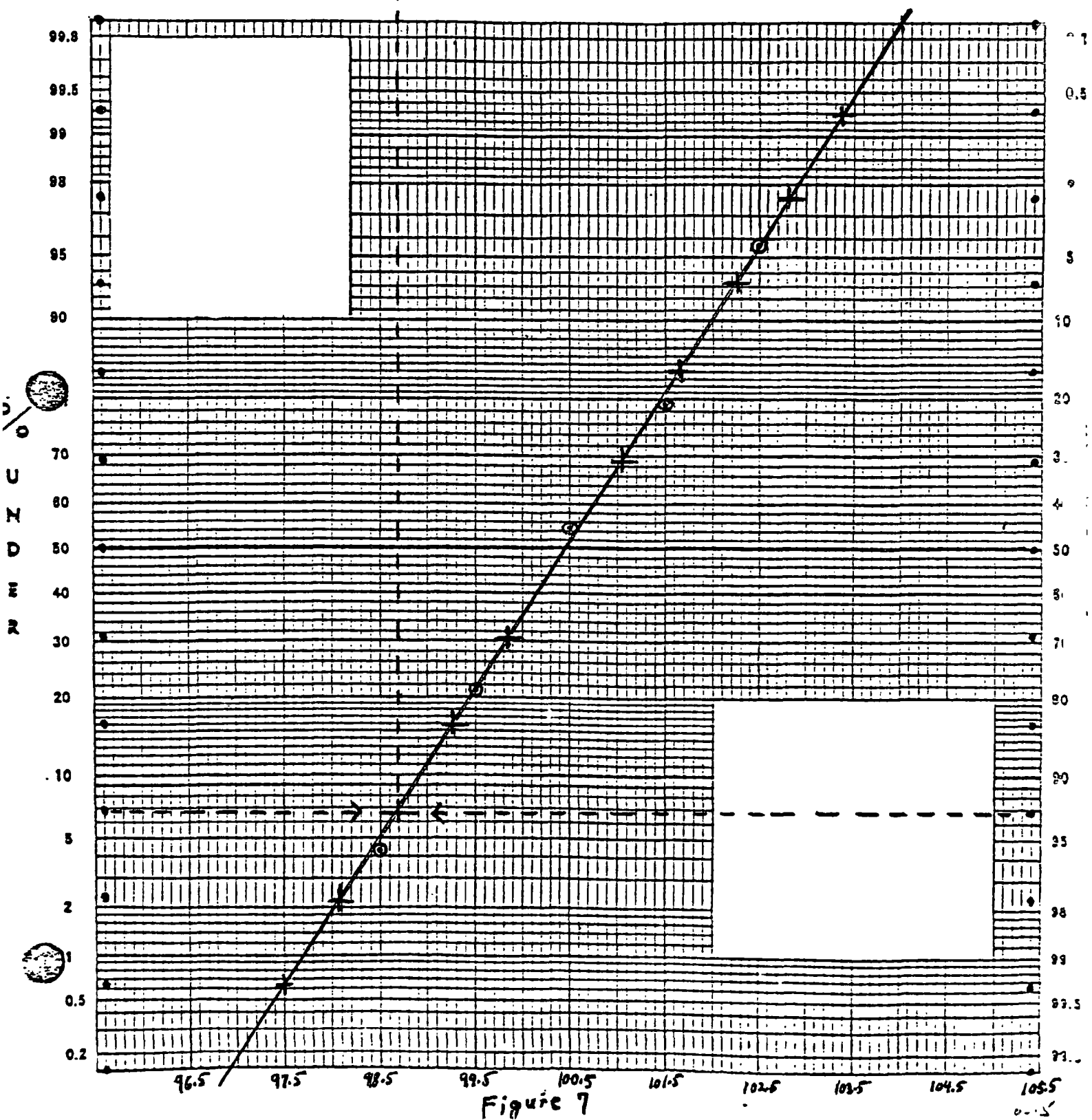
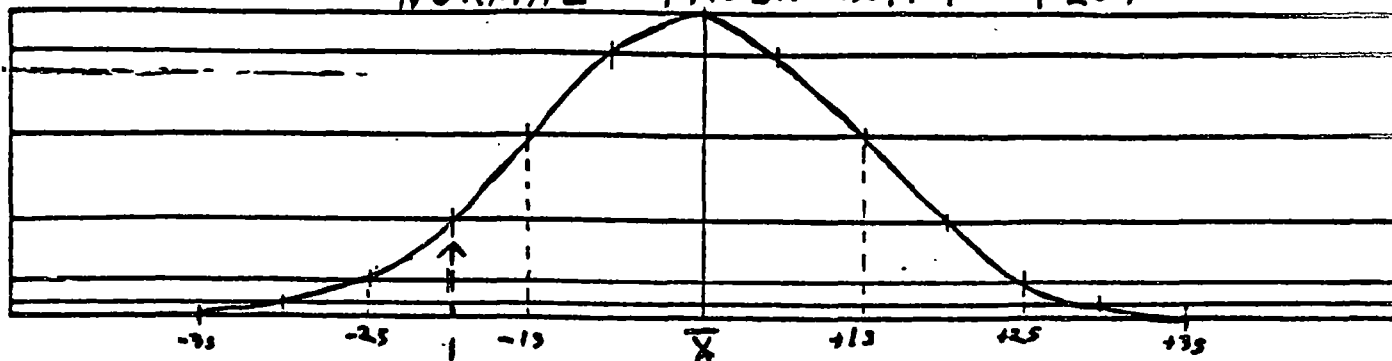


Figure 7

If data are not normally distributed, then the data will have to be transformed to make it normally distributed. Some common transformations are:

1. replacing x_i by $\log x_i$,
2. replacing x_i by $\sqrt{x_i}$
3. replacing x_i by $\frac{1}{x_i}$ or $\frac{1}{\sqrt{x_i}}$

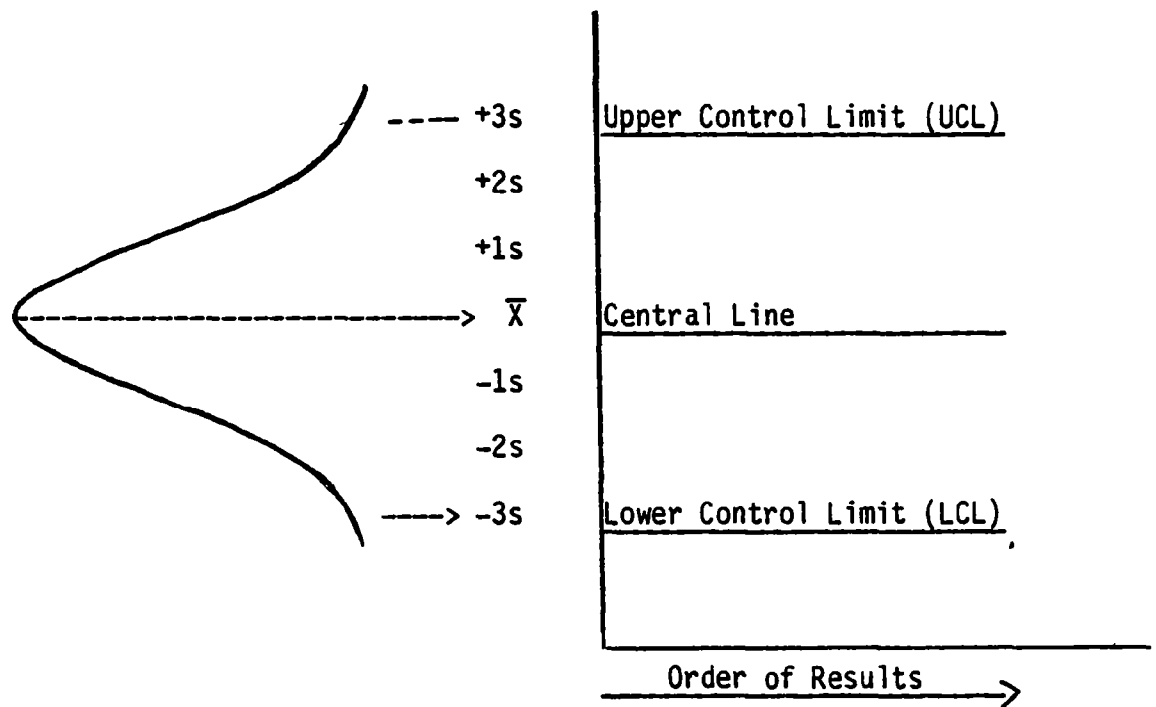
VI. CONTROL CHARTS

A. INTRODUCTION

As long as repeated samples/analysis exhibit only random errors the measurement process is in statistical control. The purpose of a quality control (QC) chart is to graphically detect lack of statistical control in the measurement process.

The relationship that exists between a normal curve and a control chart is probably best understood by looking at Figure 8 that depicts the two side-by-side.

Figure 8



Control charts may be kept on any of various characteristics (e.g., average (\bar{X}); percent recoveries (P), standard deviation (S), percent relative standard deviation (%RSD), range, percent relative range (%RR), etc.

Usually, the divisions of a control chart are not integer (whole number) factors times the standard deviation values, e.g., $3s$.

This is because s is calculated from a limited number of observations, and because the values in Table IV already have factored in $\frac{1}{\sqrt{n}}$ (this factor comes from the fact that we are concerned about fluctuations about averages – remember that the standard deviation of the mean is defined as

$$\frac{s}{\bar{x}} = \frac{s}{\sqrt{n}}$$

B. CONSTRUCTION OF CONTROL CHARTS

The American Society for Testing and Materials (ASTM) published Special Technical Publication 15D, entitled "ASTM Manual on Presentation of Data and Control Chart Analysis". This document is an excellent guide to preparing QC charts. Table III is a summary of some commonly used types of control charts.

Setting control limits

- Accumulate data by analyzing sets of replicates at a given concentration level or if historical data already exist you may use these values.
- Calculate the average of the needed characteristics.
- Look up in the appropriate table the factors for control limits (Table IV).
- Calculate central lines and the upper and lower control limits according to the formulas given in Table III:

Table III.

	<u>Central Line</u>	<u>Control Limits</u>
Averages using S	\bar{X}	$\bar{X} \pm A_3 \bar{S}$
Averages using R	\bar{X}	$\bar{X} \pm A_2 \bar{R}$
Standard Deviation	\bar{S}	$B_4 \bar{S}$ and $B_3 \bar{S}$
Ranges	\bar{R}	$D_4 \bar{R}$ and $D_3 \bar{R}$

Table IV

Observations in Sample, n	Chart for Averages		Chart for Standard Deviation		Chart for Ranges	
	Factors for Control Limits		Factors for Control Limits		Factors for Control Limits	
	A_2	A_3	B_3	B_4	D_3	D_4
2	1.880	2.659	0	3.267	0	3.267
3	1.023	1.954	0	2.568	0	2.575
4	0.729	1.628	0	2.266	0	2.282
5	0.577	1.427	0	2.089	0	2.115
6	0.483	1.287	0.030	1.970	0	2.004
7	0.419	1.182	0.118	1.882	0.076	1.924
8	0.373	1.099	0.185	1.815	0.136	1.864
9	0.337	1.032	0.239	1.761	0.184	1.816
10	0.308	0.975	0.284	1.716	0.223	1.777
11	0.285	0.927	0.321	1.679	0.256	1.744
12	0.266	0.886	0.354	1.646	0.284	1.716
13	0.249	0.850	0.382	1.618	0.308	1.692
14	0.235	0.817	0.406	1.594	0.329	1.671
15	0.223	0.789	0.428	1.572	0.348	1.652
16	0.212	0.763	0.448	1.552	0.364	1.636
17	0.203	0.739	0.466	1.534	0.379	1.621
18	0.194	0.718	0.482	1.518	0.392	1.608
19	0.187	0.698	0.497	1.503	0.404	1.596
20	0.180	0.680	0.510	1.490	0.414	1.586
21	0.173	0.663	0.523	1.477	0.425	1.575
22	0.167	0.647	0.534	1.466	0.434	1.566
23	0.162	0.633	0.545	1.455	0.443	1.557
24	0.157	0.619	0.555	1.445	0.452	1.548
25	0.153	0.606	0.565	1.435	0.459	1.541

Examples:

a. No Historical Data Given:

For example, suppose you wanted to construct a range chart (duplicates).

1. List the range (R) for each set of samples

<u>Duplicates</u>		<u>Range</u>
10.01	10.54	0.53
10.23	9.87	0.36
10.41	10.01	0.40
9.86	10.32	0.46
10.02	10.01	0.01
9.48	9.79	0.31
10.12	9.62	0.50
9.66	10.31	0.65
9.84	10.12	0.28
10.31	9.81	0.50

2. Calculate the average range by summing the list of R values and dividing by the number of sets of duplicates:

$$\bar{R} = \frac{\sum_{j=1}^m R_j}{m}$$

$$\bar{R} = \frac{4.00}{10} = 0.4$$

3. Calculate the Upper Control Limit (UCL) on the average range

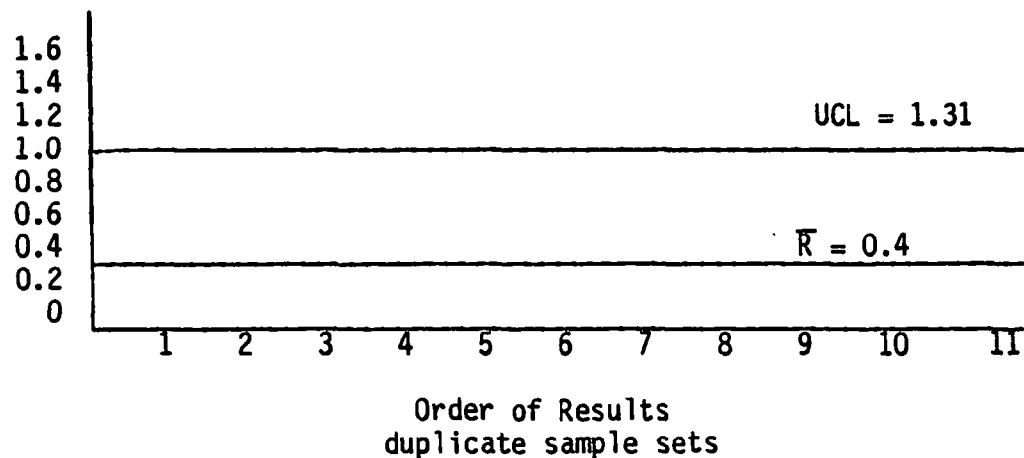
NOTE: The number of observations (n) in this sample are two (2) since duplicates were used here.

$$UCL = D_4 \bar{R} = 3.267 (0.4) = 1.31$$

4. Calculate the Lower Control Limit (LCL) on the range

$$LCL = D_3 \bar{R} = 0 (0.4) = 0$$

5. Graph R, UCL_R , and LCL_R



6. The above precision control chart is now complete, and can be used to plot R values from subsequent duplicate samples to determine if the sample/analysis is in control, out of control (plotted R value beyond UCL_R or LCL_R), and/or to detect any trends developing within the process.

b. Historical Data Given:

If a method reports or states performance characteristics, then until you can accumulate enough data to calculate your own, you could establish control limits using the reported historical data. NOTE: It is always preferable to collect enough data to calculate your own performance characteristics.

For example, suppose you wanted to construct a mean recovery (\bar{X}) using an R chart (duplicates) for the analysis of toluene using Method 503.1. Table V presents historical performance characteristics data given in the method.

1. Calculate the central line

Historical Data

spike level = 0.40 $\mu\text{g/L}$

mean % Recovery = 93%

$$\bar{X} = (\text{spike level}) (\% \text{ Recovery}) = (40\mu\text{g/L}) (0.93) = 0.37 \mu\text{g/L}$$

2. Calculate the range

$$\frac{R}{d_n} \cong s \quad R \cong s d_n$$

Historical Data

$s = .022 \mu\text{g/L}$

$$R = (.022) (1.128) = .025 \mu\text{g/L}$$

3. Calculate Upper Control Limit (UCL)

$$UCL = \bar{X} + A_2 \bar{R} = 0.37 \text{ } \mu\text{g/L} + (1.880) (.025) = 0.4170 \text{ } \mu\text{g/L}$$

4. Calculate Lower Control Limit (LCL)

$$LCL = \bar{X} - A_2 \bar{R} = 0.37 \text{ } \mu\text{g/L} - (1.880) (.025) = 0.3230 \text{ } \mu\text{g/L}$$

TABLE V

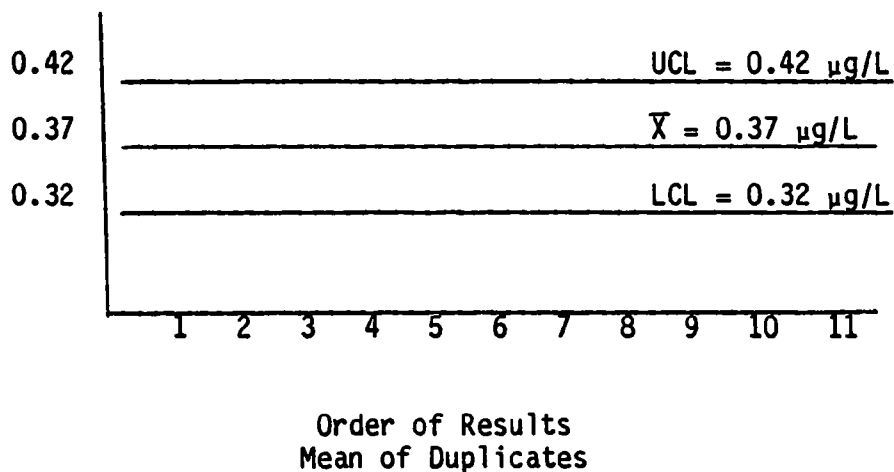
Single Laboratory Accuracy and Precision for Aged Samples Containing Aromatic Compounds
and Selected Organohalides Spiked Into Chlorinated Drinking Water

Compound	Spike Level ($\mu\text{g/L}$)	Day 1 Recovery (%)	Samples Analyzed ^a	Mean Recovery (%)	Relative Standard Deviation (%)	Standard Deviation (%)	Length of Study (days)
Benzene	0.40	100	7	100	0.082	2.1	15
Trichloroethylene	0.50	103	10	104	0.037	7.0	28
a-Trichlorotoluene	0.50	100	9	89	0.048	11.0	28
Toluene	0.40	100	7	93	0.022	5.7	15
Tetrachloroethylene	0.50	108	10	104	0.040	7.7	28
Ethylbenzene	0.40	103	7	93	0.032	8.5	15
1-Chlorocyclohexene-1	0.50	96	10	91	0.029	6.4	28
p-Xylene	0.40	95	7	85	0.029	8.7	15
Chlorobenzene	0.50	96	10	96	0.029	6.1	28
m-Xylene	0.40	95	7	90	0.028	7.7	15
o-Xylene	0.40	93	7	90	0.026	7.2	15
iso-Propylbenzene	0.40	93	7	88	0.030	8.7	15
Styrene	0.40	0.00	7	0.00			0*
p-Bromofluorobenzene	No Data						
m-Propylbenzene	0.40	90	7	83	0.030	9.3	15
t-Butylbenzene	0.40	95	7	88	0.030	8.7	15
o-Chlorotoluene	No data						
p-Chlorotoluene	0.50	94	8	93	.022	4.9	13*
Bromobenzene	0.50	96	10	93	.030	6.4	28
sec-Butylbenzene	0.40	85	7	80	0.034	11.0	15
1,3,5-Trimethylbenzene	0.50	96	10	92	0.040	8.7	28
p-Cymene	0.80	92	5	88	0.012	2.8	6*
1,2,4-Trimethylbenzene	0.40	83	7	75	0.029	8.7	15
p-Dichlorobenzene	0.50	106	10	100	0.029	8.7	28
m-Dichlorobenzene	0.50	96	10	92	0.040	8.7	28
Cyclopropylbenzene	No data						
m-Butylbenzene	0.40	90	7	78	0.049	16	15
2,3-Dibenzofuran	0.40	14	7	0.0	-	-	0*
o-Dichlorobenzene	0.50	102	9	92	0.033	7.1	28
Hexachlorobutadiene-1,3	0.50	88	10	74	0.062	17	28
1,2,4-Trichlorobenzene	0.50	94	10	88	0.047	11	28
Naphthalene	0.50	108	8	96	0.062	13	20*
1,2,3-Trichlorobenzene	0.50	100	10	85	0.046	11	28

^a Samples randomly analyzed throughout the study period.

* Maximum recommended holding time.

5. Graph \bar{X} , UCL and LCL



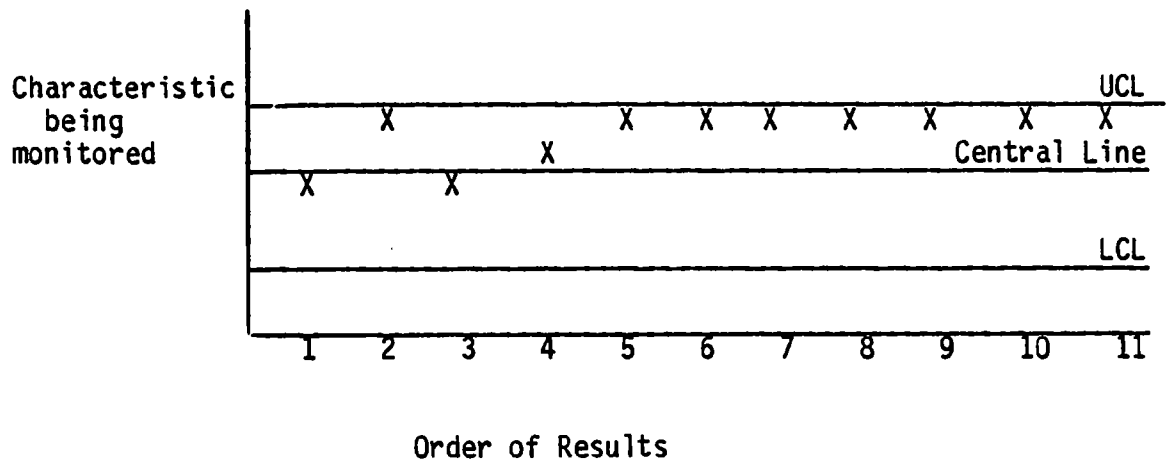
6. The above \bar{X} control chart is now complete and can be used to plot mean values of subsequent duplicates to determine if the sample/analysis is in control, out of control (plotted \bar{X} values beyond UCL or LCL), and/or to detect any trends developing within the process. Note this chart is only applicable when the dosing level is 0.40 $\mu\text{g/L}$.

NOTE: If the plotting of 30 subsequent means of duplicate indicates that your analytical system is in control, you should use your own data to construct a new chart.

VII. INTERPRETATION OF CONTROL CHARTS

Examples:

1. In this example, a trend has developed; the characteristic being monitored has changed (8 consecutive points lie to one side of the central line). If the change is detrimental then all variables in the procedure should be checked in an attempt to stop this deterioration of the process.

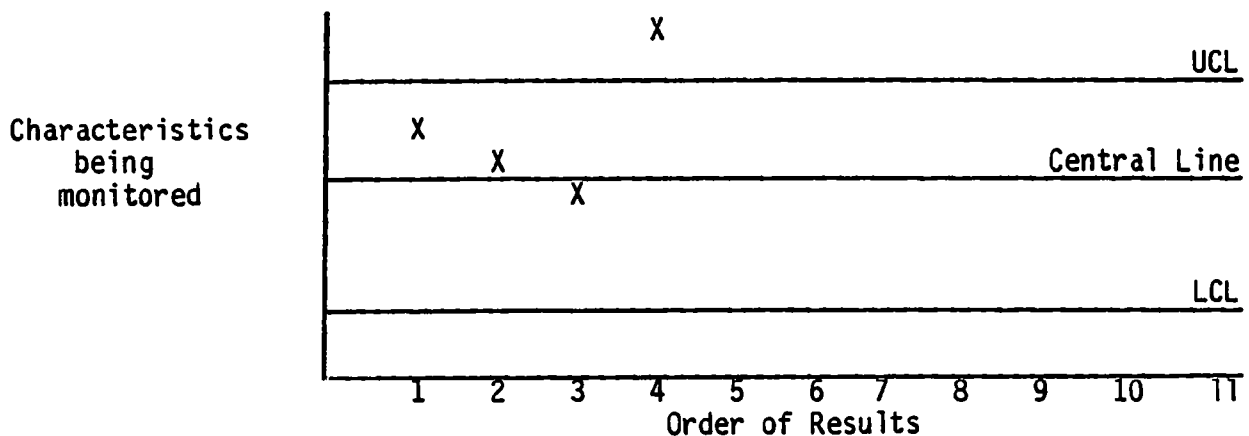


When only random errors occur the probability that a result will lie above the central line is 0.5 (50%), and the probability that a result will lie below the central line is also 0.5 (50%). The probability that seven consecutive results will lie on the same side of the central line given that the one immediately preceding the seven also lies on the same side of the central line (conditional probability) is given by the following expression:

$$\frac{(0.5)^8}{(0.5)} (0.5)^7 = .0078$$

The probability that this event would happen by chance alone is .0078, (0.78%); a very unlikely event - less than one chance out of 99.

2. In this example, a gross error has occurred, the characteristic being monitored has gone outside of the control limits. At this point the system can be stopped and all variables in the system checked. Once the system has been corrected, all samples between sample set 3 and 4 should be rerun to insure the validity of the data.



When only random errors occur the probability that a result will lie above the upper control line is 0.01 (1%); a very unlikely event - one chance out of 99.

Control chart data are normally generated by analyzing sets of quality control samples – the analytes of interest may be placed in either laboratory pure water or a standard water that matches the type of matrix normally analyzed in your laboratory. Control charts should be reconstructed (updated) periodically, because the performance characteristics may change (when 30 data points have been collected, can use newer data to construct a new chart), for the better, with time.

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Unit 10

QUALITY CONTROL

I. INTRODUCTION

The purpose of the Safe Drinking Water Act is to assure the public of an adequate supply of safe water. To achieve this, maximum levels of certain contaminants were proposed along with the prescribed methodology for analyzing for these parameters. When a laboratory performs these analyses, the laboratory should practice quality control to assure that the results being reported are true values and not in error.

Data developed from these examinations must be reliable and beyond reproach. The data can be used for making judgments on technical operations in water treatment or in legal actions involving public health hazards. For these reasons the "Criteria and Procedures" manual has set down some critical and some recommended QC procedures.

The entire critical elements for certification section contained in the "Criteria and Procedures" manual is considered as the minimum acceptable program on quality control that a laboratory can carry out and still expect reliable results. Most laboratories will want to go beyond these minimum critical requirements and include more quality control.

This outline will cover the minimum critical quality control procedures, then go into the recommended practices portions and proceed further into some ideas not in the "Criteria and Procedures" manual. The reasons for going further are to acquaint laboratory certification personnel with sufficient information to be able to evaluate whether the laboratory has complied with the minimum critical sections and allow the Certification Officer to recommend further procedures. The topic of quality control from all aspects in a laboratory is well covered in the Handbook for Analytical Quality Control in Water and Wastewater Laboratories EPA-600/4-79-019 produced by the USEPA and available from the Center for Environmental Research Information. The Certification Officer should keep in mind that technical assistance to the laboratory he/she is evaluating is of prime importance because through this assistance he/she can upgrade the laboratory to produce better results.

Assistance to state Certification Officers can be obtained from the regional certification authority, the Analytical Quality Control Officer in the region, or EMSL-CI.

II. CRITICAL ELEMENTS

A. General

1. The laboratory should prepare and follow a written QA plan. It is essential that all laboratories analyzing drinking water

compliance samples adhere to defined quality assurance procedures. This is to insure that routinely generated analytical data are scientifically valid and defensible and are of known and acceptable precision and accuracy. To accomplish these goals, each laboratory should prepare a written description of its quality assurance activities (a QA Plan). The following items should be addressed in each QA plan.

a. Sampling procedures.

b. Sample handling procedures

- specify procedures used to maintain integrity of all samples, i.e., tracking samples from receipt by laboratory through analysis to disposal.
- samples likely to be the basis for an enforcement action may require special safeguards (Chain-of-Custody procedures).

c. Instrument or equipment calibration procedures and frequency of their use.

d. Analytical procedures.

e. Data reduction, validation and reporting.

- data reduction: conversion of raw data to $\mu\text{g/L}$, picocuries/L, coliforms/100 mL, etc.
 - validation: includes insuring accuracy of data transcription and calculations.
 - reporting: includes procedures and format for reporting data to utilities, State officials, and USEPA.
- f. Types of internal quality control checks and frequency of their use.
- may include preparation of calibration curves, instrument calibrations, replicate analyses, use of EMSL-provided QC samples or calibration standards and use of QC charts.*
- g. Preventive maintenance procedures and schedules.
- h. Specific routine procedures used to determine data precision and accuracy for each contaminant measured.
- precision is based on the results of replicate analyses.

*QC chart for chemistry is explained in Handbook for Analytical Quality Control in Water and Wastewater Laboratories, EPA-600/4-79-019, March 1979.

- accuracy is normally determined by comparison of results with "known" concentrations in reagent water standards and by analyses of water matrix samples before and after adding a known contaminant "spike".

i. Corrective action contingencies.

- response to obtaining unacceptable results from analysis of PE samples and from internal QC checks.

The QA plan may consist of already available standard operating procedures (SOP's) which are approved by the laboratory director and which address the listed items, or may be a separately prepared QA document. Documentation for many of the listed QA plan items can be by reference to appropriate sections of this manual, the laboratory's SOP's or to other literature (i.e., Standard Methods for the Examination of Water and Wastewater).

If a particular listed item is not relevant, the QA plan should state this and provide a brief explanation (e.g., some laboratories never collect samples and thus have no need to describe sampling procedures). A laboratory QA plan should be concise but responsive to the above-listed items (a maximum of five pages is suggested). Minimizing paperwork while improving dependability and quality of data are the intended goals.

2. All quality assurance data should be available for inspection.

All quality control data must be available for inspection.

This statement assures the availability of the data. The person certifying the laboratory might wish to make use of these data to assure himself that the laboratory is practicing quality control and to what extent. After an amount of data have accumulated, it can serve as a record of a continuing type of quality control rather than a sporadic, hit or miss type. At any time, should there be questions on the reliability of any data, the quality control records will be available to show the reliability of the data produced during the time period in question.

The guidelines for data reporting recommend that the records of chemical analyses should be kept by the laboratory for not less than three years. It would seem prudent that all quality control data be kept for a like period of time.

Data required would include a record of the results of the yearly performance sample, a standard curve for each method the laboratory has been certified for, the records showing a check of this curve daily or each time the analysis is carried out. If the laboratory analyzes 20 or more samples per day, records should include the value of a standard run after every 20 samples. Again, this is for

a minimal program and it would be well for laboratories to adopt at least the recommended procedures listed in the "Criteria and Procedures" manual.

3. All laboratories must analyze an unknown performance evaluation sample once a year.

Laboratories must perform on an unknown performance sample once per year for parameters measured.

In a minimal program this yearly check sample would be the first external indication of a problem in a laboratory to the certifying authority. The required daily quality control data would not be sent to the certifying authority. If unacceptable answers were obtained for one or more parameters, the laboratory would be asked to analyze a follow-up performance sample. If continued problems existed, the certifying authority could offer some form of technical assistance to rectify the problem. If the data are borderline or perhaps sporadic in nature, the Certifying Officer might wish to schedule his next visit at a time when the questionable analytical method is being performed.

The principal state laboratory, as well as local laboratories, will be required to analyze an unknown performance sample. This sample will be provided by the regional authority which will certify that

laboratory in each state. The USEPA also plans to make available to states samples which can be used as performance samples for local laboratories which the state has responsibility for certifying. The performing laboratory will be given results of their analysis in terms of being within or out of the acceptable limits.

Results must be within the control limits established by USEPA for each analysis for which the laboratory wished to be certified.

The laboratory will be informed if they have or have not complied with this requirement by the authority supplying the performance sample.

4. A manual of analytical methods should be available to the analysts.

Usually the laboratory will provide to the certification team, before its arrival at the laboratory, a list of the approved methods used by the laboratory. The list should include methods for all contaminants analyzed by the laboratory. The laboratory should at least have copies of the approved methods reference. That is either the USEPA's Methods for Chemical Analysis of Water and Wastes EPA-600/4-79-020, the 14th ed of Standard Methods, or others as listed in the footnotes in Table 1 of Unit 3.

The laboratory could also prepare a methods manual of their own which would gather the approved methodology of the laboratory into one volume.

Either way, analysts should be able to have access to the approved methods. This should hold to a minimum the deviations that analysts might carry out if left to their own procedures.

5. Meters for pH should be calibrated each use period with fresh standard buffers.

Good procedures for the use of a pH meter should be followed, a good discussion is included in the Standard Methods write up of method 424.

B. Inorganic - Critical Elements

1. A standard curve must be prepared and kept for each parameters the laboratory analyzes for. This curve must be prepared with a minimum of blank and three standards. The references for the analytical methods will provide the laboratory with the range of the test. Good procedure would dictate choosing the three standards to cover this entire range. A high, low and mid-range standard would be best to run at least one of the stanards should be at or below the MCL. In order to assure

good coverage the laboratory should be encouraged to run more than the minimal requirements as listed above. A good recommended procedure is to prepare the initial curve with a blank and eight standards covering the entire range.

If more than one analyst will run the same test, it would be wise to have each analyst check their procedural technique by checking the standard curve.

2. After the initial curve has been established, it should be verified each day on which analysis are performed by the use of at least a reagent blank and one standard which is within the range of the standard curve. Again, the Certification Officer should encourage more than the required minimum daily check. The recommendation for good technique recommends a blank and two standards, one high and one low concentration.
3. These required daily checks of the standard reagent curve should be with $\pm 10\%$ of the original concentration value. For example, if the MCL was 0.50, a standard at this level analyzed as an unknown should fall between 0.55 and 0.45. If not, the analyst should check in the following order:
 - a. Any variable instrument parameters
 - b. Rerun check sample.

- c. Prepare new standard.
- d. Prepare all reagents fresh.
- e. Check shelf life of chemicals.
- f. Check instrument.

If the value persists at the new value through all this, then the analyst should prepare a new standard curve.

- 4. If 20 or more samples per day are analyzed, the working standard curve must be verified by running an additional standard at or near the MCL every 20 samples. Checks must be within ± 10 percent of original curve.

C. Organic – Critical Elements

- 1. Laboratory method blanks must be run.

For each day on which pesticides or phenoxyacid analysis are initiated or TTHM reagent water is prepared, it is essential that a laboratory method blank be analyzed with the same procedures used to analyze samples. This will assure that no TTHM's are present in the reagent water and further that no

interfering compounds are present in the reagents used in the pesticide or herbicide analysis.

2. A minimum of three calibration standards should be analyzed each day to calibrate the analytical system.

It is recommended that a blank and three standards that cover the working range be used. It would be a good idea to insert a fourth standard that would be slightly above the working range. Thus calibration series will indicate problems with reagents if the blank shows contamination and will also prove that the system is functioning properly and is linear.

If the laboratory can demonstrate that the instrument response is linear through the origin, this practice can be reduced to one standard per day, providing the response of the standard is within ± 15 percent of previous calibration.

3. Certified quality control check standards should be run each quarter for each contaminant.

If the criteria established by USEPA are not met, corrective action needs to be taken and documented. Such standards can be obtained from EMSL-CI.

4. Field blanks for trihalomethanes should be run with each set.

Several instances of accidental sample contamination have been noted and attributed to diffusion of volatile organics through the septum seal and into the sample during shipment and storage. The field blank is used as a monitor for this problem.

Impurities contained in the purge gas and organic compounds outgassing from the plumbing ahead of the trap usually account for the majority of contamination problems. The presence of such interferences are easily monitored as a part of the quality control program. When a positive TTHM response is noted in the field blank, the analyst needs to analyze a method blank in order to ascertain if the contamination problem is indigenous to the samples or to the instrument system. .

If reportable levels of TTHM's are demonstrated to have contaminated the field blank resampling is essential.

5. Ten percent of all TTHM samples should be run in duplicate.

This is a normally accepted quality control technique. A continuing record of results and subsequent actions taken needs to be maintained.

6. The laboratory needs to analyze a known TTHM laboratory control standard each day.

This will assure the analyst that the system is in control.

However, if errors exceed 20 percent of the true value, all TTHM results taken since the previous successful test are to be considered suspect.

7. Each time the TTHM analytical system undergoes a major modification or prolonged period of inactivity the precision of the system needs to be demonstrated by the analysis of replicate laboratory control standards.

By checking the system, such variables as the degree of trap conditioning, the degree of desorption from the trapping column and the purging efficiency of each compound can be compared to previous efficiencies. Small variations in purge time, purge flow rate, or purge temperature can affect analytical results. By keeping proper records of these variables the same precision of analysis can be monitored.

8. Analysis of TTHM by liquid-liquid extraction must include analysis of raw source waters.

Since the TTHM's are formed as part of the disinfection by chlorination in the plant, the raw source water must be monitored to provide data on interfering compounds. This liquid-liquid extraction technique efficiently extracts a wide boiling range of nonpolar organic compounds and, in addition, extracts the polar organic components of the sample with varying efficiencies. The absence of peaks in the raw source water analysis with retention times similar to the trihalomethanes is generally adequate evidence of an interferences - free finished drinking water analysis.

When potential interferences are noted in the raw source water analysis, an alternate analysis or the use of alternate chromatographic columns must be used to reanalyze the sample set. If interferences are still noted, qualitative identifications should be performed by using dissimilar columns or by GC/MS. If the peaks are confirmed to be other than trihalomethanes and add significantly to the total trihalomethane value in the finished drinking water analysis, then the sample set must be analyzed by another method.

9. When GC/MS analysis is used it is essential that performance tests using bromofluorobenzene be conducted once each eight-hour work shift. This test is covered in the section on Instrument and Equipment Needs and Specifications, Unit 12, and in the "Criteria and Procedures" manual.

III. RECOMMENDATIONS

The following items are classed in the "Criteria and Procedures" manual as recommended. However, a certain amount of importance must be attached to each item. The committee preparing the document felt strongly enough about these items to keep them in the document. Common laboratory practice would assure that these items be carried out.

1. Current Service Contract on All Balances

The analytical balance is of great importance in a laboratory. As reagents are weighed on this piece of equipment, care must be taken to assure that it is in good working order. The laboratory Certification Officer should question the head chemist as to the existence of a service contract on the balances. Should the laboratory Certification Officer need additional information on proper care of a balance there is a section in the Handbook for Analytical Quality Control in Water and Wastewater Laboratories EPA-600/4-79-019.

2. Class S weights Available to Make Periodic Checks on Balances

This could be included as part of the routine service contract or a set purchased and shared with the bacteriological laboratory which will also have need for them. A very complete set of directions for checking the performance of a balance is contained in Part 30 of ASTM Standards.

3. NBS - Certified Thermometer Available to Check Thermometers in Ovens, etc.

Again this item could be a shared item between chemical and bacteriological laboratories. The Certification Officer could carry this item with him and provide this service to the smaller type laboratories. Since this item is only recommended, the Certification Officer can only question if this thermometer is available and used.

4. Color Standard or Their Equivalent Available to Verify Wavelength Settings on Spectrophotometers.

The spectrophotometers should be checked for wavelength alignment. If a particular colored solution is to be used at a closely specified wavelength, considerable loss of sensitivity can be encountered if the wavelength control is misaligned. In visual instruments, an excellent reference point is the maximum absorbance for a dilute solution of potassium permanganate, which has a dual peak at 526 $m\mu$ and 546 $m\mu$. On inexpensive graphing instruments, which possess less resolution than the prism instruments, the permanganate peak appears at 525 to 550 $m\mu$ as a single flat-topped spike.

Another point that should be mentioned is the care and use of spectrophotometric absorption cells. If possible, the Certification Officer should observe the techniques of the laboratory in the use of the cells. Good techniques here could indicate good technique in all the colorimetric procedures.

5. Chemical Dated Upon Receipt of Shipment and Replaced as Needed or When Shelf Life is Exceeded.

It should not be necessary to store clean glassware or chemicals on bench tops. Floor length cabinets or about bench cabinets should be available for storage. Chemicals themselves should be of analytical reagent grade to assure good quality. Dating the chemical upon receipt will give the chief chemist an indication of the amounts to order and if the chemical can still be relied on to have its initial quality.

6. Laboratories Analyzing Water Supply Samples Other Than Its Own Should Carry Out Additional Quality Control. This section covers additional optional items for the larger laboratories.

- a. Laboratory should perform on a known reference sample (when available) once per quarter for the parameters measured.

Since the yearly known performance sample will not indicate to the laboratory how well it is doing, other than pass or fail, a known sample will show how the laboratory compares in precision and accuracy to that given for the various methods. Analysis of the known sample will allow comparison and show any trend of the quality control of the laboratory. These data should be available to the Certification Officer for inspection.

This known quality control check sample should be available to the laboratory from the principal state laboratory. If not, a synthetic sample prepared by the head chemist can be used. This control can be a large sample from a natural source known to contain the constituents of concern or a synthetic sample prepared in the laboratory from chemicals of the highest purity grade. In either case, if the control is to be kept, it should be stabilized by addition of a suitable preservative. See the section on sampling for the choice of preservative.

- b. The measured value should be within the control limits established by USEPA for each analysis for which the laboratory wishes to be certified.

Precision data can be found in one or the other standard references. That is

- 1) Standard Methods for the Examination of Water and Wastewater, 13th Edition (1971).
- 2) Manual of Methods for the Chemical Analysis of Water and Wastes EPA-600/4-79-020, 1983 edition. Not available any longer.

These data have been accumulated in Table I. If this data does not fulfill the need of the Certification Officer, he may write to the USEPA, EMSL, Cincinnati, Ohio 45268 and request additional information on accuracy and precision.

- c. At least one duplicate sample should be run every 10 samples, or with each set of samples, to verify the precision of the method. Checks should be within the control limits established by USEPA for each analysis for which the laboratory wishes to be certified.

In order to document that reproducible results are being obtained (i.e. precision of the method), it is necessary to run duplicate samples. Although the frequency of such

replicate analysis is, by nature dependent on such factors as the original precision of the method, the reliability of the instrumentation involved and the experience of the analyst, good laboratory technique is to run duplicate analysis at least 10 percent of the time. The resulting data should be within the control limits established by USEPA. If the data do not agree, the system is not under control, and results are subject to question.

- d. Standard deviation should be calculated and documented for all measurements being conducted.

This calculation will provide the upper and lower control limits for the test. Analysts can then determine whether or not the data produced is acceptable. This data can be calculated on seven replicate determinations for initial comparison. However, as additional determinations are performed, they should be added to existing data and the precision data recalculated. Twenty or more runs tend to present better statistical data.

Standard deviation calculations should be determined for each analyst to carry out the analysis. However, the data should not be collected until the analyst is familiar with the procedure. The concentration used to calculate the

standard deviation should be at the level expected in the sample for those laboratories doing only their own water. For laboratories doing determinations other than their own supply it would be best to have the standard deviation calculated at several concentrations. However, for a minimal effort, the concentration should be chosen at or close to the maximum contaminant level for the parameter.

In order to assure these data are collected, the standard run after each 20 samples could be at the concentration used to determine the standard deviation. This would produce a constant flow of this data for inclusion in future updates of the standard deviation calculation.

- e. Quality control charts or a tabulation of mean and standard deviation should be used to document the validity of data on a daily basis.

If the upper and lower control limits of ± 2 standard deviations are calculated, the analyst will have some idea as to the acceptability of each determination as the results are obtained. When outliers are found the analyst can reschedule these for analysis to assure themselves of the result before action is taken to call for a resample of the supply.

Production of quality control charts and subsequent graphing of the charts of data obtained in the laboratory will give pictorial representations of the control of the method. Tendencies toward one or the other control limit will indicate loss of control of the method.

How to produce quality control charts and a discussion of these statistical tools is covered in Basic Statistics Unit 9 and in the Handbook for Analytical Quality Control in Water and Wastewater Laboratories EPA-600/4-79-019.

IV. SUMMARY

The quality control items in the "Criteria and Procedures" manual identify a minimal effort for all types of laboratories. Since quality control is for the benefit of the laboratory in assuring valid data, it would seem wise for all laboratories to practice a good deal more quality control than is set down in the manual.

This section has discussed the quality control steps to be taken to assure proper analytical performance in the laboratory. However, a complete picture of quality control would include adherence to proper sampling techniques, including collection, preservation and handling; use of acceptable methods, and proper reporting of data to be considered. It must be recognized (and practiced) however, that quality control begins with collection and does not end until resulting data are reported.

UNIT 11
PREPARING A REPORT OF THE
LABORATORY CERTIFICATION SURVEY

I. INTRODUCTION

A narrative report should be jointly prepared by the entire certification team. Each team member is responsible for the section pertaining to his expertise. This report should contain a copy of all information pertinent to the evaluation and its disposition, including a copy of the on-site evaluation form used by each team member involved. The report should also recommend analysis for which certification can be awarded upon approval by the appropriate director of laboratory certification/QA director and/or the director of water program.

As part of the on-site evaluation, each team member should discuss the results of the on-site visit with the laboratory director. Some prediscussion time should be used by the team members to assure that complete coverage of their findings are discussed. If this is done, then the final written report will contain as little new or undiscussed material as possible.

When the evaluation is carried out by the team members of a regional inspection authority, copies of the report should be sent to the Regional Administrator for consideration. The Regional Administrator will notify the

State of his concurrence or exception and forward the entire report to the State. State evaluation of local laboratories will route the report to the officer responsible for State certification, who will in turn inform the local laboratories of the results. Copies of the report should always be retained by the Certification Officer to be used in case questions arise and to refresh his mind before the next evaluation of the laboratory.

II. THE REPORT

Since the State accepting primacy will set up its own reporting form, there is no set format for the report. However, each section of the report form should be discussed clearly, stating which items are critical and which are recommendations.

A. Personnel (Recommendation)

Under this topic the Certification Officer could summarize those personnel available to the laboratory at the present time, pointing out, if necessary, what is required to upgrade the personnel to meet the guidelines as stated in the "Criteria and Procedures" manual. If a serious understaffing exists in a laboratory, the Certification Officer should recommend the additional personnel needed by the laboratory in this section. The Certification Officer could also recommend any training he

feels would benefit the personnel to help them to better perform their duties. In this section the certification officer might designate which personnel are deemed essential and for which notification of the certifying authority is necessary if loss or replacement occurs.

B. Laboratory Facilities (Recommendation)

Discuss all topics showing where improvements or changes are suggested. For example, one of the more important items covered under this topic is the source of distilled/deionized water. The inspector might suggest a larger capacity or different type or better analysis to assure quality.

C. Laboratory Equipment and Instrument Specifications (Recommendation)

Although classified as a recommendation this area is important. If a lack of equipment is evident or if the instrument is not approved for the analysis it is being used for, this would relate directly to the methodology which is a mandatory section. The laboratory evaluator would also point out the items which might need to be updated or added to.

D. General Laboratory Practices (Recommendation)

This section would be important from the standpoint of quality

assurance. Improper glassware preparation could indicate a future trouble area in analytical analysis.

E. Methodology (Critical)

Since the methods to be used for the analysis of the various contaminants have been set down in the Federal Register, this section is mandatory until changed or until an alternate method has been approved by the proper authority. The acceptable references at this time are listed in tables I and II in the Methodology Outline (number 3). The Certification Officer should be sure to obtain all the pertinent information on this section.

F. Sample Collecting, Handling and Preservation (Critical)

This section must be looked at in depth by each member of the certification team. The proper sampling techniques may be carried out by someone other than the laboratory personnel, however, the sampling techniques must be known or the possibility of improper analytical results exists. However, it is the responsibility of the laboratory to refuse to analyze or to require a new sample if it is known or suspected that the sample was improperly collected or preserved. The preservation technique and sampling containers can be evaluated by the Certification Officer to assure compliance.

The location of sample collection is spelled out in the National Interim Primary Drinking Water Regulations as "the free flowing outlet of the ultimate user of a public water system." The required sample container and preservative as well as the holding times can be found in the "Criteria and Procedures" manual. However, each reference method should be checked for special precautions.

G. Quality Control (Critical and Recommended)

The intent of this section is to have the Certification Officer review enough data to assure that the analytical data being developed is of a reliable nature. The critical items are sufficient to provide a minimal effort of quality control. The Certification Officer should carefully review the data available to be sure that at least a minimal effort is being carried out by the laboratory. If not, or if it is deemed desirable, comments should be made here. Strong encouragement should be given to having more quality control than just a minimal effort.

H. Data Handling (Recommendation)

This section is used as a recommendation to be sure that enough information about the sample is being retained for a sufficient

time to cover any questions that might arise. It should be pointed out here that in the implementation section under other considerations it is stated that for potential enforcement actions only the chain of custody for a sample must be maintained and recorded from time of sampling through analysis to the final recording. Consequently, additional data handling would be required in this case. The laboratory should be aware of this provision and what additional information or procedures are needed.

III. LEVELS OF CERTIFICATION

The Operational Guidance section of the implementation of the "Criteria and Procedures" manual lists three levels of certification under the criteria procedures. Although these are listed for principal State laboratories, something similar could be set up for local laboratories. The three levels are:

- A. Certified – a laboratory that meets the minimum requirements listed in the technical manuals for specific parameters. A laboratory may be certified to perform only those analyses for which certification is requested. For example, a laboratory may wish to analyze for coliform bacteria and not for other contaminants. The certification should be for three years.

- B. Provisionally certified – a laboratory that has been certified subject to correction of deficiencies that do not impact the basic validity of the test results. A grace period up to one year could be awarded for deficiencies, but in no case should provisional certification be given when the laboratory does not have the capability, in the opinion of the evaluator, of performing the analysis.
- C. Not certified – a laboratory that does not have the capability of performing the analyses as determined by "Criteria and Procedures" manual. A laboratory would be placed in this category for an analysis only after the State has had an opportunity for a review of the decision and the Regional Administrator has allowed for "due process." Should the Regional Administrator uphold the "not certified" classification on a principal State laboratory after the hearing, the State must immediately correct the major deficiencies noted and then request reinspection, or the State can request inspection of another laboratory to perform the assigned analytical work.

IV. SUMMARY

The laboratory approval and certification procedure as developed by

the Administrator or his designee is part of the procedure for the determination of primary enforcement responsibility. Since the withdrawal of laboratory approval or certification may affect primary enforcement responsibility, the procedure shall include notice and the opportunity for a hearing as provided in 40 CRF 142.12 and 142.13.

UNIT 12

INSTRUMENT AND EQUIPMENT NEEDS AND SPECIFICATIONS

I. INTRODUCTION

The intent of the Safe Drinking Water Act was to place the responsibility of analysis on the treatment facility personnel (40CFR No. 248, December 24, 1975, pg. 59581). However, some states have elected to do the analysis of chemical parameters themselves. This arrangement gives rise to several possibilities: a) the treatment facility will do the analysis; b) the treatment facility will contract with an outside laboratory to do the analysis; and finally; c) that the state laboratory will do the analysis.

In the first two cases the laboratories would have to be certified by the state as being capable of doing the analysis. A further possibility could arise when a treatment facility elects to do some, but not all of the analysis and would request certification only for those parameters for which it would be doing analysis.

When a laboratory is to be certified for chemical analysis, it will need only that equipment necessary to carry out the analysis for those parameters which it has chosen to do. The "Criteria and Procedures" manual lists the capital equipment needed for a laboratory doing all the analysis.

A laboratory doing only one or a selected number of analyses would want to know what was needed for the methods chosen. This outline will list the equipment needed for each analysis. The specification for the capital equipment will not be repeated each time but referenced to the first mention of that piece of equipment.

In the case of a laboratory which has a large volume of analyses, the number of pieces of equipment should be taken into account. This would insure sufficient equipment to carry out their workload.

II. INORGANIC

A. Metals run by direct aspiration or furnace analysis

1. Atomic Absorption Spectrophotometer: An instrument having either a single or double beam design with a grating monochromator, photomultiplier detector, adjustable slits, and a wavelength range of at least 190 to 800 nm should be used. In addition, an appropriate readout system that has a response time capable of measuring the atomic absorption signal generated is required. This includes the capability to detect positive interference on the signal from intense non-specific absorption.

The system should have sufficient equipment such as regulators, tubing and gas controls to adequately monitor and deliver the proper rate of oxidant and fuel required by the method.

Sufficient hollow cathode lamps or electrodeless discharge lamps should be available.

2. Burner: The instrument should be equipped with a burner recommended by the manufacturer for the method. The instrument should also be vented about 15 to 30 cm (6 to 12 inches) above the burner to remove fumes and vapors.
3. Fuel and oxidant: nitrogen or argon, hydrogen, acetylene, air and nitrous oxide gases are needed.
4. Recorder: Having a chart width of 10 inches or 25 cm, a full scale response time of 0.5 sec or less, 10 or 100 mv input to match the instrument and a variable chart speed of 5 to 50 cm/min or equivalent. In furnace work the recorder must be used to verify adequate background correction if a CRT video readout or hard copy printer is not available.
5. Graphite Furnace: Any furnace device capable of reaching the specified temperatures is satisfactory. In addition a supply of graphite platforms and/or tubes should be available in pyrolytic and nonpyrolytic forms. Also an inert gas, argon, is needed for furnace analysis. The analyst should also have microliter pipets with disposable tips. Sizes should be available from 5 to 100 μ L. Yellow colored tips have

been found to contain Cadmium. White colored tips have been found to be acceptable for all analyses. If a large volume of analyses are expected an auto sampler is recommended. This can even provide better precision in the analysis.

A background correction system or provision for a subsequent analysis using a nonabsorbing line is required for furnace analysis.

B. Metals run by Inductively Coupled Plasma (ICP)

1. ICP instrument: either sequential or simultaneous.
2. Spare parts: a power tube for the RF generator, quartz torch, some pump tubing, photomultiplier tubes and computer disks and paper.
3. Argon gas: either liquid or dry gas.
4. A peristaltic pump: capable of at least 2 mL/min.
5. Vent for torch in order to remove toxic fumes.
6. The room should be temperature and humidity controlled.

C. Arsenic and Selenium by Gaseous Hydride

An atomic absorption instrument with argon and hydrogen gases and some form of readout device is needed. The following are also necessary.

1. Flow Meter: Capable of measuring 1 liter/minute such as Gilmont No. 12 or equivalent.
2. Medicine Dropper: Capable of delivering 1.5 mL; fitted into a size "0" rubber stopper.
3. Reaction Flask: A pear-shaped vessel with two side arms and 50 mL capacity, both arms having a ground glass T 14/20 joint (such as Scientific Glass part JM-5835 or equivalent).
4. Special Gas Inlet-Outlet Tube: Constructed from a micro cold finger condenser by cutting off that portion below the ground glass T 14/20 joint (such as Scientific Glass part JM-3325 or equivalent).
5. Hollow Cathode or Electrodeless Discharge Lamp.
6. Drying Tube: 100-mm long polyethylene tube filled with glass wool.

7. Arrangement: As in Figure I below:

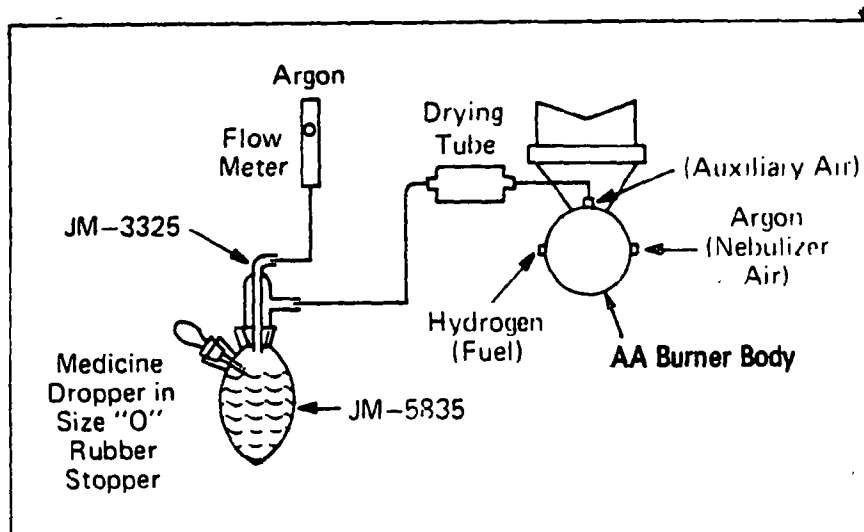


Fig. 1. Schematic Arrangement of Equipment for Determination of Arsenic and Selenium

D. Arsenic by Silver Diethyldithiocarbamate

1. Arsine generator: A Gutzeit generator (Fisher Scientific Co. No. 01-405) or equivalent used in conjunction with an absorber tube or assembly.
2. Photometer: Spectrophotometer or filter photometer, capable of measuring from 400 – 700 nm. Should be capable of using several sizes and shapes of absorption cells providing a path length of approximately 1 to 5 cm. The photometer should have a maximum spectral band width, of no more than 20 nm and a accuracy of ± 2.5 nm.

E. Mercury

1. Manual cold vapor using an atomic absorption unit:
 - a. Absorption Cell: Cells 2.5 cm in diameter and from 10 to 15 cm in length windows may be used. Suitable cells may be constructed from plexiglass tubing, 2.5 cm (1 inch) O.D. The ends are ground perpendicular to the longitudinal axis and quartz windows (2.5 cm (1 inch) diameter x 0.159 cm (1/16 inch) thickness) are cemented in place. Gas inlet and

outlet ports (also from plexiglass but .06 cm (1/4 inch) O.D.) are attached approximately 1.27 cm (1/2 inch) from each end. The cell is strapped to a burner for support and aligned to the light beam.

- b. Air Pump: A peristaltic pump capable of delivering an air flow of 1 or 2 liter/min may be used. Any other regulated compressed air system that is clean and dry (including cylinder air) is satisfactory.
- c. Flow Meter: Capable of measuring an air flow of 1 or 2 liters/min.
- d. Aeration Tubing: A straight glass frit having a coarse porosity. Tygon tubing can be used for passage of the mercury vapor from the sample bottle to the absorption cell and return.
- e. Drying Tube: A tube 15.2 cm (6 inches) x 1.9 cm (3/4 inch) diameter tube containing 20 g of magnesium perchlorate may be used. In place of the drying tube a small reading lamp with a 60 w bulb can be used to prevent condensation of moisture inside the cell. The lamp is positioned to shine on the absorption cell maintaining the air temperature in the cell about 10°C above ambient.

f. Mercury Vapor Trap: Because of the toxic nature of mercury vapor a by-pass should be included in the system to either vent the mercury vapor to an exhaust hood or pass the vapor through some absorbing media.

Liquid type, such as, equal volumes of 0.1 M KMnO_4 and 10 percent H_2SO_4 or 2.25 percent iodine in a 3 percent KI solution or

Solid type, such as, a specially treated charcoal that will absorb mercury vapor - available from Barnebey and Cheney, E. Eighth Avenue and N. Cassidy Street, Columbus, Ohio 43219, Cat. #580-22 or from Coleman Instruments, 42 Madison Street, Maywood, Illinois 60153, Cat. #50-160.

g. Arrangement: As in Figure 2 below.

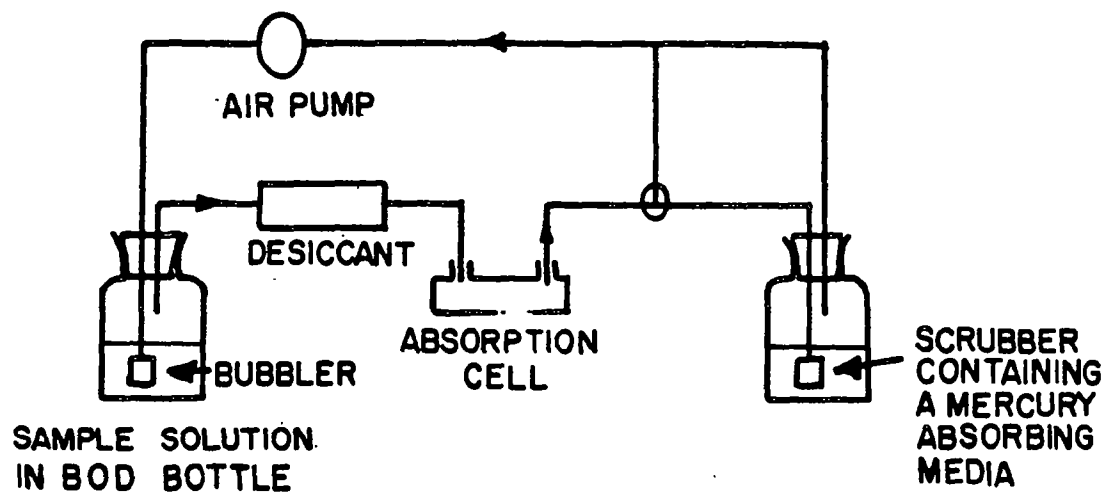


Fig. 2. Apparatus for Flameless Mercury Determination

2. Manual cold vapor using an instrument designed specifically for mercury:

a. An instrument designed specifically for the measurement of mercury using the cold vapor technique may be substituted for the atomic absorption spectrophotometer. An instrument such as the Coleman MAS-50, or its equivalent may be used.

b. Drying Tube: See specifications on previous page.

c. Mercury Vapor Trap: See 1.f. above.

3. Automated Cold Vapor Method:

a. Atomic absorption instrument or instrument specifically designed for mercury. See 2.a.

b. Autoanalyzer or equivalent: Exact equipment used is specified by the individual method, should include: sampler, proportioning pump, manifold or analytical cartridge, boiling bath with two distillation coils, vapor liquid separator, recorder.

F. Fluoride

The following items are required with this method.

1. Electrode Method:

a. Electrode: The electrode method does not require distillation when used to measure fluoride in finished drinking waters.

b. pH Meter: Must have expanded mV scale, an accuracy and readability of $\pm 1\text{mV}$. Laboratories purchasing a new pH meter are strongly advised to purchase one capable of functioning with specific ion electrodes. Unit may be line/bench or battery/portable operated.

or

c. Specific ion meter: Readable and accurate to $\pm 1\text{mV}$, unit may be line or battery operated.

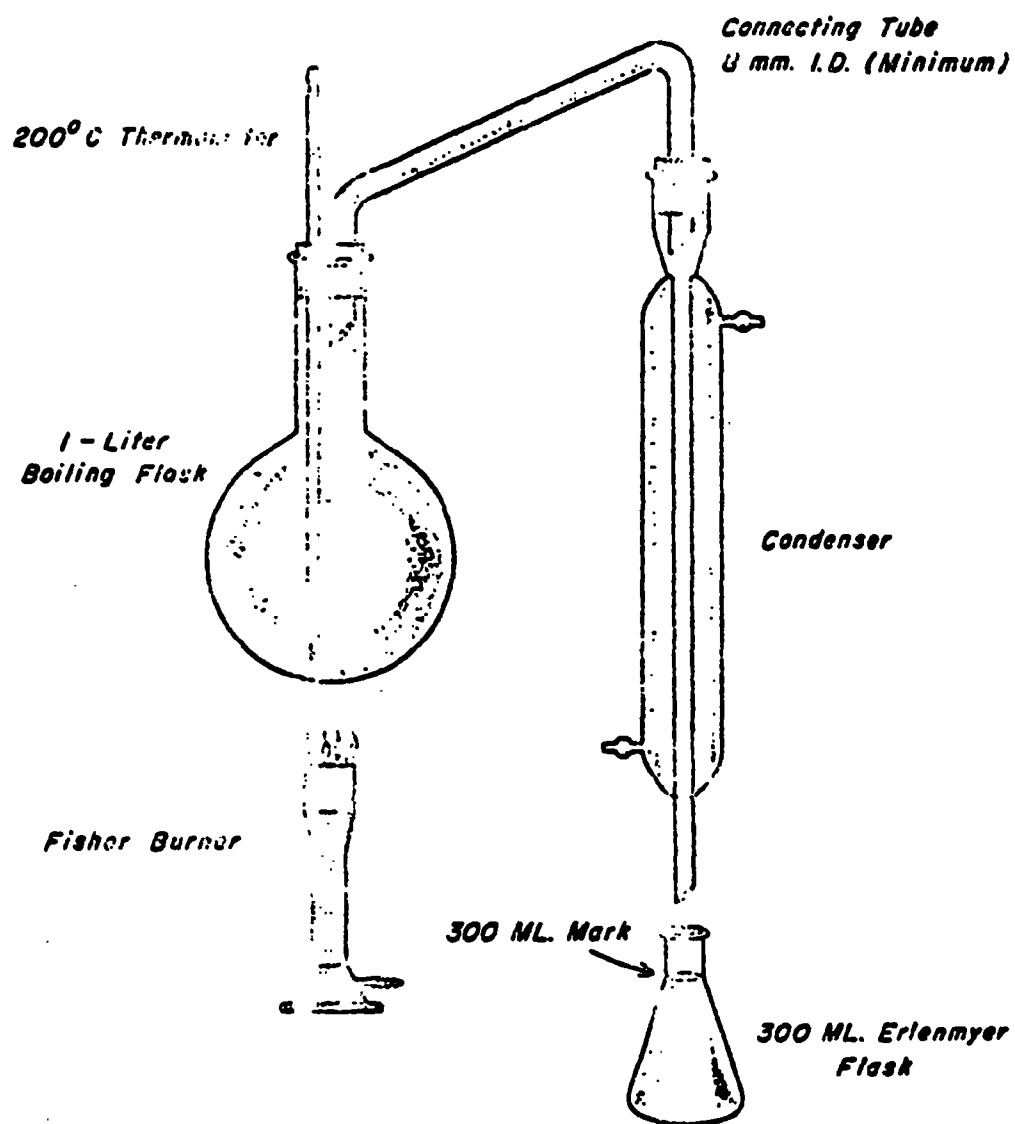


Fig. 3. Simplified Distillation Apparatus

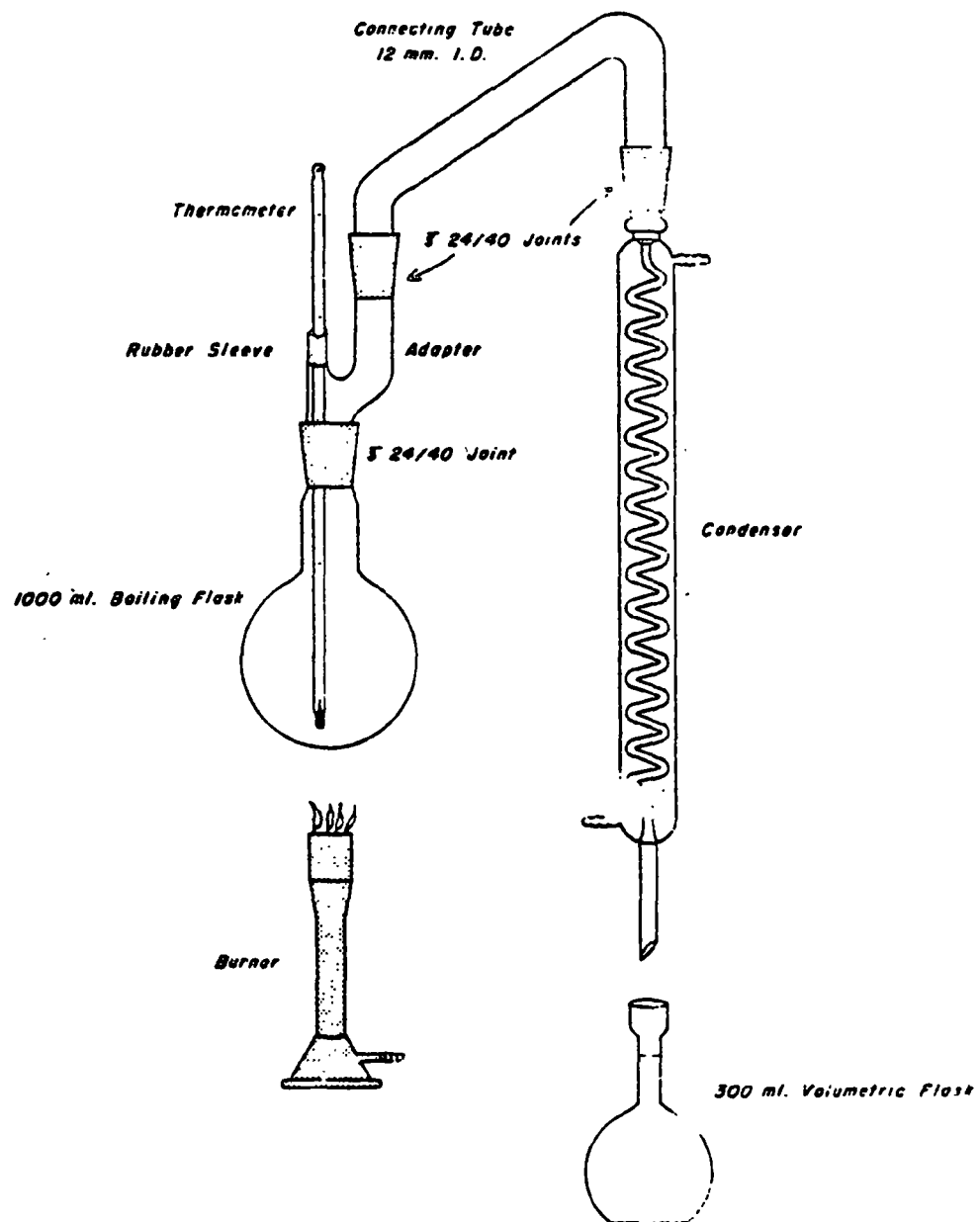


Fig. 4. Distillation Apparatus

- d. Electrodes: Fluoride and reference electrode or combination type.
 - e. Magnetic mixer: variable speed with Teflon-coated stirring bar.
2. SPADNS method with manual distillation: The following items are required.
- a. Photometer – spectrophotometer or filter photometer – see previous specifications (Unit 2, D.2).
 - b. Distillation equipment: See Figures three and four.
3. Automated methods with distillation: Autoanalyzer or equivalent with: Sampler, manifold, proportioning pump, distillation module, recorder and electrode flowthrough cell for the potentiometric procedure. The equipment is specified in the individual method.

G. Nitrate

1. Brucine:

- a. Spectrophotometer or filter photometer: suitable for measuring absorbance at 410 nm. With specifications as previously covered.
- b. Water bath: stirred with gabled lid, for use at 100°C.
- c. Water bath: for use at 10–15°C.

2. Manual cadmium reduction:

- a. Spectrophotometer: For use at 540 nm and a path length of 1 cm or longer with specifications as previously stated.
- b. Reduction Column: The column in Figure 5 was constructed from a 100-mL pipet by removing the top portion. This column may also be constructed from two pieces of tubing joined end to end. A 10 cm length of 3 cm I.D. tubing is joined to a 25 cm length of 3.5 mm I.D. tubing.

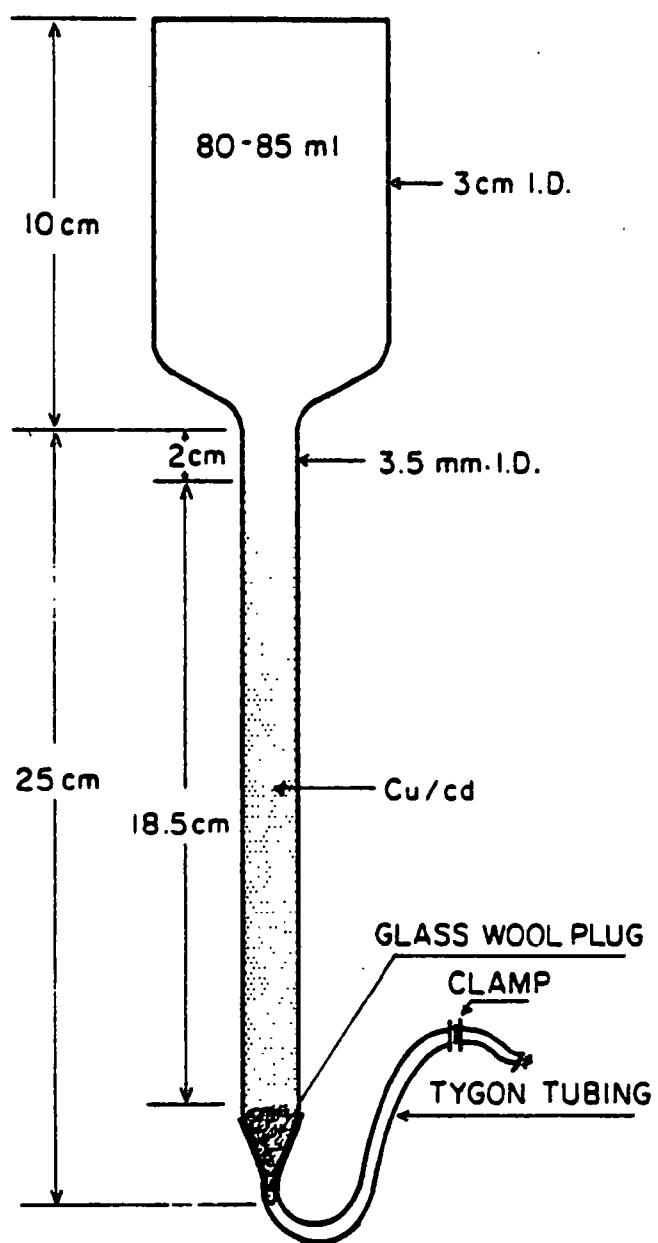


Fig. 5. Reduction Column

3. Autoanalyzer or equivalent:

- a. With sampler, manifold, pump, colorimeter, recorder, a column for the auto cadmium reduction method, plus a heating bath and continuous filter for the auto hydrazine method. Set up is specified in each method.

4. Electrode methods:

- a. pH meter or specific ion meter: As specified previously.
- b. Electrode and reference electrode or combination: As specified in specific method.
- c. Magnetic stirrer: Variable speed with Teflon coated stirring bar.

H. Turbidity

1. Nephelometric

- a. Nephelometer instrument: Ratio types are permissible but should be compared to conventional nephelometers. Measures scattered light intensity at a 90° angle to the axis of the transmitted light. Sealed liquid turbidity standards are acceptable if calibrated against prepared formazin standards at least every four months. Solid turbidity standards are not acceptable.

- b. Standards: Formazine or styrene divinyl benzene polymer standards.

I. Chlorine

1. Test kit: Using DPD or syringaldazine procedures.
2. pH meter or specific ion meter plus specified electrodes for potentiometric method.
3. Photometer as previous specified.

J. Calcium

Titrimetric: Routine laboratory glassware.

K. Sodium

1. Flame photometric method.
 - a. Flame photometer: either direct reading or internal standard type for use at 589 nm.

L. Total filterable residue

Analytical balance: capable of weighing to 0.1 mg.

Glass fiber discs: 4.7 cm or 2.1 cm without organic binder.

III. Organic Methods

A. Chlorinated hydrocarbons and chlorophenoxys

1. Gas Chromatograph: A commercial or custom designed gas chromatograph with a column oven capable of isothermal temperature control to at least 220 ± 0.2 C. The system should be equipped with accurate needle-valve, gas-flow controls, accept 1/4 inch glass columns with the option of direct on-column injection. The system must be demonstrated to be suitable for chlorinated hydrocarbon pesticides with a minimum of decomposition and loss of compounds of interest. Equipped with a glass lined injection port and either an electron capture, microcoulometric titration or electrolytic conductivity detector.
2. Recorder for gas chromatograph: Strip chart recorder, having a chart width of 10 inches or 25 cm, a full scale response time of 1 sec. or less, 1 mv (-0.05 to 1.05) signal to match the instrument and variable chart speeds of 5, 10, 25, or 50 mm per min., or equivalent.
3. Kuderna-Danish (K-D) glassware (Kontes)
Snyder Column - three-ball (macro) and two-ball (micro)
Evaporative Flasks - 500 mL
Receiver Ampules - 10-mL graduated
Ampule Stoppers

4. Water bath: Electric or steam heated capable of temperature control to within 5°C with a maximum temperature of 100°C. Concentric ring or other cover is required to support K-D concentrators.

B. TTHM's:

1. Purge and Trap Method

- a. Gas chromatograph: As above equipped with temperature program from 45°C to 220°C at about 8°C/min and with either microcoulometric titration or electrolytic conductivity detector.
- b. Recorder: as specified above.
- c. Purge and trap system: A commercial or custom designed system can be used. When interfaced to a compatible gas chromatograph, the assembly should be able to detect 0.5

µg/L of each of the individual TTHM's and measure them with a reproducibility not to exceed 8 percent relative standard deviation at 20 µg/L. The device should be designed for a 5 mL sample volume. The gas inlet should disperse finely divided gas bubbles through the sample. The trap should be capable of heating the trapping device to 180°C in one minute with less than 40°C overshoot.

2. Liquid/liquid Extraction:

- a. Gas chromatograph and recorder as specified above. The gas chromatograph should be equipped with a linearized (frequency modulated) electron capture detector.

3. Gas chromatography/mass spectrometry/data system (GC/MS/DS):

- a. The GC must be capable of temperature programming. Any column (either packed or capillary) that provides data with adequate accuracy and precision (Sect. 10) can be used. If a packed column is used, the GC usually is interfaced to the MS with an all-glass enrichment device and an all-glass transfer line, but any enrichment device or transfer line can be used if performance specifications described in this method can be demonstrated with it. If a capillary column is used, an enrichment device is not needed. A recommended packed GC column for the listed analytes is 1.8 m long by 2

mm ID glass packed with 1% SP-1000 on 60/80 mesh Carbopack

B. Recommended operating parameters for that column are: helium carrier gas flow rate of 30 mL/min and temperature of 48°C for 4 minute, increased to 230°C for at least 25 minute or until all expected analytes elute. An alternative recommended packed column is 1.8 m long by 2 mm ID glass or stainless steel packed with 0.2% Carbowax 1500 on 80/100 mesh Carbopack C.

b. Mass spectral data are obtained with electron-impact ionization at a nominal electron energy of 70 eV. The mass spectrometer must be capable of scanning from 35 to 450 amu every 7 s or less and must produce a mass spectrum that meets all criteria in Table 1 when 50 ng or less of p-bromofluorobenzene (BFB) is introduced into the GC. To ensure sufficient precision of mass spectral data, the desirable MS scan rate allows acquisition of at least five spectra while a sample component elutes from the GC. With capillary columns which produce narrower peaks than packed columns that criterion may not be feasible and adequate precision with fewer spectra per GC peak must be demonstrated.

c. An interfaced data system (DS) is required to acquire, store, reduce and output mass spectral data. The computer

software must allow searching any GC/MS data file for ions of a specific mass and plotting ion abundances versus time or scan number. This type of plot is defined as an extracted ion current profile (EICP). Software must also allow integrating the abundance in any EICP between specified time or scan number limits. A hard copy device is necessary for data output and archiving.

For each analyte, the mean accuracy should be in the range of 85 to 115 percent. Adequate precision is obtained when the relative standard deviation is ± 20 percent. For some listed analytes, this may not be feasible for low concentration measurements.

Table 1

p-Bromofluorobenzene Key Ions and Ion Abundance Criteria

Mass	Ion Abundance Criteria
50	15 to 40% of mass 95
75	30 to 60% of mass 95
95	base peak, 100% relative abundance
96	5 to 9% of mass 95
173	less than 2% of mass 174
174	greater than 50% of mass 95
175	5 to 9% of mass 174
176	96 to 100% mass 174
177	5 to 9% of mass 176

IV. General Lab Equipment

In addition to the equipment listed for each method the following equipment should also be available.

- A. Conductivity meter: Useful for checking distilled water quality. Instrument should be readable in ohms or umhos, have a range of 2-2,500,000 ohms or umhos \pm 1 percent and have a sensitivity of 0.33 percent or better. The unit may be line/bench or battery/portable operated if the above specifications are met.
- B. Drying oven: Gravity and mechanical convection units with selectable temperature control from room to 170°C or higher are satisfactory.
- C. Desiccator: Glass or plastic models may be appropriate depending on the particular application.
- D. Hot plate: Large or small units with selectable temperature control for safe heating of laboratory reagents.
- E. Refrigerator: For aqueous reagent and sample storage a standard kitchen type domestic refrigerator will be sufficient. For storing organics and flammable materials an "explosion proof" type of refrigerator should be used.

F. Glassware: All glassware purchased for laboratory use should be composed of Pyrex or Kimax type glass. This type of glass is more resistant to damage by heat, chemicals, and abuse than is regular soft glass. All volumetric glassware should be marked Class A, denoting that it meets federal specifications for volumetric glassware and need not be calibrated before use.

Unit 13
LABORATORY SAFETY PRACTICES

I. INTRODUCTION

While this is not an aspect of laboratory certification, evaluators should point out, on an informal basis, potential safety problems observed during an on-site visit. This outline is added to point out some common laboratory safety practices.

A. Safe Use, Handling, and Storage of Chemicals

1. Chemicals in any form can be safely stored, handled, and used if their hazardous physical and chemical properties are fully understood and the necessary precautions, including the use of proper safeguards and personal protective equipment are observed.
2. The management of every unit within a laboratory must give wholehearted support to a well integrated safety policy.

B. General Rules for Laboratory Safety

1. Supervisory personnel should think "safety." Their attitude toward fire and safety standard practices is reflected in the behavior of their entire staff.

2. A safety program is only as strong as the worker's will to do the correct things at the right time.
3. The fundamental weakness of most safety programs lies in too much lip service to safety rules and not enough action in putting them into practice.
4. Safety practices should be practical and enforceable.
5. Accident prevention is based on certain common standards of education, training of personnel and provision of safeguards against accidents.

II. LABORATORY DESIGN AND EQUIPMENT

A. Type of Construction

1. Fire-resistant or noncombustible.
2. Multiple story buildings should have adequate means of exit.
3. Stairways enclosed with brick or concrete walls.

4. Laboratories should have adequate exit doors to permit quick, safe escape in an emergency and to protect the occupants from fires or accidents in adjoining rooms. Each room should be checked to make sure there is no chance of a person being trapped by fire, explosions, or release of dangerous gases.
5. Laboratory rooms in which most of the work is carried out with flammable liquids or gases should be provided with explosion-venting windows.

B. Arrangement of Furniture and Equipment

1. Furniture should be arranged for maximum utilization of available space and should provide working conditions that are efficient and safe.
2. Aisles between benches should be at least 4 feet wide to provide adequate room for passage of personnel and equipment.
3. Desks should be isolated from benches or adequately protected.
4. Every laboratory should have an eyewash station and a safety shower.

C. Hoods and Ventilation

1. Adequate hood facilities should be installed where work with highly toxic or highly flammable materials are used.
2. Hoods should be ventilated separately and the exhaust should be terminated at a safe distance from the building.
3. Make-up air should be supplied to rooms or to hoods to replace the quantity of air exhausted through the hoods.
4. Hood ventilation systems are best designed to have an air flow of not less than 60 linear feet per minute across the face of the hood, with all doors open and 150, if toxic materials are involved.
5. Exhaust fans should be spark-proof if exhausting flammable vapors and corrosive resistant if handling corrosive fumes.
6. Controls for all services should be located at the front of the hood and should be operable when the hood door is closed.
7. All laboratory rooms should have the air changed continuously at a rate depending on the materials being handled.

D. Electrical Services

1. Electrical outlets should be placed outside of hoods to afford easy access and thus protect them from spills and corrosion by gases.
2. Noninterchangeable plugs should be provided for multiple electrical services.
3. Adequate outlets should be provided and should be of the three-pole type to provide for adequate grounding.

E. Storage

1. Laboratories should provide for adequate storage space for mechanical equipment and glassware which will be used regularly.
2. Flammable solvents should not be stored in glass bottles over one liter in size. Large quantities should be stored in metal safety cans. Quantities requiring containers larger than one gallon should be stored outside the laboratory.
3. Explosion proof refrigerators should be used for the storage of highly volatile and flammable solvents.

4. Cylinders of compressed or liquified gases should not be stored in the laboratory.

F. Housekeeping

1. Housekeeping plays an important role in reducing the frequency of laboratory accidents. Rooms should be kept in a neat orderly condition. Floors, shelves, and tables should be kept free from dirt and from all apparatus and chemicals not in use.
2. A cluttered laboratory is a dangerous place to work. Maintenance of a clean and orderly work space is indicative of interest, personal pride, and safety-mindedness.
3. Passageways should be kept clear to all building exits and stairways.
4. Metal containers should be provided for the disposal of broken glassware and should be properly labeled.
5. Separate approved waste disposal cans, should be provided for the disposal of waste chemicals.
6. Flammable liquids not miscible with water and corrosive materials, or compounds which are likely to give off toxic vapors should never be poured into the sink.

G. Fire Protection

1. Laboratory personnel should be adequately trained regarding pertinent fire hazards associated with their work.
2. Personnel should know rules of fire prevention and methods of combating fires.
3. Fire extinguishers (CO₂ type) should be provided at convenient locations and personnel should be instructed in their use.
4. Automatic sprinkler systems are effective for the control of fires in chemical laboratories.

H. Alarms

1. An approved fire alarm system should be provided.
2. Wherever a hazard of accidental release of toxic gases exists, a gas alarm system to warn occupants to evacuate the building should be provided.
3. Gas masks of oxygen or compressed air type should be located near exits and selected personnel trained to use them.

III. HANDLING GLASSWARE

A. Receiving, Inspection and Storage

1. Packages containing glassware should be opened and inspected for cracked or nicked pieces, pieces with flaws that may become cracked in use, and badly shaped pieces.
2. Glassware should be stored on well-lighted stockroom shelves designed and having a coping of sufficient height around the edges to prevent the pieces from falling off.

B. Laboratory Practices

1. Select glassware that is designed for the type of work planned.
2. To cut glass tubing or a rod, make a straight clean cut with a cutter or file at the point where the piece is to be severed. Place a towel over the piece to protect the hands and fingers, then break the tubing or rod by snapping with a motion directed away from the body.
3. Large size tubing is cut by means of a heated nichrome wire looped around the piece at the point of severance.

4. When it is necessary to insert a piece of glass tubing or a rod through a perforated rubber or cork stopper, select the correct bore so that the insertion can be made without excessive strain.
5. Use electric mantels for heating distillation apparatus, etc.
6. To remove glass splinters, use a whisk broom and dustpan. Very small pieces can be picked up with a large piece of wet cotton.

IV. GASES AND FLAMMABLE SOLVENTS

A. Gas Cylinders

1. Large cylinders must be securely fastened so that they cannot be dislodged or tipped in any direction.
2. Connections, gauges, regulators or fittings used with other cylinders must not be interchanged with oxygen cylinder fittings because of the possibility of fire or explosion from a reaction between oxygen and residual oil in the fitting.
3. Return empty cylinders promptly with protective caps replaced.

B. Flammable Solvents

1. Store in designated areas well ventilated.
2. Flash point of a liquid is the temperature at which it gives off vapor sufficient to form an ignitable mixture with the air near the surface of the liquid or within the vessel used.
3. Ignition temperature of a substance is the minimum temperature required to initiate or cause self-sustained combustion independently of the heating or heated element.
4. Explosive or flammable limits. For most flammable liquids, gases and solids there is a minimum concentration of vapor in air or oxygen below which propagation of flame does not occur on contact with a source of ignition. There is also a maximum proportion of vapor or gas in air above which propagation of flame does not occur. These limit mixtures of vapor or gas with air, which if ignited will just propagate flame, are known as the "lower and higher explosive or flammable limits."
5. Explosive Range. The difference between the lower and higher explosive or flammable limits, expressed in terms of percentage of vapor or gas in air by volume is known as the "explosive range."

6. Vapor Density is the relative density of the vapor as compared with air.

7. Underwriter's Laboratories Classification is a standard classification for grading the relative hazard of the various flammable liquids. This classification is based on the following scale:

Ether Class	100
Gasoline Class	90 - 100
Alcohol (ethyl) Class.....	60 - 70
Kerosene Class	30 - 40
Paraffin Oil Class	10 - 20

8. Extinguishing agents.

V. CHEMICAL HAZARDS

A. Acids and Alkalies

1. Some of the most hazardous chemicals are the "strong" or "mineral" acids such as hydrochloric, hydrofluoric, sulfuric and nitric.

2. Organic acids are less hazardous because of their comparatively low ionization potentials. However, such acids as phenol (carbolic acid), hydrocyanic and oxalic are extremely hazardous because of their toxic properties.

3. Classification of acids.

B. Oxidizing Materials

1. Such oxidizing agents as chlorates, peroxides, perchlorates and perchloric acid, in contact with organic matter can cause explosions and fire.
2. They are exothermic and decompose rapidly, liberating oxygen which reacts with organic compounds.
3. Typical hazardous oxidizing agents are:

Chlorine Dioxide

Sodium Chlorate

Potassium Chromate

Chromium Trioxide

Perchloric Acid

C. Explosive Power

1. Many chemicals are explosive or form compounds that are explosive and should be treated accordingly.
2. A few of the more common examples of this class of hazardous materials are:

Acetylides

Silver Fulminate

Peroxides

Peracetic Acid

Nitroglycerine

Picric Acid

Chlorine and Ethylene

Sodium Metal

Calcium Carbide

D. Toxicity

1. Laboratory chemicals improperly stored or handled can cause injury to personnel by virtue of their toxicity.

2. Types of exposure. There are four types of exposure to chemicals:

a. Contact with the skin and eyes

b. Inhalation

c. Swallowing

d. Injection

VI. PRECAUTIONARY MEASURES

A. Clothing and Personal Protective Equipment

1. Chemical laboratories should have special protective clothing and equipment readily available for emergency use and for secondary protection of personnel working with hazardous materials.

2. Equipment should be provided for adequate:

a. Eye protection

b. Body protection

c. Respiratory protection

d. Foot protection

e. Hand protection

B. Bodily Injury

1. Burns, eye injuries, and poisoning are the injuries with which laboratory people must be most concerned.
2. First emphasis in the laboratory should be on preventing accidents. This means observing all recognized safe practices using necessary personal protective equipment and exercising proper control over poisonous substances at the source of exposure.
3. So that a physician can be summoned promptly, every laboratory should have posted the names, telephone numbers, and addresses of doctors to be called in an emergency requiring medical care.

REFERENCES

Guide for Safety in the Chemical Laboratory, the General Safety Committee of the Manufacturing Chemists Association, Inc., Van Nostrand, New York (1954).