CALIFORNIA DEPARTMENT OF HEALTH SERVICES
ENVIRONMENTAL LABORATORY ACCREDITATION PROGRAM (ELAP)

LABORATORY PRE-VISIT INFORMATION

APPLICATION VERIFICATION

The first item to be considered during the site visit is application and information verification. Please review your application in advance for accuracy and to make sure the information presented in it is up-to-date. Additional fields of testing requested during site visit can be reviewed but will require fees and a formal written request to ELAP for certification.

FACILITIES

The laboratory facilities will be evaluated. Temperature must be controlled so as to optimize analytical performance. There should be adequate lighting, space and ventilation. All hoods must be functional. Hood flow should be monitored and documented (100 LFM). The work area should be clean, uncluttered and orderly. All reagent and sample containers should be labeled and not scattered or left open.

The laboratory water supply must be either distilled or deionized. The water must be monitored regularly for conductivity, pH and other parameters that may affect analytical results. A log must be maintained. All reagent water must meet the specifications required for each analysis.

The laboratory should have a sufficient number of electrical outlets to meet instrumental needs. There should no overloading of circuits. Surge protectors are recommended for computers and delicate instrumental needs. Gas and vacuum lines should be available. There should be an adequate plumbing system. There should be an adequate space for analysts to perform calculations and for storage of reagents, samples, glassware and containers.

BASIC LABORATORY INSTRUMENTATION/EQUIPMENT

1. **pH Meter**

   pH meters should be calibrated daily with 2 buffers in the range of interest. Buffers must not be expired and should be used only once. All calibrations must be documented and maintained. The instrument must have at least a 0.05 unit sensitivity. The electrode must be properly maintained and stored.

2. **Analytical Reagents**

   All analytical reagents should be reagent grade (AR) or better. They must be dated when first opened, stored properly and discarded after expiration date.

3. **Conductivity Meter**

   Conductivity meters must be calibrated with a 0.01 M KCL solution before each use. All calibration records must be maintained.

4. **Analytical Balance**

   Analytical balances should have at least a 0.1 mg (0.0001 g) sensitivity. The balance must be on a stable and level base. The area surrounding the balance should be kept clean at all times. In addition, an annual service contract should be obtained for each balance. A set of class "S" or "S1" weights must be available for periodic calibration checks. All calibration check records must be maintained.

5. **Drying Ovens**

A 180°C ± 5°C oven must be available for gravimetric analyses. Thermometers used for those ovens must be monitored and temperatures recorded when the ovens are in use.

6. **Refrigerators and Freezers**

The temperatures of refrigerators and freezers must be monitored daily with a accurate thermometer immersed in liquid. Records of the monitoring must include the date, temperature, initial of responsible person and the acceptable temperature range. Refrigerator should be maintained at 4 ± 2°C.

7. **Water Baths**

Chemistry water baths must be capable of maintaining a 95° to 100°C temperature. Temperature must be monitored and recorded when in use.

8. **Thermometers**

All laboratories must have a **certified thermometer** (with certificate) to perform routine calibration checks on the laboratory thermometers. All calibration checks must be documented.

9. **Glassware**

Volumetric glassware employed in the laboratory must be borosilicate, Class "A" type. All applicable preparation and cleaning procedures pertaining to specific method(s) must be followed.

10. **Desiccator**

Desiccant should be maintained. Replace and regenerate desiccant regularly.

11. **Turbidimeter**

Turbidimeters must be calibrated with primary standards (Formazin or EPA approved polymer standards) or secondary standards of appropriate range before each use. The secondary standards must be cross-referenced against primary standards on a quarterly basis.

NOTE: "Ratio" turbidimeters are not approved.

12. **Sample Containers**

All sample containers must be stored in a designated storage area; free from any source of contamination. Sample containers must be routinely checked for contamination (by lot number). Do not rely on the suppliers' quality control report! Please refer to the Method Guidelines for specific contamination monitoring requirements.

13. **Other Equipment**

Pipettors (e.g. Eppendorf, etc.) should be calibrated and adjusted on a regular basis.

TEST METHOD REFERENCES

The laboratory, at minimum, should have on hand the following references available to all personnel:

- The 16th Edition of **Standard Methods For The Examination Of Water And Wastewater** is to be used as a reference for Drinking Water analyses. The 17th edition of **Standard Methods For The Examination Of Water And Wastewater** is to be used for Wastewater analyses.

- **EPA - "Methods For Chemical Analysis of Water and Wastes"** For Drinking Water and Wastewater analyses.
- **EPA - "Handbook for Analytical Quality Control in Water and Wastewater Laboratories"** - All laboratories.
- **EPA - "Methods for the Determination of Organic Compounds in Drinking Water" (500's series)** - For Drinking Water organic analyses.
- **EPA - SW 846 3rd Edition** - For Hazardous Waste (solid) analyses. Final Update I and Proposed Update II are now available.
- **PAM Manuals, Volume I & II** - For agricultural pesticides - Food and Agriculture Program.

SAMPLE RECEIVING/STORAGE

1. **Collection Personnel/Sampling and Sample Custodian Instructions**

   All collection personnel, whether affiliated with the laboratory or clients, should be trained in using proper sampling procedures. In addition, **written** sampling instructions should be available to all sampling personnel for reference.

   A set of written procedures should be available to the sample custodian for sample receiving and storage.

   The result of any analytical determination can be no better than the sample of which it is performed.

2. **Sample Receiving**

   A designated area for receiving samples should be set up in the laboratory. The size of the area should be adequate to handle the sample load. The area must include facilities for preserving samples. The sample area should be set up in a location that will minimize potential contamination and provide easy access to sample storage area(s). The receiving area should be organized in such a way that samples can be efficiently processed and/or preserved and that sample integrity and/or identity are maintained.

   In addition, an individual should be assigned to handle the sample receiving function. A written sample processing protocol should be developed.

   A protocol for and forms for **chain-of-custody** should be developed and used if required.

3. **Posted Instructions**

   Instructions for the proper sample preservation, proper containers and holding time requirements must be clearly posted at the sample receiving area. It is recommended that additional copies of the posted instructions be made available to all personnel for their reference.

4. **Preservatives, Containers, Storage and Holding Times**

   All samples must be collected in proper containers, preserved with the appropriate preservatives if needed, stored properly and analyzed within the required holding time limit. If a preservative is used, it should be indicated on the sample container.

5. **Sample Identification/Record Keeping**

   Sample Receiving Log - A log should be maintained for sample receiving. The following information should be included: Time and date sampled, time and date received at the laboratory, sample collector, nature of sample, analyses to be performed, preservatives, condition of sample and sample recipient.

A unique laboratory identifier should be assigned to and attached securely to each sample container and indicated in the log book.

Computer/LIMS System Log - A computer log-in (LIMS) system is acceptable for sample receiving. A backup system must be available for the event of failure. All files should have backups and hardcopies must be available.

6. **Sample Tracking System**

The laboratory must have in place a system to track the samples and to monitor the holding times.

7. **Storage Facilities**

There must be adequate facilities to store all the samples properly. Samples should be stored in a fashion to minimize cross contamination. Drinking water volatile organic samples, should be isolated and stored in a separate refrigerator. Hazardous waste samples should be stored separately. All refrigerators must be maintained at $4^{\circ}C \pm 2^{\circ}C$ and must be monitored (with documentation) daily.

8. **Storage Security**

All storage facilities should be secured. Litigation samples should be stored in a locked storage area.

SAFETY

1. **Safety Equipment**

At minimum, the laboratory should have in place the following safety equipment:

- Fire Extinguishers/Fire Blankets
- Safety Shower
- Spill Kits
- Eye Wash
- First Aid Kits
- Safety Glasses

2. **Distillation, Solvent Extraction and Acid Digestion Procedures**

These procedures should always be performed under hoods. All hoods should have proper flow and are monitored on a regular basis.

3. **Chemical Storage Shelvings and Gas Cylinders**

Shelves should have rails to prevent tip overs in the event of an earthquake.

All gas cylinders should be secured either by straps, chains or floor mounts. Bungee cords are not recommended.

4. **Solvents and Acids Storage**

Solvents should be stored in flammable storage cabinets. Acids should stored in acid resistant cabinets with neutralizers available nearby. All organic extracts should be stored in explosion-proof refrigerators.

5. **Hazardous Wastes Handling**

It is vital for an environmental laboratory to dispose their hazardous waste in a responsible manner. All hazardous wastes must be stored and disposed of properly. All reactive wastes must be isolated and acidic waste should be neutralized. A waste disposal contract is strongly recommended.

NOTE: **The Occupational Safety and Health Administration published the final rule of its laboratory standard entitled "Occupational Exposures to Hazardous Chemicals in Laboratories" in the January 31, 1990 Federal Register. While ELAP has no direct control over laboratory safety, it is highly recommended that laboratories comply with the requirements outlined in the Federal Register. Copies are available to laboratories upon request from ELAP offices.**

RECORDS/DATA RETENTION

1. **Data Retention Requirements**

California requires that data for chemical analyses be retained for 10 years and 5 years for microbiological analyses.

Litigation samples and samples used for long-term studies may require indefinite retention.

Instrument printouts, chart recordings and chromatograms should be retained.

2. **Raw Data**

All raw data should be maintained on worksheets and/or permanently bound lab books. All entries must be made in indelible ink. Correction fluid is not allowed. Corrections are made by crossing out entries and initialing the corrected entry.

3. **Data Review**

There should be an adequate system of data review before final results are to be submitted. This generally involves a review by a second party. All secondary reviews should be documented.

NOTE: **Second party review is not a "rubber stamp" procedure. Data should be thoroughly reviewed. This is probably the largest single source of error in the reporting of results.**

Individual analyst lab notebooks should be periodically reviewed. They should be dated and initialed when reviewed.

4. **Corrective Actions**

All corrective actions in out-of-control situations should be documented. Documentation should include: date, analyst, samples affected, problem and resolution.

5. **Data Reduction**

Detection Limits (DLR's) should take into account all dilutions factors and interference when reported.

If bias corrections are made on data as a result of the evaluation of quality control data, the uncorrected values should also be included.

NOTE: **Laboratories should review procedures for appropriate use of significant figures. The number of significant figures should be no more than is justified by the least precise step of the procedure.**

6. **Notification and Reporting Procedures**

If a regulatory agency has no data report forms, or data reporting format, laboratories shall provide, at a minimum, the following data elements in data reports.

- Identification of the laboratory by name and Environmental Laboratory Accreditation Program certificate number.
- For each sample for which data is to be reported, the following data elements shall be provided.
- complete sample identification including any sample identification numbers assigned by the laboratory.
- Date of sample collection.
- Date of sample receive by the laboratory.
- Date of sample analysis.
- Name of analytical method.
- Analytical values including units of measure.
- Limits of detection.
- Date of report.
- Original signature by a Signatory Person.

NOTE: **In any arrangements between laboratories involving the transfer of samples, or portions of samples, the laboratory issuing the combined report shall include an original report as issued by the other laboratory.**

QUALITY ASSURANCE PLAN

The laboratory must have developed and implemented a Quality Assurance plan prior to applying for ELAP accreditation. The plan must be adhered to and reflect actual laboratory practices. It should be up-to-date (this requires frequent updating) and be accessible to all analysts.

PRIOR DEFICIENCIES REVIEW

If your laboratory is undergoing recertification, part of the on-site visit will focus on the review of your corrections (if any) to the deficiencies previously cited. Please bear in mind that the inspector will examine the corrections according to your previous response letter. Major irregularities can jeopardize your certification status.

CONFIRMATION POLICY

For gas chromatographic organic analysis, all positive results are recommended to be confirmed either by a second column or GC/MS analysis, unless exempted in the following situations:

1. The analytes of interest can produce gas chromatogram containing "pattern" peaks which match appropriate standards. These analytes include Polychlorinated Biphenyls (PCB's), hydrocarbon fuels (e.g. gasoline) and toxaphene.

2. The sample is analyzed for Benzene, Toluene and Xylenes (BTX) for gasoline tank removal purposes and the same sample was found to contain gasoline by a separate analysis. However, the presence of BTX in a sample containing no gasoline must be confirmed.

3. The samples meet all of the following requirements:

   a. All samples (liquid or solid) come form the same source, e.g. groundwater samples from the same well, for continuous monitoring. However, samples of same matrix form the same site but from different sources (different sampling locations) are not exempted.

   b. All chemical parameters have been previously analyzed, identified and confirmed by a second column or GC/MS. The laboratory must have the necessary documents indicating previous confirmation.

   c. The resulting gas chromatograms are relatively simple and do not contain complex or overlapping peaks.

   d. Chromatograms are largely unchanged from those for which confirmation was carried out.

   e. Representative samples must be periodically confirmed at a frequency of at least 5%.

   f. For Drinking Water analyses, refer to the individual method for confirmation criteria.

EXTRACTION TESTS OF HAZARDOUS WASTE
(Field of Testing #11)

INTRODUCTION

There are currently two (2) extraction procedures used for evaluating hazardous materials:

1. Toxicity Characteristic Leaching Procedure (TCLP), EPA Method 1311.

2. Waste Extraction Test (WET), Title 22.

The Federal Government (EPA-RCRA) has replaced the EP-Toxicity test with the TCLP test. Please note that for the newly regulated volatile compounds, a zero-headspace extractor (ZHE) is required.

WARNING: Please be aware that the acetic acid used in the TCLP extraction solution can be damaging to your GC equipment (i.e. columns, fittings, etc.). Increased maintenance and/or replacement parts may be needed.

Extraction procedures may be required for Hazardous Waste analysis. It should be noted that extraction tests are to be applied only when the results are between the Total Threshold Limit Concentration (TTLC) and Soluble Threshold Limit Concentration (STLC) action levels.

If the TTLC analysis of the waste indicates that the constituent concentration in the waste extract cannot exceed the STLC level, extraction is not required.

The Toxicity Characteristic Leaching Procedure (TCLP) has been adopted by the Department of Toxic Substance Control (Title 22, Section 66261.24).

INSTRUMENTATION/EQUIPMENT

For the Waste Extraction Test (WET), either a horizontal or rotary shaker is acceptable.

Toxicity Characteristic Leaching Procedure (TCLP) requires a rotary (end-over-end) extractor/shaker capable of 30 ± 2 RPM.

The ZHE for volatile analysis must be an **approved** device. It must be able to hold a minimum volume of 500 ml and 50 P.S.I. pressure for one (1) hour with no leaks. The "O" - rings must be maintained and replaced on a regular schedule. The device must be equipped with a built-in pressure gauge.

Extracts must be collected using syringes or Tedlar^{R} bags.

PROCEDURE

1. **Standard Operating Procedures (SOPs)**

   There should be a SOP developed for **all** procedures. This would include any particle size reduction, filtration, extraction, etc. A flowchart is recommended.

2. **Sample Collection/Preservation**

   Samples must **not** to be preserved before extraction. Samples must be preserved after extraction or promptly analyzed.

3. **Sample Preparation/Extraction/Handling**

The proper sample sizes to use are as follows:

	WET	TCLP
Non-volatile samples:	50 g to 500 ml (10:1) 25 g to 250 ml (10:1)	100 g to 2000 ml (20:1) 25 g to 500 ml (20:1)
Volatile samples:	Not Applicable	25 g to 500 ml (20:1)

All preparation information such as weight of sample, matrix type/sample description, preparer, any preliminary tests such as % solids determination and particle size reduction must be documented and available for inspection.

NOTE: For analysis of volatile compounds, milling and sieving if not recommended. Samples must be kept cold and all handling must be performed with minimal air contact.

4. **Filtration Requirements**

It is **strongly recommended** that filtration be done in hoods.

0.6 - 0.8 micron glass fiber filters should be used. The filter should be acid washed for inorganic analysis. The proper filter system must have 300 to 1500 ml holding capacity and be 50 to 100 mm in diameter. Filtration should be by either vacuum or positive pressure (recommended).

NOTE: Only <u>one</u> filter is used per sample. Do not replace a filter if flow is restricted.

5. **Extraction Reagents**

For the WET test, a citric acid solution is required.

For the TCLP test, the requirements are pH dependent. Either Glacial acetic acid with NaOH (pH=5) and glacial acetic acid only (pH=2.9) may be required. Refer to method for specific requirements on the extraction reagents.

6. **Extraction Period**

The WET test has an extraction period of forty eight (48) hours. TCLP has an extraction period of eighteen (18) hours ± two (2) hours.

QUALITY CONTROL

An extraction blank must analyzed with each sample batch. Spikes must be introduced **after** filtration and **before** preservation. For TCLP, there is a correction factor based on recovery.

The Q.A. plan developed for the laboratory must be followed and reflect actual laboratory practices. It must be up-to-date and made accessible to all analysts.

GENERAL MINERAL/WET CHEMISTRY
(Fields of Testing #2 and #16)

INTRODUCTION

This section covers gravimetric, titrimetric, spectrophotometric, ion-selective electrode, ion-chromatographic, automated and manual wet chemical methods.

General mineral/wet chemistry results are reported to the Office of Drinking Water (ODW) (Potable Water Field of Testing #2) and to the Regional Water Quality Control Boards (RWQCB's) (Wastewater-Field of Testing #16).

For potable water, the sample is liquid and total recoverable analysis is required. Wastewater analysis may be for total or filtrable recoveries.

For the most part the analytes are in easily detectable quantities. Detection levels are not critical.

Analytical precision, especially with manual methods, can be varied and must be monitored for and kept within an acceptable range.

Phosphate and MBAS (Methylene Blue Active Substances) analyses are susceptible to laboratory contamination. A set of dedicated hot HCl washed glassware for those analyses is strongly recommended.

INSTRUMENTATION/METHODS

1. GRAVIMETIRC METHODS

For gravimetric methods, the required equipment includes: An analytical balance, oven(s) maintained at 180°C (Total Dissolved Solids) or 105°C (suspended solids), desiccator with fresh desiccants, and glass fiber filters.

2. TITRIMETRIC METHODS

For titrimetric methods, adequate backlighting must be available for performing titrations. Titrations must be performed with Class "A" burettes with the appropriate volume for the titration range. Magnetic stirrers should be used. All indicators must be stored properly, be in good condition and not past expiration date.

3. SPECTROPHOTOMETRIC METHODS

The wavelength settings in the spectrophotometer must be checked for accuracy periodically (e.g. with Holmium Oxide filters) and documented.

The appropriate type of cuvette (i.e. glass, quartz, etc.) for the wavelength of interest must be used.

Matched cuvettes must be used for dual beam instruments or established curves.

4. ION-SELECTIVE ELECTRODE METHODS

pH/Ion Specific meters must be readable to 1 mV and capable of temperature compensation/monitoring and proper decade response (50 to 60 mV range).

Electrodes must be stored properly and be in good operating condition. The membrane must be maintained and replaced as per manufacturer's instructions. All electrodes must be conditioned before any analysis.

Appropriate buffers should be used for analysis as per methods.

5. ION-CHROMATOGRAPH (IC)

ELAP approves IC as a technique for anions only in Drinking Water. Note that IC is not approved for Fluoride (F) in Drinking Water.

IC's must be equipped with the appropriate detectors and have adequate control for the water dip. In addition, laboratories must have the appropriate columns for the methods. Suppressor columns, separator columns and guard columns must be available as needed.

The eluent should be made freshly daily.

Phosphate (PO_4^-) and nitrite (NO_2^-) standards must be prepared fresh daily. All other standards can be held for one week.

***As of January 1, 1993, Ion Chromatography is now approved for the analysis of anions in wastewater.**

6. AUTOMATED ANALYTICAL SYSTEMS

Automated analytical systems must be equipped with the following features: Sampler, proportioning pump, manifold/cartridge, colorimeter with the required filter and flow-cell, recorder/printer or data handling system, adequate chemical/waste drainage for the instrument and any other accessories as required by the specific automated method.

With automated systems, it is crucial to determine the level of analyte that will cause carry-over contamination.

INSTRUMENT OPERATION/MAINTENANCE

Instrument operation manuals must be complete and accessible to the analyst. Instrument operating conditions must be established, documented and made available to the analyst.

Instruments are to be in good operating condition. Instrument repair and maintenance logs should be kept.

GLASSWARE/CONTAINERS

The appropriate glassware and containers must be available.

All samples must be collected in proper containers with the proper preservatives.

Glassware should be stored in an area free from dust and other contamination. Acid washed glassware must be segregated from other types of glassware.

CALIBRATION

1. FOR ALL METHODS:

   a. A **Standard Preparation Log** should be maintained. The logbook should include the following information: Source of the standard, lot number, purity, dilutions, final concentration, preparer, date prepared and expiration date. All calibration standards must be checked with a secondary standard that has been ultimately referenced to be certified standard.

   b. All standard solutions should be properly labeled with all pertinent information including: Date made, expiration date, concentration and preparer's initials.

2. SPECTROPHOTOMETRIC, ION-SELECTIVE ELECTRODE, ION-CHROMATOGRAPHIC AND AUTOMATED WET CHEMICAL METHODS:

   a. The standard curve must be constructed from a reagent, method blank and a minimum of three (3) standards each time. Alternatively, a standard reference curve may be employed but cannot be more than one year old; one standard is run each time and must be within set acceptance limits of the established curve. The range of standards must encompass the entire linear range or the range of interest. Standards must be in the DLR to MCL range for the samples.

   b. All samples quantitated must be within the calibration standard range or else the results are invalid. Sample dilution or the construction of a new calibration curve is required.

   c. The calibration curve needs to be evaluated for linearity by correlation factor ($r > 0.995$), %RSD or equivalent.

   d. An external reference sample should be run with each sample batch to confirm standard accuracy.

3. TITRIMETRIC METHODS

   Titrants need to be standardized each use or as per method requirements. The titrants must be dated, in good condition and stored properly.

4. GRAVIMETRIC METHODS

   A blank must be run with each batch of samples. All samples must be dried to a constant weight before final determination.

QUALITY CONTROL

1. QUALITY ASSURANCE PLAN

   The Q.A. plan developed for the laboratory must be followed and reflect actual laboratory practices. It must be up-to-date and made accessible to all analysts.

2. REPLICATES

   Drinking Water: 10% (f) or at least once per set
   Wastewater: 5% (f) or at least once per set

   The recommended maximum range for replicate precision is 20%.

3. SPIKE RECOVERIES

Samples should be spiked at a level not exceeding the action level for the analyte. Gravimetric and titrimetric methods do not require recovery analysis. For analytes where no action levels are established, spike with midrange standard.

Spiking standards should be prepared independently of the calibration standards.

Drinking Water: 10% (f) or at least once per set
Wastewater: 5% (f) or at least once per set

The recommended recovery range should be 80-120%.

Duplicate matrix spikes are recommended.

4. ACCEPTANCE GUIDELINES/CONTROL CHARTS

Acceptance guidelines and control charts must be established for each analyte in each matrix type and for each instrument.

5. CHECKING CORRECTNESS OF ANALYSES

For complete general mineral analysis of potable water, it is vital to check for correctness by evaluating the anion-cation balance (ion-balance). The acceptable difference is ± 5%. The appropriate procedures are outlined in **Standard Methods For The Examination Of Water And Wastewater**, 17th Edition 1989, Section 1030F, p. 1-20 to 1-21.

PROCEDURES

Analyses must be performed by acceptable methods and be referenced in the final report. No variation in reagents, instrumentation and conditions as described in the approved method is allowed.

TOXIC INORGANIC TESTING
(Field of Testing #3, 10, 17)

REGULATORY AGENCIES REQUIREMENTS

1. DRINKING WATER (FIELD OF TESTING #3)

The sample is liquid. Total recoverable analysis is required (no filtration). The sample is acid preserved in its original container. Interferences are minimal. No digestion is required unless the sample is visibly turbid. Sensitivity is **crucial** and any potential for contamination (i.e. from reagents, sample containers, glassware) must be monitored, documented and kept at acceptable levels. Laboratories should be prepared to demonstrate MDLs (Method Detection Limits) at or below established Detection Limit For Reporting Purposes (DLR). Calibration standards and recoveries should be at or below the Maximum Contaminant Level (MCL).

Graphite Furnace Atomic Absorption Spectrophotometer (GFAA) (EPA 2XX.2 series methods) and **simultaneous** Inductively Coupled Plasma Spectrophotometer (ICP) (EPA 200.7) are the instruments of choice for most analytes.

Mercury (Hg) must be analyzed by the cold vapor technique (EPA 245.X). A rigorous digestion is required.

Arsenic (As) and Selenium (Se) should be analyzed by either hydride generation or GFAA. EDL lamps are strongly recommended. Selenium cannot be analyzed by ICP. Arsenic analysis by ICP is subject to strong spectral interferences.

Flame Atomic Absorption Spectrophotometry (Flame AA) for the most part, has inadequate sensitivity for drinking water trace element analysis. Concentration of samples to meet the detection limits is <u>not</u> recommended due to the potential for strong spectral interferences. For alkali and alkaline earth elements, ion suppressors are required.

Sequential ICP does not have adequate sensitivity for the analysis of most trace elements except for Barium (Ba) and possibly Chromium (Cr). An ultrasonic nebulizer greatly increases sensitivity.

ELAP is now certifying for Sb, Be, Ni, and Tl, however, these elements are not regulated (as of 1-1-92) for drinking water in California.

California (1-1-92) has not adopted the Federal Lead and Copper Rule (6-29-91 Federal Register). ELAP will inform all certified laboratories well in advance of formal implementation of the rule.

EPA has recently published, "*Methods for the Determination of Metals in Environmental Samples*" EPA/600/4-91/1010. New procedures for sample preparation and updated versions of EPA 200 series methods are presented

Methods for the preparation of drinking water samples for analysis are described:

- *EPA 200.1 - Determination of Acid Soluble Metals - NITRIC DIGESTION FOR GFAA
- *EPA 200.2 - Determination of Total Recoverable Metals - FOR ICP-AES ONLY DUE TO HCl

*May be required for certain potable water systems.

200.7

Please note that EPA 200.2 calls for the use of HCl. If graphite furnace methods are to be employed, use of a matrix modifier is **crucial** to minimize spectral interferences and low recoveries.

EPA 200.8 (ICP/MS) is now approved for Pb, Fe, Cu, Mn, Zn, Sb, Be, Ni, and Tl (1-1-92).

EPA 200.9 (Stabilized Platform GFAA) is approved for Sb, Be, Ni, Tl, Pb, and Cu (1-1-92).

2. WASTEWATER (FIELD OF TESTING #17)

The sample is either liquid or solid. Total or filtrable analysis is required. Mild digestion followed by filtration is recommended for liquid samples. Rigorous digestion followed by filtration is recommended for solid samples. There is a potential for chemical and matrix interferences. Method of standard addition (MSA) may be required. Laboratories should be prepared to demonstrate MSA. Sensitivity is not crucial. Many elements are monitored. The laboratory **must** have lamps for all the elements applied for in the application form.

All types of instrumentation (except ICP/MS) are acceptable.

Mercury (Hg) must be analyzed by the cold vapor technique (EPA 245.X). A rigorous digestion is required.

Arsenic and Selenium should be analyzed by either hydride generation or GFAA. EDL lamps are strongly recommended. Selenium analysis by ICP is not approved. Arsenic is subject to strong spectral interferences with ICP analysis.

3. HAZARDOUS WASTE (FIELD OF TESTING #10)

Highly varying levels of target analytes and inferring elements may be present in samples. A strategy for dealing with trace analysis vs. macro analysis should be devised. This should include screening of samples, choice of instrumentation, dilution or concentration of the samples and adjustment of the size of the sample prepared for analysis. Monitoring for and correction of matrix effects should be well documented.

*Sample matrices should be classified as:

- Aqueous
- Sludges
- Multi-phasic
- Groundwater
- Oil or Organic Liquid
- Sandy Soil
- Clay Soil
- EP, WET or TCLP extracts

*SW 846 Final Update I, 1990.

Total or extractable (WET or TCLP) analysis is required. All samples must be digested by the applicable 3000 series method. Method of sample preparation must be described in the final report.

Detection limits (MDLs) **must** be clearly established for **each** matrix type analyzed.

For EP, WET or TCLP extraction analyses, Reporting Limits should be no more than 10% of STLC action levels.

Solids samples must be made homogenous by sifting (#USS 10 mesh) and/or milling and all extraneous materials should be removed. Proper preparation of samples is crucial and must be documented in sample preparation records.

All major instrumental categories are acceptable.

Mercury (Hg) must be analyzed by the cold vapor technique. A rigorous digestion is required.

Arsenic (As) and Selenium (Se) should be analyzed by either hydride generation or GFAA. EDL lamps are strongly recommended. For Arsenic and Selenium, ICP (EPA 6010) is an acceptable method. However, if adequate detection limits (10% of STLC values) cannot be achieved, alternative methods (GFAA and Hydride generation) are also required.

Hydride generation for hazardous samples is not recommended because of interferences due to the high acid levels.

A Laboratory Control Sample (LCS) of a matrix that is representative of the samples being tested should be analyzed with each set of digestates to evaluate digestion efficiency. It must emphasized that some sample matrices do not lend themselves to the recommended digestion procedures. If acceptable recoveries cannot be achieved and the LCS is in control, results of the sample analysis must either be rejected or submitted with a written qualifier.

KEY ELEMENTS OF PROPER ANALYSIS

1. Calibration: Establishes the linear range (working range) for analysis.

2. External Reference Sample: Establishes the accuracy of the calibration standards.

3. Method Detection Limit (MDL): Establishes the sensitivity of the method. MDLs must be veri by matrix.

4. Laboratory Control Sample (LCS): A reference sample of known value and appropriate matrix establish the efficiency of the digestion/extraction procedure.

5. Matrix Spike/Matrix Spike Duplicates (MS/MSD): Evaluates the effects of the sample matrix on the sample analysis. Duplicates and recoveries assess the precision and bias of the analysis.

WARNING

Reporting limits for soils must be carefully scrutinized. It has often been observed that laboratories tend to report unreasonably low values based on MDL data generated from reagent water or interference-free soil (i.e. Ottawa sand). MDL's data must be generated from matrices that reflect the actual sample matrices being analyzed.

INSTRUMENTATION

1. FLAME ATOMIC ABSORPTION SPECTROPHOTOMETRY (FLAME AA)

Flame AA's, should be supplied with the proper oxidant gases (for N_2O, a heater is required). The acetylene tank should be grounded and pressure should be maintained above 75 P.S.I.

The instrument(s) should be equipped with the proper burner heads (kept clean), and have a safety trap, background correction capability, strip chart recorder/printer and autosampler (optional).

Ion suppressors should used for analyses of the alkali and refractory elements.

2. GRAPHITE FURNACE ATOMIC ABSORPTION SPECTROPHOTOMETRY (GFAA)

GFAA's should be supplied with the proper grade of Argon/Nitrogen carrier gases.

The furnace area/tubes should be well maintained and in good condition.

The instrument(s) should be equipped with background correction capability, strip chart or recorder/printer, HGA accessory and autosampler (optional).

HCl should not be used for sample digestions.

GFAA analysis is subject to matrix effects. Serial dilutions and method of standard additions may be required.

Matrix modifiers are strongly recommended for GFAA analysis. Some form of background correction is **required**.

The sensitivity and limited linear range of GFAAs often requires sample dilution. The actual magnitude of the dilution as well as the cleanliness of the laboratory glassware and reagents can dramatically influence the quality of analytical results. Large dilutions should be avoided and screening procedures by alternate methods is recommended for suspected high level samples.

3. INDUCTIVELY COUPLED PLASMA SPECTROPHOTOMETRY (ICP)

The ICP should have an adequate argon gas supply (liquid argon is highly recommended).

The ICP can either be "simultaneous" or "sequential". Accessories such as an ultrasonic nebulizer increase sensitivity.

The instrument(s) should be equipped with background correction capability, a data acquisition system, printer and autosampler (optional).

An inter-element interference check standard should be run with each batch of samples (Field of Testing #10 only).

Interferences can occur because of:

- Overlap of spectral lines from another element.
- Unresolved overlap of molecular band spectra.
- Background from contamination or recombination phenomena.
- Stray light from line emission of high concentration elements.

The following procedures must be implemented to minimize the effects of chemical and matrix bias:

- Computer compensation after measuring the level of interferring elements.
- Selection of alternate wavelength.
- Manual background correction adjacent to the analyte line.

Serial dilution and method of standard additions may be required.

A high solids nebulizer is recommended for hazardous wastes samples. Due to potential for chemical and spectral interferences, hazardous waste samples results should be confirmed by an alternate wavelength or alternate method. All spectra should be closely examined by the analyst.

4. **INDUCTIVELY COUPLED PLASMA/MASS SPECTROPHOTOMETRY (ICP/MS)**

The ICP/MS should have an adequate argon gas supply (liquid argon is highly recommended).

The instrument should have a 5 - 250 AMU range with 1 AMU peak resolution at 5% peak height.

A peristaltic pump with mass flow controllers is required for sample introduction.

Tuning solution (Be, Mg, Co, In, Pb-100 ppb) is required for evaluating isotopic resolution at 20 - 200 AMU range.

Internal standards are required to compensate for drift and physical interferences (3 standards are required for a 5 - 250 AMU range).

Data system requirements are based on meeting Q.C. performance criteria. Consult with manufacturers guidelines for specifics.

Dissolved solids should not exceed 2000 mg/L.

Isobaric elemental and polyatomic interferences should be minimized by choice of isotope for measurement.

Physical effects of viscosity, aerosol formation and surface tension must be monitored with internal standards.

"Memory effects" must be monitored and minimized.

5. **MERCURY COLD VAPOR APPARATUS/HYDRIDE GENERATOR**

The Mercury Cold Vapor apparatus should have a trap and adequate ventilation for the vapors. Proper digestion procedures must be employed.

6. **LAMPS**

All lamps listed in the application must be present and in good condition. They should be dated when first placed into service.

EDL lamps are recommended for As and Se analyses. An appropriate power source must be available for the EDL lamps.

INSTRUMENT OPERATION/MAINTENANCE

Instrument operation manuals must be complete and accessible to the analyst. Instrument operating conditions must be established, documented and made available to the analyst.

Instruments are to be in good operating condition. Instrument repair and maintenance logs must be kept. Proper venting should be provided for all the instruments.

GLASSWARE/CONTAINERS/FACILITIES

Sample containers can be either plastic or glass. They should be new or acid washed. All samples are to be preserved with HNO_3 at pH < 2; preservative may be added to sample container before or after sampling.

Glassware must be acid washed (1 + 1 HNO_3), followed with D.I. water rinse.

An **acid resistant** hood is recommended for all digestion procedures. Digestion covers are strongly recommended to minimize air-borne contamination.

Batches or Lot numbers of sample containers must be monitored for contamination.

SAMPLE PREPARATION

A Sample Preparation Log must be maintained and should include the following information: Sample ID#, sample preparer, weigh of the soil or volume of the liquid, digestion method employed, date, matrix type, any pre-treatment and the final volume for analysis.

Digestates of Sn, Sb, Mo, Ba and Ag are less stable and analysis should be completed as soon as possible.

For Hazardous Waste samples (Field of Testing #10), a rigorous digestion using the appropriate SW 846 Method 3000 Series Methods is required.

For Wastewater liquids (Field of Testing #17), a mild nitric acid digestion is required. Solids require a vigorous (EPA 3050 or equivalent) digestion.

Closed Vessel Microwave Digestion (Fed. Reg. Vol., 56, No. 207, p. 55410 - 55414, October 25, 1991) has been proposed but is not approved (as of 4-1-92) for both Wastewater and Hazardous Waste testing.

EPA Methods 3015 (liquids) and 3051 (solids) have not yet been approved (January 1, 1992) for hazardous materials digestions.

CALIBRATION

1. STANDARDS

A standard preparation log must be maintained. The logbook should include the following information: Source of the standard, lot number, purity, dilutions, final concentration, preparer, date prepared and expiration date. All calibration standards must be cross-referenced with standards or check samples from a different source or lot number.

2. STANDARD CURVE

The standard curve must be constructed from a calibration blank and a minimum of three (3) standards each time. The range of the standards must encompass the entire linear range or the range of interest. Standard ranges should be adjusted accordingly for Drinking Water, Wastewater and Hazardous Waste samples.

All samples quantitated must be within the calibration standard range or the results are invalid. Sample dilution or the construction of a new calibration curve is required.

The calibration curve needs to be evaluated for linearity by correlation factor ($r > 0.995$), %RSD, or equivalent.

Daily sensitivity or Response Factor (RF) check samples should be analyzed to ensure proper instrument performance.

An external reference sample must be analyzed with each run. For Hazardous Waste analysis (Field of Testing #10), a "Laboratory Control Sample" must be prepared. The LCS must be of an appropriate matrix and made with standards from a second source. A standard check should be analyzed every 15 samples and at the end of the run.

NOTE: For ICP calibration, a blank and high range standard may be employed. A low and midrange solution must be then run as samples and be within acceptance limits.

3. METHOD BLANK

A volume of Type II reagent water processed through each step of sample preparation. A method blank must be run with each batch of samples.

4. CALIBRATION BLANK

A volume of Type II reagent water with the same amounts of acids as the samples and standards.

QUALITY CONTROL

1. QUALITY ASSURANCE PLAN

The Q.A. plan developed for the laboratory must be followed and reflect actual laboratory practices. It must be up-to-date and made accessible to all analysts.

2. DETECTION LIMITS

Reporting Limits (RLs) and Method Detection Limits (MDLs) must be established by matrix type and instrumentation. The RLs must be documented and "reasonable". (See enclosed appendix on MDL/DLR).

3. REPLICATES

Replicate analysis must be performed at a 10% (f) or at least once per batch for Drinking Water samples. For Wastewater and Hazardous Waste samples, the requirement is 5% or at least once per batch.

4. RECOVERIES

Samples should be spiked at a level not exceeding the MCL for the analyte. The spike must be from a source separate from the calibration standard.

Spikes should be tested at a 10% (f) or at least once per batch for Drinking Water samples. For Wastewater and Hazardous Waste samples, the requirement is 5% or at least once per batch.

Duplicate spikes are recommended.

Minimum recommended recovery ranges are:

a. Drinking Water: 80-120% with a precision of ± 20%.

b. Hazardous Waste: 70-130% with a precision of ± 30% (Sb and Ag: 60-140% with a precision of ± 40%); EPA 3055 (draft method) yields higher recoveries for Ag and Sb and is available upon 2request

c. Wastewater: 75-125% with a precision of ± 25%.

5. ACCEPTANCE GUIDELINES/CONTROL CHARTS

Acceptance guidelines and control charts must be established for each analyte in each matrix type and for each instrument.

PROCEDURES

Analyses must be performed by acceptable methods and referenced in the final report. No variation in method, reagents, instrumentation and conditions as described in the approved method is allowed.

A separate Quality Assurance Plan for handling each of the various regulatory agency samples may need to be developed.

WASTEWATER INORGANIC CHEMISTRY

NUTRIENTS AND DEMANDS
(Field of Testing #16)

INTRODUCTION

Wastewater nutrient and demand results are reportable to the State Regional Water Quality Control Boards (RWQCB's). Maximum Contamination Level's (MCL's) and Detection Levels for Reporting Purposes (DLR's) can be varied. Please verify reporting levels with the boards.

The sample is either liquid or solid. Either total or recoverable analysis is required.

The holding times and/or sample preservation are crucial (e.g. BOD, oil and grease, cyanide and sulfide). All samples should be refrigerated. Analyze all samples as soon as possible.

The potential for interferences to affect analytical results especially for cyanide, sulfide and BOD analyses is high. Samples must be evaluated for potential interferences prior to analysis. Any adjustments made to the sample must be documented.

For distillations, extractions, and digestion procedures, a method blank, method standard and matrix spikes are essential for proper evaluation of methods.

For distillation and digestion procedures, the appropriate safety precautions should taken such as working in an efficient hood, wearing safety glasses and having spill kits available.

Reporting limits (see appendix - MDL/RL) are matrix dependent. These limits should be above the Method Detection Limit (MDL) and should be validated with actual work on the matrices involved. Limits must be confirmed by spiking blanks at RL levels and taking the fortified blank through all analytical steps. Any validation work should be documented and be available for inspection.

Please refer to the General Laboratory Information Guidelines for procedures relating to recording keeping, glassware and reagents, quality control and reporting of results.

BIOCHEMICAL OXYGEN DEMAND (BOD) (FoT #16.4)

EQUIPMENT/REAGENTS

The incubator must be capable of maintaining a temperature of 20°C ± 1°C. The incubator temperature must be monitored during the 5-day incubation period. Please note that there is significant temperature variation in most refrigerators. You should monitor the temperature at different levels in the incubator to verify uniform temperature.

The BOD bottles should be 300 ml in volume. They **must not** be washed with chromic acid for **any** reason. The bottles should have water seals, be capped with plastic covers, and not cracked. BOD bottles used for Mercury analysis should be segragated from those used for BOD analysis.

The dilution water must be either freshly made or stored properly (out of light). If algal growth is observed, discard the water and thoroughly wash and rinse the holding container before reuse.

For carbonaceous BOD, a nitrogen inhibitor (2-chloro-6-(trichloromethyl) pyridine (TCMP)) is required.

PROCEDURE

Prior to analysis, the sample must be tested for pH and residual Cl_2. If the pH range is unacceptable or if residual Cl_2 is detected, the sample must be treated. A dynamic range of volumes must be employed for samples that are not routinely analyzed.

Seeding is usually needed only for treated effluent. The seed should be introduced after the pH is adjusted and all interferences have been removed. Untreated primary effluent or commercial seed sources (i.e. polyseed) are acceptable. Oxygen demand from the seed must be compensated for in final calculations.

Dissolved oxygen can be determined by the modified Winkler method or be dissolved oxygen probe.

For the modified Winkler Method, the Sodium Thiosulfate ($Na_2S_2O_3$) titrant must be routinely standardized. The Dissolved Oxygen Probe must be properly stored and in good condition. The probe must be calibrated on a periodic basis against the Winkler Method. Air calibration alone is **prohibited**. The probe should be recalibrated after each membrane change.

Key Elements Of B.O.D. Analysis Include:

1. The oxygen depletion of the dilution water blank should be less than 0.2 mg/L after five (5) days. **No compensation is allowed** for a Dissolved Oxygen (DO) difference of greater than 0.2 mg/L.

2. For results to be valid, the residual DO must be greater than 1.0 mg/L and the depletion must be greater than 2.0 mg/L.

3. The Glucose/Glumatic acid test should be performed periodically (acceptable range: 167-233 mg/L).

NOTE: **Samples results that show a decreasing BOD value with increased amount of sample should be evaluated for "toxic effects".**

WARNING: It is **strongly recommended** that gloves be worn when handling samples for BOD analysis. Samples may contain toxic and/or infectious materials (biohazard) that may be potential health hazards for the analyst.

CHEMICAL OXYGEN DEMAND (COD) (FoT #16.9)

Digestion can be done either by open reflux or closed block digestion (micro digestion). Open reflux digestion should be performed in a hood. Air-borne contamination must be minimized. For micro digestion, the sample must be homogenized with an osterizer if there is suspended material in the sample. It is recommended that all samples be done in duplicate to monitor contamination and precision.

The temperature in the closed digestion heating block must be monitored (150° C).

SAFETY WARNINGS: a) **Properly mix reagents and samples before digestion; super heating can occur!**

b) **Always wear safety glasses!**

A calibration curve or external reference standard using Potassium Acid Phthalate should be used. Titrametric or spectrophotometric analysis may be employed. Chloride should be complexed with Mercuric Sulfate ($HgSO_4$) to minimize interference. Saline samples requires special treatment (see EPA 410.3). The normality of the dichromate solution should be adjusted to match expected the COD level for the sample.

WARNING: **The potential for positive contamination is high and should be monitored for and kept at acceptable levels.**

CYANIDE (FoT #16.12)

NOTE: As of January 1, 1992, microdistillation (membrane) systems are not approved for cyanide analysis.

Liquid samples must be preserved with NaOH.

All samples must be tested for the presence of oxidizing agents and other potential interferences and properly treated prior to analysis. Any pre-treatment steps must be documented.

Reflux distillation is required for both manual and automated wet analysis. Vacuum flow rates can fluctuate and must be constantly monitored to ensure acceptable recoveries. The distillation should be performed in a hood.

A method blank, method standard and duplicate matrix spikes must be performed with each batch of samples.

A new calibration curve and reference standard must be run with each batch of samples.

Reporting limits must be verified by matrix and be at reasonable levels.

Cyanide analysis by ion-chromatography and ion specific electrode are not approved as of 1/1/92.

Cyanide samples analyzed by automated wet methods must be manually distilled (UV promoted distillation is not allowed).

AMMONIA/TOTAL KJELDAHL NITROGEN (TKN) (FoTs 16.3, 16.16)

The sample is preserved with Sulfuric Acid (H_2SO_4) and should be analyzed as soon as possible.

Reagent water must be monitored for potential ammonia contamination.

For saline samples, standards and blanks should be prepared in Synthetic Ocean Water (SOW).

For EPA Methods 350.1 (automated wet analysis), EDTA must be added to complex and remove Calcium and Magnesium ions.

For EPA Method 350.2 (manual wet analysis), distillation (micro- or macro-) is required.

For EPA Method 350.3 (potentiometric, I.S.E.), **no** distillation is required.

Organic Kjeldahl Nitrogen (OKN) can be determined by subtracting free ammonia from TKN values.

Automated digestion, block digestion and macro- Kjeldahl digestion systems are all approved for TKN analysis.

A method blank, method standard and duplicate matrix spikes must be performed with each batch of samples.

A new calibration curve and reference standard must be run with each batch of samples.

PHENOLS (FoT 16.24)

NOTE: Micro distillation and UV promoted automated distillation are not approved as of 1/1/92.

The sample should be preserved with H_3PO_4 and Cu SO_4 to minimize biological degradation (EPA 420.1 Section 4.1).

The sample should be tested for the presence of oxidizing and interfering agents prior to analysis. Any pre-treatment steps must be documented.

A method blank, method standard and duplicate matrix spikes must be performed with each batch of samples.

A new calibration curve and reference standard must be run with each batch of samples.

OIL AND GREASE (FoT 16.20)

Samples must be collected in **glass** containers and preserved with either HCl or H_2SO_4.

The sample container should be rinsed with an aliquot of freon and combined with the sample extract.

A freon blank must be analyzed. It is permissible to subtract blank values from sample results.

All extracts should be passed through anhydrous Sodium Sulfate prior to analysis.

Quantitation can be by either gravimetric (EPA 413.1) or infrared, spectrophotometric (EPA 413.2) methods.

NOTE: Recycling of Freon is strongly encouraged. This practice not only is cost effective but also good for the environment. Information on recycling systems is available from the ELAP office upon request.

TOTAL ORGANIC CARBON (TOC) (FoT 16.21)

The samples should be collected in glass containers and preserved with HCl or H_2SO_4.

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

Samples must be made homogenous prior to analysis.

Organic carbon is converted to CO_2 by either catalytic combustion or wet chemical oxidization.

CO_2 may be analyzed directly by a infrared detector or converted to CH_4 and analyzed by a Flame Ionization Detector.

Potassium hydrogen phthalate is used for standard calibration.

Procedures as recommended by instrument manufacturer should be adhered to.

TOTAL RECOVERABLE PETROLEUM HYDROCARBONS (TRPH) (FoT 16.44)

NOTE: **EPA 418.1 is not an acceptable method for Total Petroleum Hydrocarbon (TPH) analysis for Leaking Underground Fuel Tank (LUFT) compliance and is recommended only as a screening method.**

Liquid samples should be collected in glass one-liter bottles and preserved with HCl.

The sample container should be rinsed with an aliquot of freon and combined with the sample extract.

Solid samples should be collected in 4 oz. (120 ml) wide-mouth, teflon lined jars or Shelby core tubes.

Solids are to be extracted with Freon 113 (3 times) and combined with anhdrous sodium sulfate prior to analysis.

Clean-up using silica gel adsorbent may be required to remove interferences.

Fixed or scanning infrared spectrophotometers are acceptable.

If the mixed standard (N-hexadecane, iso-octane and chlorobenzene) does not adequately match hydrocarbons present in the sample, significant bias can occur.

Reporting limits (esp. for soils) must be scrutinized. The suggested reporting limits are 1-5 mg/L for liquids and 25-50 mg/Kg for soils.

PHYSICAL PROPERTIES
(Field of Testing #9)

INTRODUCTION

As part of California's Title 22, Article 10, Sections 66261.21-66261.23, the physical property tests are part of the criteria for identifying hazardous wastes.

The Tests Involved Are:

1. Ignitability (Flashpoint determination)
2. Corrosivity (pH determination)
3. Corrosivity towards steel
4. Reactivity

IGNITABILITY (FLASHPOINT) - Title 22 Section 66261.21

Either the Pensky-Martens closed-cup or the Setaflash closed-cup flash testers are acceptable for flashpoint determination. The apparatus must be equipped with a stirrer thermometer. The thermometer must be calibrated periodically and all calibrations must be documented.

Pensky-Martens testers are recommended for liquids including those that tend to form surface film under test conditions and for liquids that contain suspended solids.

Setaflash testers are preferred for lower flash point and less viscous liquid test samples.

Flashpoint must be done in an area free of draft and under a vented area.

For quality control, a duplicate must be analyzed once per set with acceptable precision (± 10%). The reference standard (p-xylene with a flashpoint of 25°C or 77°F) must be determined at least once per batch and documented.

CORROSIVITY - pH DETERMINATION - Title 22 Section 66261.22 (EPA 9040)

The pH meter must be properly maintained and calibrated before any determinations are made. The electrode should be properly stored in a buffer and cleaned after contact with hazardous material.

For safety, pH determination should be done in a hood if the characteristics of the material is unknown to the analyst.

Solid samples must be mixed with an equivalent weight of reagent water or calcium chloride solution depending on the nature of the soil (see EPA 9045) prior to analysis.

CORROSIVITY TOWARDS STEEL - Title 22 Section 66261.22

Required Equipment Includes:

- A flask with a 500 to 5000 ml capacity
- A reflux condenser
- A thermowell and temperature regulating device (e.g. Rheostat)
- A heating device
- Specimen supporting system

The system must be capable of holding the test temperature of 55°C.

Test coupons (SAE 1020 steel) must be available.

For quality control, a duplicate and a blank (check for sound metal lost) must be run per set of samples. The ratio of the test material to the surface area must be at least 40 ml/cm. The procedure for cleaning the surface before weighing must be established and written into the SOP.

REACTIVITY - Title 22 Section 66261.23

A solid waste exhibits the characteristic of reactivity if it has any of the following properties:

1. Is unstable and readily undergoes violent change.
2. Will react violently with water.
3. Forms a potentially explosive mixture with water.
4. When mixed with water, is capable of generating toxic gas vapors.
5. **Is a sulfide or cyanide bearing waste capable of generating toxic gases, vapors or fumes when exposed to pH conditions between 12.5 and 2.**
6. Is capable of detonation or explosion if heated or is subject to confinement.
7. Is capable of detonation or explosive decomposition.
8. Is classified as a forbidden explosive as defined in CFR 173.51, 53, 88.
9. Has an EPA Hazardous Waste number of D003.

For purposes of ELAP certification, only Item Number 5 will be evaluated for certification purposes.

1. **Determination of Hydrogen Cyanide released from Wastes (Total Releasable Cyanide) (Chapter 7, 7.3.3.2 -SW 846, 3rd Edition).**

   An aliquot of waste is acidified to pH 2 and cyanide is collected and evaluated by EPA Method 9010 (please refer to FoT 16 for analytical procedures for the determination of cyanide)

   Please refer to Section 4.D (see Figure 1) for required equipment.

   A stirring apparatus, round bottom flask, separatory funnel, two-stage regulator supply of nitrogen and a rotometer are required.

   As a System Performance Check, a cyanide reference sample (Paragraph 5.2) must be run. Fifty percent or greater recovery is required.

2. **Determination of Hydrogen Sulfide release for Wastes (Total Releasable Sulfide) (Chapter 7, 7.3.4.2 - SW 846 3rd Edition).**

An aliquot of waste is acidified to pH 2 and sulfide and evaluated by EPA Method 9030 (please refer to FoT 16 for analytical procedures for the determination of sulfide).

Please refer to Section 4.0 (see Figure 2) for required equipment.

A stirring apparatus, round bottom flask, separatory funnel, two-stage regulator supply of nitrogen, rotometer and detector tube for sulfide are required.

As a System Performance Check, a sulfide reference solution (Paragraph 5.2) must be run. ≥ 50% recovery is required.

GENERAL QUALITY CONTROL

The Quality Assurance plan developed for these methods must be adhered to and reflect actual laboratory practices. It must be up-to-date and accessible to all analysts.

ORGANIC CHEMISTRY
(Field of Testing #4, 5, 12, 13, 18, 19)

REGULATORY AGENCY REQUIREMENTS

1. DRINKING WATER (FIELD OF TESTING #4 AND 5)

The sample is liquid. Total recoverable analyses is required. There are few chemical and matrix inferences and sample recoveries are not required. Low-level, contamination-free analysis is required. Drinking water samples should be segragated from and analyzed independently of hazardous waste samples. **The potential for laboratory contamination of samples must be minimized.**

Analysis is by the EPA 500 series methods. All requirements for initial demonstration of proficiency as described in the method must be complied with.

Analyzing laboratories must use ODW reporting forms for submitting compliance results. Detection Limits for Reporting Purposes (DLRs) as established by ODW must be used.

Sensitivity is crucial for drinking water and analysis. This is especially true of compounds such as EDB and DBCP (EPA 504) and Endrin, Heptachlor, and Heptachlor Epoxide (EPA 505, 508) which have required reporting limits at or near MDLs under optimum instrument performance conditions.

Liquid-solid phase extraction (LSE) is required for EPA 506 and 525.1.

EPA Methods 504 and 505 require micro extraction.

Diethylhexyl phthalate (DEHP) is now regulated in drinking water. This is common in plastic products. Steps must be taken to minimize the potential for contamination.

2. WASTEWATER (FIELD OF TESTING #18, 19)

The sample is either liquid or solid. Analyses is by the EPA 600 series methods. Capillary columns may be substituted for packed columns.

Second column or GC/MS confirmation is required for samples tested by 600 series methods. (See Confirmation Policy).

Duplicate matrix spikes are required. Clean-up procedures may be necessary to remove interferences.

3. HAZARDOUS WASTES (FIELD OF TESTING #12 AND #13)

Highly varying levels of target analytes and inferring elements may be present in samples. A strategy for dealing with trace analysis vs. macro analysis should be devised. This should include screening of samples, choice of instrumentation, dilution or concentration of the samples and adjustment of the size of the sample prepared for analysis. Monitoring for and correction of matrix effects should be well documented.

*Sample matrices should be classified as:

- Aqueous
- Sludges
- Multi-phasic
- Groundwater
- Oil or Organic Liquid
- Sandy Soil
- Clay Soil
- EP, WET or TCLP extracts

*SW 846 Final Update I, 1990.

Method Detection Limits (MDLs) **must** be clearly established for **each** matrix type analyzed.

For EP, WET or TCLP extraction analyses, MDLs must be 10% of STLC action levels.

Organic samples are prepared for introduction into the instrument by EPA 3500 series (extraction) or EPA 5000 (purge and trap) methods. Clean-up, if necessary, must be performed by EPA 3600 series methods. All preparation of samples including clean-up procedures must be documented.

Analysis is by the EPA 8000 series of methods. Capillary columns may be substituted for packed columns.

Second column or GC/MS confirmation is strongly recommended for samples tested by the 8000 series method (See Confirmation Policy).

All quality control and demonstration of proficiency requirements described in Section 8000 must be complied with for all Hazardous Wastes methods.

Final Update I (November 1990) for SW 846, 3rd Edition, is now available to laboratories. Methods 8011 (EDB, DBCP), 8021 (ELCD and PID detectors in series) and 8260 (GC/MS-Volatiles) are now approved methods.

EPA 1311, the Toxicity Characteristic Leaching Procedure (TCLP) has been adopted by DTSC. An approved Zero-Headspace-Extractor (ZHE) is required for extractable volatile analysis. Please refer to Extraction Procedures for more information.

4. LEAKING UNDERGROUND FUEL TANK (LUFT) PROGRAM COMPLIANCE

Hydrocarbon fuel testing is required for LUFT compliance. The LUFT program is administered by various regulatory agencies and as such reporting requirements may vary. Please contact the agency for more information.

Total Petroleum Hydrocarbons (TPH) is usually performed by GC-FID (DHS method or modified 8015) with BTXE identification by PID. The PID-FID detectors may be run in series. EPA methods 8240 and 8260 (P&T, GC/MS) are recognized as equivalent methods for TPH analysis.

Gasoline is usually analyzed by purge and trap procedures. Soils may be directly purged (1 gram into 5 ml water) or extracted with methanol (10 grams into 20 ml, 50 μl/5 ml). Higher boiling point fuels such as kerosene, jet fuels, and diesel are usually extracted ($MeCl_2$ recommended). Concentration steps may be necessary to achieve acceptable detection limits for extractables.

Total Recoverable Petroleum Hydrocarbon (TRPH) analysis by IR (EPA 418.1) will yield low recoveries for the volatile fraction of fuels and should be used for screening purposes only, unless requested by the regulatory agency.

It is crucial that a site sampling plan be clearly established before beginning a clean-up project. Data quality objectives must be clearly defined. GC/MS is recommended for initial characterization of the site. This is especially true if complex or uncharacteristic chromatograms are generated. Less rigorous methods may be used for remediation or monitoring conditions once matrix factors and analytes have been determined.

Due to weathering factors, etc., "aged" fuels will tend to yield varying results when calibrated with fresh standards.

It is recommended that reference chromatographic "profiles" for the various fuels be maintained.

INSTRUMENTATION

NOTE: All procedures and equipment as described in the methods must be strictly followed. Variations only as permitted in the method are allowed and only after demonstration of equivalency.

1. GAS CHROMATOGRAPH (GC)

The GC should be equipped with an integrator/data handling system capable of peak resolution and baseline adjustment; glass-lined injection ports, 0.2 °C oven control, temperature programming capability and appropriate detectors.

For VOC analysis, the instrument(s) should have the capability for sub-ambient oven temperatures and an appropriate purge and trap device.

2. HIGH PERFORMANCE LIQUID CHROMATOGRAPH (HPLC)

The HPLC should be equipped with a recorder/integrator for data handling and solvent programming capability.

The HPLC should have either UV or Fluorescence (required for EPA 531.1) detectors. Post-Column derivatization is required for methods employing the fluorescense detector.

3. GAS CHROMATOGRAPH/MASS SPECTROMETER (GC/MS)

The GC/MS should be equipped with a recording device and an appropriate software/computer system for data acquisition and manipulation; and capable of plotting ion-abundance vs. time or scan number (Extracted Ion Current Profile - EICP). The spectrometer should be capable of scanning from 35 to 300 AMU every 2 seconds or less using 70 volts (nominal) electron ionization energy for volatile methods and 35-500 AMU every second for extractable methods.

The computer must also have a library of compounds. With automated quantitation and search routines, manual verification is required.

The instrument should have all glass transfer lines and enrichment devices.

For volatile analytical methods, Bromofluorobenzene (BFB) tuning is required. For semi-volatile analytical methods, deca-fluorotriphenylphosphine (DFTPP) tuning is required. Tuning should be performed every 8-12 hours depending on method.

A sub-ambient over controller or cryogenic focusing (liquid N_2) may be required for volatile analyses.

Qualitative identification is achieved by analyzing standards under the same conditions as samples and using both the mass spectra and GC retention times.

Internal standard calibration for quantification is required.

System Performance Check Compounds (SPCCs) are required for EPA Methods 8260 and 8270. SPCCs evaluate response factors (RFs). All SPCC compounds must have an average RF greater than 0.3 (0.250 bromoform) for volatile analysis and 0.050 for semi-volatile analysis.

Calibration Check Compounds (CCCs) are required to evaluate the instrument calibration (EPA 8260, 8270). Percent RSDs should not exceed 30% for CCCs.

Quadrapole, magnetic sector and ion-trap spectrometers are all acceptable.

INSTRUMENT OPERATION/MAINTENANCE

Instrument operation manuals must be complete and accessible to the analyst. Instrument operating conditions must be established, documented and made available to the analyst.

Instruments should be in good operating condition. All instrument repair and maintenance logs should be kept. For instruments used in extractable analyses, the septa should be changed on a regularly scheduled basis. For instruments used in volatile analysis, the traps should be well-maintained and the packing material should be replaced at regularly scheduled intervals. It is recommended that all instruments be vented to minimize contamination.

GLASSWARE/CONTAINERS/REAGENTS/PREPARATION

1. VOLATILE ORGANIC COMPOUNDS (VOCs)

Liquid VOC samples must be collected in duplicate along travel blanks in 40 ml, Teflon lined septum vials with no headspace. The vials must be new or baked out at 105°C. If vials are reused, a new Teflon liner must be used each time. Samples to be analyzed, must be stored separately from volatile organic standards and extracts.

Soil samples should be collected in 4 ounce (120 ml) wide-mouth jars with Teflon liners.

Soil samples for VOC analysis should **not** be composited.

2. EXTRACTABLE ANALYSES

Liquid samples must be collected in one liter amber glass bottles with Teflon-lined caps. The bottles must be new, baked out at 400°C or solvent (acetone) rinsed.

Soil samples should be collected in 4 ounce (120 ml) wide-mouth jars with Teflon liners.

Special handling should be applied if SHELBY (brass) tubes are used for core samples. Make sure of electrical or duct tape is **not** used to seal the sample container (toluene contamination). The top two inches of soil must be removed before taking the sample aliquot for analysis.

Please refer to the individual method for extraction procedures; Macro, Micro, and Liquid-Solid Extraction (LSE) with or without concentration steps may be required. Extraction efficiency should be evaluated through the use of surrogates and method standards. Extraction efficiency must meet acceptance criteria and cannot be compensated for.

The appropriate glassware must be available for extractions (i.e. separatory funnels, K-D apparatus, etc.). The glassware must be either baked out at 400°C or solvent (acetone) rinsed.

A water/steam bath must be available for sample concentration steps. All concentration and extraction steps must be performed in a hood.

All extracts should be stored securely in an explosion-proof refrigerator.

Surrogate compounds as specified in the methods (and spiking compounds if necessary) are added to the sample **prior** to extraction.

CLEAN-UP PROCEDURES

Interferences from co-extracted compounds vary from sample to sample. If analysis is prevented due to interferences, further clean-up of the sample extract may be necessary. The laboratory shall be prepared to document clean-up procedure capability by EPA 3600 Series Methods. Method of clean-up should be cited in the final report.

Clean-up procedures are necessary for the isolation of analytes to minimize extraneous peaks; to reduce deterioration of resolution and column efficiency, loss of detection sensitivity and to prolong the life of the column.

3. **REAGENTS**

Laboratories must use organic-free reagent water. The organic-free water can either be prepared in-house or purchased.

All solvents, reagents, sample containers and glassware must be evaluated for contamination before use.

BLANKS/CONTAMINATION

The potential for contamination in organic analyses is high. Laboratories must take all steps necessary to ensure that contamination is kept at minimal levels. Contamination is a problem that should be resolved, not worked around!

Contamination is monitored through the use of method blanks and travel blanks (VOC analysis only). If a reportable analyte is detected in either blank, the result of the sample analysis for that analyte may be invalidated. **SUBTRACTION OF BLANK CONTAMINANT LEVELS IS NOT PERMITTED.**

The "Golden Rule" in organic analysis is **"ANALYZE AS SOON AS POSSIBLE!"** The faster that a sample is analyzed, the less likely there will be either sample loss or contamination.

Common laboratory contaminants are Methylene Chloride, Chloroform, Benzene, Freons and Acetone. If blank contamination is detected, you should examine your laboratory for the following:

1. The solvent containers must be capped and stored in a ventilated area. Methanol used to prepare standards for volatile analysis should be stored away from other solvents, especially methylene chloride.

2. Extractions must be done in a hood with adequate flow (100 LFM - monitored on a regular basis) and in an area as far away from the instrumentation as possible.

3. The laboratory must have adequate hoods and proper ventilation (preferably positive pressure)in the analytical area.

4. Samples must be stored separately from sources of contamination. They must not be stored in the same refrigerator as the standards or solvent extracts. Hazardous waste samples may or may not contain VOC compounds at high levels.

5. The organic-free lab water must be kept free of contamination at all times. The water should be freshly prepared. If necessary, the water can be held if it is boiled, cooled and purged with nitrogen before use.

6. Empty sample containers must be stored in an area free from possible sources of contamination.

7. Concurrent analyses of extractables (MBAS, oil and grease and solvent extraction for GC procedures) should be minimized if possible.

8. Carry-over contamination from the trap, column and the detector should be monitored.

9. Each lot of solvents (methanol, methylene chloride, etc.) must be tested for interferences and contaminants and the results documented.

10. Use of Tygon tubing and reagents such as sodium sulfate stored in plastic containers must be avoided for extraction procedures to minimize the effects of phthalate contamination.

SAMPLE PREPARATION/EXTRACTION

A sample log must be maintained and should include the following information:

1. Sample ID#
2. Date
3. Sample Preparer
4. Matrix Type
5. Any Pre-Treatment
6. Weight of Soil
7. Volume of Original Sample
8. Preparation/Extraction Method
9. Final Volume

CALIBRATION

1. STANDARDS

A standard preparation log must be maintained. The logbook should include the following information:

a. Source of the Standard
b. Lot Number
c. Purity
d. Dilutions
e. Final Concentration
f. Preparer
g. Date Prepared
h. Expiration Date

Volatile standards must be stored with minimal headspace. All neat standards for VOCs must be frozen. All standards must be refrigerated. All standards must be labeled, dated and stored properly.

2. STANDARD CURVE

The standard curve must be constructed from a calibration blank and a minimum of five (5) standards. The range of the standards must encompass the entire linear range or the range of interest. Standards must be in the appropriate range for Drinking Water, Hazardous Waste and Wastewater samples.

All samples quantitated must be within the calibration standard range or else the results are **invalid.** Sample dilution or the construction of a new calibration curve is required.

The calibration curve needs to be evaluated for linearity statistically (%RSD or equivalent).

For daily runs, a midrange standard can be used for calibration verification provided that the Average Response Factor criteria are met.

A standard check should be analyzed every 15 samples or at the end of the run.

Retention times should be monitored and "windows" for R.T. limits for specific compounds should be clearly established.

3. METHOD BLANK

A volume of Type II reagent water processed through each step of sample preparation. A method blank must be run with each batch of samples.

*Results for analytes are invalid if they are detected in the method blank at:

- The Detection Limit (DLR), or
- 5% of the action level, or
- 5% of the measured concentration in the sample.

*SW 846

4. CALIBRATION BLANK

A volume of Type II reagent water with the same amounts of acids as the samples and standards.

QUALITY CONTROL

1. QUALITY ASSURANCE PLAN

The Q.A. plan developed for the laboratory must be followed and reflect actual laboratory practices. It must be up-to-date and made accessible to all analysts.

2. METHOD DETECTION LIMITS

Method Detection Limits (MDLs) must be established by matrix type and instrument.

3. REPORTING LIMITS

Reporting limits must be based on the entire method. Distillations, clean-ups, extractions, dilutions or concentration steps and all matrix (interferences) effects must be taken into account. Failure to record dilutions and not taking them into account in final report is a common laboratory error.

False positive results should be fully explained in the comment section along with the uncorrected data.

Method of sample preparation must be cited in the final report and will affect reporting limits.

The RLs must be documented and "reasonable".

4. SIGNIFICANT FIGURES

Laboratories should review the reporting of significant figures in final results. The number of significant figures reported should be no more than the number justified by the **least** precise step in the procedure. Automated data reported to four to five figures should be reviewed and corrected manually for final reports.

5. REPLICATES

Replicate analyses must be performed at a 10% level or at least once per batch for Drinking Water samples. For Wastewater and Hazardous Waste samples, the requirement is 5% or at least once per batch.

6. RECOVERIES

Samples should be spiked at a level not exceeding the MCL for the analyte. The spiking solution must be from a source made independently from the calibration standard.

Matrix spikes are not required for Drinking Water analysis. For Wastewater and Hazardous Waste analyses, recoveries should performed a 5% (f) or at least once per batch. Duplicate matrix spikes are recommended.
For Hazardous Waste and Wastewater methods, a minimum of three (3) compounds or 10% of the target compounds should be spiked, whichever is greater. The spikes should encompass the chromatographic range (i.e. early eluting vs. late eluting). All compounds spiked must be in control.

7. EXTERNAL REFERENCE AND LABORATORY CONTROL SAMPLES (LCS)

An external reference sample must be analyzed with each run.

For Hazardous Waste Analysis (Field of Testing #12 and 13), a "Laboratory Control Sample" must be prepared. The sample must be of a representative matrix and made with standards from a secondary source.

8. ACCEPTANCE GUIDELINES/CONTROL CHARTS

Acceptance guidelines and control charts must be established for each analyte in each matrix type and for each instrument.

9. CORRECTIVE ACTION/DATA REVIEW

All resolutions of out-of-control situations must be documented by an established "Corrective Action" protocol.

All data (raw and final results) should be reviewed by a second party before they are released. Documentation of that review is needed. This is particularly important with automated data. Data must be reviewed manually and initialed by the reviewer before submission of results.

10. INSTRUMENT RUN LOG

A Run Log must be maintained for all instruments involved in organic analysis. Instrument, analyst, date and sample sequence should be indicated.

11. CHROMATOGRAM QUALITY

To assure high data quality, the chromatograms for an analysis must have a stable baseline with no rises and dips, and be **well-resolved** and have symmetrical (non-tailing) peaks.

Carrier gas flow rates and oven temperatures that are higher than recommended in the method may speed up run times but can make integration, peak selection and peak resolution very difficult. Please use good judgement.

Detector saturation levels must be established and documented. The optimum range for detector quantification should be established. Some detectors have very limited linear dynamic ranges.

12. PEAK SELECTION FOR MULTIPEAK COMPOUNDS

Many congeners of complex compounds may be linear and representative in a standard or in one sample matrix but not in another. The decision as to which peaks are chosen should be made with each sample matrix. It is recommended that the peaks be carefully chosen for every analysis and for every sample matrix.

13. PEAK INTEGRATION

Forcing a base-line across a number of peaks and measuring all of the area is inappropriate for quantifying complex organic compounds in soils where large amounts of interfering materials are present in the sample but not in the standard.

PROCEDURES

Analyses must be performed by acceptable methods and referenced in the final report. No variation in method, reagents, instrumentation and conditions as described in the approved method is allowed.

A separate Quality Assurance Plan for handling each of the various regulatory agency samples may need to be developed.

SOLVENT RECYCLING

Laboratories are strongly encouraged to recycle all the solvents used in their laboratories. This practice not only is cost effective but also good for the environment.

CONFIRMATION POLICY (January 1, 1992)

For gas chromatographic organic analysis, all positive results are recommended to be confirmed either by a second column or GC/MS analysis, unless exempted in the following situations:

1. The analytes of interest can produce gas chromatogram containing "pattern" peaks which match appropriate standards. These analytes include Polychlorinated Biphenyls (PCB's), hydrocarbon fuels (e.g. gasoline) and toxaphene.

2. The sample is analyzed for Benzene, Toluene and Xylenes (BTX) for gasoline tank removal purposes and the same sample was found to contain gasoline by a separate analysis. However, the presence of BTX in a sample containing no gasoline must be confirmed.

3. The samples meet all of the following requirements:

    a. All samples (liquid or solid) come form the same source, e.g. groundwater samples from the same well, for continuous monitoring. However, samples of same matrix form the same site but from different sources (different sampling locations) are not exempted.

    b. All chemical parameters have been previously analyzed, identified and confirmed by a second column or GC/MS. The laboratory must have the necessary documents indicating previous confirmation.

    c. The resulting gas chromatograms are relatively simple and do not contain complex or overlapping peaks.

    d. Chromatograms are largely unchanged from those for which confirmation was carried out.

    e. Representative samples must be periodically confirmed at a frequency of at least 5%.

    f. For Drinking Water analyses, refer to the individual method for confirmation criteria.

PROCEDURE TO DETERMINE METHOD DETECTION LIMIT (MDL)

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

1. Make an estimate of the detection limit using either:
   a. A concentration value that corresponds to an instrument signal/noise ratio in the range of 2.5 to 5:1.
   b. A low concentration value showing a break in the slope of the calibration curve.

2. Prepare reagent (blank) water that is as free of analyte as possible.

3. a. If the MDL is to be determined in reagent water (blank), prepare a laboratory standard (analyte in reagent water) at a concentration which is between 1 and 5 times the estimated MDL. Proceed to step 4.
   b. If the MDL is to be determined in another sample matrix, analyze the sample. If the measured level of the analyte is in the recommended range of 1 to 5 times the estimated MDL, proceed to step 4.

4. Take a minimum of seven aliquots and process each through the entire analytical method.

5. Calculate the standard deviation(s) of the replicate measurements.

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

$$S = (S^2)^{\frac{1}{2}}$$

where Xi, i = 1 to 7 are the analytical results from the seven sample aliquots

MDL = S x (3.143)

6. A lower concentration of the analyte will not result in a significantly lower calculated MDL.

Example of the MDL Calculation:

Run #	Xi	Xi^2
True Value = 1.5 mg/L		
1.	1.2310	1.515
2.	1.3620	1.855
3.	1.5192	2.292
4.	1.5776	2.488
5.	1.6621	2.762
6.	1.7226	2.962
7.	1.7383	3.021
	$\overline{Xi} = 10.807$	$\overline{(X_i^2)} = 16.895$

$(Xi)^2 = 116.79$

$\frac{(Xi)^2}{n} = 16.68$

$S^2 = \frac{0.215}{6}$

$S = 0.189$

$MDL = (3.143) \times S = 0.594$ mg/L

Reference: Glaser, J.A., Foerst, D.L., McKee, G.D. Quave, S.A., and Budde, W.L., "Trace Analysis for Waste Waters," Environmental Science and Technology, 15. 1426, 198.

REPORTING LIMITS (RL)

- Reporting Limits must be established for all reportable parameters. All final reports should have established RL's.
- For potable water, there are established reporting limits. These limits must be used.
- For wastewater and hazardous wastes, as of (1-1-92) there are no set reporting limits (consult with the regulating agency or client for special reporting requirements).
- If the target analyte is not detected or detected below the Reporting Limits, it should be reported as N.D. (not detected) and be followed by the Reporting Limit Value.
- The RL is not to be confused with the MDL (see handout). All RLs must be equal to or preferably higher than the MDL value. The RL should be thought of as a Practical Quantitation Limit (PQL).
- Ideally, RL should be ten times the MDL and at most, one tenth the MCL.
- Reporting Limits are **matrix** and **method** dependent. RL's must be established for each matrix and method employed and take into account any dilution factor used in preparing the sample for analysis.
- Reporting Limits must be **verifiable**. A blank (for each matrix to which a RL will be used) must be "fortified" at the RL level and recovery values must be documented.

WARNING: It has been observed that many laboratories have used RL's for certain analytes in soil matrices that were absolutely impossible to achieve. Please scrutinize and verify all RLs before employing them on regulatory sample results. Reporting limits in final reports must be legally defensible.

INITIAL DEMONSTRATION OF PROFICIENCY

Initial demonstration of proficiency is required for all methods for which first time ELAP accreditation is sought.

The applicant laboratory should be prepared to demonstrate method proficiency at the time of the on-site visit.

Lack of documentation or incomplete development of methods applied for will be indicated as a deficiency to be addressed by a written corrective action response in the form of a data package.

All initial demonstration of proficiency requirements as specified in the individual method must be performed. Refer to the individual methods for more details.

In addition, the applicant laboratory should be prepared to demonstrate the following requirements:

1. The appropriate instrumentation and reagents as required to perform the analysis.
2. A written Standard Operating Procedure must be developed and implemented for each method. (See "Standard Operating Procedures").
3. Results from any recent performance evaluation samples.
4. Properly documented Quality Control guidelines and Q.C. analyses as applied to the method.
*5. Four replicate analyses of a suitable control sample. All results must be within the listed acceptance limits of the control sample or ± 20% if no limit is listed.
*6. Results from the analysis of duplicate matrix spikes. Note that matrix spikes should reflect the actual sample matrices to be analyzed and reported by the applicant laboratory to the respective state regulatory agencies.
*7. Proper calibration procedure.
*8. Properly documented Method Detection Limits (MDL's) and Reporting Limits. (See Appendices - "Method Detection Limit Determination" and "Reporting Limits").
*9. Each analyst must make an initial one-time demonstration of their ability to generate data of acceptable accuracy and precision.

*May or may not be required, refer to individual method for specific requirements.

ADDITIONAL NOTES:

1. Each time a method is changed (only as permitted in the method), the laboratory must demonstrate equivalence of analysis. The initial demonstration of proficiency must be repeated.
2. All raw data, calculations, printouts, graphs, chromatograms, etc. used to generate any of the above data must be maintained by the laboratory and must be available at the time of the on-site visit.
3. Laboratories seeking initial ELAP certification must prepare an example of a "Final Report" for each regulatory agency to which results are to be submitted. The final report must be available for review upon request.
4. Microbiological analyses (Fields of Testing No. 1 and 7), Bioassay analyses (Field of Testing No. 8), and any other non-chemical procedures may have special requirements for initial demonstration of method proficiency. This appendix does not apply to those methods.

OPERATING PROCEDURES

The laboratory shall describe or make reference to all laboratory activities that may affect data quality. For routinely performed activities, SOPs are often prepared to ensure consistency and to save time and effort. Any deviation from an established procedure during a data collection activity must be documented. The procedures shall be available for the indicated activities, and shall include, at a minimum, the information described below. A suggested SOP format is included in this appendix.

1. **Sample Management**

   The procedures describing the receipt, handling, scheduling, and storage of samples shall be specified.

2. **Sample Receipt and Handling**

   These procedures describe the precautions to be used in opening sample shipment containers and how to verify that chain-of-custody has been maintained, examine samples for damage, check for proper preservatives and temperature, and log samples into the laboratory sample streams.

3. **Sample Scheduling**

   These procedures describe the sample scheduling in the laboratory and includes procedures used to ensure that holding time requirements are met.

4. **Sample Storage**

   These procedures describe the storage conditions for all samples, verification and documentation of daily storage temperature, and how to ensure that custody of the samples is maintained while in the laboratory.

5. **Reagent/Standard/Glassware Preparation**

   The procedures describing how to prepare standards and reagents shall be specified. Information concerning specific grades of materials used in reagent and standard preparation, appropriate glassware and containers for preparation and storage, and labeling and recordkeeping for stocks and dilutions shall be included.

6. **General Laboratory Techniques**

   The procedures describing all essentials of laboratory operations that are not addressed elsewhere shall be specified. These techniques shall include, but are not limited to, glassware cleaning procedures, operation of analytical balances, pipetting techniques, and use of volumetric glassware.

7. **Test Methods**

   Procedures for test methods describing how the analyses are actually performed in the laboratory shall be specified. A simple reference to standard methods is not sufficient, unless the analysis is performed exactly as described in the published method.

8. **Sample Preparation and Analysis Procedures**

   These include applicable holding time, extraction, digestion, or preparation steps as appropriate to the method procedures for determining the appropriate dilution to analyze; and any other information required to perform the analysis accurately and consistently.

9. **Instrument Standardization**

This includes concentration(s) and frequency of analysis of calibration standards, linear range of method, and calibration acceptance criteria.

10. **Sample Data**

This includes recording requirements and documentation including sample identification number, analyst, data verification, date of analysis and computational method(s).

11. **Precision and Bias**

This includes all analytes for which the method is applicable and the conditions for use of this information.

12. **Detection and Reporting Limits**

This includes all analytes in the method.

13. **Test-Specific QC**

This describes QC activities applicable to the specific test and references any applicable QC procedures.

14. **Equipment Calibration and Maintenance**

The procedures describing how to ensure that laboratory equipment and instrumentation are in working order shall be specified. These procedures include calibration procedures and schedules, maintenance procedures and schedules, maintenance logs, service arrangements for all equipment, and spare parts available in-house. Calibration and maintenance of laboratory equipment and instrumentation shall be in accordance with manufacturer's specifications or applicable test specifications and shall be documented.

15. **Quality Control**

The type, purpose, and frequency of QC samples to be analyzed in the laboratory and the acceptance criteria shall be specified. Information should include the applicability of the QC sample to the analytical process, the statistical treatment of the data, and the responsibility of laboratory staff and management in generating and using the data.

16. **Corrective Action**

The procedures describing how to identify and correct deficiencies in the analytical process shall be specified. These should include specific steps to take in correcting the deficiencies such as preparation of new standards and reagents, recalibration and restandardization of equipment, reanalysis of samples, or additional training of laboratory personnel in methods
and procedures. The procedures shall specify that each corrective action must be documented with a description of the deficiency and the corrective action taken, and should include the person(s) responsible for implementing the corrective action.

17. **Data Reduction and Validation**

The procedures describing how to review and validate the data shall be specified. They shall include procedures for bias correction, computing and interpreting the results from QC samples, and independent procedures to verify

that the analytical results are reported correctly. In addition, routing procedures used to monitor precision and bias, including evaluations of reagent, equipment rinsate, and trip blanks, calibration standards, control samples, duplicate and matrix spike samples, and surrogate recovery, should be detailed in the procedures.

18. **Reporting**

    The procedures describing the process for reporting the analytical results shall be specified.

19. **Records Management**

    The procedures describing the means for generating, controlling, and archiving laboratory records shall be specified. The procedures shall detail record generation and control, and the requirements for record retention, including type, time, security, and retrieval and disposal authorities.

20. **Project-specific records** may include correspondence, chain-of-custody records, request for analysis, calibration data records, raw and finished analytical and QC data, data reports, and procedures used.

21. **Laboratory operations records** may include laboratory notebooks, instrument performance logs and maintenance logs in bound notebooks with prenumbered pages; laboratory benchsheets; software documentation; control charts; reference material certification; personnel files; laboratory procedures; and corrective action reports.

22. **Waste Disposal**

    The procedures describing the methods for disposal of chemicals including standard and reagent solutions, process waste, and samples shall be specified.