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HANFORD ENVIRONMENTAL ANALYTICAL METHODS (METHODS AS OF MARCH 1990)

APPENDIX A2-I

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May 1993

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WHC/222-S Laboratory: Inorganics

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A2-I.20	LA-505-151	Inductively Coupled Plasma (ICP) Emission Spectrometer Operations and Analysis	Ag, Al, As, B, Ba, Bi, Ca, Cd, Ce, Co, Cr, Cu, Eu, Fe, Hg, K, La, Li, Mg, Mn, Mo, Na, Nd, Ni, P, Pb, Pu, S, Se, Si, Sm, Sn, Sr, Ta, Th, Ti, W, V, Zn, Zr
A2-I.30	SW-846 3050	Acid Digestion of Sediments, Sludges, and Soils	Al, Ba, Be, Cd, Ca, Cr, Co, Cu, Fe, Pb, Mg, Mn, Mo, Ni, K, Na, Tl, V, Zn, As, Be, Se
A2-I.40	LA-355-101	Spectrophotometric Determination of Phosphorous in High Salt Waste Samples	P
A2-I.50	LA-533-101	Anion Analysis on Dionex Model 10	F ⁻ , Cl ⁻ , PO ⁻³ , NO ⁻ , NO ₂ ⁻ , SO ₄ ⁻²⁴
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A2-I.140	LA-507-141	Operation of the Link XR300 for Quantitative X-Ray Fluorescence Analysis	XRF Operation
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A2-I.190	LA-564-101	Percent Water in Tank Farm Samples and Pilot Evaporatory Samples	Water

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A2-I.240	LA-514-121	Softening Point Determination by DSC	Softening Point
A2-I.250	LA-514-112	Differential Thermal Analysis of Caustic Samples	Thermal Analysis
A2-I.260	LA-519-132	Percent Solids by Centrifuge	Solids
A2-I.280	LA-905-101	Spectrophotometric Determination of Thorium with Arsenazo III	Total Th
A2-I.290	LA-645-001	Spectrophotometric Determination of Nitrite	NO ₂ ⁻

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Appendix Number	Lab Number	Method Name	Analytes
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A2-I.340	LA-344-105	Determination of Carbon in Solutions by Combustion and Coulometry	C
A2-I.360	LA-634-102	Ammonia by Kjeldahl	NH ₃
A2-I.380	LA-505-122	Sample Preparation and Analysis, High Activity AA-6 Atomic Absorption Spectrophotometer	Sample Preparation, AA Operation
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ANALYTICAL LABORATORIES

Issued By: T. A. Lane

Manager,
Analytical Laboratory

Title

DETERMINATION OF pH ON SINGLE-SHELL TANK
CORE SAMPLES

Author: C.M. Seidel

SUMMARY

This procedure describes the method used to measure pH of single-shell tank core samples. Sludge or solid samples are mixed with deionized water. The pH electrode used combines both a sensor and reference electrode in one unit. The meter amplifies the input signal from the electrode and displays the pH visually. Procedures to operate a specific type of pH meter can be found in the Laboratory Analytical Procedure Manual.

LIMITATIONS

The pH of any solution may be measured but care must be used in assessing the significance and meaning of the value. At the extremes of the pH scale (<1 or >10), pH is not a good measure of acidity or alkalinity. Use of a low sodium error electrode will reduce incorrectly low reading at the high end of the pH scale.

Temperature fluctuations will cause measurement errors.

Errors will occur when the electrode becomes coated with any oily material or clogged with material that will not rinse free. The electrode can be cleaned in an ultrasonic bath; or washed with detergent, followed by a water rinse, followed by 1:10 HCl solution soak, and then rinsed with water.

SAFETY

All activities described in this procedure are supported by safety instructions contained in SD-CP-LB-003, "Safety in the Analytical Laboratory."

Follow the requirements and good practices set forth in WHC-CM-4-15, Radiation Work Requirements and Permits Manual, and WHC-CM-10, Radiation Protection. The handling of radioactive samples will be controlled by the relevant radiation work permits

S-003, "Rooms with Open Faced Hoods (Excluding 2B Decon and Slurp Hood and Room 1GB) Routine Work/Maintenance Performed Inside Open Faced Hoods";

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SAFETY (Continued)

S-008, "Building Cubicles Load In/Out of Samples, Waste and Equipment from Cubicles."

The handling of radioactive samples will be monitored by RPTs whenever sample radiation levels exceed 100 mr/hr.

All appropriate safety standards as listed in WHC-CM-4-3, Industrial Safety Manual, shall be followed.

In compliance with WHC-CM-1-3, Management Requirements and Procedures, (MRP 5.43), an Impact Level 03 has been assigned to this procedure.

REAGENTS

1. "Q-water": Deionized water reading more than 16.5 micro-ohms.
2. Standard buffers prepared from NIST salts or purchased as solutions from commercial vendors and validated by comparison with NIST standards.
3. Electrode filling solutions; see electrode operating instructions. These solutions can be obtained from electrode vendors.

EQUIPMENT

1. pH meter with means for temperature compensation.
2. Combination pH electrode.
3. Glass enclosed stir bar and magnetic stirrer.

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PROCEDURE

NOTE: Samples must be ground, sieved, and blended before starting this procedure. Samples will be provided from the hot cell with a known weight (5.0 g) weighed into a 25 mL glass vial.

1. The pH meter when used must be Calibrated at a minimum of two points that bracket the expected pH of the sample being measured. Calibration buffer solutions used must be approximately three pH units or more apart. Calibration must be repeated until the buffer solutions readings are within 0.05 pH units of the buffer solutions values. Because of the wide range and types of pH meters in use, detailed operating procedures will not be incorporated in this method. See the laboratory analytical method for the operation of the pH meter in use for detailed instructions.

NOTE: If the exposure level of the bottles and samples are low enough to work with the samples outside of the hot cell, the samples are moved to a ported hood. If a sample contains 20% water, or more, determine the pH directly as per LA-212-102. If temperature of samples differ by more than 2°C from calibration buffers, the measured pH values must be corrected for temperature.

2. Add a volume "Q-water" to each sample bottle equal to the weight of the sample $\pm 3\%$.
3. If a glass sealed magnetic stirring bar was not added to the sample vial before the sample was placed in the vial, add one now and place vial on stirrer. Stir for 30 minutes at low to medium speed.
4. Stop stirring and let sample stand for one hour.
5. Lower electrodes into sample and measure pH. Report results as "core pH measured in water."
6. Duplicate samples and check standards must be analyzed routinely.

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DISCUSSION

See SD-CP-LB-025, "Determination of pH Values," for detailed discussion of pH determinations.

REFERENCES

Procedure:

LA-212-102, "Determination of pH Direct Measurement."

Source Documents:

SD-CP-LB-003, "Safety in the Analytical Laboratory."

SD-CP-LB-025, "Determination of pH Values."

WHC-CM-1-3, Management Requirements and Procedure.

WHC-CM-4-3, Industrial Safety Manual.

WHC-CM-4-15, Radiation Work Requirements and Permits Manual.

WHC-CM-10, Radiation Protection.

Winters, W. I., et al., "Waste Characterization Plan (Waste Analysis Plan) for the Hanford Site Single-Shell Tanks," predecisional draft Westinghouse Hanford Company, WHC-EP-0210; Feb. 1989.

"pH Electrometric Measurement," Method 9040, SW 846, Sept. 86.

"Soil pH," Method 9045, SW 846, Sept. 86.

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T. A. Lane

INDUCTIVELY COUPLED PLASMA
(ICP)EMISSION SPECTROMETER
OPERATIONS AND ANALYSIS

Author: S. A. Jones 4

SUMMARY

This procedure describes the steps involved in the instrument operation and sample analysis using the polychromator section of the ARL Model 3580 Inductively Coupled Plasma (ICP) at 222-S/RCRA Laboratory. The polychromator section of the instrument is used to determine forty elements (Al, As, Ba, Bi, B, Ca, Cd, Ce, Cr, Co, Cu, Eu, Fe, La, Li, Pb, Mg, Mn, Hg, Mo, Nd, Ni, P, K, Pu, Sm, Se, Si, Ag, Na, Sr, S, Ta, Th, Sn, Ti, W, U, Zn, and Zr) simultaneously. Other elements can be determined sequentially using the monochromator section of the instrument. This procedure covers the operations necessary to back up computer discs and restore calibration data after system failure or operator error. Additionally, this procedure provides some general guidelines about what to do if the computer misbehaves. The quality assurance/quality control requirements for ICP analysis to environmental protocol are specified. The standards which must be analyzed and the frequency of analysis are included.

APPLICATIONS AND LIMITATIONS

This procedure is applicable to the analysis of aqueous samples in an acid matrix. Solids must first be dissolved. All environmentally significant samples must be appropriately digested prior to introduction into the ICP. Any sample which can be analyzed on the ICP can be analyzed using the QA/QC requirements of this procedure. Environmentally significant samples must be analyzed using the QA/QC requirements in this procedure.

SAFETY

There are no unusual safety concerns associated with this procedure.

EQUIPMENT

Inductively coupled argon plasma emission spectrometer, ARL Model 3580

Argon gas supply

REAGENTS

Hydrochloric Acid (conc), HCl (MSDS #1250)

Hydrochloric Acid (1:1), HCl

Add 500 mL concentrated HCl to 400 mL water and dilute to 1 L.

Nitric acid (conc), HNO₃ (MSDS #1384)

Nitric acid (1:1), HNO₃

Add 500 mL concentrate HNO₃ to 400 mL water and dilute to 1 L.

ASTM Type II Water (ASTM D1193-77 (1983))

All references to water in this procedure refer to ASTM Type II water unless otherwise specified.

Standard stock solutions purchased containing elements at concentrations found on label and certificate of analysis.

PROCEDURE USE GUIDE

The ICP is controlled through the use of a small computer, with data input through a terminal and results accessed through a printer. The following conventions will be used in this procedure to clarify the use of the computer.

The system prompt is a ">", located on the left hand side of the screen, and signifies that the computer is running in the DPS program and will accept system commands. If other prompt symbols are seen, the system is not running correctly. If the computer is accidentally running DEC's RT-11 software, the system prompt is a period ("."). Any other prompts indicate the computer is "lost" and should be rebooted.

A carriage return is represented by a <CR> in this procedure and is a key on the terminal, usually labeled RETURN, NEWLINE, or both. A carriage return is used after each input, to signal the computer to read the input. A carriage return without any input is used as an exit. One space must be left between commands and other input. An example is SAMPLE ICPROG, where SAMPLE is the command and ICPROG is the program it will use.

<CTRL P> instead of <CR> is used to print all screen output to the printer between system prompts. This is done by holding down the CTRL key (the CTRL key is located on the left side of the keyboard) and pressing the P key once.

In order to differentiate between the terminal's output to the screen and the user's input, for this procedure all screen output is in bold while user's input is in bold and underlined.

A menu is simply a list of options that can be performed under a specific command. System commands can be shortened, as long as the abbreviated command is still unique. For example, CALIBRATE can be shortened to CAL or CA, but not C, as there are other commands that begin with C, but not CA. Most of the time, the system will supply default responses for the user, mainly for yes/no questions. The default value is always the first one displayed. For example, Yes is the default for Print (Y/N)?.

PROCEDURE USE GUIDE (Continued)

The following table of contents is included to facilitate finding individual sections of this procedure.

PART I.	Startup and Warmup Operations.	5
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PROCEDURE STEPS

PART I. STARTUP AND WARMUP OPERATIONS

NOTE: This section gives instructions to bring into service the ICP which has been partially (routinely) switched off.

A. Startup/Shutdown Procedure

NOTE: When the ICP is shut down due to an abnormal condition, make a note in the instrument log book and notify management.

1. Confirm magnehelic gauge reads 0.5-4.5 inches water. If the gauge reads outside the range, proceed no further and notify management.
2. Assure argon supply is adequate.
3. Confirm that argon tank valve is open and that the regulator outlet pressure is adjusted to 80-95 psig.
4. Read the instrument log book and assure that the instrument was operating properly the last time it was run. If there were problems which have not been corrected, do not operate the instrument.
5. Inspect and fill with deionized water (if necessary) humidifier and tip wash water reservoirs.
6. Confirm that spectrometer bleed valve is CLOSED.
7. Confirm that the following breakers and/or switches are set as indicated. If not, set in the order listed below.

a. Autostart:	RUN-1
b. Nebulizer:	NO. 2
c. Spectrometer heater breaker:	ON
d. Electronics breaker:	ON
e. HVPS breaker:	ON
f. Computer breaker:	ON
g. SAMI power:	ON
h. VT-240:	ON
i. LA-210:	ON
j. Pump breaker:	ON
k. ICP Stand breaker:	ON
8. Confirm that gas distribution box argon supply valve is fully open. The ARGON status light emitting diode (LED) should light.
9. Press START button on face of ICP and assure that light flashes. The function of this step is to purge air from the torch, spray chamber assembly, and argon supply line. Lighting the torch with entrained atmospheric gases is difficult.

PROCEDURAL STEPS (continued)

10. Confirm computer is operating. (Terminal responds to typed commands.)

11. Type PEARL <CR>.

The status channel values will be printed. Verify that all status channels are within limits. If not, shut down ICP and document problem in the instrument log book.

The position calibration is performed by the POSITION command. The POSITION CALIBRATE facility allows the sequential controller of the 3580 to check and update its wavelength positioning data.

The torch must be off or the optical gate closed before the POSITION command is used.

The position calibration can take up to 10 minutes to complete. During this time the scanner controller display gives information on the operation.

12. Save status channel and RPOS printout in the log book.

13. Jet sample trap solution to waste.

NOTE: The jet-and-flush operations are to be performed routinely before the ICP torch is lighted and after the torch is extinguished. The flush-and-jet operations are also performed after analyzing radioactive samples.

- a. Open Sanitary Water Valve (MAIN_SW).
- b. Press foot-operated Jet Valve 3-4 seconds.
- c. Press hand-operated Flush Valve 20-30 seconds.
- d. Repeat steps 2-3, as necessary, to reduce radiation levels.
- e. Close Sanitary Water Valve.

14. Confirm that the following controls of the RF generator are in the indicated position. If not, set as indicated.

- a. NORMAL/START switch is in POWER 1.
- b. Regulated drive knob is fully counterclockwise.
- c. Unregulated drive knob is fully counterclockwise.
- d. Multimeter is switched to PA FIL.

15. Assure that the RF generator AC MAINS light is on. If not, turn on the AC MAINS breaker. At the end of 90 seconds, the yellow STANDBY light will light.

PROCEDURAL STEPS (continued)

16. Assure STANDBY light is on.

17. Don and wash gloves.

NOTE: Gloves must be washed each time gloves are put on to prevent samples from being contaminated with glove powder.

18. Survey the hood. If smearable contamination is found, clean it before proceeding.

19. Exchange the contents of the water and nitric acid beakers for fresh ones.

20. Set up and start the peristaltic pump with the uptake tube in water.

21. Verify that there is a pulse-free mist being produced in the spray chamber. If not, adjust the pressure on the pump tubing to produce a desired mist, shut down the pump, make a note in the log book, and do not proceed with this procedure.

B. Torch Lighting

NOTE: Do not start plasma until position calibration is complete and message

 Start the Plasma Now Please

 is issued by the computer.

1. Press and hold green START torch button.

The Tesla coil should start after a delay of about two seconds. This will be noted by a buzzing sound from within the torch box.

If the plasma fails to form in five seconds, released the button, wait about 30 seconds, and try again. A total of three tries is permitted without contacting management.

2. Confirm the following readings on the RF generator. If any reading is outside the tolerance window, terminate the plasma immediately and notify management.

- a. Reflected Power indicator shows less than 15 watts.
- b. Incident Power indicator shows 1150-1250 watts.
- c. Plate Current reads 0.72-0.95 amperes.
- d. Filament Voltage (PA FIL) reads 7.1-8.2 volts.
- e. Plate Voltage (PA VOLT) reads 3800-4500 volts.
- f. Grid Current (PA GRID) reads less than 240 ma.

3. Confirm that the TCU indicating LED has gone out. If not, terminate the plasma.

PROCEDURAL STEPS (continued)

4. Confirm the following gas control readings. If any are out of tolerance, terminate the plasma.
 - a. Nebulizer flow gauge reads at least 0.3 arbitrary units.
 - b. Coolant Gas pressure is 40-30 psi.
 - c. Plasma Gas pressure is 15-20 psi.

PART II. CALIBRATION

A. Profile

NOTE: The plasma must be ON before executing the IPROF command.

1. Enter IPROF<CR> at the terminal.

NOTE: If SAMI does not move, something is wrong. Notify management.

2. Verify that SAMI rotates.
3. Enter I<CR> in response to the computer prompt:

Scan integration time (per step) = I<CR>

4. Aspirate 5 mg/L Mn (profile solution).

5. Enter <CR> in response to the computer prompt:

Press <CR> when ready to start measurement <CR>

6. Verify (again) that SAMI rotates. This time, SAMI should move over a very short range.

NOTE: When finished a plot of intensity versus SAMI steps will be generated at the terminal.

7. Respond to the terminal prompt as appropriate:

PRINT (N/Y)?

- a. Respond with Y<CR> if an unusual plot is obtained, if the peak is "ragged," or if you have reason to believe that something "strange" happened during the data collection period. Save for the responsible scientist.
- b. Respond with N<CR> if the plot appears to be normal.

PROCEDURAL STEPS (continued)

8. Decide to accept, repeat, or reject the calculated peak position based on the criteria below:
 - a. Accept the peak position if it is between -8 to +8 steps from the previous location, and the peak shape was smooth and symmetrical (Option 1).
 - b. Repeat the scan if the peak position is between -16 to -9 or +9 to +16 steps (Option 2).
 - c. Notify management if the peak position is off by more than 16 steps, or if the peak position is not reproducible. Do not operate the ICP.

C. Calibrate

NOTE: Calibration should be performed only at the direction of the responsible scientist.

1. Enter CALIBRATE Name<CR> at the system prompt, where "Name" is the name of the program being calibrated.

EXAMPLE

<CALIBRATE ICPROG<CR>

2. Enter 1<CR> in response to the menu and prompt:
 1. ICP mode f operation
 2. OE mode of operation <CR> Exit
Option = 1<CR>
3. Enter 1<CR> in response to the menu and prompt:

Options:

 1. Run all standards/regressions/plots
 2. Run a single standard
 3. Run all regressions/plots
 4. Refit

<CR> Exit
Option = 1<CR>
4. Aspirate the request standard 30 seconds.
5. Enter <CR> in response to the prompt for the calibration standard:
Enter <CR> when ready to start measurements CR>.
6. After measurement is complete, rinse the system by aspirating some of the solvent in which the standards were prepared.

PROCEDURAL STEPS (continued)

7. Repeat steps 3,4, and 5 for each standard prompted.
8. Enter <CR> in response to the menu:

Options:

1. Run all standards/regressions/.plots
2. Run a single standard
3. Run all regressions/plots
4. Refit
- <CR> Exit

Option = <CR>

9. Analyze QC standards and blanks.
10. Evaluate the QC results for the elements of interest.
 - a. Proceed with samples if the results of the QC standards are acceptable.
 - b. Archive the CALIBRATION printout in the appropriate binder.
 - c. Notify management if QC is not satisfactory.

PART III. Sample Analysis

NOTE: Appropriate dose rate monitoring of sample must be performed.

NOTE: Contamination of samples, particularly with sodium and calcium, is a rather insidious problem which must be avoided. Rinse gloves sample vials, and pipets to avoid contamination of samples.

NOTE: Run appropriate QC checks prior to analyzing samples.

1. Prepare sample dilutions.
2. At the system prompt enter SAMPLE ICPROG.
3. Enter payroll number and carriage return in response to prompt:
Result file (<CR> for no storage) =
4. Enter sample serial number (e.g., S118) in response to prompt:
Sample Name =
5. Enter 1 in response to prompt:
Sample Number =

PROCEDURAL STEPS (continued)

6. Enter sample dilution in response to prompt:

Sample Code 1 =

NOTE: Additional sample information can be inserted in sample fields Sample Code 2 and Sample Code 3, if desired.

7. Enter carriage return in response to prompt:

Sample Code 2 =

8. Enter carriage return in response to prompt:

Sample Code 3 =

9. Enter sample volume taken for dilution (or carriage return for no dilution) in response to prompt:

Weight =

10. Enter volume of sample plus diluent in response to prompt:

Volume =

EXAMPLE: A sample was received which required a 200-10 dilution (200 μ L was added to 10.00 mL 1 M HNO_3 nitric acid.) Thus, for the prompts one should respond:

Weight = 0.2

Volume = 10.2

The computer will calculate a dilution corrected concentration using these values.

11. Insert nebulizer tube in sample.

12. Enter carriage return in response to prompt:

Press <CR> when ready to start measurement.

Unless one is sample-limited, it is preferable to enter the carriage return about 15 seconds after the sample has reached the spray chamber.

13. Remove nebulizer tube when measurement is complete.

14. Rinse with nitric acid for at least one minute before the analysis of each sample.

PROCEDURAL STEPS (continued)

15. Respond to prompt:

More samples [Y/N] ?

as appropriate.

16. Analyze the instrument check standard and the calibration blank after each 10 samples.

PART VI. QUALITY ASSURANCE/QUALITY CONTROL (QA/QC)

For QA/QC procedures, an "analytical sample" is each "analysis" performed (i.e., each solution run through the ICP for which a result is produced). A "frequency of 10%" means once every 10 analytical samples.

Calibration blanks and calibration verification samples are not counted as analytical samples when determining 10% frequency.

If any QC measurement fails to meet specified criteria, the analytical measurement may not be repeated prior to taking the appropriate corrective action as specified in this procedure.

1. Instrument calibration

Instruments must be calibrated daily or once every 24 hours and each time the instrument is set up. The instrument standardization date and time must be included in the raw data.

2. Initial calibration verification (ICV) and continuing calibration verification

a. Initial calibration verification (ICV)

Immediately after the ICP system has been calibrated, the accuracy of the initial calibration shall be verified and documented for every analyte by the analysis of Initial Calibration Verification Solutions at each wavelength used for analysis. When measurements exceed the control limits of 90% to 110% of True Value, the analysis must be terminated, the problem corrected, the instrument recalibrated, and the calibration reverified.

Analyses shall be conducted on an independent standard at a concentration other than that used for instrument calibration, but within the calibration range. An independent standard is defined as a standard composed of the analytes from a different source than those used in the standards for the instrument calibration.

PROCEDURAL STEPS (continued)

b. Continuing calibration verification

To ensure calibration accuracy during each analysis run, one of the following standards is to be used for continuing calibration verification and must be analyzed for every wavelength used for the analysis of each analyte, at a frequency of 10% or every 2 hours during the analysis run, whichever is more frequent. The standard must also be analyzed for every wavelength used for analysis at the beginning of the run and after the last analytical sample. The analyte concentrations in the continuing calibration standard must be a solutions at or near the mid-range levels of the calibration curve.

If the deviation of the continuing calibration verification is greater than $\pm 10\%$ of true value. The instrument must be recalibrated and the preceding 10 analytical samples or all analytical samples analyzed since the last good calibration verification must be performed for the analytes affected. Information regarding the continuing verification of calibration shall be recorded on FORM II-IN for ICP.

3. RDL standards for ICP (CRI)

To verify linearity near the RDL for ICP analysis, the operator must analyze an ICP standard at two times the RDL or two times the IDL, whichever is greater, at the beginning and end of each sample analysis run, or a minimum of twice per 8 hour working shift, whichever is more frequent, but not before Initial calibration verification. This standard must be run for ICP for every wavelength used for analysis, except those for Al, Ba, Ca, Fe, Mg, Na, and K.

4. Initial Calibration Blank (ICB), Continuing Calibration Blank (CCB) and Preparation Blank (PB) Analyses

a. Initial Calibration Blank (ICB) and Continuing Calibration Blank (CCB) Analyses

A calibration blank must be analyzed at each wavelength used for analysis immediately after every initial and continuing calibration verification, at a frequency of 10% or every 2 hours during the run, whichever is more frequent. The blank must be analyzed at the beginning of the run and after the last analytical sample. The results for the calibration blanks shall be recorded on FORM III-IN for ICP. If the magnitude (absolute value) of the calibration blank exceeds the IDL, the result must be so reported in ug/L on FORM III-IN, otherwise report as IDL-U. If the absolute value blank result exceeds the RDL (Exhibit C), terminate analysis, correct the problem, recalibrate and reanalyze the preceding 10 analytical or all analytical samples analyzed since the last good. calibration blank.

PROCEDURAL STEPS (continued)

b. Preparation Blank (PB) Analysis

At least one preparation blank (or reagent blank), consisting of deionized distilled water processed through each sample preparation and analysis procedure (See Exhibit D, Section III), must be prepared and analyzed with every Sample Delivery Group, or with each batch of samples digested, whichever is more frequent.

The first batch of samples in an SDG is to be assigned to preparation blank one, the second batch of samples to preparation blank two, etc. Each data package must contain the results of all the preparation blank analyses associated with the samples in the SDG.

This blank is to be reported for each SDG and used in all analyses to ascertain whether sample concentrations reflect contamination in the following manner.

- (1) If the absolute value of the concentration of the blank is less than or equal to the RDL, no correction of sample results is performed.
- (2) If any analyte concentration in the blank is above the RDL, the lowest concentration of the analyte in the associated samples must be 10x the blank concentration. Otherwise, all samples associated with the blank with the analytes concentration less than 10x the blank concentration and above the RDL, must be redigested and reanalyzed for that analyte (except for an identified aqueous soil field blank). The sample concentration is not to be corrected for the blank value.
- (3) If the concentration of the blank is below the negative RDL, then all samples reported below 10x RDL associated with the blank must be redigested and reanalyzed.

The values for the preparation blank must be recorded in ug/L for aqueous samples and in mg/Kg for solid samples.

5. ICP Interference Check Sample (CS) Analysis

To verify interelement and background correction factors, the analyst must analyze and report the results for the ICP Interference Check Samples at the beginning and end of each analysis run or a minimum of twice per 8 hour working shift, whichever is more frequent, but not before Initial Calibration Verification.

PROCEDURAL STEPS (continued)

The Interference Check Samples consist of two solutions: Solution A and Solution AB. Solution A consists of the interferents, and Solution AB consists of the analytes mixed with the interferents. An ICS analysis consists of analyzing both solutions consecutively (starting with solution A) for all wavelengths used for each analyte reported by ICP.

Results for the ICP analyses of Solution AB during the analytical runs must fall within the control limit of $\pm 20\%$ of the true value for the analytes include in the Interference Check Samples. If not, terminate the analysis, correct the problem, recalibrated the instrument, and reanalyze the analytical samples analyzed since the last good ICS.

6. Spike Sample Analysis

The spike sample analysis is designed to provide information about the effect of the sample matrix on the digestion and measurement methodology. The sample is added before the digestion, (i. e., prior to the addition of other reagents). At least one spike sample analysis must be performed on each group of samples of a similar matrix type (i.e., water, soil) and concentration (i.e., low, medium) or for each Sample Delivery Group, whichever is more frequent.

If the spike analysis is performed on the same sample that is chosen for the duplicate sample analysis, spike calculations must be performed using the results of the sample designated as the "original sample". The average of the duplicate results cannot be used for the purpose of determining percent recovery. Samples identified as field blanks cannot be used for spiked sample analysis.

If the spike recovery is not within the limits of 75-125%, the data of all samples received associated with that spike sample and determined by the same analytical method must be flagged with the letter "N" on the forms. An exception to this rule is granted in situation where the sample concentration exceeds the spike concentration by a factor of four or more. In such an event, the data shall be reported unflagged even if the percent recovery does not meet the 75-125% recovery criteria.

$$\% \text{Recovery} = \frac{(\text{SSR} - \text{SR})}{\text{SA}} \times 100$$

Where, SSR = Spiked Sample result
 SR = Sample Result
 SA = Spike added

PROCEDURAL STEPS (continued)

7. Duplicate Sample Analysis (D)

One duplicate sample must be analyzed from each group of samples of a similar matrix type (i.e., water, soil) and concentration (i.e., low, medium).

The relative percent difference (RPD) for each component are calculated as follows:

$$RPD = \frac{|S - D|}{(S + D)/2} \times 100$$

Where, RPD = Relative Percent Difference
S = First Sample value (original)
D = Second sample Value (duplicate)

A control limit of 20% for RPD shall be used for original and duplicate sample values greater than or equal to 5x RDL. A control limit of ($\pm$) The RDL must be used for sample values less than 5x RDL.

If one result is above the 5x RDL level and the other is below, use the $\pm$ RDL criteria. If both sample values are less than the IDL, the RPD is not calculated.

If the duplicate sample results are outside the control limits, flag all the data for samples received associated with that duplicate sample.

8. Quality Control Reference Sample

A quality control reference sample is a sample prepared from an independent standard at a concentration other than that used for calibration, but within the calibration range. An independent standard is defined as a standard composed of the analytes of interest from a different source than that used in the preparation standards for use in the standard curve. A quality control reference sample is intended as an independent check of technique, methodology, and standards and should be run with every analytical batch or every 20 samples, whichever is greater.

9. ICP Serial Dilution Analysis (L)

Prior to reporting concentration data for the analyte elements, the operator must analyze and report the results of the ICP Serial Dilution Analysis. The ICP Serial Dilution Analysis must be performed on each group of samples of a similar matrix type and concentration or for each Sample Delivery Group, whichever is more frequent. Samples identified as field blanks cannot be used for Serial Dilution Analysis.

PROCEDURAL STEPS (continued)

If the analyte concentration is sufficiently high (minimally a factor of 10 above the instrumental detection limit in the original sample), an analysis of a 5-fold dilution must agree within 10% of the original determination. If the dilution analysis for one or more analytes is not within 10%, a chemical or physical interference effect must be suspected, and the data for all affected analytes in the sample received associated with that serial dilution must be flagged.

The percent differences for each component are calculated as follows:

$$\% \text{Difference} = \frac{|I-S|}{I} \times 100$$

where, I = Initial sample result
 S = Serial Dilution Result (Instrument Reading x 5)

10. Method Detection Limit (MDL) Determination

For operational purposes, when it is necessary to determine the method detection limit in the sample matrix, the MDL shall be determined by multiplying by 7 the standard deviation obtained from the triplicate analyses of a matrix spike containing the analyte of interest at a concentration three to five times the estimated MDL.

Determine the estimated MDL as follows:

Obtain the concentration value that corresponds to:

- a) an instrument signal/noise within the range of 2.5 to 5.0, or
- b) the region of the standard curve where there is a significant change in sensitivity, i.e., a break in the slope of the standard curve.

11. Interelement Correction for ICP

The interelement correction factors must be determined before any samples are analyzed and at least annually thereafter. Correction factors for spectral interferences due to Al, Ca, Fe, and Mg must be determined at all wavelengths used for each analyte reported by ICP. Correction factors for spectral interference due to analytes other than Al, Ca, Fe, and Mg must be reported if they were applied.

PROCEDURAL STEPS (continued)

12. Linear Range Analysis (LRA)

For ICP analysis, a linear range verification check standard must be analyzed and reported quarterly (every 3 calendar months) for each element. The standard must be analyzed during a routine analytical run. The analytically determined concentration of this standard must be within $\pm 5\%$ of the true value. This concentration is the upper limit of the ICP linear range beyond which results cannot be reported without dilution of the analytical standard.

13. All quality control data should be maintained and available for easy reference or inspection.
14. Dilute and reanalyze samples that are more concentrated than the linear calibration limit.
15. Employ a minimum of one laboratory blank per sample batch to determine if contamination or any memory effects are occurring.
16. Analyze one duplicate sample for every 20 samples. A duplicate sample is a sample brought through the whole sample preparation and analytical process.
17. If the analyte concentration is sufficiently high (minimally a factor of 10 above the instrument detection limit after dilution), an analysis of a 1:4 dilution should agree within $\pm 10\%$ of the original determination. If not, a chemical or physical interference effect should be suspected.

The percent differences for each component are calculated as follows:

$$\% \text{Difference} = \frac{|I-S|}{I} \times 100$$

where, I = Initial sample result
 S = Serial Dilution Result (Instrument Reading x df)
 df = dilution factor

18. An analyte spike added to a portion of a prepared sample, or its dilution, should be recovered within 75% to 125% of the known value. The spike addition should produce a minimum level of 10 times an a maximum of 100 times the instrumental detection limit. If the spike is not recovered within the specified limits, a matrix effect should be suspected.

PROCEDURAL STEPS (continued)

19. Check the instrument standardization by analyzing appropriate quality check standards as follows.
 - a. Check instrument calibration using a calibration blank and two appropriate standards.
 - b. Verify calibration every 10 samples and at the end of the analytical run, using a calibration blank and a single point check standard.

The results of the check standard are to agree within 10% of the expected value; if not, terminate the analysis, correct the problem, and recalibrate the instrument.

The results of the calibration blank are to agree within three standard deviations of the mean blank value. If not, repeat the analysis two more times and average the results. If the average is not within three standard deviations of the background mean, terminate the analysis, correct the problem, recalibrate, and reanalyze the previous 10 samples.

20. Verify the interelement and background correction factors at the beginning and end of an analytical run or twice during every 8-hour shift, whichever is more frequent. Do this by analyzing the interference check sample. Results should be within $\pm 20\%$ of the true value obtained in step 7a.

PART V. ROUTINE SHUTDOWN

1. Aspirate 2% nitric acid for about 5 minutes to rinse spray chamber.
2. Press red STOP button on spectrometer or yellow STANDBY button on RF generator.
3. Push the green START button briefly to restart the argon flow. The green light will flash. Allow the argon to cool the torch for two minutes after plasma termination, then press the STOP button.
4. Jet sample tank solution to waste using Part III.
5. Turn off the peristaltic pump and unhook the pump tubing.
6. Turn off the STAND breaker.

PROCEDURAL STEPS (continued)

PART VI. NONROUTINE STARTUP AND SHUTDOWN

A. Complete (Nonroutine) Startup

NOTE: An off-standard magnehelic gauge reading indicates failure of the off-gas containment system.

1. Confirm that the magnehelic gauge reads between 0.5-4.5 inches of water. If the gauge reads outside the range, proceed no further; notify management.
2. Turn the line conditioner "LOSS OF POWER SHUT-OFF" switch from "OFF" to "ON".
3. Switch on the electronics power (switch labeled "ELECTRONICS").
4. Switch on the computer power (switch labeled "COMPUTER").

NOTE: If the vacuum system has been opened to atmospheric pressure, up to 24 hours may be required for the instrument to pump down to a workable vacuum. The system is usable only if the pressure is less than 75 mtorr and the IPROF position result is within ± 8 steps.

5. Switch on the vacuum pump power (switch labeled "PUMP").
6. Switch on the high voltage power supply (switch labeled "HVPS").

NOTE: The spectrometer must have a temperature of 36-38°C. To determine when the instrument is ready for use, check and correct the profile every 1/2 hour until the position is within ± 8 steps. If the current interruption has not lasted long (less than one hour) and the spectrometer has not been opened, the stabilization time roughly equals the interruption time. The current spectrometer temperature can be displayed on the screen through the command STLOG<CR>.

7. Switch on the spectrometer heater (switch labeled "HEATER").
8. Ensure the "AUTOSTART" switch is in the "RUN-1" position.
9. Ensure the "NEBULIZER" switch is in the "NO. 2" position.
10. Confirm that the following controls of the RF generator are in the indicated position. If not, set as indicated.
 - a. Mode switch is in "POWER 1".
 - b. Regulated, drive knob is fully counterclockwise.
 - c. Unregulated, drive knob is fully counterclockwise.
 - d. Multimeter is switched to "PA FIL."

PROCEDURAL STEPS (continued)

NOTE: The "AC MAINS" breaker will be in the "ON" position if the shutdown was caused by an unexpected power failure.

11. Switch on the RF generator "AC MAINS" breaker and allow to warm up at least 5 minutes.
12. Switch on the "SAMI" power.
13. Turn on the video terminal.
14. Turn on the printer.

NOTE: If an error in time or date is made, this can be corrected using the TIME and DATE commands.

15. "Boot" the computer.

- g. Push "RESTART" button.
- h. When terminal displays "START?" respond by typing "DLO<CR>."
- i. When terminal displays prompts for date and time, respond in the format requested by the computer. Note that the computer uses a 24-hour clock. This means that 9:00 pm is entered as 21:00.

16. Continue with PART I, "Routine Startup and Shutdown of the Inductively Coupled Plasma (ICP) Emission Spectrometer," to complete the startup.

B. Complete (Nonroutine) Shutdown

NOTE: The ICP is not normally shut down completely after use. The activities outlined below should only be done if a power outage is anticipated. The ICP can be shut down on an emergency basis (fire, smoke, or flood) by simply throwing the breakers outside 1-J(X-Panel). Contact laboratory manager if this is necessary.

NOTE: If the plasma is going, it should be terminated using Part V, Routine Shutdown, of this procedure.

1. Turn the components off in the indicated order:

j. Video terminal	e. "PUMP" switch
k. Printer	f. "HVPS power supply switch
l. "ELECTRONICS" switch	g. Spectrometer "HEATER" switch
m. "COMPUTER" switch	h. "SAMI" power switch

2. Turn off "RF MAINS" breaker.
3. Open the spectrometer bleed valve.
4. Turn off argon at laboratory valve.

PROCEDURAL STEPS (continued)

PART VII. COMPUTER OPERATIONS FOR THE ICP

The operations listed here are to backup the floppy disks, backup calibration data, restore "lost" calibration data, and render the computer operational if (when) it "hangs up."

A. BACKUP Command

The BACKUP command makes copies of selected files including those containing calibration curves and the wavelength library.

Type BACKUP at system prompt.

1. Insert backup floppy disk into disk drive and close drive door.
2. Enter carriage return.
3. Remove floppy disk when prompted to do so.
4. Repeat steps 2-5 for each backup copy.

Normally, only one backup will contain all the important data.

5. Return floppy disk to binder.

B. RELOAD Command

The RELOAD command transfers data from the floppy disk to the Winchester disk. This operation is not done routinely--it is done only to restore data lost through instrument malfunction or operator error.

1. Turn on disk drive.
2. Type RELOAD at system prompt.
3. Insert floppy disk with backup data into drive and close door.
4. Enter carriage return.
5. Remove floppy disk when prompted to do so.
6. Turn off disk drive.
7. Return disk to binder.

PROCEDURAL STEPS (continued)

C. Recovery from Computer Malfunction

The computer on the ICP sometimes fails to respond to commands or fails to complete a task in a normal fashion. When this happens, certain operations can be attempted to correct the situation. These operations are listed below in the order in which they should be attempted.

- .1. Confirm that there really is a problem by checking that none of the following are causing the apparent lack of response.
 - a. No disk operations are in progress (no read light).
 - b. No monochromator operations are in progress (changing information in monochromator status motion.)
 - c. No SAMI operations in progress (SAMI motion).
 - d. Printer is online.
2. Try recovery by attempting the following in the order given. There are no guarantees that any of the below will work.
 - a. Repeat last item input.
 - b. Type Control-D.
 - c. Type Control-C.
 - d. Press green RESET button.
 - e. Shut off printer.
 - f. Reboot computer
 - g. Shut off VT-240 terminal.
 - h. Switch off 24V power breaker
 - i. Obtain assistance from management or responsible scientist.

Table 1. Example of Sample Order Including QC Check Standards.

Sample Number	Description	Sample Number	Description
1	ICS	20	Sample Blank (dup)
2	ICB	21	Spike Check A
3	ICV	22	Spike Check B
4	ICB	23	CCV
5	2 x CRDL	24	CCB
6	ICS(A)	25	LCS
7	ICS(AB)	26	Sample
8	CCV	27	Sample (dup)
9	CCB	28	Sample + Spike
10	Spike Check A	29	Sample (1/5 dilution)
11	Spike Check B	30	2 x CRDL
12	LCS	31	ICS(A)
13	Sample	32	ICS(AB)
14	Sample (dup)	33	CCV
15	Sample + Spike	34	CCB
16	Sample (1/5 dilution)	35	ICS
17	CCV	36	2 x ICS
18	CCB	37	CCV
19	Sample Blank	38	CCB

Table 2. Maximum Calibration Standards for the ICP SST Program.

ELEMENTS	Maximum Standard (ppm)	ELEMENTS	Maximum Standard (ppm)	ELEMENTS	Maximum Standard (ppm)
Aluminum	50	Lanthanum	100	Sodium	20
Antimony	100	Lead	100	Strontium	20
Arsenic	100	Lithium	20	Sulfur	100
Barium	20	Magnesium	20	Tantalum	50
Beryllium	20	Manganese	20	Thallium	100
Bismuth	100	Mercury	50	Thorium	100
Boron	50	Molybdenum	50	Tin	100
Cadmium	20	Neodymium	20	Titanium	50
Calcium	20	Nickel	20	Tungsten	50
Cerium	20	Phosphorous	50	Uranium	100
Chromium	20	Potassium	20	Vanadium	20
Cobalt	20	Samarium	20	Zinc	20
Copper	20	Selenium	100	Zirconium	50
Europium	20	Silicon	50		
Iron	20	Silver	20		

DISCUSSION

The purpose of laboratory QC is to provide information about the quality of the data as they are being produced. Data quality is usually expressed in terms of accuracy, precision, and detection limit of the analytical method. Accuracy is a measure of the closeness of an individual measurement, or an average of a number of measurements to the true value. Accuracy is generally represented as percent recovery.

Precision is defined as a measure of reproducibility among individual measurements of the same analyte under specified conditions. Instrument and overall method precision are often expressed as the coefficient of variation, standard deviation, percent difference, and/or relative standard deviation.

Results from QC procedures are used to document data quality, to verify that the analytical system is working well on a given matrix/analyte combination, to indicate whether instruments are operating properly, and to indicate when additional sample cleanup or other corrections need to be made. The QC data are indicators, but they do not change the quality of the analytical data.

METHOD 3050

ACID DIGESTION OF SEDIMENTS, SLUDGES, AND SOILS

1.0 SCOPE AND APPLICATION

1.1 This method is an acid digestion procedure used to prepare sediments, sludges, and soil samples for analysis by flame or furnace atomic absorption spectroscopy (FLAA and GFAA, respectively) or by inductively coupled argon plasma spectroscopy (ICP). Samples prepared by this method may be analyzed by ICP for all the listed metals, or by FLAA or GFAA as indicated below (see also Paragraph 2.1):

<u>FLAA</u>		<u>GFAA</u>
Aluminum	Magnesium	Arsenic
Barium	Manganese	Beryllium
Beryllium	Molybdenum	Cadmium
Cadmium	Nickel	Chromium
Calcium	Potassium	Cobalt
Chromium	Sodium	Iron
Cobalt	Thallium	Molybdenum
Copper	Vanadium	Selenium
Iron	Zinc	Thallium
Lead		Vanadium

2.0 SUMMARY OF METHOD

2.1 A representative 1- to 2-g (wet weight) sample is digested in nitric acid and hydrogen peroxide. The digestate is then refluxed with either nitric acid or hydrochloric acid. Dilute hydrochloric acid is used as the final reflux acid for (1) the ICP analysis of As and Se, and (2) the flame AA or ICP analysis of Al, Ba, Be, Ca, Cd, Cr, Co, Cu, Fe, Mo, Pb, Ni, K, Na, Tl, V, and Zn. Dilute nitric acid is employed as the final dilution acid for the furnace AA analysis of As, Be, Cd, Cr, Co, Pb, Mo, Se, Tl, and V. A separate sample shall be dried for a total solids determination.

3.0 INTERFERENCES

3.1 Sludge samples can contain diverse matrix types, each of which may present its own analytical challenge. Spiked samples and any relevant standard reference material should be processed to aid in determining whether Method 3050 is applicable to a given waste.

4.0 APPARATUS AND MATERIALS

- 4.1 Conical Phillips beakers: 250-mL.
- 4.2 Watch glasses.
- 4.3 Drying ovens: That can be maintained at 30°C.
- 4.4 Thermometer: That covers range of 0 to 200°C.
- 4.5 Whatman No. 41 filter paper (or equivalent).
- 4.6 Centrifuge and centrifuge tubes.

5.0 REAGENTS

5.1 ASTM Type II water (ASTM D1193): Water should be monitored for impurities.

5.2 Concentrated nitric acid, reagent grade (HNO_3): Acid should be analyzed to determine level of impurities. If method blank is $\leq$ MDL, the acid can be used.

5.3 Concentrated hydrochloric acid, reagent grade (HCl): Acid should be analyzed to determine level of impurities. If method blank is $\leq$ MDL, the acid can be used.

5.4 Hydrogen peroxide (30%) (H_2O_2): Oxidant should be analyzed to determine level of impurities.

6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

6.1 All samples must have been collected using a sampling plan that addresses the considerations discussed in Chapter Nine of this manual.

6.2 All sample containers must be prewashed with detergents, acids, and Type II water. Plastic and glass containers are both suitable. See Chapter Three, Section 3.1.3, for further information.

6.3 Nonaqueous samples shall be refrigerated upon receipt and analyzed as soon as possible.

7.0 PROCEDURE

7.1 Mix the sample thoroughly to achieve homogeneity. For each digestion procedure, weigh to the nearest 0.01 g and transfer to a conical beaker a 1.00- to 2.00-g portion of sample.

7.2 Add 10 mL of 1:1 HNO_3 , mix the slurry, and cover with a watch glass. Heat the sample to 95°C and reflux for 10 to 15 min without boiling. Allow the sample to cool, add 5 mL of concentrated HNO_3 , replace the watch glass, and reflux for 30 min. Repeat this last step to ensure complete oxidation.

Using a ribbed watch glass, allow the solution to evaporate to 5 mL without boiling, while maintaining a covering of solution over the bottom of the beaker.

7.3 After Step 7.2 has been completed and the sample has cooled, add 2 mL of Type II water and 3 mL of 30% H_2O_2 . Cover the beaker with a watch glass and return the covered beaker to the hot plate for warming and to start the peroxide reaction. Care must be taken to ensure that losses do not occur due to excessively vigorous effervescence. Heat until effervescence subsides and cool the beaker.

7.4 Continue to add 30% H_2O_2 in 1-mL aliquots with warming until the effervescence is minimal or until the general sample appearance is unchanged.

NOTE: Do not add more than a total of 10 mL 30% H_2O_2 .

7.5 If the sample is being prepared for (a) the ICP analysis of As and Se, or (b) the flame AA or ICP analysis of Al, Ba, Be, Ca, Cd, Cr, Co, Cu, Fe, Pb, Mg, Mn, Mo, Ni, K, Na, Tl, V, and Zn, then add 5 mL of concentrated HCl and 10 mL of Type II water, return the covered beaker to the hot plate, and reflux for an additional 15 min without boiling. After cooling, dilute to 100 mL with Type II water. Particulates in the digestate that may clog the nebulizer should be removed by filtration, by centrifugation, or by allowing the sample to settle.

7.5.1 Filtration: Filter through Whatman No. 41 filter paper (or equivalent) and dilute to 100 mL with Type II water.

7.5.2 Centrifugation: Centrifugation at 2,000-3,000 rpm for 10 min is usually sufficient to clear the supernatant.

7.5.3 The diluted sample has an approximate acid concentration of 5.0% (v/v) HCl and 5.0% (v/v) HNO_3 . The sample is now ready for analysis.

7.6 If the sample is being prepared for the furnace analysis of As, Be, Cd, Cr, Co, Pb, Mo, Se, Tl, and V, cover the sample with a ribbed watch glass and continue heating the acid-peroxide digestate until the volume has been reduced to approximately 5 mL. After cooling, dilute to 100 mL with Type II water. Particulates in the digestate should then be removed by filtration, by centrifugation, or by allowing the sample to settle.

7.6.1 Filtration: Filter through Whatman No. 41 filter paper (or equivalent) and dilute to 100 mL with Type II water.

7.6.2 Centrifugation: Centrifugation at 2,000-3,000 for 10 min is usually sufficient to clear the supernatant.

7.6.3 The diluted digestate solution contains approximately 5% (v/v) HNO_3 . For analysis, withdraw aliquots of appropriate volume and add any required reagent or matrix modifier. The sample is now ready for analysis.

7.7 Calculations:

7.7.1 The concentrations determined are to be reported on the basis of the actual weight of the sample. If a dry weight analysis is desired, then the percent solids of the sample must also be provided.

7.7.2 If percent solids is desired, a separate determination of percent solids must be performed on a homogeneous aliquot of the sample.

8.0 QUALITY CONTROL

8.1 For each group of samples processed, preparation blanks (Type II water and reagents) should be carried throughout the entire sample preparation and analytical process. These blanks will be useful in determining if samples are being contaminated.

8.2 Duplicate samples should be processed on a routine basis. Duplicate samples will be used to determine precision. The sample load will dictate the frequency, but 20% is recommended.

8.3 Spiked samples or standard reference materials must be employed to determine accuracy. A spiked sample should be included with each group of samples processed and whenever a new sample matrix is being analyzed.

8.4 The concentration of all calibration standards should be verified against a quality control check sample obtained from an outside source.

9.0 METHOD PERFORMANCE

9.1 No data provided.

10.0 REFERENCES

10.1 None required.

METHOD 3050
ACID DIGESTION OF SEDIMENTS, SLUDGES, AND SOILS

METHOD 3050
ACID DIGESTION OF SEDIMENTS, SLUGGIES, AND SOILS
(Continued)

3.3 METHODS FOR DETERMINATION OF METALS

This manual contains six analytical techniques for trace metal determinations: inductively coupled argon plasma emission spectrometry (ICP), direct-aspiration or flame atomic absorption spectrometry (FAA), graphite-furnace atomic absorption spectrometry (GFAA), hydride-generation atomic absorption spectrometry (HGAA), cold-vapor atomic absorption spectrometry (CVAA), and several procedures for hexavalent chromium analysis. Each of these is briefly discussed below in terms of advantages, disadvantages, and cautions for analysis of wastes.

ICP's primary advantage is that it allows simultaneous or rapid sequential determination of many elements in a short time. The primary disadvantage of ICP is background radiation from other elements and the plasma gases. Although all ICP instruments utilize high-resolution optics and background correction to minimize these interferences, analysis for traces of metals in the presence of a large excess of a single metal is difficult. Examples would be traces of metals in an alloy or traces of metals in a limed (high calcium) waste. ICP and Flame AA have comparable detection limits (within a factor of 4) except that ICP exhibits greater sensitivity for refractories (Al, Ba, etc.). Furnace AA, in general, will exhibit lower detection limits than either ICP or FLAA.

Flame AAS (FLAA) determinations, as opposed to ICP, are normally completed as single element analyses and are relatively free of interelement spectral interferences. Either a nitrous-oxide/acetylene or air/acetylene flame is used as an energy source for dissociating the aspirated sample into the free atomic state making analyte atoms available for absorption of light. In the analysis of some elements the temperature or type of flame used is critical. If the proper flame and analytical conditions are not used, chemical and ionization interferences can occur.

Graphite Furnace AAS (GFAA) replaces the flame with an electrically heated graphite furnace. The furnace allows for gradual heating of the sample aliquot in several stages. Thus, the processes of desolvation, drying, decomposition of organic and inorganic molecules and salts, and formation of atoms which must occur in a flame or ICP in a few milliseconds may be allowed to occur over a much longer time period and at controlled temperatures in the furnace. This allows an experienced analyst to remove unwanted matrix components by using temperature programming and/or matrix modifiers. The major advantage of this technique is that it affords extremely low detection limits. It is the easiest to perform on relatively clean samples. Because this technique is so sensitive, interferences can be a real problem; finding the optimum combination of digestion, heating times and temperatures, and matrix modifiers can be a challenge for complex matrices.

Hydride AA utilizes a chemical reduction to reduce and separate arsenic or selenium selectively from a sample digestate. The technique therefore has the advantage of being able to isolate these two elements from complex samples which may cause interferences for other analytical procedures. Significant interferences have been reported when any of the following is present: 1) easily reduced metals (Cu, Ag, Hg); 2) high concentrations of transition metals (>200 mg/L); 3) oxidizing agents (oxides of nitrogen) remaining following sample digestion.

Cold-Vapor AA uses a chemical reduction to reduce mercury selectively. The procedure is extremely sensitive but is subject to interferences from some volatile organics, chlorine, and sulfur compounds.

ANALYTICAL LABORATORIES

Issued By:

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Title

SPECTROPHOTOMETRIC DETERMINATION OF PHOSPHORUS
IN HIGH-SALT WASTE SAMPLES

SUMMARY

Total phosphorus is determined colorimetrically as orthophosphate (PO_4^{3-}) by formation of the molybdophosphoric acid complex. Sample pretreatment is necessary to insure that the phosphorus is completely converted to PO_4^{3-} .

The sample is first fumed down with concentrated HCl and CuCl_2 . The dried sample is then dissolved in dilute HCl (0.7 M) and masking agents (EDTA and KF) are also added. Ammonium molybdate solution is added to complex the phosphorus which is then extracted into butyl acetate and read against a reagent blank on a UV-visible spectrophotometer. The complex absorbs ultraviolet light at about 305 nm.

LIMITATIONS

The use of masking agents and the organic extraction make this procedure quite specific for phosphorus. However, the following limits must be observed:

Species

Maximum

Citrate

10 mg

NO_3^-

1 mg (after fume down)*

NO_3^-

0.5 mg (after fume down)*

Pu

20 mg**

* See Discussion section

** See Applications section

Tantalum, tungsten, zirconium and titanium may interfere if present in greater than trace amounts, but the limits have not been determined.

The HCl concentration during the extraction step should be within the limits of 0.9 to 1.1 M HCl was used to dissolve the dried sample.

The butyl acetate used in this procedure must be spectroquality or better, as certain impurities in inferior grades (even some "reagent" grade) can seriously interfere by UV absorption in the region of the sample. Check for impurities by scanning the butyl acetate and checking for the interference peak at 310 nm.

Release Date

06/15/88

Expires

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APPLICATIONS

This method is intended primarily for high-salt samples containing up to moderate amounts of phosphorus (3.5×10^{-5} M up to 0.1 M), but should work in other matrices. A suspect matrix should be checked out with an appropriate standard before samples are attempted.

Samples with concentrations higher than 0.1 M phosphorus may be run, but the large dilution required must be done very carefully, to minimize dilution error. Samples containing high levels of plutonium should not be run by this method. A separate procedure with an additional preliminary fume-down, PSPU-01, has been prepared for this purpose. (2)

The optimum range of phosphorus in the sample aliquot is 3.5×10^{-5} to 6.5×10^{-4} moles, although the detection limit is about 5×10^{-6} moles. Ten values from the LSR Data Base for a clean phosphorus standard resulted in an accuracy of 101.4% and estimate of precision of a single observation at + 9.7%. (1)

SAFETY

Concentrated hydrochloric acid is toxic and corrosive. In addition, it emits highly noxious fumes of hydrogen chloride gas when heated. The fume-downs in this procedure should be performed only in a well-ventilated hood using vacuum dome in line with a caustic scrubber. (See Figure 1)

The provisions of "General Regulations and Practices for Radiation Work," RHO-GM-MA-2, Volume 6, Book 1, Standard Requirements and Procedures Section 61-02.5, and Radiation Work Permit SL-3 found in RHO-MA-172 apply to all work performed under this procedure and must be followed at all times.

REAGENTS

NOTE: Except as noted, all reagents should be prepared from reagent grade chemicals and stored in glass. All reagents are stable indefinitely except as noted.

1. Phosphorus Calibration Standard, 1.25×10^{-4} - 1.20×10^{-4} M P

Prepare a Stock Phosphorus Standard that is 1.25×10^{-2} - 1.30×10^{-2} M P using primary standard grade potassium dihydrogen phosphate (KH_2PO_4) that has been dried for at least two hours at 105°C . Prepare 100 ml of Phosphorus Calibration Standard by making a 100 fold dilution with 1 M HCl of the Stock Phosphorus Standard. A new Phosphorus Calibration Standard should be prepared just prior to calibration.

2. Hydrochloric Acid, concentrated (37 wt. percent)
3. Hydrochloric Acid, 1 M
4. Hydrochloric Acid, 0.70 M

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REAGENTS (continued)

5. Ethylenediaminetetraacetic Acid (EDTA), 10 g/l

Use the disodium dihydrate form. Store in polyethylene bottle.

6. Potassium Fluoride, 2 M

7. Cupric Chloride, 0.1 M in 0.006 M HCl

8. Ammonium Molybdate Solution, 120 g/l in 5 M HCl

Ammonium heptamolybdate, $(\text{NH}_4)_6 \text{MO}_7 \text{O}_{24} \cdot 4\text{H}_2\text{O}$ must be completely dissolved in concentrate HCl before adding water.

Store in a refrigerator. This reagent deteriorates with time and should be replaced when standard recoveries drop to 95 percent or less. Store in polyethylene.

9. n-Butyl Acetate, Spectroquality Grade, Eastman No. 13085 (or equivalent)

Check each new batch by scanning against water as reference from 320 to 200 nm. If the absorbance at 310 nm is above 0.1 absorbance, the batch should be rejected.

EQUIPMENT

1. Doublebeam Spectrophotometer, capable of UV absorbance measurements at 305 nm.
2. Vials, Specimen, 22 ml, with caps.
3. UV Quartz Spectrophotometer Cells, matched set of at least 6.
4. Magnetic Stirrer--capable of giving good emulsions in about 15 ml.
5. Heating mantle for dessicator.
6. Dry seal vacuum dessicator.
7. Caustic scrubber.

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PROCEDURE

1. Carry a standard through all steps of the procedure with the samples(s).
2. Carry a blank through all steps of the procedure.
3. Add 1 ml of concentrated HCl to each vial. Vials will be required for each sample, blank, and a standard.
4. Survey sample. Pipet the sample containing 3.5×10^{-5} to 6.5×10^{-4} moles of P into the vial, rinsing the pipet 2 or 3 times in acid.
5. Add 1 drop 0.1 M CuCl_2 to each vial. Swirl gently to mix.
6. Place in the heated dessicator and evaporate to dryness with the temperature held at 100° to 120°C and then continue heating for about 10 minutes. Be certain the dessicator is open to vacuum through the trap system as in Figure 1.
7. Cool vials and add 7 ml of 0.70 M HCl to each.
8. Add 1 ml of 10 g/l EDTA and 250 μl of 2 M KF to each vial. Add a glass covered stir bar to each and then cap.

NOTE: A non-glass covered stir bar should never be used. If the glass stir bar breaks or cracks in the steps that follow, the sample should be discarded because the result will be low. (12)

9. Stir for one minute and allow to stand for 15 minutes.

NOTE: The following steps should be performed just prior to reading the absorbances.

10. Remove cap and add 1 ml of ammonium molybdate solution (in refrigerator) to each vial. Stir.
11. Add exactly 4 ml of n-Butyl Acetate to each vial. Cap vials.
12. Stir each vial to complete emulsion for at least three minutes.
13. Allow phases to disengage completely. This typically takes 15-20 minutes.

NOTE: If there is a pronounced yellow color in the organic layer (top layer) the sample will be too high to read, and should be rerun using a smaller sample size. If the organic layer is cloudy, the vial should be centrifuged until the phases are clear. Do not attempt to read a cloudy sample. Your reading will be biased high.

14. Transfer enough of the organic layer to fill a 1 cm quartz cell about 2/3 full.

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PROCEDURE (continued)

15. Check to see that none of the water layer was transferred (droplets on sides of cell). If this is observed, the solution should be transferred back to the vial. The quartz cell should be cleaned and dried before another attempt at transferring the organic layer into the cell.

NOTE: Save the two cells containing blank until all sample have been run. This will enable rebalancing or repeating an auto baseline if a malfunction occurs.

16. Measure absorbance of the samples against the blank at 305 nm according to the "Analytical Procedure" for the spectrophotometer.
17. When a group of samples have been run, slurp the solution from the cells and wash the cells with alcohol then water and then alcohol. Dry the cells before placing more samples in them.
18. When all samples are completed, clean and dry cells as instructed in step 17 and then place the cells in their boxes.

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CALCULATIONS

A. Samples and Standards

$$P \text{ (as PO}_4^{3-}), \underline{M} = \frac{(\text{Rdg}-a)}{b} \times \text{D.F.}$$

where:

Rdg = Sample reading in absorbance units
a = Y-intercept in absorbance units
b = Slope in absorbance units/ $\underline{M}$
D.F. = Dilution Factor (1/sample size in ml)

NOTE: See Calibration section on determination of a and b.

B. Percent Recovery of Standard

$$\% \text{ Recovery of Standard} = \frac{(\underline{M} \text{ P observed})(100\%)}{\text{Standard Value, } \underline{M} \text{ P}}$$

C. Calculation Example

a = .007756
b = 6161.27
Sample Rdg. = 1.204
Sample D.F. = 1010 (100-10-100 Sample size)
Std. Rdg. = .398
Std. D.F. = 2 (500 μ l)
Std. Value = $1.305 \times 10^{-4} \underline{M} \text{ P}$

$$\text{Std. } (\underline{M} \text{ P}) = \frac{(.398 - .007756)}{6161.27} \times 2$$

$$= 1.267 \times 10^{-4} \underline{M}$$

$$\% \text{ Recovery of Std.} = \frac{(1.267 \times 10^{-4} \underline{M})(100\%)}{1.305 \times 10^{-4} \underline{M}}$$

$$= 97.1\% \text{ Recovery}$$

$$\text{Sample } (\underline{M} \text{ P}) = \frac{(1.204 - .007756)}{6161.27} \times 101$$

$$= 0.1961 \underline{M}$$

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CALIBRATION

NOTE: A new calibration is to be performed when a new batch of ammonium molybdate reagent is prepared.

1. Add 1 ml of concentrated HCl to each of 9 vials.
2. Using the Phosphorus Calibration Standard, pipet into the series of vials the following samples sizes.

NOTE: The Calibration Curve will be more accurate if calibrated pipets are used.

<u>Vial No.</u>	<u>Volume (ml)</u>
1	0.100
2	0.200
3	0.300
4	0.500
5	0.750
6	1.000
7	1.500
8	2.000
9	2.500

3. Prepare a blank as instructed in the procedure.
4. Carry all vials through the procedure, starting with step 5.
5. Determine the slope and y intercept for the curve by fitting a straight line to the data by the method of Least Squares. This can be done by using the H.P. Calculator Curve fitting program. The curve fit should be greater than .9990.

DISCUSSION

A. Chemical Pretreatment

Phosphorus is determined in this method only when in the form of orthophosphate, PO_4^{3-} (or H_3PO_4 in an acid solution). A fume-down with concentrated HCl and a slight excess of cupric ion (as CuCl_2) oxidizes to orthophosphate any lower valence states of phosphorus which may be present: (3,4)

Excess copper up to 1 mg does not interfere. (5,6)

The HCl fume-down is also presumed to at least partially hydrolyze any pyrophosphate present, although this has not been verified:

The fume-down with HCl serves also to destroy the nitrate and nitrite in the sample, which are generally present in large amounts in these high-salt samples. Experimentally, it was found that the HCl fume-down would destroy up to 5 M NO_2 and 5 M NO_3 in a 0.500 ml direct sample size, so that no interference was observed. (11) In Table I, Limitations section, the amounts given for nitrate and nitrite are those following the fume-down. If present in higher amounts, nitrite will bias the results high, due presumably to UV absorption of extractable species tailing into the region of interest (300 to 310 nm). Nitric acid or nitrate in excess inhibit the extraction, causing low results. (2,6)

By dissolving the dried sample in 7 ml of 0.7 M HCl, the acid concentration is optimized for the extraction step. This acid plus that present in the ammonium molybdate reagent gives a final concentration of about 1 M.

The purpose of EDTA and KF is to complex metals which might otherwise form inextractable phosphate complexes. Aluminum is the main concern in high-salt samples, but this also applies to many metallic impurities.

DISCUSSION (continued)

B. Complexation and Extraction

Several other chemical species (e.g., silicate) also form colored complexes with ammonium molybdate. However, only the phosphate complex is extracted by butyl acetate. (7)

The useful life of the molybdate reagent has not been determined, but it is known that it gradually deteriorates. Standards should be run with each sample or series of samples to verify the validity of the calibration. When standard recoveries are 95 percent or less, the solution should be replaced and a new calibration performed.

C. UV Absorption Problems and Interfaces

The purity of the butyl acetate has been found to be quite critical in this method. (8) Only "spectro" grade butyl acetate should be used, as some inferior grades have been shown to contain impurities absorbing in the region of 275 nm. This absorption peak is sometimes so intense in the sample that it completely masks the molybdophosphate absorption at 305 nm. Each batch of butyl acetate should be checked by scanning it from 320 to 300 nm against water as a reference. The absorbance should be less than 0.1 absorbance unit at 310 nm.

Occasionally, the organic layer will be cloudy when the phases separate. This cloudiness is presumably due to entrained water or salts and must be removed by centrifuging before the sample can be read. A cloudy sample will always read high, due to the scattering of light by the suspended droplets of the dispersed phase.

Previous experience has shown that the absorbance of the sample versus the blank will change with time. It is not known how fast this happens, but at present it is recommended that the samples be read within two hours following addition of the molybdate reagent.

Cells should be washed with ethyl alcohol followed by water followed by ethyl alcohol. Acetone must never be used for cleaning the cells, for a number of reasons:

1. Acetone absorbs strongly in the near UV region, and even traces left in the cell will bias the results.
2. Acetone inherently leaves a film on the optical surfaces of the cells upon evaporation.
3. Some cements used in optical cells are dissolved by acetone.

For a basic discussion of the theory of UV and visible light absorption and derivation of Beer's Law, the reader is referred to Willard, Merritt, and Dean (9) and other appropriate texts.

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Figure 1. PO₄ VACUUM DOME AND CAUSTIC SCRUBBER SET-UP

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ANALYTICAL LABORATORIES

Issued By: T. A. Lane

Title ANION ANALYSIS ON DIONEX MODEL 10

Manager,

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SUMMARY

This procedure describes the operation of the Dionex Model 10 Ion Chromatograph for the determination of fluoride, chloride, phosphate, nitrite, nitrate, and sulfate anions. Anions of interest are separated, measured, and detected by means of a guard column, a separator column, a suppressor, and a conductivity cell.

LIMITATION

Table I lists the anion concentrations used in calibration. Samples that have concentrations greater than the highest calibration standard, must be diluted with E2 eluent. The procedure is designed to give a precision of $\pm 10\%$ for each of the five anions.

Interferences can be caused by substances with retention times that are similar to and overlap those of the anions of interest. Some samples have very high concentrations of certain anions that interfere with other anions by shifting the retention times, thus causing an identification problem. Interfering ions include sulfite, chromate, perchlorate, iodide, iodate, iron, arsenate, aluminum, zirconium, calcium, strontium, barium, and several organic compounds.

Samples known to contain particles greater than 0.45 microns and reagents known to contain particles greater than 0.20 microns require filtration to prevent damage to the flow systems and columns. Any visible particles in the sample should be filtered out.

APPLICATIONS

Anions in waters for cooling basins, boilers, industrial waste waters, as well as surface waters and well waters may be determined by ion chromatography. When this procedure is used in analyzing unfamiliar samples for any of the anions, anion identification should be supported by addition of a spike solution containing a known concentration of mixed anions to be determined.

SAFETY

The following safety concern is associated with this procedure.

- o Radioactive samples reading greater than 10 mRAD/h should not be run on the ion chromatograph without special planning involving appropriate technical and supervisory personnel.

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REAGENTS

| Label all reagents according to Procedure LO-120-001.

| Stock standards are stable for at least one month when stored at 4°C. Dilute working standards should be prepared weekly except those that contain nitrite and phosphate should be prepared fresh daily.

| E2 CONCENTRATE 0.300 M Sodium Bicarbonate (MSDS #1480) M Sodium Carbonate (MSDS #1484)

| To prepare reagent grade 0.300 M sodium bicarbonate and 0.240 M sodium carbonate, weigh out 50.40 g of sodium bicarbonate and 50.90 g of sodium carbonate and dissolve in a 2 liter volumetric flask containing 1500 mL of deionized H₂O (>=16 megohm). Bring to total volume of 2 liters using >=16 megohm deionized H₂O. The E2 concentrate will depreciate after two months from the time of preparation.

| E2 ELUENT: 0.003 M Sodium Bicarbonate and 0.0024 M Sodium Carbonate

| To prepare 0.003 M sodium bicarbonate and 0.0024 M sodium carbonate, add 200 mL of E2 concentrate to a 20 liter plastic reservoir. Bring to total volume of 20 liters using Q-H₂O (>=16 megohm). Blend for at least 8 - 10 minutes. Measure the conductance of the previous eluent against the conductance of the new eluent. The new eluent must be analyzed as a sample in order to prove that no anions are added. The E2 eluent will depreciate after two months from the time of preparation.

| REGENERANT CONCENTRATE: 0.5 M Sulfuric Acid (MSDS #1529)

| To prepare 0.5 M sulfuric acid, add 110 - 115 mL of reagent grade concentrated sulfuric acid to a 4 liter plastic bottle containing 3 to 3 1/2 liters of deionized water (>=16 megohm). Dilute to a 4 liter volume with remaining deionized water. Mix for at least 8 - 10 minutes. The 0.5 M sulfuric acid is usually prepared by Standards Laboratory. The regenerant will depreciate two months from the time of preparation.

| WORKING REGENERANT: 0.0124 M Sulfuric Acid

| Prepare 0.0125 M sulfuric acid by adding 250 ± 5 mL of 0.5 M sulfuric acid to enough deionized water to make 10 liters. Mix for at least 8 - 10 minutes.

REAGENTS (continued)

CALIBRATION STOCK STANDARD SOLUTIONS:

NOTE: Good for one month. Store each solution separately in polyethylene bottle. Dry all powder chemicals overnight in 100-110°C drying oven. High Purity reagents to be used are "Baker Analyzed".

Chloride (Cl) 10,000 mg/L: (MSDS #1485)

Dissolve 1.6485 g of sodium chloride (NaCl) in Q-water in a 100 mL calibrated volumetric flask and stir at least 2 - 5 minutes. Dilute to 100 mL with Q-water.

Phosphate (PO₄) 10,000 mg/L: (MSDS #2286)

Dissolve 0.7165 g potassium phosphate (KH₂PO₄) in Q-water in a 50 mL calibrated volumetric flask and stir at least 2 - 5 minutes. Dilute to 50 mL with Q-water.

Nitrate (NO₃) 10,000 mg/L: (MSDS #1506)

Dissolve 0.3427 g sodium nitrate (NaNO₃) in Q-water in a 25 mL calibrated volumetric flask and stir at least 2 - 5 minutes. Dilute 25 mL with Q-water.

Sulfate (SO₄) 10,000 mg/L: (MSDS #1844)

Dissolve 0.4535 g potassium sulfate (K₂SO₄) in Q-water in a 25 mL calibrated volumetric flask and stir at least 2 - 5 minutes. Dilute 25 mL with Q-water.

Fluoride (F) 10,000 mg/L: (MSDS #1491)

Dissolve 0.5525 g sodium fluoride (NaF) in Q-water in a 25 mL calibrated volumetric flask and stir at least 2 - 5 minutes. Dilute 25 mL with Q-water.

Nitrite (NO₂) 10,000 mg/L: (MSDS #1495)

Dissolve 0.3749 g sodium nitrite (NaNO₂) in Q-water in a 25 mL calibrated volumetric flask and stir at least 2 - 5 minutes. Dilute 25 mL with Q-water.

CALIBRATION WORKING STANDARDS (continued)

This standard is a working standard in the ion concentrations listed below and stored in a polyethylene bottle. Using the solutions from step 10, dilutings are made as listed using eluent to bring the mark of 100 mL calibrated volumetric flask. The working standard is in a clean matrix.

SOLUTION	CONCENTRATION (ppm)	mL NEEDED/100mL
NaF	(F ⁻) 50	5 mL
NaCl	(Cl ⁻) 60	6 mL
KH ₂ PO ₄	(PO ₄ ⁻) 500	5 mL
NaNO ₃	(NO ₃ ⁻) 500	5 mL
Na ₂ SO ₄	(SO ₄ ⁻²) 500	5 mL
NaNO ₂	(NO ₂ ⁻) 500	5 mL

EQUIPMENT

Dionex Ion Chromatograph, Model 10, with one system equipped with a cell for detection, a pre-column, a separator column and a suppressor.

Hewlett-Packard, 3390-A reporting integrator.

| Vials, polyethylene, 1 oz size, with screw caps, stock room part #57-9000-025.

| Syringes, plastic disposable, 5 cc Luer-lok tip.

Dispenser, 1 liter with 10 mL dispensette

Eppendorf pipets, sizes: 10/25/50/75 through 1000 uL with appropriate tips

Carboys-plastic reservoirs with attached spigots. One 20 liter size for eluent storage and preparation.

Glass bottles 1 gallon size for waste effluent.

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PROCEDURE

A. INSTRUMENT START-UP AND SAMPLE ANALYSIS:

1. Check to see if the eluent and regenerant reservoirs are full. The E2 eluent reservoir must be > 3 liters.
2. Tighten cap on regenerant bottle.
3. Turn on air at valve on air cylinder.
4. Check the pressure readings on the compressed air tank. The cylinder should have a pressure of 200 psi and the regulator gauge should read between 80 - 90 psi. Adjust the regulator pressure by turning the handle clockwise for increasing the pressure and the opposite way for decreasing the pressure.
5. Check waste container in the hood.
6. Toggle levers should be in the following positions: (See Figure II.)
 - a. On the ion chromatograph console:
Power - OFF
Pump - OFF
Air - ON
Red "ready" LED light - OFF
Inject- LOAD
7. On the Hewlett-Packard 3390-A Integrator press "List", "Meth", and "Enter" keys to list the integration parameter. Verify that the parameters agree with those listed in Figure I of the procedure. Figure V illustrates the 3390-A Keyboard.
8. If there is a disagreement, then follow the steps listed below:
 - a. press "ZERO" on the keyboard, then "0" and "ENTER".
 - b. Press "ATT 2", then "10" and "ENTER".
 - c. Press "CHT SP", then "0.5" and "ENTER".
 - d. Press "PK WD", then "0.16" and "ENTER".
 - e. Press "THRSH", then "7" and "ENTER".
 - f. Press "AR REJ", then "50000" and "ENTER".
 - g. Press "OP()", then "4" and "ENTER". This changes the response to "yes".
 - h. Press "OP()", then "1" and "ENTER". The integrator responds with "M-D-Y" and "DATE". M-Month, D-Date, Y-Year.

PROCEDURE (continued)

- i. Press N-month, N-day, N-year, than "ENTER". For example: If the date is March 4, 1987, press "03-04-87" and then press "ENTER". The integrator responds with "H-M-S". H=Hours, M=Minutes, S=Seconds.
 - j. Press N-hours, N-minutes, N-seconds, then "ENTER". For example: The time is 8:30:40. press "08-03040", then "ENTER".
 - k. Press "STOP" and "TIME", then the time listed in Figure I and "ENTER".
 - l. Press "LIST", "METH" and then "ENTER". Compare the parameters with those listed in Figure I.
9. On the ion chromatograph console the toggle levers must be set in the following positions: (See Figure I.)

Power - ON
Pump - ON

WARNING: THE PRESSURE READING ON THE PUMP GAUGE MUST NOT EXCEED 600 PSI OR BE LESS THAN 400 PSI. WHEN PRESSURES FALL OUTSIDE THESE LIMITS, TURN THE PUMP TOGGLE LEVER "OFF" AND NOTIFY THE RESPONSIBLE SCIENTIST. SERIOUS INSTRUMENT DAMAGES MAY OCCUR WHEN THE INSTRUMENT IS OPERATED UNDER THESE CONDITIONS.

10. Set the mode switch inside the hood next to the conductivity meter to "LIN". (See Figure III.)

NOTE: Allow the instrument to equilibrate for 1 hour so that eluent can circulate throughout the system. The conductivity may increase and then decrease. When the system has equilibrated the conductivity usually stays at 0.04 micro MHO/cm which is about two small divisions past the zero line. MHO is synonymous with OHM. MHO is the terminology specific with the Model 10 instrument.

11. Turn the fine offset knob (not the course adjustment knob) on the meter module until the meter reads a 0.04 micro MHO/cm only if the conductivity is not 0.04 micro MHO/cm after equilibration.
12. Prepare a LMCS standard using 100 uL of the standard with a mixed concentration of anions to 10 mL of E2 eluent in a 1 oz plastic vial and mix thoroughly. Samples are prepared the same as the LMCS standards; however, dilutions may vary dependent on the anion concentrations in the samples.
13. Fill a 5 mL disposable syringe with LMCS standard assuring that no air bubbles are in the syringe. If air is in the syringe refill until air is gone.

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PROCEDURE (continued)

14. Place the syringe on the Luer-lock fitting located in the hood on the sample injection part. Turn the syringe so that the syringe interlocks with the sample port.
15. Check to see that the toggle lever on the ion chromatograph console is in the load position before loading the sample. Load the sample (about 2 - 3 mL of sample).
16. Identify the sample by pressing the "ID" key on the integrator, then the sample number, the dilution, and then press "ENTER".
17. In succession, press the "START" key on the integrator and switch the injector toggle lever on the ion chromatograph console to the injection mode.
18. The elution order for the five anions is fluoride, chloride, phosphate, nitrate, and sulfate. See Figure IV for the chromatogram illustrating the peaks and their elution order.
19. If the sample requires a direct injection with no dilutions, then add 50 uL of E2 Concentrate to 5 mL of the sample. Dilutions are required when the concentrations of the samples are higher than the highest calibration standard concentration.

NOTE: Sample-Plus-Spike concentration must fall within calibration range.

20. After first sample has been analyzed to determine dilution factor, spike this sample with 50 uL (or an amount determined by the responsible scientist) of calibration standard. Every following tenth sample must also be spiked.

NOTE: The concentration for the spike will be calculated on the M-600 using the DIONEX program. The % recoveries of the spike will be calculated after both the spike results and the sample results are tabulated.

21. Repeat steps 14 - 21 for additional samples or standards.
22. Inject an LMCS standard at the end of all sample analysis. The % recoveries must fall within the 10% control limits. Log the % recoveries of the LMCS samples and a description of the samples analyzed in the log book.
23. Record the condition of the instrument and any problems occurring during the operation of the instrument in the log book.

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PROCEDURE (continued)

B. INSTRUMENT SHUT-DOWN

1. Place the toggle lever on the ion chromatograph console in the load mode. Load the sample port with 10 - 15 mL of deionized water at the end of the analysis in order to thoroughly flush the sample loop.
2. Turn the switch on the meter module in the hood to "ZERO".
3. Turn the pump switch on the ion chromatograph console to the "OFF" position.
4. Turn the power switch on the ion chromatograph console to the "OFF" position.
5. Turn the air off on the valve at the air cylinder.
6. Loosen cap on regenerant bottle so air pressure is released.
7. Clean work area.

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CALCULATIONS

Calculate the results using the M600 computer. Those samples that have been spiked with a known mixed anion calibration standard will be treated as an unknown sample, and calculated using the M600 computer. The responsible scientist will calculate the % recoveries using the samples and the spike concentrations. Since the peak height measurement technique has been selected as the form of detector response, it is necessary to analyze standards to obtain a reference for detector response versus standard concentration. When the reference points are graphed, the calibration curve is formed and the range of linear response can be determined. The one-point calibration technique may be used in calculating the concentration of the unknown simply by taking the response ratio of both the unknown and the standard samples and multiplying by the concentration of the standard, as shown below.

$$\text{Concentration Of Unknown} = \frac{(\text{Response of unknown}) (\text{Concentration of Standard})}{(\text{Response of Standard})}$$

One-point calibrations are not recommended for accurate quantitation because the linear response range is not known in many cases. However, if the linear range is known, then a one-point calibration may be adequate. The response of the unknown should fall within the linear response range of the calibration curve so that the concentration may be adequately determined.

NOTE: Only the responsible scientist or a qualified technician fully familiar with the calibration procedure will calibrate the instrument. A new calibration is required when one of the following is changed:

- 1) Guard column.
- 2) Separator column.
- 3) Eluent.

1. Prepare a series of calibration dilutions using the mixed calibration standard prepared by Standards Laboratory (F^- : 50 ppm, Cl^- : 60 ppm, PO_4^{3-} : 500 ppm, NO_3^- : 500 ppm, SO_4^{2-} : 500 ppm). Dispense 10 mL of E2 eluent into six (1 oz) successive plastic vials. To each successive vial add 25, 50, 100, 250, and 750 μL of the mixed anion calibration standard and mix thoroughly. See actual concentrations of the dilutions in Table I.
2. Record peak heights and retention times for all the anions in the log book. Also record the % recoveries on the LMCS standards.
3. Enter the calibration into the M600 computer, print the results, and enter the peak heights in the log book of each anion at each concentration level.

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DISCUSSION

Ion Chromatography quantitatively determines certain anions through the process of ion separation and eluent suppression.

As the sample is loaded into the 100 uL sample injection loop and the injection valve is activated, eluent carries the sample through a series of resin packed columns, called a pre-column (guard column), a separator column, and an anion suppressor. The anions in solution compete for cationic exchange sites and momentarily become bound to selective sites until they become replaced by the eluent. The competitive ion exchange process recurs several times as the sample continues through the columns.

The greater the selectivity for a particular ion, the longer it will remain attached to the resin exchange sites. Elution of the anions depends on this attachment time. These preferred sites and times of attachment permit separation of the different anions in solution.

Retention times are used to identify anions and is the time elapsed from the sample injection time to the maximum peak. Pre-knowledge of a known sample's retention time prior to analysis of an unknown sample make it possible to identify an anion by its retention time.

Shifts in retention times are observed problems in ion chromatography. These peak shifts may be evident in highly concentrated samples, samples whose matrix interacted with the eluent, and temperature changes. The best approach to minimizing the peak shifts is to dilute the sample such that the total quantity of anions are kept reasonably low for the separator column. Phosphate and nitrate in high concentrations have high affinities for the resin and are two of the main constituents for causing retention time shifting.

The conductivity of a solution is directly affected by its temperature. A change in temperature causes a change in solution conductivity. As the solution conductivity increases, the effect on temperature changes becomes more pronounced. Therefore, the effects on temperature variation may be further reduced by normalizing all measured conductivities to 25°C.

It is, at times, desirable to vary the concentration of the eluent. As separator columns age, retention of analytes weaken and retention times shorten. This causes a loss in peak resolution. A simple remedy is to use a more dilute eluent. With a more dilute eluent, resolution between peaks may improve; however, peak broadening may also occur.

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REFERENCES

Section A-Procedures

1. LO-120-001, "Labeling of Standards and REagents".

Section B - Source Documents

1. Dionex Model 10 and 14, Operator's Instrument Manual, Sunnyvale, CA, 1983.
2. Dionex Model 10 Ion Chromatography Training Course Manual, Dionex Corp., Sunnyvale, CA, 1987.
3. O'Dell, J., Pfaff, J., Gales, M. and McKee, G., January 1984. Test Method-The Determination of Inorganic anions in Water by Ion Chromatography Method 300.0. 300.01 - .0.5, Research and Development E.P.A.
4. Smith, F., Chang, R., 1983, "The Practice of Ion Chromatography", 13 - 74.

TABLE I

APPROXIMATE ANION CONCENTRATIONS RANGES USED TO CALIBRATE
THE ION CHROMATOGRAPH

<u>ANION</u>	<u>CONCENTRATION RANGE (mg/L)</u>
F ⁻	0.125 - 3.488
Cl ⁻	0.150 - 4.186
PO ₄ ⁻³	1.247 - 23.810
NO ₃ ⁻	1.247 - 23.810
SO ₄ ⁻²	1.247 - 23.810

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FIGURE I
INTEGRATION PARAMETERS

ZERO - 0
ATT2 - 10
CHT SP - 0.5
PK WD - 0.16
THRSH - 7
AR REG - 50000

RPRT OPTNS:

2. RF UNC PKS - 0.0000E+00
3. MUL FACTOR - 1.0000E+00
4. PK HEIGHT MODE YES
5. EXTEND RT NO
6. RPRT UNC PKS NO

TIME TBL
.10.00 STOP

CALIB TBL
EMPTY

FIGURE II

Power, Regeneration and Operations Panels (Model 10)

A - Power and Regeneration Panel

B - Fuses

C - POWER switch

D - PUMP switch

E - AIR air toggle

F - Regeneration Control Buttons

G - Regeneration Timer Switches

H - Operations Panel

J - Air Toggles

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FIGURE III

Conductivity Meter

- A - Adjustment Screw to Set Meter Zero
- B - Log Scale
- C - Linear Scale
- D - Calibration Mark
- E - MODE switch
- F - Course Offset Dial
- G - Offset Range Switch
- H - Fine Offset Dial
- I - PIP Button (Event Marker)
- J - Full Scale Switch

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FIGURE VI

FIGURE V

STOP												START											
1111	10	DEL	1000	ENTER	CLEAR	ESC																	
1000	0000	1000	0000	7	8	9	1000																
DEL	0011	1110	0011	4	5	6	1000																
1000	1000	1110	1000	1	2	3	1011																
1100	1010	1000	1000	0	.	-	1011																

ANALYTICAL LABORATORIES

Issued By:

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Title

MERCURY ANALYSIS BY HYDRIDE GENERATION ATOMIC
ABSORPTION

SUMMARY

This procedure describes the operation of the Perkin-Elmer Model 2280 atomic absorption spectrometer using the MHS-20 Mercury/Hydride System with the amalgam attachment. This method is used for the determination of mercury in aqueous solution using the amalgam technique. Mercury is determined using stannous sulfate solution as the reductant. The determination is performed according to the established method of HATCH and OTT (Anal. Chem., 40. 2085 (1968)).

LIMITATIONS

This procedure is used for the analysis of aqueous solutions. The detection limit and precision are dependent on the sample matrix but are usually in the range of 5 to 40 ng of mercury and 5% to 20%, respectively.

The total prepared volume of sample must not exceed 50 mL.

Potassium permanganate is added to eliminate possible interference from sulfide. Concentrations as high as 20 mg/L of sulfide as sodium sulfide do not interfere with the recovery of added inorganic mercury from Type II water.

Copper has also been reported to interfere; however, copper concentrations as high as 10 mg/L had no effect on recovery of mercury from spiked samples.

Certain volatile organic materials that absorb at this wavelength may also cause interference. A preliminary run without reagents should determine if this type of interference is present.

APPLICATIONS

This method is a cold-vapor atomic absorption procedure approved for determining the concentration of mercury in mobility-procedure extracts, aqueous wastes, and ground waters. All samples must be subjected to an appropriate dissolution step prior to analysis. This method has not been tested on other sample matrices; therefore, contact the responsible scientist if other than environmental samples are to be analyzed.

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SAFETY

All activities described in this procedure are supported by safety instructions contained in SD-CP-LB-003, "Safety in the Analytical Laboratory." For safe handling and use of the chemicals in this procedure, review the Hanford Environmental and Health Foundation's Material Safety Data Sheets (MSDSs) for those chemicals listed in the Reagents Section.

Follow the requirements and good practices set forth in WHC-CM-4-15, Radiation Work Requirements and Permits Manual, and WHC-CM-4-10, Radiation Protection. The RWP applicable to this procedure is:

S-003, "Room with Open Faced Hoods (Excluding 2B Decon and Slurp Hood and Room 1GB) Routine Work Maintenance Performed Inside Open Faced Hoods,"

No chemicals from WHC-CM-4-3, Volume 2, Industrial Safety Manual, carcinogen list (Guide C-2, Rev. 1, Table) are used in this procedure.

In compliance with WHC-CM-1-3, Management Requirements and Procedures, (MRP 5.43), an Impact Level 03 has been assigned to this procedure.

Do not overfill the reaction flask. The maximum prepared sample volume is 50 mL.

Ensure that the sample transfer hose between the Analyzer Assembly and the quartz cell is not restricted in any way.

Make certain that the venting hoses from the cell are not restricted in any way. Check them periodically to see that they have not become full with condensed water.

Never push START button when a reaction flask or vessel is not placed underneath the immersion tube.

At the end of the working day, purge the reductant transfer system with deionized water to remove any reductant residues.

EQUIPMENT

Perkin-Elmer Model 2280 Atomic Absorption Spectrometer with Model MHS-20 Mercury/Hydride Option and Mercury Amalgam Attachment.

Hollow Cathode Lamp (HCL)

Amalgam attachment

Compressed air

Argon

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EQUIPMENT (continued)

Quartz tube with quartz windows and silicon sleeves

Reaction flasks with covers

Transfer hose with flashback arrestor

Pipets, glass or Eppendorf, various sizes

Vials, 22 mL disposable

Beakers, 15 and 30 mL disposable

Filter units, disposable

Glass stir rods, medium

REAGENTS

Note: Label reagents according to LO-120-001, Ref. A.2

Nitric acid (HNO₃), concentrated, MSDS #1384

Reagent grade of low mercury content. If a high reagent blank is obtained, it may be necessary to distill the nitric acid. No expiration.

Nitric acid, 1.5% (v/v), MSDS #1384

Dilute 15 mL of concentrated nitric to 1 L with deionized water. Store in glass or plastic. Shelf life one year.

Sulfuric acid (H₂SO₄), concentrated, MSDS #1529

Reagent grade. As received. No expiration.

Sulfuric acid, 0.5 N, MSDS #1529

Dilute 14.0 mL of concentrated sulfuric acid to 1.0 L. Store in glass or plastic. Shelf life one year.

Stannous sulfate solution, MSDS #N/A

Add 25 g stannous sulfate to 250 mL of 0.5 N H₂SO₄. This mixture is a suspension and should be stirred continuously during use. (Stannous chloride may be used in place of stannous sulfate.) Store in glass or plastic. Should be prepared fresh daily.

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REAGENTS (continued)

Sodium chloride-hydroxylamine sulfate solution, MSDS #1688 and MSDS #1485

Dissolve 12 g of sodium chloride and 12 g of hydroxylamine sulfate in deionized water and dilute to 100 mL. (Hydroxylamine hydrochloride may be used in place of hydroxylamine sulfate.) Store in glass. Shelf life three months.

Potassium permanganate, 5% solution (w/v), MSDS #1445

Dissolve 5 g of potassium permanganate (mercury free) in 100 mL of deionized water. Store in glass bottle. Shelf life three months.

Potassium persulfate, 5% solution (w/v), MSDS #146

Dissolve 5 g of potassium persulfate in 100 mL of deionized water. Store in glass bottle. Shelf life three months.

Stock mercury solution, MSDS #1323

Dissolve 0.1354 g of mercuric chloride in 75 mL of deionized water. Add 10 mL of concentrated HNO_3 and adjust the volume to 100.0 mL using a Class A volumetric flask, store in glass. Should be prepared fresh daily.

Mercury working standard, MSDS #1323

Dilute 1 mL of the stock mercury solution to 1 L using a Class A volumetric flask. Acidity of the working standard should be maintained at 0.15% nitric acid. This acid should be added to the flask, as needed, before addition of the aliquot. Store in glass, should be prepared fresh daily.

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PROCEDURE

This procedure contains seven sections:

- I. Cleaning the Cell Windows
- II. Cell Cleaning Procedures
- III. Amalgam Attachment Installation
- IV. Instrument Setup
- V. Preparation of Standards and Samples
- VI. Analysis
- VII. Instrument Shutdown

I. Cleaning the Cell Windows

NOTE: The windows are optical devices, forming a part of the optical system of the instrument with which they are used. They must be accorded the same careful treatment applied to any optical component.

The windows normally exhibit a small absorption, which increases slightly toward shorter wavelengths. Dirt, fingermarks, scratches, lint, etc., can easily introduce substantial analytical errors. The windows should be checked regularly for contamination and cleaned as required.

If cleaning is necessary, proceed as follows:

1. Switch OFF the MHS-20.

NOTE: The Heating Mantle and the cell may be hot. RISK OF BURNS. Wear protective hand covering, if required.

2. Open the Heating Mantle by swinging the cover back.
3. Lift out the cell.
4. Remove the quartz windows by very carefully pulling them out of the sleeves.
5. Place the windows in the ultrasonic cleaner for 2 minutes.
6. Remove from the ultrasonic cleaner and rinse with distilled water followed by ethyl alcohol.
7. Place windows on a clean surface and allow to air dry.
8. Wipe down windows with a soft, lint free cloth.
9. Replace the windows by carefully pushing them into the sleeves.

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II. Cell Cleaning Procedures

NOTE: Under normal working conditions the quartz cell should only be cleaned if it becomes seriously contaminated (e.g., through sample solution being transported to the cell). Do not perform this section without first consulting the responsible scientist.

WARNING: THE HEATING MANTLE AND CELL MAY BE HOT. RISK OF BURNS! WEAR PROTECTIVE HAND COVERING, IF NECESSARY.

1. Switch OFF the MHS-20.
2. Open the Heating Mantle by swinging the cover back and lift out the cell.
3. Disconnect the three hoses from the cell (see Figure 1).
4. Remove the quartz windows from the sleeves. Remove the sleeves from the cell ends.
5. Wash the cell out well with running water. Then rinse the cell thoroughly with deionized water and ethyl alcohol. Allow the cell to air dry.
6. Replace the sleeves and the quartz windows.
7. Reconnect the three hoses to the correct cell nipples.
8. Place the cell in the Heating Mantle and close the cover.

III. Amalgam Attachment Installation

The Amalgam Attachment is permanently mounted in the back of the Analyzer Assembly. It is necessary to change hose connections when the Amalgam mode is chosen for mercury analysis.

The Amalgam Attachment is installed on the Analyzer Assembly as shown in Figure 2.

1. Connect the transfer hose coming from the reaction flask to the upper right-hand nipple on the Amalgam Attachment.
2. Connect the transfer hose going to the quartz cell to the upper left-hand nipple on the Amalgam Attachment.
3. Connect the compressed air coolant hose to the lower left-hand nipple on the Amalgam Attachment.
4. This completes the hose connections on the Amalgam Attachment.

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IV. Instrument Setup

1. Turn the LAMP 1 control fully counterclockwise.
2. Install the Mercury Hollow Cathode Lamp (HCL) in the lamp compartment and plug into LAMP 1 connector.
3. Switch the POWER on.
4. Make the following control settings:
 - SIGNAL - LAMP 1
 - BKGD CORR - AA
 - GAIN - Fully counterclockwise
5. Turn the LAMP 1 control until the LAMP/ENERGY display shows the proper lamp current as given on the lamp.
6. Set the SIGNAL control to ABS.
7. Adjust the LAMP/ENERGY to a maximum of 70 using the GAIN control.
8. Allow about 30 minutes for the HCL to stabilize.
9. Clean the cell and cell windows under direction of the responsible scientist. See Sections I and II of this procedure.
10. Set the WAVELENGTH to 253.7 nm and the slit to 0.7 nm (NORMAL setting). See Figure 3.
11. Perform the following lamp alignment and wavelength adjustments. The quartz cell must be removed, and the heating mantle left open while these steps are being performed. The reaction flask should also be removed.
 - a. Open the lamp compartment door and turn the two alignment knobs on the lamp holder (see Figure 4) to maximize the LAMP/ENERGY display.
 - b. Adjust the reading to a maximum of 69-71 with the GAIN control (see Figure 5). If the gain should become too high, an over range reading of "EE" will be displayed.
 - c. Peak the wavelength setting by turning the WAVELENGTH ADJUST (see Figure 3) slowly to obtain a maximum reading on the LAMP/ENERGY display or minimum absorbance reading on the Digital Display (see Figure 5).

IV. Instrument Setup (continued)

- d. Again, adjust the reading to a maximum of 69-71 with the GAIN control.
- e. Close the lamp compartment door.
- 12. Lay the quartz cell in the Heating Mantle and close the cover.
- 13. Adjust the LAMP/ENERGY to a maximum to 69-71 using the GAIN control.

NOTE: As the lamp warms up, the display value will change.
Readjust as in Step 13 above.

- 14. Turn the MODE selector switch to CONT on the spectrophotometer (see Figure 5).
- 15. Make incremental adjustments, alternately, to the VERTICAL, HORIZONTAL, and ROTATIONAL controls (see Figure 6) to obtain a minimum absorbance reading on the display. This is to fine adjust the quartz cell.
- 16. Turn on the nitrogen gas supply and increase the pressure to 36 psig.
- 17. Turn on the compressed gas supply and increase the pressure to 36 psig.
- 18. Turn the POWER switch on the controller to ON (see Figure 7) and push the Amalgam button.
- 19. Make the following settings on the MHS-20 controller:

PURGE I -----40 seconds
REACTION -----10 seconds
PURGE II -----30 seconds
TEMP -----180°C

NOTE: See Figure 8 for all recorder buttons.

- 20. Turn on the recorder and check that the RANGE and CHART SPEED are set to 10 mV and 10 mm/minute, respectively.
 - a. The RANGE is adjusted by pushing the RNGE button.
 - b. The CHART SPEED is adjusted by pushing the SPD button.
- 21. To START recording data, push the RUN button.

IV. Instrument Setup (continued)

22. To STOP recording data, push the STOP and PEN LIFT buttons.
23. Fill the reductant reservoir bottle to the shoulder with stannous sulfate. Screw the bottle into the fitting on the analyzer assembly (see Figure 9).

NOTE: ALWAYS zero the absorbance reading by pushing the AZ button AFTER attaching the reaction flask onto the flange on the analyzer assembly.

24. Adjust the LAMP/ENERGY display to 69-71 using the GAIN control.
25. Push the AZ button on the spectrophotometer (see Figure 5) to zero the absorbance reading, if necessary.
26. To zero the pen on the chart paper, push and hold the ZERO ADJ button and turn the zero adjust knob.
27. Place an empty reaction flask onto the flange on the analyzer assembly and push the START button on the controller.
28. After the START light goes out, remove and empty the reaction flask in the waste bottle.
29. Repeat Steps 24-28 three times.

NOTE: Periodically check the lamp watts and adjust, if necessary.

V. Preparation of Standards and Samples

A. Standard and Sample Preparation

1. Prepare the calibration solutions by dispensing 10 mL of 6 M HCl, 1 mL of 6 M HNO₃ and 1 mL of 1 M HSO₃NH₂ and pipetting the appropriate number of microliters (0, 10, 20, or 40) of the calibration standard into the corresponding reaction flask.

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V. Preparation of Standards and Samples (continued)

2. Prepare the sample and LMCS standard solutions according to the following.
 - a. Label duplicate 35 mL vials with the sample number. Mark one vial with an X to indicate that the sample is spiked.
 - b. Add 20 mL of deionized water and pipet an aliquot of sample into the appropriate vial. The sample size is selected to give a result within the range of concentrations of the calibration curve. When no estimate of sample concentration is available, use 200 μ L.
 - c. Add 25 μ L of the mercury LMCS standard to the 35 mL vial marked with an X.
3. Add 1 mL of sulfuric acid (H_2SO_4) to each vial and mix.
4. Add 0.5 mL of nitric acid (HNO_3) to each vial and mix.
5. Add 3 mL of potassium permanganate (KMnO_4) to each vial and allow to stand for 15 minutes.
6. Add 1.6 mL of potassium persulfate ($\text{K}_2\text{S}_2\text{O}_8$) to each vial and mix.
7. Heat each vial in a dry-bath for 2 hours maintained at 95°C .
8. Cool and add 1.2 mL of sodium chloride-hydroxylamine sulfate solution. Mix.
9. When the solution has decolorized, wait 30 seconds.
10. Transfer the solution to a reaction flask.
11. Rinse the 35 mL vial 2 times with 1.5% nitric acid and add to the reaction flask.
12. Go to the analysis section.

VI. Analysis

All standards and samples are to be treated the same.

1. Condition the gold/platinum gauze on the Amalgam Attachment by attaching an empty reaction flask to the Analyzer Assembly and pushing the MAN HEAT button on the MHS-20 controller.

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VI. Analysis (continued)

2. With the REACTION FLASK off, adjust the lamp energy to 69-71, and zero the absorbance reading.
3. Attach a reaction flask containing the blank and push the START button on the controller.
4. Label the chart paper with the information requested on the list on the recorder.

NOTE: Use a metric ruler with mm graduations to measure the peak height. Measure the difference between the baseline just before the peak and peak maxima. Measure to the nearest 1/2 mm.

5. Check the absorbance reading on the chart paper. The blank must not give a signal higher than 10 mm. Higher blank values indicate contaminated chemicals or a contaminated flask or dirty cell and windows or combination of above.

NOTE: Dispose of sample and rinse waste into the appropriately labelled bottle.

6. Remove the reaction flask after the START light goes out, rinse the dispenser tip with 1.5% HNO₃ then deionized water.
7. Rinse the reaction flask thoroughly with 1.5% HNO₃ and deionized water.
8. Wait for the air coolant to stop flow through the Amalgam Attachment.
9. Repeat Step 2.
10. Attach a reaction flask containing a blank and push the START button on the controller.
11. Label the chart paper with Sample I.D. and Size.
12. Check the absorbance reading on the chart paper. You must get a minimum signal as posted on the instrument. If not, contact the responsible scientist.
13. Repeat Steps 6-9.

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VI. ANALYSIS (continued)

14. If the initial checks prove satisfactory, then repeat the above process for the rest of the calibration standards, LMCS standards, and samples.

VII. Instrument Shutdown

1. Remove the reduction (NaBH_4) bottle and replace it with a bottle containing deionized water.
2. Place an empty reaction flask on the analyzer assembly.
3. Rinse the reductant out of the transfer lines by setting both PURGE I and II to their minimum values and REACTION to its maximum and then go through the REACTION cycle 3 times.
4. Close the valve on the nitrogen regulator.
5. Close the valve on the compressed air regulator.
6. Set the PURGE I to its maximum value and REACTION and PURGE II to their minimums and then go through the REACTION cycle until the START light blinks (until the N_2 pressure is zero).
7. Turn off the recorder power. Remove and cap pen.
8. Turn the HCL lamp wattage off.
9. Turn off the power to the spectrometer.
10. Turn MHS-20 controller OFF.
11. Clean up the work area.

CALCULATION

1. Plot the absorbance (peak height in mm from the strip chart) versus the ng (number of microliters) of standard added.
2. Draw a best fit straight line through the points using a ruler and check the linearity. Notify the responsible scientist if the data is not linear.
3. Calculate the mercury concentrations using the HP-97 calculator and the Curve Fit program as follows:
 - a. Load Side 1 and 2 of the Curve Fit program card.
 - b. Press f(A); then press f(B).
 - c. Press DSP; then press 4.
 - d. Enter the ng of mercury and push ENTER.
 - e. Enter the absorbance (mm) and push A.
 - f. Repeat Steps d and e for each standard.
 - g. Push C to compute r^2 , slope, and intercept.
 - h. Enter the sample absorbance (mm) and push D to calculate the ng of mercury in the sample.
 - i. Calculate the sample concentration in parts per billion (ppb) by dividing the value obtained in Step h by the sample aliquot volume (in mL). See Step 4.b on the next page.
 - j. Enter the sample + spike absorbance (mm) and push D to calculate the ng of mercury.
 - k. Calculate the spike recovery as shown in Step 4.c on the next page.
 - l. Repeat Steps h through k for all samples and enter the information on the sample cards.
 - m. Turn in the sample cards.

CALCULATIONS (continued)

4. Example

a. Sample Analysis

A sample was received for analysis. A 0.1 mL (100 microliters) aliquot was taken into the procedure with a resulting absorbance of 24.0 mm. Likewise, a 0.1 mL aliquot was spiked with 25 uL of 1 ppm Hg standard; the resulting absorbance was 73 mm. The calibration standards were measured.

Calibration Data:

Blank (0.0 ng)	:	0.0 mm
10.0 ng	:	20.0 mm
20.0 ng	:	40.0 mm
40.0 ng	:	80.0 mm

From the calibration data, one finds that the sample absorbance corresponds to 12.0 ng of Hg and the sample-plus-spike corresponds to 36.5 ng.

b. Calculation of original Sample Concentration (ppb):

$$\begin{aligned}\text{ppb} &= (\text{ng Hg in sample aliquot}) / \text{mL sample aliquot} \\ &= (12.0 \text{ ng}) / (0.1 \text{ mL}) = 120 \text{ ppb}\end{aligned}$$

c. Calculation of Spike recovery

Spike recovery =

$$\frac{(\text{ng sample} + \text{spike}) - (\text{ng sample})}{(\text{ng spike})} \times 100$$

$$\frac{(36.5 \text{ ng} - 12.0 \text{ ng})}{(25.0 \text{ ng})} \times 100 = 98.0\%$$

Acceptable spike recoveries are:

Without ion exchange	85 - 115%
With ion exchange	75 - 125%

5. Alternative concentration units:

To convert from ppb to ppm: $\text{ppm} = \text{ppb} / 1000$

To convert from ppb to g/L: $\text{g/L} = \text{ppb} / 1,000,000$

DISCUSSION

The Amalgam Attachment is connected between the reaction flask and the quartz cell. The mercury liberated during the reaction is transported to the Amalgam Attachment where it is quantitatively amalgamated on the gold/platinum gauze. At the end of the reaction the solution is further purged with inert gas for a short period to ensure that the maximum possible quantity of mercury is transported to the gold/platinum gauze. The gauze is then rapidly heated to about 600°C. The mercury is released and transported by the carrier gas to the quartz cell. The absorption signal so generated gives a tall, peak-shaped tracing on the recorder.

In the Amalgam Mode the maximum cell temperature is limited to 200°C. The cell temperature cannot be increased to above 200°C, even if CELL TEMP slider is set to a higher value. If the cell temperature is above 200°C when either stannous sulfate or AMALGAM Mode is selected, the START FUNCTION is inhibited. The cell must cool to 200°C before the determination can be started.

Mercury, but not metallic hydride-forming elements, may be determined using stannous sulfate solution as reductant. The determination is performed according to the established method of HATCH and OTT (Anal. Chem., 40. 2085 (1968)). According to the type of matrix, the sample solution is treated so that the mercury is present in ionic form. Residual organically bound mercury can be oxidized with potassium permanganate. Reductant is dispensed into the sample solution and mercury is reduced to the metallic state.

Metallic mercury vapor is driven out of the sample solution by the carrier gas transported to the quartz cell where its absorption is measured. The cell is heated to around 180 °C to prevent condensation.

The detection limits attainable with the MHS-20 are often a function of the level of contamination rather than instrument capability. When working at the ppb levels, contamination is usually the major source of error. Careful handling of the apparatus and careful technique will minimize this problem. The following precautions help to avoid sample contamination:

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DISCUSSION (continued)

1. Use only deionized water.
2. Collect all samples in Teflon or polyethylene containers that have been thoroughly rinsed with 1.5% HNO₃.
3. Use only reagents found to be free of mercury. Measure blanks before analyzing samples.
4. All glassware and apparatus must be scrupulously clean.

The hydride apparatus performs an analysis of ng levels of mercury. Total sample volumes of up to 50 mL can be accommodated to provide greater sensitivity. In practice, however, interference levels, radiation levels in some samples (including waste tank), and amount of sample available limits the sample size substantially.

REFERENCES

Section A - Procedures

LA-505-124, "Application of the Method of Standard Additions to Atomic Absorption."

LO-120-001, "Labeling of Standards and Reagents."

Section B - Source Documents

Operators Manual, Perkin-Elmer Model 2280 Atomic Absorption Spectrometer.

Operators Manual, MHS-20 Mercury/Hydride System.

SW-846 Method 7470, "Mercury in Liquid Waste (Manual Cold-Vapor Technique)."

SD-CP-LB-003, "Safety in the Analytical Laboratory."

WHC-CM-1-3, Management Requirements and Procedures.

WHC-CM-4-3, Industrial Safety Manual.

WHC-CM-4-10, Radiation Protection.

WHC-CM-4-15, Radiation Work Requirements and Permits Manual.

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Figure 1. Schematic of Hose Connections

Figure 2. Amalgam Attachment Installed in the Analyzer Assembly

AMALGAM ATTACHMENT INSTALLATION

The Amalgam Attachment is installed in the Analyzer Assembly as given below.

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Figure 3. Wavelength Adjust and Slit Width

- 1 SLIT Width Selector
- 2 BKGD CORReCTOR Switch
- 3 Optics Compartment Access Screw
- 4 BKGD CORR INTENSITY Control
- 5 WAVELENGTH ADJUST Control
- 6 WAVELENGTH Counter

Figure 4. Lamp Compartment with Universal HCL Mount

- 1) Filter Attenuator Control
- 2) Alignment Knob
- 3) Spring
- 4) Lamp 1 Connector
- 5) Front Holddown Screw
- 6) Universal Lamp Mount
- 7) Catch Release
- 8) Lamp Mount Button/Screw

Figure 5. Instrument Controls and Indicators

1	Digital Display and Indicators	13	PRNT (Print) Key and Signal Dot
2	AZ (Auto Zero) Key and Signal Dot	14	Numerical Keyboard
3	S1 Key and Signal Dot	15	CE (Clear Entry) Key
4	S2 Key and Signal Dot	16	Electronics Compartment Access
5	S3 Key and Signal Dot		Screws
6	AVERage Key and Signal Dot	17	SIGNAL Switch
7	CV (Coefficient of Variation)	18	READ Key and Signal Dot
	Key and Signal Dot	19	MODE Switch
8	SD (Standard Deviation) Key and	20	LAMP/ENERGY Display
	Signal Dot	21	RECORDER Switch
9	RSLP (Reslope) Key and Signal Dot	22	GAIN Control
10	t (Time) Key	23	LAMP 1 Control
11	EXpansion Key and Signal Dot	24	LAMP 2 Control
12	CHK (Check) Key	25	POWER Switch

Figure 6. Heating Mantle Assembly with Quartz Cell Installed in the Sample Compartment (shown without the drain trap assembly)

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Figure 7. Front Panel of MHS-20 Controller

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Figure 8. Recorder Left Front Control Panel

Figure 9. Analyzer Assembly Positioned in Front of the Sample Compartment

ANALYZER ASSEMBLY

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SAFETY

All activities described in this procedure are supported by safety instructions contained in SD-CP-LB-003, "Safety in the Analytical Laboratory." For safe handling and use of the chemicals in this procedure, review the Hanford Environmental and Health Foundation's Material Safety Data Sheets (MSDSs) for those chemicals listed in the Reagents Section.

Follow the requirements and good practices set forth in WHC-CM-4-15, Radiation Work Requirements and Permits Manual, and WHC-CM-10, Radiation Protection. The RWP applicable to this procedure is:

S-003, "Rooms with Open Faced Hoods (Excluding 2B Decon and Slurp Hood and Room 1GB) Routine Work/Maintenance Performed Inside Open Faced Hoods";

No Chemicals from WHC-CM-4-3, Volume 2, Industrial Safety Manual, carcinogen list (Guide C-2, Rev. 1, Table) are used in this procedure.

In compliance with WHC-CM-1-3, Management Requirements and Procedures, (MRP 5.43), an Impact Level 03 has been assigned to this procedure. EQUIPMENT

Since this procedure is applicable to radioactive samples, standard practices to contain radioactivity and limit personnel exposure must be followed.

EQUIPMENT

Disposable glass vials, 22 mL with poly seal caps

Disposable or glass cuvettes

Spectrophotometer capable of absorption measurement at 540 nm

REAGENTS

Potassium Dichromate Stock Solution MSDS #1434

Dissolve 141.4 mg of dried potassium dichromate (analytical reagent grade), in deionized water and dilute to 1 L in a Class A volumetric flask. Store in glass. (1 mL = 50 ug Cr).

Potassium Dichromate Standard Solution MSDS #1434

Dilute 10.00 mL potassium dichromate stock solution to 100 mL with deionized water in a Class A volumetric flask. Store in glass. (1 mL = 5 ug Cr).

Sulfuric Acid 10% (v/v) MSDS #1529

Dilute 10 mL of distilled reagent grade of spectrograde quality sulfuric acid to 100 mL with deionized water. Store in glass.

REAGENTS (continued)

Diphenylcarbazide Solution MSDS #1724

Dissolve 250 mg 1,5-diphenylcarbazide in 50 mL acetone. Store in brown bottle. Discard when the solution becomes discolored.

Acetone MSDS #1005

Analytical reagent grade. As received.

Sulfamic Acid (1 M) MSDS #1623

Prepare by dissolving 9.7 g of sulfamic acid (HSO_3NH_2) in deionized water And diluting to 0.10 L. This solution is good for three months.

PROCEDURE STEPS

A. Calibration

1. Prepare the potassium dichromate standard solution by diluting 10.00 mL of potassium dichromate stock solution to 100 mL with deionized water in a Class A volumetric flask.
2. Dispense exactly 9.3 mL of deionized water into each of seven vials. Pipet the following amounts of potassium dichromate standard solution into the separate vial: 50, 100, 250, 500, 1000, 1500, 2000, 2500.
3. Carry the calibration standards through the procedure starting with Step 4.
4. Determine the slope and y-intercept for the curve by fitting a straight line to the data by the method of Least Squares. The curve fit should be greater than 0.9980. See Appendix A for further details.

B. Sample Preparation and Measurement

NOTE: Carry a reagent blank (0 mL) and QC standard through the procedure with every batch of samples. Verify calibration with an independently prepared check standard every ten samples. LABEL VIALS before starting.

NOTE: Run one spike duplicate for every five samples. (Add 1.0 mL of calibration standard as a sample spike).

1. Dispense exactly 9.3 mL of deionized water to each 22 mL disposable vial.
2. Pipet sample containing 0.025 ppm to 1 ppm of Cr(VI) into the deionized water in the vial.

PROCEDURE STEPS (continued)

3. Record dilution size if used.
4. Dispense 0.4 mL of 1 M sulfamic acid.
5. Dispense 0.2 mL of diphenylcarbazide solution.
6. Dispense 0.1 mL of 10% sulfuric acid.
7. Add stir bar, cap vial, and stir mixture for 1-2 minutes.
8. Let solution stand 5-10 minutes for full color development.
9. Transfer a portion of each sample to a cuvette and measure the absorbance at 540 nm. Use the reagent blank to zero the instrument.
10. Slurp the solution from the cuvettes and vials, dispose of the disposable cells and vials according to SO-170-002, "Slurping of Radioactive Liquid Waste." If glass cuvettes are used, rinse the cells with Q-water and ethanol.

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CALCULATIONS

1. Samples

$$\text{ppm Cr(VI)} = \frac{\text{Absorbance @ 540 nm} - y \text{ intercept}}{\text{slope}} \times \text{D.F.}$$

D.F. = Dilution Factor

2. Percent Recovery of Standard

$$\% \text{ Recovery of std} = \frac{\text{ppm Cr(VI) observed}}{\text{ppm Std Value}} \times 100$$

3. Spike Recovery

$$\text{ug Cr(VI) in Sample} = (\text{ppm Cr(VI) in sample}) (\text{Total Volume})$$

$$\text{ug Cr(VI) in Sample + Spike} = (\text{ppm Cr(VI) in Sample + Spike}) (\text{Total Volume})$$

$$\text{ug Cr(VI) in Spike} = (\text{ppm of Cr(VI) in Spike}) (\text{Volume of Spike added mL})$$

$$\% \text{ Spike Recovery} = \frac{(\text{ug Cr(VI) in Sample + Spike}) - (\text{ug Cr(VI) in Sample})}{\text{ug Cr(VI) in Spike}} \times 100$$

Example Calculations for Spike Recoveries:

Spike Standard Concentration is 5 ppm (1 mL = 5 ug)

The following data was obtained from TK 106 AN samples. Calculated concentrations were derived from the calibration parameters shown in Appendix A.

<u>Sample</u>	<u>Absorbance</u>	<u>Calculated Conc(ppm)</u>
TK 106 AN (0.1 mL)	0.064	0.0813
TK 106 AN (0.1 mL) + spike (1.0 mL)	0.414	0.5286

Spike recovery for 1.0 mL Spike:

$$\text{ug Cr(VI) in Sample} = (0.0813) (10.1) = 0.8211$$

$$\text{ug Cr(VI) in Sample + Spike} = (0.5286) (11.1) = 5.8670$$

$$\text{ug Cr(VI) in Spike} = (5.0) (1.0 \text{ mL}) = 5.0$$

$$\% \text{ Spike recovery} = \frac{5.8670 - 0.8211}{5.0} \times 100 = 100.92\%$$

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DISCUSSION

The reaction with diphenylcarbazide is nearly specific for chromium. Hexavalent molybdenum and mercury salts will react to form color with the reagent, but the intensities are much lower than that for chromium at the specified pH. Concentrations of molybdenum and mercury up to 200 mg/L can be tolerated. Vanadium interferes strongly, but concentrations up to 10 times that of chromium will not cause trouble.

The sample size selected should contain 0.025 ppm to 1.0 ppm of Cr(VI).

REFERENCES

Source Documents:

SD-CP-LB-003, "Safety in the Analytical Laboratory."

WHC-CM-1-3, Management Requirements and Procedures.

WHC-CM-4-3, Industrial Safety Manual.

WHC-CM-4-10, Radiation Manual.

WHC-CM-4-15, Radiation Work Requirements and Permits Manual.

American Public Health Association, American Water Works Association, Water Pollution Control Federation, Standard Methods For the Examination of Water and Wastewater, Fourteenth edition, pp. 192-195, 1975.

Test Methods for Evaluating Solid Waste (SW-846), Volume 1, section A, Rev. 0, Method 7196, Chromium, Hexavalent (Colorimetric), pp. 1-6, Sept 1986.

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Appendix A

Example Calibration:

1. Concentration of Cr(VI) in calibration solution is 5 ppm. (1 mL = 5 ug)

<u>mL Calibration Solution</u>	<u>Conc. (ppm)</u>	<u>Absorbance</u>
0	0	0
0.050	0.0248	0.019
0.100	0.0495	0.040
0.250	0.1220	0.089
0.500	0.2381	0.192
1.000	0.4545	0.366
1.500	0.6522	0.496
2.000	0.8333	0.664
2.500	1.000	0.778

$$r^2 = 0.9992$$

$$a = 0.0004$$

$$b = 0.7827$$

The slope and y-intercept for the curve were determined by fitting a straight line to the data by the method of Least Squares. The curve fit should be greater than 0.9980.

ANALYTICAL LABORATORIES

Issued By:**T. A. Lane****Manager,****Analytical Laboratory****Author: C. M. Seidel****Title****ANION ANALYSIS ON DIONEX MODEL 40001**

SUMMARY

Refer to SD-CP-LB-008, "Ion Chromatography at the 222-S Laboratory" for background and discussion of this procedure.

SAFETY

All activities described in this procedure are supported by safety instructions contained in SD-CP-LB-003, "Safety in the Analytical Laboratory."

All work with chemical reagents will conform to Material Safety Data Sheets, 1484 (for handling sodium carbonate), 1529 (for sulfuric acid), and 1506 (for nitrates and nitrites).

Compliance with RWP S0003 is mandatory when performing this procedure.

Compressed gas used in the performance of this procedure is handled in accordance with WHC Industrial Safety Standard WHC-CM-4-3, PS-2, Vol. 1.

REAGENTS

NOTE: Label all reagents according to Procedure LO-120-001.

NOTE: Stock standards are stable for at least one month when stored at 4°C. Dilute working standards should be prepared weekly except those that contain nitrite and phosphate should be prepared fresh daily.

1. Reagent water (Q-Water): Deionized water, free of anions of interest. Water should contain no particles larger than 0.20 microns. This water shall have a resistance equal to or greater than 16 megohm.
2. 0.020 Molar Sodium Bicarbonate: Pipet 50 mL of 0.400 Molar sodium bicarbonate into a 1 L volumetric flask. Dilute to mark with Q-Water.
3. 0.020 Molar Sodium Carbonate: Pipet 50 mL of 0.400 Molar sodium carbonate into a 1 L volumetric flask. Dilute to mark with Q-Water.
4. 0.0125 Molar Sulfuric Acid (Regeneration Solution): Transfer 250 mL 0.5 Molar sulfuric acid into a plastic bottle and add Q-Water to make 10 L. Mix well. Replenish the regenerant reservoir with this solution labeled 0.0125 Molar sulfuric acid. The expiration date should be approximately two months.

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REAGENTS (continued)

5. 0.50 Molar Sulfuric Acid: Prepared by Standards Laboratory. Dilute 112.0 mL conc. sulfuric acid to 4 L with Q-Water.
6. 0.400 Molar Sodium Bicarbonate: Prepared by Standards Laboratory. Weigh 67.20 g of sodium bicarbonate, dissolve and dilute with Q-Water to volume in a 2 L volumetric flask.
7. 0.400 Molar Sodium Carbonate: Prepared by Standards Laboratory. Weigh 84.83 g of sodium carbonate, dissolve and dilute with Q-Water to volume in a 2 L volumetric flask.
8. Eluant: Pipet 8.00 mL of 0.020 Molar sodium carbonate and 8.00 mL of 0.020 Molar sodium bicarbonate into a 100 mL volumetric flask and dilute with Q-Water to volume. Stable two weeks.
9. COMPRESSED GAS:
 - 9.1 Purified nitrogen.
 - 9.2 Helium
10. STOCK STANDARD SOLUTIONS:
 - 10.1 Chloride (Cl^-) 10,000 mg/L: Dissolve 16.485 g of sodium chloride (NaCl reagent grade) in reagent grade water and dilute to 1 L. Store in a polyethylene bottle.
 - 10.2 Phosphate (PO_4^{3-}) 10,000 mg/L: Dissolve 14.330 g of potassium phosphate (KH_2PO_4 reagent grade) in reagent grade water and dilute to 1 L. Store in a polyethylene bottle.
 - 10.3 Nitrate (NO_3^-) 10,000 mg/L: Dissolve 13.708 g sodium nitrate (NaNO_3 reagent grade) in reagent grade water and dilute to 1 L. Store in a polyethylene bottle.
 - 10.4 Sulfate (SO_4^{2-}) 10,000 mg/L: Dissolve 18.141 g potassium sulfate (K_2SO_4 reagent grade) in reagent grade water and dilute to 1 L. Store in a polyethylene bottle.
 - 10.5 Fluoride (F^-) 10,000 mg/L: Dissolve 22.100 g sodium fluoride (NaF) in reagent water and dilute to 1 L. Store in a polyethylene bottle.
 - 10.6 Nitrite (NO_2^-) 10,000 mg/L: Dissolve 14.997 g sodium nitrite (NaNO_2) in reagent water and dilute to 1 L. Store in a polyethylene bottle.

REAGENTS (continued)

11. CALIBRATION WORKING STANDARD

This standard is prepared in the ion concentrations listed below and stored in a polyethylene bottle. Using the solutions from Step 10 above.

	Concentration (ppm)	<u>mL of 10000 ppm Stock</u> per L
NaF	(F ⁻) 50	5.00
NaCl	(Cl ⁻) 60	6.00
KH ₂ PO ₄	(PO ₄ ⁻³) 500	50.0
NaNO ₃	(NO ₃ ⁻) 500	50.0
K ₂ SO ₄	(SO ₄ ⁻²) 500	50.0

EQUIPMENT

1. Dionex Ion Chromatograph, System 4000i, equipped with conductivity cell for detection, an AG4A guard-column, an AS4A separator column and membrane suppressor. A Dionex AutoIon Controller and software.
2. Vials, polyethylene, 22 mL size with screw caps, stock room part #57-9000-025.
3. Syringes, plastic disposable, 5 cc and 10 cc, Luer-lok tip.
4. Dispenser, 1 L with 10 mL dispensette.
5. Eppendorf pipets, with appropriate tips.
6. Sample bottles: Glass or polyethylene of sufficient volume to allow replicate analyses of anions of interest.
7. Dionex sample vials, 5 ml Dionex part number 38141.
8. Dionex caps for 5 ml vials, Dionex part number 039528.
9. Dionex autosampler.

PROCEDURE

1. Instrument Start-Up

- 1.1 Wash all glass or polyethylene labware, if not pre-washed, in a ultrasonic bath filled with Q-water. Dry before using. Follow LO-080-114.
- 1.2 Check to see if eluant reservoirs are full. If half full or less, fill with more eluant according to directions in Appendix I and Figure I.
- 1.3 Empty waste bottles.
- 1.4 Turn on nitrogen gas (80 - 85 psi) and the helium gas (30 - 50 psi). The regenerant is pressure fed at 80 - 85 psi; be sure the cap on the regenerant is tight.
- 1.5 Eluant Degas Module.
 - 1.5.1 Turn on Eluant Degas Module system power switch to "ON."
 - 1.5.2 The Sample Reservoir switch must be in the "ON" position.
 - 1.5.3 Eluant switches 1, 2, and 3 must be in the "ON" position and other eluant switches 4, 5, and 6 must be in the "OFF" position.
 - 1.5.4 The Degas rate switch must be in the "LOW" position.
 - 1.5.5 The Pressure Regulator must be set at 7 - 8 psi.

CAUTION: To prevent damage to system do not apply pressures greater than 10 psi. Pressures above 10 psi will be vented by the safety relief valve and will only waste gas.

- 1.6 Turn on the Power Module.
- 1.7 Turn on solenoid A and B on the Chromatography Module.
- 1.8 Pump Module.
 - 1.8.1 Wait 5 minutes after turning on the Eluant Degas Module before turning on the Pump Module.

PROCEDURE (continued)

- 1.8.2 Check readings on the gradient pump module. If readings for %1, %2, %3, and %4 are 0.0 press the "START" button. This will reset the pump readings to the default settings.

Note: The default readings are:

Flow	=	2.0
Time	=	0.0 *
High Pressure	=	2000
%1	=	84
%2	=	8
%3	=	8
%4	=	00
%5	=	Off
%6	=	Off

* Pump cannot be started unless Time = 0.0

- 1.8.3 Press the "START" button. If pump does not start, contact scientist.
- 1.8.4 Check flow to see that it is 2.0 mL/min.
- 1.8.5 When the pressure is stable at ± 10 psi, the instrument has equilibrated. If there is a pressure problem (i.e., pressure exceeds 2000 psi or less than 200 psi), the pump module will turn off the pump. Contact the scientist in charge.

1.9 Computer Module

NOTE: See SD-CP-LB-008, Appendix II, for detailed instructions on the use of the computer mouse and the Windows program.

- 1.9.1 Turn power "ON" for computer, CRT, and printer. If the computer is already on, restart by holding down the "Alt", "Ctrl", and pressing the "Del" key.
- 1.9.2 The computer will do a systems test and auto-boot. This will take less than 2 minutes.
- 1.9.3 The computer will boot into the Windows program. A list of files will be displayed on the CRT.

PROCEDURE (continued)

2. Sample Analysis Schedule

- 2.1 Point at the "SCHEDULE.EXE" program file. Open this file by double clicking.
- 2.2 Use the menu and mouse to fill out the schedule. The SCHEDULE.EXE is used to create, store, and edit a schedule of analyses. Each line in a schedule specifies the sample name, the method of analysis, and correction factors.

NOTE: The schedule may be completed by recalling an old schedule and editing it for use.

2.2.1 Samples are entered under the following protocols:

- 2.2.1.1 The first sample must be "set-up" when using the autosampler. No sample is loaded the sample tray for this sample. This is used to aline the computer with the autosampler.
- 2.2.1.2 The second sample position is "system blank." This is an eluant blank prepared as in 2.2.5.2 by spiking Q-water.
- 2.2.1.3 The tenth sample is repeated as a spike analysis. Not less than one sample will be run as a spike with each batch/analysis of samples. The dilution of a sample spiked will be the same as that sample without the spike. The spike is performed by the addition of 0.050 mL of the calibration standard into 5.00 mL of sample.
- 2.2.1.4 One sample for each 15 analyzed will be run in duplicate, but not less than one sample duplicate will be run for each batch/analysis of samples.
- 2.2.1.5 The SAMPLE NAME is entered by typing in the name using up to 30 characters, with no spaces.

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PROCEDURE (continued)

- 2.2.2 METHOD: Type in "C:\Windows\ai400\method\WATER01".
- 2.2.3 DATA FILE: Type in the date in the form
C:\ data\YYMMDD00
- 2.2.3.1 YY = year (1965 = 65, 1988 = 88)
- 2.2.3.2 MM = month (May = 05, June = 06)
- 2.2.3.3 DD = Day (1st = 01, 10th = 10)
- 2.2.3.4 00 = number of batch run for that day. Always enter "00". The computer will automatically change to next number. So no two files will have the same number.
- 2.2.4 VOLUME: Enter 0.
- 2.2.5 DILUTION: Enter the dilution factor for correction of dilution effects.
- 2.2.5.1 Samples are diluted with a known volume of eluant until the analyte falls within the calibration range for that analyte. The dilution factor is entered into the sample schedule.
- 2.2.5.2 Samples that are not diluted are spiked with a volume equal to 0.5% of the sample volume with 0.400 Molar sodium carbonate and 0.400 Molar sodium bicarbonate.
- 2.2.6 INT. STD.: Enter 0.
- 2.3 Pull down FILE menu and select SAVE. Save as
C:\windows\ai400\schedule\YYMMDD00. Use format from 2.2.3 above.
- 2.4 Pull down box menu in upper left corner and close the SCHEDULE.EXE.

PROCEDURE (continued)

- 2.5 Open the RUN.EXE window by pointing to the center of RUN.EXE and double-click to load.
- 2.6 Switch conductivity, pump, and chromatography modules to Remote Operation.
- 2.7 Pull down the LOAD menu and select "Schedule...". A list of options will be displayed on the left side of the CRT. Use the mouse to select the schedule directory and double-click. Select the schedule saved in Section 8.3.3 above and double-click to load.

- 2.7.1 The computer will display the CIM Method settings. These are;

CIM Address #1
System #1
Number of loops for the schedule ? 1
Starting Inject # for the schedule ? 1

Accept these settings.

- 2.7.2 The computer will now display:

Cim	Sys	Inj	E.Time	R.Time	Sample Name	Status	Method	Schedule
1	1	001	0.00	0.00	SETUP	READY	WATER01.MET	YYMMDD00
1	2	000	0.00	0.00		NOT LOADED		

If any display other than the one shown above is on the screen, call the scientist for help, otherwise proceed.

- 2.8 Load samples into the autosampler for analysis.

- 2.8.1 The samples to be run are loaded into 5 mL plastic tubes. Fill the tubes with 2.5 to 5.0 mL of sample to be analyzed. Do not fill tubes above the 5.0 mL mark on the side of the tubes. Tubes filled above this mark may overflow when capped.
- 2.8.2 The tubes are then placed in the cassette tube holders. The positions in the holders are numbered 1 to 6, and there is a white dot next to position number 1. Be sure to load the tubes in the same order as shown in the schedule from Section 2.2.

PROCEDURE (continued)

2.8.3 Cap the tubes using the tube capping tool. The top of the caps must be flush with the top of the sample tubes.

2.8.4 Place the cassettes into the left side of the auto-sampler. The number one position (the white dot) must be placed next to the center divider of the autosampler.

3. Start Analysis:

3.1 Pull down the RUN menu and select "START". The computer interface will control the analysis.

3.2 After the Load/Inject indicator indicates injection, but before the instrument is 2 minutes into the run, turn on the autosampler power switch.

3.3 Press the Bleed Switch on the front of the autosampler. The indicator will show bleed "ON".

3.4 Press the HOLD/RUN switch on the front of the autosampler. The indicator will show "RUN".

3.5 At 8.1 minutes into the run, the instrument will recycle printing the results of the sample run and injecting and analyzing the next sample on the schedule.

3.6 The analysis can be interrupted by pulling down the run menu and selecting "STOP". Otherwise the instrument will continue until it reaches the end of the analyses schedule.

3.7 After all standards/samples are analyzed. Turn off instrument as per Section 4. System power down below.

4. System Power Down

4.1 Put all modules in the LOCAL mode.

4.2 Turn OFF the computer.

4.2.1 Pull down the menu box in the upper left corner of the RUN.EXE window and select close. This closes this program.

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PROCEDURE (continued)

- 4.2.2 Drag the DOS icon to the center of the screen. Pull down the menu box in the upper left corner of the DOS window and select close. This closes the Windows program. The computer will prompt "Do you wish to exit windows?" Answer OK.
- 4.2.3 Type "park" and press "ENTER."
- 4.2.3 Turn off the power to CRT and printer. Leave the computer turned on.
- 4.3 Put the Gradient Pump into the Stop mode.
- 4.4 Turn OFF valve B and then valve A on the Chromatography Module. Wait until you hear the solenoids close before proceeding.
- 4.5 Turn OFF the Degas Module. Gas will be vented automatically.
- 4.6 Turn OFF the power Module.
- 4.7 Turn OFF all compressed gas at the cylinders.

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CALCULATIONS

1. Calculations of results are performed by the Dionex AutoIon Controller and confirmed by the Dionex scientist or appointee. All sample results must be reviewed and confirmed by a scientist or other appointed qualified personnel before any results are reported into the laboratory data base or to the customer.
2. Since the peak height measurement technique has been selected as the form of detector response, it is necessary to analyze standards to obtain a reference for detector response versus standard concentration. When the reference points are graphed, the calibration curve is formed. See calibration below.
3. Results are reported in ug/mL.
4. Spike recovery should not be calculated for peaks reading more than 200% of the spiked value.

$$\text{Percent recovery} = \frac{(\text{SSR} - \text{SR}) * 100}{\text{SA}}$$

SSR = Spiked sample result
SR = Sample result
SA = Spike added

If the spike recovery is not within 20% of the spiked value, the analysis of that type of sample, or samples from that sample point, should be stopped until the reason for the low recovery can be determined.

5. The width of the retention time window used to make identifications shall be based upon measurements of actual retention times. Three times the standard deviation of a retention time will be used to calculate the retention window. However, experience will weigh heavily in the interpretation of chromatograms. Wherever there is a question as to peak identification, the peak will be identified by re-running spikes of that sample.

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CALCULATIONS (continued)

6. Results of analysis of the Laboratory Measurement Control System (LMCS) standard are stored in the LMCS laboratory data base. When entering results into LMCS, use the following electronic data processing codes:

F-	R974
Cl-	R972
NO ₂ ⁻	to be issued
PO ₄ ⁻³	R976
NO ₃ ⁻	R978
SO ₄ ⁻²	R970

Be sure to note instrument #4 when entering data.

7. Single operator precision will be tabulated by calculation of percent recovery and the standard deviation(s) of the percent recovery for each analyte. If data is not comparable with the laboratory norm, potential problem areas must be reviewed and corrected.

CALIBRATION AND STANDARDIZATION

NOTE: Only the responsible scientist or a qualified technician fully familiar with the calibration procedure will calibrate the instrument. A new calibration is required whenever the Guard Column or Separator Column is changed, or whenever it has been determined that the instrument has drifted from the calibration being used.

1. Prepare a series of calibration dilutions using the mixed calibration standard prepared by Standards Laboratory. Dispense 10 mL of eluant into six (22 mL) polyethylene vials. To the successive vials add 20, 50, 100, 200, 400, and 800 uL of the mixed anion calibration standard. Mix dilutions thoroughly.

Sample Name	uL Cal. Standard	mL Eluant
AUTOCALC1R	20	10.00
AUTOCALC2R	50	10.00
AUTOCALC3R	100	10.00
AUTOCALC4R	200	10.00
AUTOCALC5R	400	10.00
AUTOCALC6R	800	10.00

CALIBRATION AND STANDARDIZATION (continued)

2. Recalibration is performed automatically whenever these sample names are placed in a sample schedule. A "Calsched" is stored in the schedule to be used for calibration. Instrument recalibration is performed at the completion of data analysis of any sample called AUTOCALC. Previous data is replaced with the new data whenever the sample name ends in R.

REFERENCES

Section A - Procedures

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ANALYTICAL LABORATORIES

Issued By:

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Title

SPECTROPHOTOMETRIC DETERMINATION OF
CYANIDE

SUMMARY

Hydrogen cyanide (HCN) is liberated from an acidified sample by distillation and collection in a sodium hydroxide (NaOH) absorption solution. Cyanide (CN^-) is converted to CNCI by reaction with chloramine-T which reacts with a pyridine-barbituric acid reagent to form a purple dye. The absorbance of this dye is proportional to the cyanide concentration and is measured at 580 nm using a spectrophotometer.

LIMITATIONS

Cyanide forms very stable complexes with many of the transition and heavy metals; i.e., chromium, aluminum, iron, cobalt, molybdenum, nickel, copper, silver, zinc, and cadmium within various Hanford wastes (double shell slurry, salt cake, and terminal liquor). Aluminum and chromium could prevent free cyanide from existing; thereby, requiring a distillation process to break up metal cyanide complexes and to separate the cyanide for measurement of total cyanide. Other possible interferences are sulfide, nitrites, and nitrate. Nitrates are destroyed by sulfamic acid. The detection limit of the procedure is dependent on the distillation blank. With careful monitoring of the blank, a lower detection limit of 1 micrograms of cyanide (CN^-) is possible.

The average percent recovery of seven non-distilled replicate 10 microgram cyanide standards was 99.96% with a standard deviation of $\pm 0.47\%$. The precision of the method at the 95% confidence level is $\pm 0.92\%$.

The average percent recovery of five distilled replicate 10 microgram cyanide standards was 99.90% with a standard deviation of $\pm 1.28\%$. The precision of the method at the 95% confidence level is $\pm 2.50\%$.

APPLICATIONS

The primary source of cyanide in Hanford wastes is from a cesium scavenging process that was used in the 1950's using ferrocyanide [$\text{Fe}(\text{CN})_6^{-4}$] precipitates to remove cesium-137 from the waste in single shell tanks (SST). An estimated 100 metric tons of cyanide was added to the tanks during this operation. Cyanide analyses are also needed to help prepare environmental documentation for long-term performance assessment of the grout waste program.

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SAFETY

There are no unusual laboratory safety concerns associated with this procedure.

REAGENTS

Sodium Phosphate, 138 g/L

Dissolve 138 g of $\text{NaH}_2\text{PO}_4 \cdot \text{H}_2\text{O}$ in 800 mL of deionized water. Dilute to 1 L with deionized water. Store in a plastic bottle and refrigerate. Shelf life is 6 months.

Chloramine-T, 10 g/L

Dissolve 1 g of chloramine-T powder (white) in 80 mL of deionized water and dilute to 100 mL with deionized water. Store in an amber bottle and refrigerate. Shelf life is 1 week.

Pyridine-Barbituric Acid

Place 15 g of barbituric acid in a 250 mL volumetric flask and add just enough deionized water to wash the sides of the flask and wet the barbituric acid. Add 75 mL of pyridine and mix. Add 15 mL of concentrated hydrochloric acid, mix, and cool to room temperature, (white precipitate). Dilute to 250 mL with deionized water and mix (precipitate dissolves). Store in an amber glass bottle and refrigerate. Shelf life is 6 months.

Sodium Hydroxide, 0.125 M

Dissolve 5 g of NaOH in 900 mL of deionized water and dilute to 1 L with deionized water. Store in plastic bottle. Shelf life is 1 year.

Sodium Hydroxide, 1.0 M

Dissolve 40 g of NaOH in 900 mL of deionized water and dilute to 1 L. Use CAUTION when adding water to the solid NaOH as it is a very exothermic reaction. Store in a plastic bottle. Shelf life is 1 year.

Acetate Buffer

Dissolve 54 g of $\text{NaC}_2\text{H}_3\text{O}_2 \cdot 3\text{H}_2\text{O}$ and 125 mL of glacial acetic acid in 900 mL of deionized water. Adjust the pH to 4 with NaOH or acetic acid. Store in a plastic bottle. Shelf life is 1 year.

$\text{Na}_4\text{EDTA} \cdot 2\text{H}_2\text{O}$, 100 g/L

Dissolve 10 g of $\text{Na}_4\text{EDTA} \cdot 2\text{H}_2\text{O}$ in deionized water and dilute to 1 L. Store in a plastic bottle. Shelf life is 1 year.

REAGENTS (Continued)

Methyl Red Indicator, 0.1%

Dissolve 0.1 g of methyl red indicator in 100 mL of ethanol. Store in amber glass bottle. Shelf life is 1 year.

Sulfuric Acid, 2.5 M

Add 140 mL of concentrated sulfuric acid very slowly with stirring into 800 mL of deionized water. Cool and dilute to the 1 L volume in a volumetric flask with deionized water. Store in a glass bottle. Shelf life is 1 year.

Sulfamic Acid, 2 M

Dissolve 19.4 g of $\text{NH}_2\text{SO}_3\text{H}$ in 80 mL of deionized water and dilute to 100 mL with deionized water. Store in an amber glass bottle. Shelf life is 1 month.

Potassium Cyanide, 1000 ug/mL CN

Dissolve 0.2505 g of KCN and 0.2 g of potassium hydroxide (KOH) in 80 mL of deionized water and dilute to 100 mL in a volumetric flask. Standardize by titration with standard silver nitrate (AgNO_3). Store in 100 mL amber glass bottles. Shelf life is 6 months. Check titer weekly.

Potassium Cyanide, 10 ug/mL CN

Pipet 100 μL or 0.1 mL into a 10 mL volumetric flask containing 8 mL of 0.125 M NaOH and dilute to volume with 0.125 M NaOH. Transfer to a 30 mL glass bottle and mix. Shelf life is 1 day.

EQUIPMENT

Distillation apparatus, dual setup, (Figure 1)

Hot Plate, Corning or equivalent

Flasks, volumetric, 50 mL

Bottles, glass, 30 mL

Spectrophotometer, UV-Visible, Milton Roy Spec 21 or equivalent, with 3-cell sample compartment

Cells, spectrophotometer, 1 cm, disposable

Dispensers, 3 mL, 10 mL, and 25 mL, Oxford or equivalent

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PROCEDURAL STEPS

I DISTILLATION STARTUP

1. Turn on water bath for still condenser.
 - a. Turn on main Power Switch on back of unit.
 - b. Turn on Water Pump Switch on upper front of unit.
 - c. Set Pump Motor Speed Switch to Low range on back of unit.
 - d. Set Temperature Knob to approximately 10°C for low temperature range (equivalent to 60°C on high range).
 - e. Turn on Temperature Controller Switch on lower front of unit.
 - f. Observe water temperature with bath thermometer (10-14°C).
2. Close flask slurp Stopcock #2.
3. Set Vacuum Flowmeter to 0.8 mL/minute.
4. Set 3-Way Vacuum Release Stopcock #4 to outside Air position.

II DISTILLATION PROCEDURE

- NOTE: Employ a minimum of one blank per sample batch to determine if contamination or any memory effects are occurring.
- NOTE: Every 15 samples, verify apparatus operation with an independently prepared check standard.
- NOTE: Run one spike duplicate sample for every 10 samples. A duplicate sample is a sample brought through the whole sample preparation process.
- NOTE: Perform all Steps 1 through 35 of this procedure with both distillation units (Figure 1).

1. Remove the small stopper on the delivery tube.
2. Add 25 mL of 0.125 M NaOH by dispenser with a funnel to the trap tube (absorbent) via the delivery tube keeping the solution from entering the condenser sidearm.
3. Replace the small stopper on the delivery tube.
4. Close reagent reservoir Stopcock #1.
5. Add 5 mL of deionized water by wash bottle to reagent reservoir.

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PROCEDURAL STEPS (Continued)

6. Pipet sample solution aliquot or add solid sample into reservoir water.
 7. Open reagent reservoir Stopcock #1.
 8. Set 3-Way Vacuum Release Stopcock #4 to Vacuum position.
 9. Turn on Hood Vacuum Valve.
 10. Adjust vacuum air flow through the flask by setting reagent reservoir Stopcock #1 so the flask solution is readily mixed but not spattered during the next addition.
 11. Rinse reagent reservoir with 4 X 5 mL of deionized water.
 12. Add 4 drops of 0.1% methyl red indicator and rinse with 1 mL water into flask.
 13. Add 2 M sulfamic acid dropwise until flask solution turns red, then dispense 2 mL of additional 2 M sulfamic acid. Rinse with 1 mL of water. Mix for 5 minutes.
 14. Dispense 5 mL of 100 g/L EDTA and rinse with 1 mL water. Mix for 5 minutes.
 15. Add slowly dropwise 2.5 M sulfuric acid (H_2SO_4) with intermittent water rinses (yellow to red color).
 16. Add slowly dropwise 1.0 M NaOH with intermittent water rinses (red to orange).
 17. Dispense 10 mL of pH 4 acetate buffer and rinse with 1 mL water.
 18. Adjust vacuum air flow to 5-10 bubbles per second in the trap tube by adjusting the reagent reservoir Stopcock #1 at position marked.
 19. Turn on hot plate to 3.6 ± 0.2 setting and boil vigorously for 1 hour.
 20. Observe the air bubble rate closely for the first 15 minutes of heating. Increase air flow as needed to prevent sample from backing up into the reagent reservoir. Bubble rate needs to be checked only occasionally when solution is boiling.
 21. Turn off hot plate and allow flask to cool for 15 minutes.
- CAUTION: PERFORMS STEPS 22 THROUGH 24 SEQUENTIALLY IN RAPID SUCCESSION TO RELEASE ALL THE VACUUM WITHIN THE SYSTEM IMMEDIATELY.
22. Close, then open slowly the Reagent Reservoir Stopcock #1 without spattering the trap tube solution.
 23. Set 3-Way Vacuum Stopcock #4 to outside Air position.

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PROCEDURAL STEPS (Continued)

24. Remove immediately the small stopper on delivery tube.

CAUTION: AVOID TOUCHING HOT PLATE WHEN DRAINING TRAP TUBE.

25. Open trap tube Stopcock #3 and drain the NaOH trap solution into a 50 mL volumetric flask. Close Stopcock #3.

26. Disconnect trap tube by removing metal balljoint clamp and loosen 3-prong clamp.

27. Lower trap tube to rest on 50 mL flask.

28. Rinse delivery tube with 2 ± 1 mL deionized water.

29. Open Trap Tube Stopcock #3 and drain into the 50 mL flask. Close Stopcock #3.

30. Rinse trap tube with 7 ± 1 mL deionized water.

31. Open Trap Tube Stopcock #3 and drain into the 50 mL flask. Close Stopcock #3.

32. Place a stopper on the 50 mL flask and set aside for the spectrophotometric measurement procedure.

NOTE: Carefully center the delivery tube within the trap tube.

33. Reconnect the trap tube using (1) metal balljoint clamp first; (2) the 3-prong clamp secondly.

34. Replace the small delivery tube stopper.

35. Set 3-Way Vacuum Stopcock #4 to Vacuum position.

36. Close both reagent reservoir Stopcocks #1 on each distillation unit.

37. Open the flask slurp Stopcock #2 on one unit only.

38. Close Stopcock #5 on delivery tube vacuum line to allow more vacuum to slurp the distillation flask solution to the waste bottle.

39. Open the reagent reservoir Stopcock #1 to flush out waste lines.

40. Open Stopcock #5 on delivery tube vacuum line.

41. Add 20-25 mL deionized water to reagent reservoir for rinsing the distillation flask and allow to drain into flask.

42. Close reagent reservoir Stopcock #1.

43. Close Stopcock #5 on delivery tube vacuum line to evacuate flask.

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PROCEDURAL STEPS (Continued)

44. Open reagent reservoir Stopcock #1 to empty flask.
45. Repeat Steps 40 through 44 twice more.
46. Open Stopcock #5 on delivery tube vacuum line.
47. Close the Flask Slurp Stopcock #2.
48. Close Reagent Reservoir Stopcock #1.
49. Repeat Steps 37 through 47 with remaining distillation unit.
50. Set 3-Way Vacuum Stopcock #4 to Air position.
51. Remove small stopper on delivery tube on one unit only.
52. Add slowly 25 mL deionized water to trap tube using plastic funnel while keeping the water level below the condenser sidearm.
53. Open trap tube Stopcock #3 and drain into waste beaker.
54. Empty beaker into a separate waste bottle.
55. Repeat Steps 52 through 54 twice more.
56. Replace the small delivery tube stopper.
57. Repeat Steps 51 through 56 with remaining distillation unit.

III DISTILLATION SHUTDOWN

1. Set 3-Way Vacuum Release Stopcock #4 to Air position, if necessary.
2. Turn off Hood Vacuum Valve.
3. Turn off water bath for distillation condenser.
 - a. Turn off Temperature Controller Switch on lower front of unit.
 - b. Turn off Water Pump Switch on upper front of unit.
 - c. Turn off main Power Switch on back of unit.

IV SPECTROPHOTOMETRIC COLOR DEVELOPMENT

NOTE: Carry reagent blank containing 25 mL of 0.125 M NaOH in a 50 mL volumetric flask through all steps of the procedure with every batch of samples.

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PROCEDURAL STEPS (Continued)

NOTE: Pipet each non-distilled calibration standard (1-20 ug CN^-) into a 50 mL volumetric flask. Dispense 25 mL of 0.125 M NaOH into flask.

1. Turn on the Power Switch on the spectrophotometer (Figure 2).
2. Dispense 7.5 mL of NaH_2PO_4 (138 g/L) solution to the sample in the 50 mL volumetric flask from the distillation. Swirl to mix for 10-15 seconds.
3. Dispense 1 mL of 10 g/L of Chloramine-T reagent and swirl to mix for 5-10 seconds.
4. Immediately dispense 2.5 mL of Pyridine-Barbituric Acid reagent and swirl to mix for 5-10 seconds.
5. Dilute to volume with deionized water.
6. Invert flask several times or add stir bar and stir 5 minutes.

NOTE: Purple color develops in 8 minutes, and its absorbance must be read within 20 minutes.

7. Set wavelength to 580 nm on the spectrophotometer.
8. Zero the spectrophotometer using deionized water in 1 cm disposable plastic cells. Refer to Section V for the Spectrophotometer Operation.
9. Record the absorbance of the solution on the analytical card.
10. Dispose of cell solution into a waste bottle.
11. Discard the plastic cell into solid waste container.
12. Clean all glassware by rinsing with deionized water.

V SPECTROPHOTOMETER OPERATION

1. Turn on the Mode Selector Knob to the Absorbance position.

NOTE: The analytical card for this procedure will probably indicate the wavelength appropriate for this analytical method.

NOTE: View the Wavelength Dial from directly above to avoid a reading error.

2. Set the wavelength by rotating the Wavelength Selector Knob until the desired wavelength in nanometers (350-1000 nm) is indicated on the dial.

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PROCEDURAL STEPS (Continued)

NOTE: Be sure that the spectrophotometer cells used are matched to each other.

3. Fill a disposable plastic cell with water.
4. Insert the cell into one end of the 3-position cell holder inside the spectrophotometer cell compartment (Figure 3).
5. Use the Control Rod on the front of the sample compartment to position the cell into the spectrophotometer light beam (Figure 4).
6. Close the cell compartment cover.
7. Set the Sensitivity Switch to LO.
8. Adjust the Zero A Control Knob to obtain a zero reading on the digital display.
 - a. If a zero reading cannot be obtained, move the Sensitivity Switch to M (medium) position, and again try to obtain a zero reading with the Zero Knob.
 - b. If a zero reading still cannot be obtained, move the Sensitivity Switch to HI (high) position, and try once more.
 - c. If a zero reading cannot be obtained with any Sensitivity setting, call the manager. The instrument is malfunctioning.
9. Fill a clean disposable cell with the prepared sample solution.
10. Insert the cell into the center position in the 3-position cell holder inside the spectrophotometer light beam (Figure 3).
11. Use the Control Rod on the front of the sample compartment to position the cell into the spectrophotometer light beam (Figure 4).
12. Close the cell compartment cover.

NOTE: Normally the absorbance of a reagent blank will be recorded on the analytical card also.

13. Read the digital display and record the reading on the analytical card.
14. Turn off the Power Switch when all sample absorbencies have been measured.

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CALCULATIONS

1. The slope and y-intercept are obtained according to the Calibration Section of this procedure.
2. Micrograms of Cyanide(μgCN^-) = $\frac{(\text{Total Absorbance} - \text{Blank Abs}) - (\text{y-intercept})}{\text{Slope}}$
3. $\mu\text{g/mL CN}^- = \text{mg/L CN}^- = \frac{\text{Micrograms CN}^-}{\text{Sample Size (mL)}} \times \text{D. F.}$

where D. F. = Dilution Factor

$$\text{D. F. (using flasks)} = \frac{\text{Flask Volume (mL)}}{\text{Original Sample Aliquot (mL)}}$$

$$\text{D. F. (using vials)} = \frac{A + B}{B}$$

where: A = Dispensed Volume (mL)

B = Original Sample Aliquot (mL)

4. Percent Recovery of Standard = $\frac{\mu\text{g/mL CN}^- \text{ Observed}}{\mu\text{g/mL CN}^- \text{ Std. Value}} \times 100$

Example

A standard was run using a 1 mL aliquot.
The total absorbance was found to be 0.663 at 580 nm.
The reagent blank was 0.016 absorbance units.
The slope is 0.076317.

$$\text{The dilution factor is } 100 = \frac{10 \text{ mL}}{0.1 \text{ mL}}$$

The y-intercept is 0.016827.

The true mg/L value for the standard is 817 mg/L.

$$\text{Micrograms of CN}^- = \frac{(0.663 - 0.016) - 0.016927}{0.076317}$$

$$\text{Micrograms of CN}^- = 8.2574$$

$$\mu\text{g/mL} = \text{mg/L} = \frac{8.2574 \mu\text{g}}{1 \text{ mL}} \times 100 = 825.74$$

$$\text{Standard \% Recovery} = \frac{825.74}{817.00} \times 100$$

$$\text{Standard \% Recovery} = 101.06\%$$

5. Percent Spike Recovery = $\frac{(\mu\text{g CN}^- \text{ in Sample} + \text{Spike}) - (\mu\text{g CN}^- \text{ in Sample})}{\mu\text{g CN}^- \text{ in Spike}} \times 100$

CALIBRATION

1. The Working CN^- Calibration Standard (10 ug/mL CN^-) was used to prepare a calibration curve by carrying these standards through Section IV and V of this procedure.

Example - Typical data are as follows:

<u>Pipet Size (mL)</u>	<u>Micrograms Cyanide</u>	<u>Total Absorbance</u>	<u>Net Absorbance</u>
Blank	0	.016	0
100	0.82	.091	0.075
200	1.63	.150	0.134
500	4.08	.354	0.338
1000	8.17	.663	0.647
2000	16.34	1.275	1.259
3000	24.51	1.720	*1.704

* Non Linear

The calibration curve remains linear to above 20, but less than 30 micrograms of cyanide per sample aliquot.

2. The y-intercept, slope, and correlation coefficient are obtained by inserting the net absorbance versus the micrograms of cyanide for each calibration point into a Linear Fit Program. This program performs a linear regression on the calibration points and gives a curve fit, slope, and y-intercept.

DISCUSSION

Standard methods for cyanide analysis which use high acid distillation of HCN and spectrophotometric measurement of cyanide were evaluated for Hanford waste matrices. The high nitrate concentrations in Hanford waste oxidized cyanide to cyanate in the high acid distillation procedure resulting in zero recovery of the cyanide.

A low acid distillation procedure was developed which uses ethylenediaminetetraacetic acid (EDTA) to break up cyanide complexes and an acetate buffer to control the pH at 4.0.

The analysis of cyanide requires three to four hours per sample; therefore, the method is not amenable to large sample loads. Multiple distillation systems could improve throughput but would require additional hood space. Therefore, a dual or tandem distillation apparatus has been utilized in the laboratory. An adjacent hood has been reserved for the color development and spectrophotometric measurement technique.

The standard methods to analyze for total cyanide use distillation of HCN from strong sulfuric acid to break up metal cyanide complexes and to separate the cyanide from these interferences. These methods use large sample sizes (500 mL) and large distillation flasks which are not suitable for small highly radioactive samples that must be handled in the confined space of a hood. Therefore, the equipment and procedure had to be scaled down a factor of 10 from existing technology in order to be applicable and convenient for analysis of Hanford wastes.

Samples to be analyzed for cyanide must be preserved by making basic with NaOH (pH greater than 12). This is normally not a problem because most Hanford waste was neutralized before storage.

An interferant that can be carried through the distillation is sulfide. Sulfide ion is easily oxidized by air, nitrate, and nitrite even in basic solution unless stabilized by strong reducing agents or as insoluble metal sulfides. Standard methods add lead carbonate to the sample if they test positive for sulfide with lead acetate papers.

Just about all Hanford waste contains some nitrite. Nitrite has been reported to react with some organics to form cyanide. In addition, it could also oxidize cyanide to cyanate under the acid distillation conditions. In this method 2 mL of 2 M sulfamic acid was added to reduce nitrites to nitrogen gas.

The distillation procedure normally operated smoothly. The only problem that occasionally arose was liquid backing up in the flask air inlet tube into the reagent reservoir during initial heat up of the flask. This was caused by pressure in the flask increasing with heat which reduced air flow and pushed liquid up the tube. The air flow during the first 10 to 15 minutes of the distillation must be closely watched to prevent this from happening.

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DISCUSSION (Continued)

The EPA-Pyridine-Barbituric Acid Method is based on the reaction of cyanide with Chloramine-T reagent to form CNCl. In this procedure the CNCl reacts with pyridine-barbituric acid reagent to form a red-blue dye that absorbs at 580 nm. The major advantage over the EPA Pyridine Pyrazolone Method is that the pyridine-barbituric acid reagent is easier to prepare and more stable than the pyrazolone. Another major difference in the procedures is the color development time and stability.

A less acidic medium for the distillation is attractive since under these condition thiocyanate is stable and many oxidants (nitrate) are weaker. This method uses a distillation at pH 4.0 coupled with the addition of EDTA for displacing cyanide in metal complexes to separate cyanide. An acetate buffer is used to maintain the pH and sulfamic acid is added to remove nitrite interferences.

The low acid distillation procedure gave good recoveries in the presence of nitrite, nitrate, aluminum, and other components of a synthetic waste. Distillation time studies indicate that the distillation is complete within 30 minutes; however, a one hour distillation time has been selected for this method.

While attempting to prepare a calibration curve, difficulties were encountered in duplicating any previous given standard's absorbance value. A subsequent pH study of several mixtures of NaOH and NaH_2PO_4 was then made. The mixture of 0.25 M NaOH and NaH_2PO_4 had a pH of 7.1, while a mixture of 0.125 M NaOH and NaH_2PO_4 gave a pH of 6.4. Since the upper range (pH) allowable is 8.0, the lower pH range was selected using the 0.125 M NaOH instead of the previously used 0.25 M NaOH. This cyanide-chloramine-T-pyridine-barbituric acid dye complex formed very readily and was reproducible. The resulting absorbance using 0.125 M NaOH produced values 70% greater than previous methods; thereby, greatly increasing the sensitivity of the method.

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FIGURE 1

CYANIDE DISTILLATION EQUIPMENT

SPECTRONIC 21 UV Operating Controls

Figure 2

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GENERAL PURPOSE SAMPLE COMPARTMENT

Figure 3

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Interior of GPSC Showing Location of Multiple
Sample Holder

Figure 4

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ANALYTICAL LABORATORIES

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Title
ARSENIC ANALYSIS BY HYDRIDE GENERATION ATOMIC
ABSORPTION

SUMMARY

This procedure describes the operation of the Perkin-Elmer Model 2280 atomic absorption spectrometer using the MHS-20 Mercury/Hydride system. The procedure is used for the quantitative determination of the hydride-forming element arsenic.

LIMITATIONS

This procedure is used for the analysis of aqueous solutions. Organic solvents are not allowed. The detection limit and precision are dependent on the sample matrix, but are usually in the range of 10 to 100 ng of arsenic and 5 to 20 percent, respectively.

The total prepared volume of sample must not exceed 50 mL.

Metal ions that can be reduced to the free metal might interfere. Some examples are Cu, Ni, Fe, Pd, Bi, Se, Hg and Co. Spiked samples are used as a check for interferences.

AN ICP ANALYSIS MUST BE PERFORMED ON ALL SAMPLES BEFORE ATTEMPTING THIS METHOD. THE RESPONSIBLE SCIENTIST WILL THEN DETERMINE IF ANY INTERFERING ELEMENTS ARE PRESENT. IF POTENTIAL INTERFERENCES ARE PRESENT THEN THE ION EXCHANGE SECTION WILL HAVE TO BE USED.

Arsenic absorbs light in the far ultraviolet. Air in the cell path and dirty optics affect the performance of the method. Other gases such as oxides of nitrogen which have broad absorption bands in the UV will cause high results and possibly unstable baselines.

APPLICATIONS

This procedure is applicable to a wide variety of aqueous solutions, including environmental waters and waste tank core samples. The method measures only inorganic arsenic. Analysis of organic samples requires an oxidation step prior to hydride generation.

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SAFETY

The provisions of General Regulations and Practices for Radiation Work (GEN-0) and applicable Radiation Work Permits (SL-3 and SL-8), found in RHO-MA-172, RHO-GM-MA-2, SRP 61-02.5 apply to all work performed under this procedure. All work with chemical reagents will conform to RHO-MA-221, Volume 2, Chemical Safety Guides 11 (sodium hydroxide) and 51 (hydrogen).

Read the Material Safety Data Sheets (MSDS's) for HCl (1250), HNO₃ (1384), and HF (1251). The appropriate care must be used when handling all acids. Special care must be exercised when handling HF. Wear PVC or neoprene gloves and use only in a hood. HF has a latent period. In concentrations of 20-50 %, the burn may not be felt for 1-8 hours following the exposure. HF burns are painful and VERY SLOW to heal.

Arsenic and its salts are toxic and must be handled accordingly. Surgeon's gloves must be worn to prevent direct contact with the materials. Operations such as heating or hydride generation must be done under controlled ventilation conditions so that vapors are trapped or released in hoods.

NaBH₄ is used as a reductant in the MHS-20/Hydride system. Sodium borohydride is a strong reducing agent and liberates hydrogen gas on contact with acids. Solutions of sodium borohydride are relatively unstable and decompose liberating hydrogen. This decomposition increases with temperature. Literature indicates that significant changes occur in the reactivity of sodium borohydride solutions stabilized with 1-2% sodium hydroxide in three weeks.

Sodium borohydride solutions must be disposed of carefully. The solutions must not be disposed of in acidified slurp bottles. Waste solutions of basic sodium borohydride must be stored in special ventilated bottles and disposed of by dilution in water and pouring down a ventilated drain that has first been rinsed with large amounts of water. These same procedures apply to sample waste from this procedure which may contain some unreacted sodium borohydride. These acidified waste solutions must not be slurped into the normal waste traps but stored in a separate waste bottle before properly diluting and disposing.

During the course of a determination a chemical reaction takes place and hydrogen is liberated. Hydrogen can form explosive mixtures with air. The method includes equipment and steps that are important in preventing an explosive reaction of hydrogen with air. To prevent the buildup of air/hydrogen mixtures, the following precautions must be strictly observed:

1. Never select SnCl₂ mode when using NaBH₄ as reductant.
2. NaBH₄ liberates hydrogen on contact with acids. It must be stored away from heat and sealed to prevent entrance of acid fumes and water. Sodium borohydride solutions must be kept basic and prevented from mixing with acids except under the controlled conditions of this procedure.

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SAFETY (continued)

3. Continuous ventilation must be provided in the operating area.
4. Do not overfill the reaction flask. The maximum prepared sample volume is 50 mL.
5. Once the reaction has been started, do not remove the reaction flask from the Analyzer Assembly and then reconnect it. Air entrained in the flask may lead to the formation of a potentially explosive air/hydrogen mixture.

If it becomes necessary to remove the flask before the determination is complete (e.g. due to excessive foam development), leave it in the hood until the release of hydrogen has ceased. The determination should be repeated on a fresh sample.

6. Do not empty the reaction flask directly into the laboratory's waste water system. There may be an excess of NaBH_4 in the flask.
7. Ensure that the sample transfer hose between the Analyzer Assembly and the quartz cell is not restricted in any way.
8. Ensure that the flashback arrestor is not blocked.
9. Make certain that the venting hoses from the quartz cell are not restricted in any way. Check them periodically to see that they have not become full with condensed water.
10. Never push START button when a reaction flask or other vessel is not placed underneath the immersion tube.
11. At the end of the working day, purge the reductant transfer system with deionized water to remove any reductant residues.

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EQUIPMENT

Perkin-Elmer Model 2280 Atomic Absorption Spectrometer with Model MHS-20 Mercury/Hydride option and Mercury Amalgam attachment.

Hollow Cathode Lamp (HCL)

Quartz tube with quartz windows and silicon sleeves

Reaction flasks with covers

Transfer hose with flashback arrestor

Pipets, glass or Eppendorf, various sizes

Vials, 22 mL disposable

Beakers, 15 and 30 ml disposable

Filter units, disposable

Glass stir rods, medium

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REAGENTS

For all the following reagents: put into a plastic bottle and label with reagent name, concentration, creation date and preparer's initials.

1.0 ppm As in 2.0% HCl calibration standard is prepared by diluting a 1000 ppm 0.100 ml of As stock solution (Spex or equivalent) to 100.0 ml with 2.0% HCl. This solution is good for two weeks.

6.0 M HCl is prepared by diluting 520 ml of concentrated (11.6 M) HCl to 1.0 l with deionized water. This solution is good for 6 months.

0.010 M NaOH is prepared by dissolving 0.40 g NaOH in deionized water and diluting to 1.0 l. This solution is good for 6 months.

6.0 M HNO₃ is prepared by diluting 390 ml concentrated (15.4 M) HNO₃ to 1.0 l with deionized water. This solution is good for 6 months.

1.0 M HSO₃NH₂ is prepared by dissolving 9.7 g HSO₃NH₂ in deionized water and diluting to 0.10 l. This solution is good for 2 months.

0.10 M EDTA is prepared by dissolving 3.72 g EDTA-disodium salt, dihydrate in deionized water and diluting to 100 ml. This solution is good for 6 months.

0.10 M Acetate Buffer is prepared by dissolving 13.6 g NaC₂H₃O₂ * 3H₂O in deionized water, adding 5.8 ml of 17.4 M CH₃COOH and diluting to 1.0 l. This solution is good for 6 months.

1.0% Sodium Borohydride in 0.010 M NaOH Reagent.

CAUTION: Sodium borohydride reacts with acid to form hydrogen gas which could explode. Clean up spills with water only. Dispose of excess sodium borohydride in acid-free waste bottles and sinks. See SAFETY section.

Add 5.0 g sodium borohydride (15 pellets, about 0.35 g each) to 500 ml of 0.010 M NaOH and mix until dissolution is complete. Filter through a 0.45 um filter and transfer to the reductant reservoir. Prepare fresh daily.

PROCEDURE

This procedure contains seven sections:

- I. Preparation of the Quartz Cell and Windows
- II. Instrument Setup
- III. Preparation of Standards and Samples Not Requiring Ion Exchange
- IV. Preparation of Standards and Samples Requiring Ion Exchange
- V. Analysis
- VI. Instrument Shutdown
- VII. Calculations

I. Preparation of the Quartz Cell and Windows

1. Disassemble and assemble and clean the cell and windows as instructed by the responsible scientist.

CAUTION: Handle HF carefully. See the SAFETY section.

2. A new cell and windows must be conditioned by soaking in concentrated HF for 10-15 minutes (NO LONGER).
3. Rinse the cell and windows thoroughly with deionized water then alcohol and let air dry.

II. Instrument Setup

1. Turn the LAMP 1 control fully counterclockwise.
2. Install the arsenic HCL in the lamp compartment and plug into LAMP 1 connector.
3. Switch the POWER on.
4. Make the following control settings:
 - SIGNAL - LAMP 1
 - BKGD CORR - AA
 - GAIN - Fully counterclockwise
5. Turn the LAMP 1 control until the LAMP/ENERGY display shows the proper lamp current as given on the lamp.
6. Set the SIGNAL control to ABS.
7. Allow about 30 minutes for the HCL to stabilize.
8. While the instrument is stabilizing, the cell and windows MUST be cleaned by thoroughly rinsing with 6 M HNO₃ then deionized water. This MUST be done at the start of each day.

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PROCEDURE (continued)

II. Instrument Setup (continued)

9. Set the wavelength and slit at 193.7 nm and 0.7 nm, respectively (see Figure 1).
10. Perform the following lamp alignment and wavelength adjustments. The quartz cell must be removed and the heating mantle left open while these steps are being performed. The reaction flask should also be removed.
 - a. Peak the wavelength setting by turning the WAVELENGTH ADJUST (see Figure 1) slowly to obtain a maximum reading on the LAMP/ENERGY display (see Figure 2).
 - b. Adjust the reading to a maximum of 70 with the GAIN control (see Figure 2). If the gain should become too high, an over range reading of "EE" will be obtained.
 - c. Open the lamp compartment door and turn the two alignment knobs on the lamp holder (see Figure 3) to maximize the LAMP/ENERGY display.
 - d. Again, adjust the reading to a maximum of 70 with the GAIN control.
 - e. Close the lamp compartment door.

NOTE: As the lamp warms up the display value will change. Readjust as in "d" above.

11. Lay the quartz cell in the heating mantle and close the cover.
12. Select the absorbance mode and continuous signal handling on the spectrophotometer (see Figure 2).
13. Make incremental adjustments, alternately, to the VERTICAL, HORIZONTAL and ROTATIONAL controls (see Figure 4) to obtain a minimum absorbance reading on the display. This is to fine adjust the quartz cell.
14. Turn on the nitrogen gas supply and increase the pressure to 36 psig.
15. Switch the POWER on the controller to ON (see Figure 5) and push the NaBH_4 button.

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PROCEDURE (continued)

II. Instrument Setup (continued)

16. Set the TEMP, PURGE I, REACTION and PURGE II sliders to 900, 20, 20 and 40, respectively. The temperature is ready when the TEMP indicator light comes on (about 5 minutes).

NOTE: See Figure 7 for all recorder buttons.

17. Turn on the recorder and check that the Range and Chart Speed are set to 10 mV and 10 mm/minutes, respectively.
- a. The Range is adjusted by pushing the RNGE button.
 - b. The Chart Speed is adjusted by pushing the SPD button.
18. To Start or Stop recording data, push the RUN or STOP and PEN LIFT buttons.
19. To zero the pen on the chart paper, push and hold the ZERO ADJ button and turn the zero adjust knob.
20. Fill the reductant reservoir bottle to the shoulder with 1% NaBH₄ in 0.01 M NaOH. Screw the bottle into the fitting on the analyzer assembly (see Figure 6).

NOTE: ALWAYS zero the absorbance reading by pushing the AZ button BEFORE attaching the reaction flask onto the flange on the analyzer assembly.

21. Push the AZ button on the spectrophotometer (see Figure 2) to zero the absorbance reading, if necessary.
22. Place an empty reaction flask onto the flange on the analyzer assembly and push the START button on the controller.
23. Remove and empty (in the NaBH₄ waste bottle) the reaction flask from the flange after the START light goes out.
24. Repeat Steps 21-23 three times.

NOTE: Periodically check the lamp watts and adjust if necessary.

NOTE: VERY IMPORTANT. ICP results for the samples MUST be checked for the presence of interfering elements. If none are present, proceed with Section III. If ANY interfering elements are present, skip to Section IV.

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PROCEDURE (continued)

III. Preparation of Standards and Samples Not Requiring Ion Exchange

NOTE: It is absolutely essential to use scrupulously clean glassware and reaction equipment to ensure valid analyses.

NOTE: There are specifically labelled reaction flasks to be used only for the arsenic calibration solutions.

1. Prepare the calibration solutions by dispensing 10 ml of 6 M HCl, 1 ml of 6 M HNO₃ and 1 ml of 1 M HSO₃NH₂ and pipetting the appropriate number of microliters (0, 25, 50 or 75) of the calibration standard into the corresponding reaction flask.
2. Prepare the sample and LMCS standard solutions according to the following.
 - a. Label duplicate reaction flasks with the sample number. Mark one of the flasks with an X to indicate that the sample is spiked.
 - b. Dispense 10 ml of 6 M HCl, 1 ml of 6 M HNO₃ and 1 ml of 1 M HSO₃NH₂ and pipet an aliquot of the sample into the appropriate flask. The sample size is selected to give a result within the range of concentrations of the calibration curve. When no estimate of sample concentration is available, use 100 microliters.

NOTE: Never use more than 100 microliters of sample without first consulting the responsible scientist.

- c. Add 25 microliters of the As calibration standard to the reaction flasks marked with an X.
- d. Go to the analysis section.

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PROCEDURE (continued)

IV. Preparation of Standards and Samples Requiring Ion Exchange

NOTE: When ion exchange is required all calibration standards, LMCS standards and samples must be treated the same.

NOTE: It is absolutely essential to use scrupulously clean glassware and reaction equipment to ensure valid analyses.

1. Prepare the calibration solutions according to the following.
 - a. Label duplicate filter apparatus and 15 and 30 ml beakers with the volume of As to be added, 0, 25, 50 or 75 microliters.
 - b. Add 10 ml of 0.1 M acetate buffer and 500 microliters of 0.1 M EDTA to a 15 ml labelled disposable beaker then pipet in the appropriate number of microliters of the calibration standard.
 2. Prepare the sample and LMCS standard solutions according to the following:
 - a. Label duplicate filter apparatus and 15 and 30 ml beakers with the sample number. Mark one set with an X to indicate that the sample is spiked.
 - b. Add 10 ml of 0.1 M acetate buffer and 500 microliters of 0.1 M EDTA to a 15 ml labelled disposable beaker then pipet in an aliquot of the sample. The sample size is selected to give a result within the range of concentrations of the calibration curve. When no estimate of the sample concentration is available, use 100 microliters.
- NOTE:** Never use more than 100 microliters of sample without first consulting the responsible scientist.
- c. Add 25 microliters of the As calibrations standard to the beakers marked with an X.
3. Weigh approximately 13 g of Chelex 100 into a 30 ml plastic disposable beaker, add the above sample, swirl and let sit for 15 minutes.
4. Stir the slurry with a glass rod and pour into a filter apparatus.
5. Rinse off the glass rod with 0.1 M acetate buffer (from the squirt bottle) into the 30 ml beaker.
6. Apply vacuum to remove 3-4 ml of liquid off the Chelex. DO NOT LET THE CHELEX GO DRY.

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PROCEDURE (continued)

IV. Preparation of Standards and Samples Requiring Ion Exchange (continued)

7. Add 5 ml of 0.1 M acetate buffer to the 30 ml beaker, swirl, add to the filter unit.
8. Repeat Step 6.
9. Repeat Step 7 and vacuum dry. The final volume should be about 20 ml.
10. Dispense 10 ml of 6 M HCl, 1 ml of 6 M HNO₃, and 1 ml of 1 M HSO₃NH₂ into a clean reaction flask, add the above filtered solution and go to the analysis section.

V. Analysis

All standards and samples are to be treated the same.

1. WITH THE REACTION FLASK OFF:
 - a. Adjust the lamp energy to 69-70, if necessary, and zero the absorbance reading.
2. Attach a reaction flask containing the blank and push the START button on the controller.
3. Label the chart paper with the information requested on the list on the recorder.

NOTE: Use a metric ruler with mm graduations to measure the peak height. Measure the difference between the baseline just before the peak and the peak maxima. Measure to the nearest 1/2 mm.

4. Check the absorbance reading on the chart paper. The blank must not give a signal higher than 5 mm. Higher blank values indicate contaminated chemicals (water, acids, NaBH₄) or a contaminated flask or dirty cell and windows.

NOTE: Dispose of sample and rinse waste into the appropriately labelled bottle.

5. Remove the reaction flask after the START light goes out, rinse the dispenser tip with 6 M HNO₃ then deionized water and wipe with a Kimwipe.
6. Rinse the reaction flask thoroughly with 6 M HNO₃ and deionized water.
7. Repeat Step 1.

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PROCEDURE (continued)

V. Analysis (continued)

8. Attach a reaction flask containing a 50 ng calibration standard and push the START button on the controller.
9. Label the chart paper.
10. Check the absorbance reading on the chart paper. You must get a minimum signal as posted on the instrument. If not, contact the responsible scientist.
11. Repeat Steps 5-7.
12. If the initial checks prove satisfactory, then repeat the above process for the rest of the calibration standards, LMCS standards and samples.

VI. Instrument Shutdown

1. Turn off the recorder power. Remove and cap pen.
2. Turn off the power to the spectrometer.
3. Turn the HCL lamp wattage off.
4. Remove the reduction (NaBH_4) bottle and replace it with a bottle containing deionized water.

NOTE: Dispose of NaBH_4 waste in the NaBH_4 waste bottle ONLY.

5. Place an empty reaction flask on the analyzer assembly.
6. Rinse the reductant out of the transfer lines by setting both PURGE I and II to their minimum values and REACTION to its maximum then go through the REACTION cycle 3-5 times.
7. Close the valve on the nitrogen regulator.
8. Set PURGE I to its maximum value and REACTION and PURGE II to their minimums then go through the REACTION cycle until the START light blinks (until the N_2 pressure is zero).
9. Turn off the controller.
10. Clean up the work area.

PROCEDURE (continued)

VII. Calculations

1. Plot the absorbance (peak height in mm from the strip chart) versus the ng (number of microliters) of standard added.
2. Draw a best fit straight line through the points using a ruler and check the linearity. Notify the responsible scientist if the data is not linear.
3. Calculate the arsenic concentrations using the HP-97 calculator and the Curve Fit program as follows:
 - a. Load side 1 and 2 of the Curve Fit program card.
 - b. Press f(A) then press f(B).
 - c. Press DSP then press 4.
 - d. Enter the ng of As and push ENTER.
 - e. Enter the absorbance (mm) and push A.
 - f. Repeat steps d and e for each standard.
 - g. Push C to compute r^2 , intercept and slope.
 - h. Enter the sample absorbance (mm) and push D to calculate the ng of As in the sample.
 - i. Calculate the sample concentration in parts per billion (ppb) by dividing the value obtained in step h by the sample aliquot volume (in ml). See No. 2 on the next page.
 - j. Enter the sample + spike absorbance (mm) and push D to calculate the ng of As.
 - k. Calculate the spike recovery as shown in No. 3 on the next page.
 - l. Repeat steps h through k for all samples and enter the information on the sample cards.
 - m. Turn in the sample cards and pat yourself on the back.

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PROCEDURE (continued)

VII. Calculations (continued)

EXAMPLE

1. Sample Analysis

A sample was received for analysis. A 0.1 ml (100 microliters) aliquot was taken into the procedure with a resulting absorbance of 24.0 mm. Likewise, a 0.1 mL aliquot was spiked with 25 microliters of 1000 ng/mL (1 ppm) arsenic standard; the resulting absorbance was 43.5 mm. The calibration standards were measured.

Calibration Data:

Blank (0.0 ng)	:	0.0 mm
25.0 ng	:	20.0
50.0 ng	:	40.0
75.0 ng	:	60.0

From the calibration data, one finds that the sample absorbance corresponds to 30.0 ng arsenic and the Sample-plus-spike corresponds to 54.4 ng.

2. Calculation of original Sample Concentration (ppb)

$$\begin{aligned}\text{ppb} &= (\text{ng As in sample aliquot})/(\text{mL sample aliquot}) \\ &= (30.0 \text{ ng})/(0.1 \text{ mL}) = 300 \text{ ppb}.\end{aligned}$$

3. Calculation of Spike recovery

Spike recovery =

$$\frac{(\text{ng sample} + \text{spike}) - (\text{ng sample})}{(\text{ng spike})} \times 100\% =$$

$$\frac{(54.4 \text{ ng} - 30.0 \text{ ng})}{(25.0 \text{ ng})} \times 100\% = 97.6\%$$

Acceptable spike recoveries are:

- a. Without ion exchange - 85 - 115 %,
- b. with ion exchange - 75 - 125 %.

4. Alternative concentration units:

To convert from ppb to ppm: $\text{ppm} = \text{ppb}/1000$

To convert from ppb to g/L: $\text{g/L} = \text{ppb}/1000000$

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DISCUSSION

Sodium borohydride (NaBH_4) is used as the reductant for the determination of metallic hydride-forming elements and may also be used with advantage for the determination of mercury. Sodium borohydride liberates hydrogen on contact with acids. The reaction mechanisms involved in the reduction of metal ions are complicated and almost certainly take place via the formation of intermediate radicals. The following equations represent simplifications of the reduction processes.

M is a metallic element that forms a volatile hydride (e.g. As, Bi, Sb, Se, Te, etc.)

For determining metallic elements that form volatile hydrides, the sample solution is first treated so that the metal under study is present in ionic form in acid solution. Reductant is dispensed into the sample solution where it reacts to liberate hydrogen. The metal ions are reduced to the volatile hydride. The nitrogen stream flushes the hydride into the heated quartz cell where it is decomposed and the absorption of the metal measured. The cell is heated to between 900°C and 1000°C .

The detection limits attainable with the MHS-20 are often a function of the level of contamination rather than instrument capability. When working at the ppb levels, contamination is usually the major source of error. Careful handling of the apparatus and careful technique will minimize this problem. The following precautions help to avoid sample contamination:

1. Use only deionized water.
2. Collect all samples in Teflon or polyethylene containers that have been thoroughly rinsed with 6 M HNO_3 .
3. Use only reagents found to be free of mercury, arsenic and selenium. Measure blanks before analyzing samples.
4. All glassware and apparatus must be scrupulously clean.

The hydride apparatus performs an analysis of ng levels of arsenic. Total sample volumes of up to 50 ml can be accommodated to provide greater sensitivity. In practice, however, interference levels, radiation levels in some samples (including waste tank) and amount of sample available limits the sample size substantially.

DISCUSSION (continued)

Applications of hydride generation spectroscopic techniques have been reviewed⁽⁴⁾. All hydride methods are subject to interferences caused by the presence of electropositive ions. One mechanism for this interference is the reduction of these ions to finely divided metal particulates which absorb or interact with the hydride vapors and cause low results. The removal of these ions from solution by ion exchange before analysis eliminates or reduces the interference.

REFERENCES

1. LA-505-124, "Application of the Method of Standard Additions to Atomic Absorption."
2. Operators Manual, Perkin-Elmer Model 2280 Atomic Absorption Spectrometer.
3. Operators Manual, MHS-20 Mercury/Hydride System.
4. T. Nahahara, "Applications of Hydride Generation Techniques in Atomic Absorption, Atomic Fluorescence, and Plasma Atomic Emission Spectroscopy," Progress Analytical Atomic Spectroscopy, Vol. 6, pp. 163-223, 1983.

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Figure 1. Left Front Control Panel

- 1 SLIT Width Selector
- 2 BKGD CORReCTOR Switch
- 3 Optics Compartment Access Screw
- 4 BKGD CORR INTENSITY Control
- 5 WAVELENGTH ADJUST Control
- 6 WAVELENGTH Counter

Figure 2. Right Front Control Panel

1	Digital Display and Indicators	13	PRNT (Print) Key and Signal Dot
2	AZ (Auto Zero) Key and Signal Dot	14	Numerical Keyboard
3	S1 Key and Signal Dot	15	CE (Clear Entry) Key
4	S2 Key and Signal Dot	16	Electronics Compartment Access
5	S3 Key and Signal Dot		Screws
6	AVERage Key and Signal Dot	17	SIGNAL Switch
7	CV (Coefficient of Variation) Key and Signal Dot	18	READ Key and Signal Dot
8	SD (Standard Deviation) Key and Signal Dot	19	MODE Switch
9	RSLP (Reslope) Key and Signal Dot	20	LAMP/ENERGY Display
10	t (Time) Key	21	RECORDER Switch
11	EXPansion Key and Signal Dot	22	GAIN Control
12	CHK (Check) Key	23	LAMP 1 Control
		24	LAMP 2 Control
		25	POWER Switch

Figure 3. Universal Lamp Mount

- 1 Filter Attenuator Control
- 2 Alignment Knob
- 3 Spring
- 4 Lamp 1 Connector
- 5 Front Holddown Screw
- 6 Universal Lamp Mount (0057-0271)
- 7 Catch Release
- 8 Lamp Mount Button/Screw

Figure 4. Heating Mantle Assembly with Quartz Cell Installed

Figure 5. Front Panel of the Controller

Figure 6. Analyzer Assembly

Figure 7. Recorder Left Front Control Panel

ANALYTICAL LABORATORIES

Issued By:

T. A. Lane

Manager,

Analytical Laboratory

Author: R. L. Wilson

Title

SELENIUM ANALYSIS BY HYDRIDE GENERATION ATOMIC ABSORPTION

SUMMARY

This procedure describes the operation of the Perkin-Elmer Model 2280 atomic absorption spectrometer using the MHS-20 Mercury/Hydride system. The procedure is used for the quantitative determination of the hydride-forming element selenium.

LIMITATIONS

This procedure is used for the analysis of aqueous solutions. Organic solvents are not allowed. The detection limit and precision are dependent on the sample matrix, but are usually in the range of 10 to 100 ng of selenium and 5 to 20 percent, respectively.

The total prepared volume of sample must not exceed 50 mL.

Metal ions that can be reduced to the free metal might interfere. Some examples are Cu, Ni, Fe, Pd, Bi, Se, Hg and Co. Spiked samples are used as a check for interferences.

AN ICP ANALYSIS MUST BE PERFORMED ON ALL SAMPLES BEFORE ATTEMPTING THIS METHOD. THE RESPONSIBLE SCIENTIST WILL THEN DETERMINE IF ANY INTERFERING ELEMENTS ARE PRESENT. IF POTENTIAL INTERFERENCES ARE PRESENT THEN THE ION EXCHANGE SECTION WILL HAVE TO BE USED.

Selenium absorbs light in the far ultraviolet. Air in the cell path and dirty optics affect the performance of the method. Other gases such as oxides of nitrogen, which have broad absorption bands in the UV, will cause high results and possibly unstable baselines.

APPLICATIONS

This procedure is applicable to a wide variety of aqueous solutions, including environmental waters and waste tank core samples. The method measures only inorganic selenium. Analysis of organic samples requires an oxidation step prior to hydride generation.

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SAFETY

The provisions of "General Regulations and Practices for Radiation Work," RHO-GM-MA-2, Volume 6, Book 1, Standard Requirements and Procedures Section 61-02.5, and Radiation Work Permits SL-3 and SL-8 found in RHO-MA-172 apply to all work performed under this procedure and must be followed at all times. All work with chemical reagents will conform to RHO-MA-221, Volume 2, Chemical Safety Guides 11 (sodium hydroxide) and 51 (hydrogen).

Read the Material Safety Data Sheets (MSDS's) for HCl (1250), HNO₃ (1384) and HF (1251). The appropriate care must be used when handling all acids. Special care must be exercised when handling HF. Wear PVC or neoprene gloves and use only in a hood. HF has a latent period. In concentrations of 20-50%, the burn may not be felt for 1-8 hours following the exposure. HF burns are painful and VERY SLOW to heal.

Selenium and its salts are toxic and must be handled accordingly. Surgeon's gloves must be worn to prevent direct contact with the materials. Operations such as heating or hydride generation must be done under controlled ventilation conditions so that vapors are trapped or released in hoods.

NaBH₄ is used as a reductant in the MHS-20/Hydride system. Sodium borohydride is a strong reducing agent and liberates hydrogen gas on contact with acids. Solutions of sodium borohydride are relatively unstable and decompose liberating hydrogen. This decomposition increases with temperature. Literature indicates that significant changes occur in the reactivity of sodium borohydride solutions stabilized with 1-2% sodium hydroxide in three weeks.

Sodium borohydride solutions must be disposed of carefully. The solutions must not be disposed of in acidified slurp bottles. Waste solutions of basic sodium borohydride must be stored in special ventilated bottles and disposed of by dilution in water and pouring down a ventilated drain that has first been rinsed with large amounts of water. These same procedures apply to sample waste from this procedure which may contain some unreacted sodium borohydride. These acidified waste solutions must not be slurped into the normal waste traps, but stored in a separate waste bottle before properly diluting and disposing.

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SAFETY (continued)

During the course of a determination a chemical reaction takes place and hydrogen is liberated. Hydrogen can form explosive mixtures with air. The method includes equipment and steps that are important in preventing an explosive reaction of hydrogen with air. To prevent the buildup of air/hydrogen mixtures, the following precautions must be strictly observed:

1. Never select SnCl_2 mode when using NaBH_4 as reductant.
2. NaBH_4 liberates hydrogen on contact with acids. It must be stored away from heat and sealed to prevent entrance of acid fumes and water. Sodium borohydride solutions must be kept basic and prevented from mixing with acids except under the controlled conditions of this procedure.
3. Continuous ventilation must be provided in the operating area.
4. Do not overfill the reaction flask. The maximum prepared sample volume is 50 mL.
5. Once the reaction has been started, do not remove the reaction flask from the Analyzer Assembly and then reconnect it. Air entrained in the flask may lead to the formation of a potentially explosive air/hydrogen mixture.

If it becomes necessary to remove the flask before the determination is complete (e.g., due to excessive foam development), leave it in the hood until the release of hydrogen has ceased. The determination should be repeated on a fresh sample.

6. Do not empty the reaction flask directly into the laboratory's waste water system. There may be an excess of NaBH_4 in the flask.
7. Ensure that the sample transfer hose between the Analyzer Assembly and the quartz cell is not restricted in any way.
8. Ensure that the flashback arrestor is not blocked.
9. Make certain that the venting hoses from the quartz cell are not restricted in any way. Check them periodically to see that they have not become full with condensed water.
10. Never push START button when a reaction flask or other vessel is not placed underneath the immersion tube.
11. At the end of the working day, purge the reductant transfer system with deionized water to remove any reductant residues.

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EQUIPMENT

Perkin-Elmer Model 2280 Atomic Absorption Spectrometer with Model MHS-20 Mercury/Hydride option and Mercury Amalgam attachment

Hollow Cathode Lamp (HCL)

Quartz tube with quartz windows and silicon sleeves

Reaction flasks with covers

Transfer hose with flashback arrestor

Pipets, glass or Eppendorf, various size

Vials, 22 mL disposable

Beakers, 15 and 30 ml disposable

Filter units, disposable

Glass stir rods, medium

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REAGENTS

For all the following reagents: put into a plastic bottle and label with reagent name, concentration, creation date and preparer's initials.

1.0 ppm Se in 2.0% HCl calibration standard is prepared by diluting a 1000 ppm 0.100 ml of Se stock solution (Spex or equivalent) to 100.0 ml with 2.0% HCl. This solution is good for two weeks.

6.0 M HCl is prepared by diluting 520 ml of concentrated (11.6 M) HCl to 1.0 l with deionized water. This solution is good for 6 months.

0.010 M NaOH is prepared by dissolving 0.40 g NaOH in deionized water and diluting to 1.0 l. This solution is good for 6 months.

6.0 M HNO₃ is prepared by diluting 390 ml concentrated (15.4 M) HNO₃ to 1.0 l with deionized water. This solution is good for 6 months.

1.0 M HSO₃NH₂ is prepared by dissolving 9.7 g HSO₃NH₂ in deionized water and diluting to 0.10 l. This solution is good for 2 months.

0.10 M Acetate Buffer is prepared by dissolving 13.6 g NaC₂H₃O₂ * 3H₂O in deionized water, adding 5.8 ml of 17.4 M CH₃COOH and diluting to 1.0 l. This solution is good for 6 months.

1.0% Sodium Borohydride in 0.010 M NaOH Reagent.

CAUTION: Sodium borohydride reacts with acid to form hydrogen gas which could explode. Clean up spills with water only. Dispose of excess sodium borohydride in acid-free waste bottles and sinks. See SAFETY section.

Add 5.0 g sodium borohydride (15 pellets, about 0.35 g each) to 500 ml of 0.010 M NaOH and mix until dissolution is complete. Filter through a 0.45 um filter and transfer to the reductant reservoir. Prepare fresh daily.

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PROCEDURE

This procedure contains seven sections:

- I. Preparation of the Quartz Cell and Windows.
- II. Instrument Setup
- III. Preparation of Standards and Samples Not Requiring Ion Exchange
- IV. Preparation of Standards and Samples Requiring Ion Exchange
- V. Analysis
- VI. Instrument Shutdown
- VII. Calculations

I. Preparation of the Quartz Cell and Windows

1. Disassemble and assemble and clean the cell and windows as instructed by the responsible scientist.

CAUTION: Handle HF carefully. See the SAFETY section.

2. A new cell and windows must be conditioned by soaking in concentrated HF for 10-15 minutes (NO LONGER).
3. Rinse the cell and windows thoroughly with deionized water then alcohol and let air dry.

II. Instrument Setup

1. Turn the LAMP 1 control fully counterclockwise.
2. Install the selenium HCL in the lamp compartment and plug into LAMP 1 connector.
3. Switch the POWER on.
4. Make the following control settings:

SIGNAL - LAMP 1
BKGD CORR - AA
GAIN - Fully
counterclockwise
5. Turn the LAMP 1 control until the LAMP/ENERGY display shows the proper lamp current as given on the lamp.
6. Set the SIGNAL control to ABS.
7. Allow about 30 minutes for the HCL to stabilize.
8. While the instrument is stabilizing, the cell and windows MUST be cleaned by thoroughly rinsing with 6 M HNO₃ then deionized water. This MUST be done at the start of each day.

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PROCEDURE (continued)

II. Instrument Setup (continued)

9. Set the wavelength and slit at 196.0 nm and 0.7 nm, respectively (see Figure 1).
 10. Perform the following lamp alignment and wavelength adjustments. The quartz cell must be removed and the heating mantle left open while these steps are being performed. The reaction flask should also be removed.
 - a. Peak the wavelength setting by turning the WAVELENGTH ADJUST (see Figure 1) slowly to obtain a maximum reading on the LAMP/ENERGY display (see Figure 2).
 - b. Adjust the reading to a maximum of 70 with the GAIN control (see Figure 2). If the gain should become too high, an over range reading of "EE" will be obtained.
 - c. Open the lamp compartment door and turn the two alignment knobs on the lamp holder (see Figure 3) to maximize the LAMP/ENERGY display.
 - d. Again, adjust the reading to a maximum of 70 with the GAIN control.
 - e. Close the lamp compartment door.
- NOTE: As the lamp warms up the display value will change. Readjust as in "d" above.
11. Lay the quartz cell in the heating mantle and close the cover.
 12. Select the absorbance mode and continuous signal handling on the spectrophotometer (see Figure 2).
 13. Make incremental adjustments, alternately, to the VERTICAL, HORIZONTAL and ROTATIONAL controls (see Figure 4) to obtain a minimum absorbance reading on the display. This is to fine adjust the quartz cell.
 14. Turn on the nitrogen gas supply and increase the pressure to 36 psig.
 15. Switch the POWER on the controller to ON (see Figure 5) and push the NaBH_4 button.

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PROCEDURE (continued)

II. Instrument Setup (continued)

16. Set the TEMP, PURGE I, REACTION and PURGE II sliders to 900, 30, 10 and 40, respectively. The temperature is ready when the TEMP indicator light comes on (about 5 minutes).

NOTE: See Figure 7 for all recorder buttons.

17. Turn on the recorder and check that the Range and Chart Speed are set to 10 mV and 10 mm/minutes, respectively.
 - a. The Range is adjusted by pushing the RNGE button.
 - b. The Chart Speed is adjusted by pushing the SPD button.
18. To Start or Stop recording data, push the RUN or STOP and PEN LIFT buttons.
19. To zero the pen on the chart paper, push and hold the ZERO ADJ button and turn the zero adjust knob.
20. Fill the reductant reservoir bottle to the shoulder with 1% NaBH₄ in 0.01 M NaOH. Screw the bottle into the fitting on the analyzer assembly (see Figure 6).

NOTE: ALWAYS zero the absorbance reading by pushing the AZ button BEFORE attaching the reaction flask onto the flange on the analyzer assembly.

21. Push the AZ button on the spectrophotometer (see Figure 2) to zero the absorbance reading, if necessary.
22. Place an empty reaction flask onto the flange on the analyzer assembly and push the START button on the controller.
23. Remove and empty (in the NaBH₄ waste bottle) the reaction flask from the flange after the START light goes out.
24. Repeat Steps 21-23 three times.

NOTE: Periodically check the lamp watts and adjust, if necessary.

NOTE: VERY IMPORTANT. ICP results for the samples MUST be checked for the presence of interfering elements. If none are present, proceed with Section III. If ANY interfering elements are present, skip to Section IV.

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PROCEDURE (continued)

III. Preparation of Standards and Samples Not Requiring Ion Exchange

NOTE: It is absolutely essential to use scrupulously clean glassware and reaction equipment to ensure valid analyses.

NOTE: There are specifically labelled reaction flasks to be used only for the selenium calibration solutions.

1. Prepare the calibration solutions by dispensing 10 ml of 6 M HCl, 1 ml of 6 M HNO₃ and 1 ml of 1 M HSO₃NH₂ and pipetting the appropriate number of microliters (0, 25, 50 or 75) of the calibration standard into the corresponding reaction flask.
2. Prepare the sample and LMCS standard solutions according to the following.
 - a. Label duplicate reaction flasks with the sample number. Mark one of the flasks with an X to indicate that the sample is spiked.
 - b. Dispense 10 ml of 6 M HCl, 1 ml of 6 M HNO₃ and 1 ml of 1 M HSO₃NH₂ and pipet an aliquot of the sample into the appropriate flask. The sample size is selected to give a result within the range of concentrations of the calibration curve. When no estimate of sample concentration is available, use 100 microliters.

NOTE: Never use more than 100 microliters of sample without first consulting the responsible scientist.

- c. Add 25 microliters of the Se calibration standard to the reaction flasks marked with an X.
- d. Go to the Analysis section.

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PROCEDURE (continued)

IV. Preparation of Standards and Samples Requiring Ion Exchange

NOTE: When ion exchange is required all calibration standards, LMCS standards and samples must be treated the same.

NOTE: It is absolutely essential to use scrupulously clean glassware and reaction equipment to ensure valid analyses.

1. Prepare the calibration solutions according to the following.
 - a. Label duplicate filter apparatus and 15 and 30 ml beakers with the volume of Se to be added, 0, 25, 50 or 75 microliters.
 - b. Add 10 ml of 0.1 M acetate buffer to a 15 ml labelled disposable beaker then pipet in the appropriate number of microliters of the calibration standard.
 2. Prepare the sample and LMCS standard solutions according to the following.
 - a. Label duplicate filter apparatus and 15 and 30 ml beakers with the sample number. Mark one set with an X to indicate that the sample is spiked.
 - b. Add 10 ml of 0.1 M acetate buffer to a 15 ml labelled disposable beaker then pipet in an aliquot of the sample. The sample size is selected to give a result within the range of concentrations of the calibration curve. When no estimate of the sample concentration is available, use 100 microliters.
- NOTE: Never use more than 100 microliters of sample without first consulting the responsible scientist.
- c. Add 25 microliters of the Se calibration standard to the beakers marked with an X.
 3. Weigh approximately 13 g of Chelex 100 into a 30 ml labelled plastic disposable beaker, add the above sample, swirl and let sit for 30 minutes.
 4. Stir the slurry with a glass rod and pour into a filter apparatus.
 5. Rinse off the glass rod with 0.1 M acetate buffer (from the squirt bottle) into the 30 ml beaker.
 6. Apply vacuum to remove 3-4 ml of liquid off the Chelex. DO NOT LET THE CHELEX GO DRY.

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PROCEDURE (continued)

IV. Preparation of Standards and Samples Requiring Ion Exchange (continued)

7. Add 5 ml of 0.1 M acetate buffer to the 30 ml beaker, swirl and add to the filter unit.
8. Let sit for 5 minutes and vacuum dry. The final volume should be about 15 ml.
9. Dispense 10 ml of 6 M HCl, 1 ml of 6 M HNO₃ and 1 ml of 1 M HSO₃NH₂ into a clean reaction flask, add the above filtered solution and go to the Analysis section.

V. Analysis

All standards and samples are to be treated the same.

1. WITH THE REACTION FLASK OFF:

- a. Adjust the lamp energy to 69-70, if necessary, and zero the absorbance reading.

2. Attach a reaction flask containing the blank and push the START button on the controller.
3. Label the chart paper with the information requested on the list on the recorder.

NOTE: Use a metric ruler with mm graduations to measure the peak height. Measure the difference between the baseline just before the peak and the peak maxima. Measure to the nearest 1/2 mm.

4. Check the absorbance reading on the chart paper. The blank must not give a signal higher than 3 mm. Higher blank values indicate contaminated chemicals (water, acids, NaBH₄) or a contaminated flask or dirty cell and windows.

NOTE: Dispose of sample and rinse waste into the appropriately labelled bottle.

5. Remove the reaction flask after the START light goes out, rinse the dispenser tip with 6 M HNO₃ then deionized water and wipe with a Kimwipe.
6. Rinse the reaction flask thoroughly with 6 M HNO₃ and deionized water.
7. Repeat Step 1.

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PROCEDURE (continued)

V. Analysis (continued)

8. Attach a reaction flask containing a 50 ng calibration standard and push the START button on the controller.
9. Label the chart paper.
10. Check the absorbance reading on the chart paper. You must get a minimum signal as posted on the instrument. If not, contact the responsible scientist.
11. Repeat Steps 5-7.
12. If the initial checks prove satisfactory, then repeat the above process for the rest of the calibration standards, LMCS standards and samples.

VI. Instrument Shutdown

1. Turn off the recorder power. Remove and cap pen.
2. Turn off the power to the spectrometer.
3. Turn the HCL lamp wattage off.
4. Remove the reduction (NaBH_4) bottle and replace it with a bottle containing deionized water.

NOTE: Dispose of NaBH_4 waste in the NaBH_4 waste bottle ONLY.

5. Place an empty reaction flask on the analyzer assembly.
6. Rinse the reductant out of the transfer lines by setting both PURGE I and II to their minimum values and REACTION to its maximum then go through the REACTION cycle 3-5 times.
7. Close the valve on the nitrogen regulator.
8. Set PURGE I to its maximum value and REACTION and PURGE II to their minimums then go through the REACTION cycle until the START light blinks (until the N_2 pressure is zero).
9. Turn off the controller.
10. Clean up the work area.

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PROCEDURE (continued)

VII. Calculations

1. Plot the absorbance (peak height in mm from the strip chart) versus the ng (number of microliters) of standard added.
2. Draw a best fit straight line through the points using a ruler and check the linearity. Notify the responsible scientist if the data is not linear.
3. Calculate the arsenic concentrations using the HP-97 calculator and the Curve Fit program as follows:
 - a. Load side 1 and 2 of the Curve Fit program card.
 - b. Press f(A) then press f(B).
 - c. Press DSP then press 4.
 - d. Enter the ng of Se and push ENTER.
 - e. Enter the absorbance (mm) and push A.
 - f. Repeat steps d and e for each standard.
 - g. Push C to compute r^2 , slope and intercept.
 - h. Enter the sample absorbance (mm) and push D to calculate the ng of Se in the sample.
 - i. Calculate the sample concentration in parts per billion (ppb) by dividing the value obtained in step g by the sample aliquot volume (in ml). See No. 2 on the next page.
 - j. Enter the sample + spike absorbance (mm) and push D to calculate the ng of Se.
 - k. Calculate the spike recovery as shown in No. 3 on the next page.
 - l. Repeat steps h and k for all samples and enter the information on the sample cards.
 - m. Turn in the sample cards and pat yourself on the back.

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PROCEDURE (continued)

VII. Calculations (continued)

EXAMPLE

1. Sample Analysis

A sample was received for analysis. A 0.1 ml (100 microliters) aliquot was taken into the procedure with a resulting absorbance of 24.0 mm. Likewise, a 0.1 mL aliquot was spiked with 25 microliters of 1000 ng/mL (1 ppm) selenium standard; the resulting absorbance was 43.5 mm. The calibration standards were measured.

Calibration Data:

Blank (0.0 ng)	:	0.0 mm
25.0 ng	:	20.0
50.0 ng	:	40.0
75.0 ng	:	60.0

From the calibration data, one finds that the sample absorbance corresponds to 30.0 ng selenium and the Sample-plus-spike corresponds to 54.4 ng.

2. Calculation of original Sample Concentration (ppb)

$$\begin{aligned}\text{ppb} &= (\text{ng Se in sample aliquot})/(\text{mL sample aliquot}) \\ &= (30.0 \text{ ng})/(0.1 \text{ mL}) = 300 \text{ ppb}.\end{aligned}$$

3. Calculation of Spike recovery

Spike recovery =

$$\frac{(\text{ng sample} + \text{spike}) - (\text{ng sample})}{(\text{ng spike})} \times 100\% =$$

$$\frac{(54.4 \text{ ng} - 30.0 \text{ ng})}{(25.0 \text{ ng})} \times 100\% = 97.6\%$$

Acceptable spike recoveries are:

- a. Without ion exchange - 85 - 115 %,
- b. with ion exchange - 75 - 125 %.

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PROCEDURE (continued)

VII. Calculations (continued)

4. Alternative concentration units:

To convert from ppb to ppm: $\text{ppm} = \text{ppb}/1000$

To convert from ppb to g/L: $\text{g/L} = \text{ppb}/1000000$

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DISCUSSION

Sodium borohydride (NaBH_4) is used as the reductant for the determination of metallic hydride-forming elements and may also be used with advantage for the determination of mercury. Sodium borohydride liberates hydrogen on contact with acids. The reaction mechanisms involved in the reduction of metal ions are complicated and almost certainly take place via the formation of intermediate radicals. The following equations represent simplifications of the reduction processes.

M is a metallic element that forms a volatile hydride (e.g. As, Bi, Sb, Se, Te, etc.)

For determining metallic elements that form volatile hydrides, the sample solution is first treated so that the metal under study is present in ionic form in acid solution. Reductant is dispensed into the sample solution where it reacts to liberate hydrogen. The metal ions are reduced to the volatile hydride. The nitrogen stream flushes the hydride into the heated quartz cell where it is decomposed and the absorption of the metal measured. The cell is heated to between 900°C and 1000°C .

The detection limits attainable with the MHS-20 are often a function of the level of contamination rather than instrument capability. When working at the ppb levels, contamination is usually the major source of error. Careful handling of the apparatus and careful technique will minimize this problem. The following precautions help to avoid sample contamination:

1. Use only deionized water.
2. Collect all samples in Teflon or polyethylene containers that have been thoroughly rinsed with 6 M HNO_3 .
3. Use only reagents found to be free of mercury, arsenic and selenium. Measure blanks before analyzing samples.
4. All glassware and apparatus must be scrupulously clean.

The hydride apparatus performs an analysis of ng levels of selenium. Total sample volumes of up to 50 ml can be accommodated to provide greater sensitivity. In practice, however, interference levels, radiation levels in some samples (including waste tank) and amount of sample available limits the sample size substantially.

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DISCUSSION (continued)

Application of hydride generation spectroscopic techniques have been reviewed⁽⁴⁾. All hydride methods are subject to interferences caused by the presence of electropositive ions. One mechanism for this interference is the reduction of these ions to finely divided metal particulates which absorb or interact with the hydride vapors and cause low results. The removal of these ions from solution by ion exchange before analysis eliminates or reduces the interference.

REFERENCES

1. LA-505-124, "Application of the Method of Standard Additions to Atomic Absorption."
2. Operators Manual, Perkin-Elmer Model 2280 Atomic Absorption Spectrometer.
3. Operators Manual, MHS-20 Mercury/Hydride System.
4. T. Nahahara, "Applications of Hydride Generation Techniques in Atomic Absorption, Atomic Fluorescence, and Plasma Atomic Emission Spectroscopy," Progress Analytical Atomic Spectroscopy, Vol. 6, pp. 163-223, 1983.

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Figure 1. Left Front Control Panel

- 1 SLIT Width Selector
- 2 BKGD CORReCTOR Switch
- 3 Optics Compartment Access Screw
- 4 BKGD CORR INTENSITY Control
- 5 WAVELENGTH ADJUST Control
- 6 WAVELENGTH Counter

Figure 2. Right Front Control Panel

1	Digital Display and Indicators	13	PRNT (Print) Key and Signal Dot
2	AZ (Auto Zero) Key and Signal Dot	14	Numerical Keyboard
3	S1 Key and Signal Dot	15	CE (Clear Entry) Key
4	S2 Key and Signal Dot	16	Electronics Compartment Access
5	S3 Key and Signal Dot		Screws
6	AVERage Key and Signal Dot	17	SIGNAL Switch
7	CV (Coefficient of Variation)	18	READ Key and Signal Dot
	Key and Signal Dot	19	MODE Switch
8	SD (Standard Deviation) Key and	20	LAMP/ENERGY Display
	Signal Dot	21	RECORDER Switch
9	RSLP (Reslope) Key and Signal Dot	22	GAIN Control
10	t (Time) Key	23	LAMP 1 Control
11	EXPanSion Key and Signal Dot	24	LAMP 2 Control
12	CHK (Check) Key	25	POWER Switch

Figure 3. Universal Lamp Mount

- 1 Filter Attenuator Control
- 2 Alignment Knob
- 3 Spring
- 4 Lamp 1 Connector
- 5 Front Holddown Screw
- 6 Universal Lamp Mount (0057-0271)
- 7 Catch Release
- 8 Lamp Mount Button/Screw

Figure 4. Heating Mantle Assembly with Quartz Cell Installed

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Figure 5. Front Panel of the Controller

Figure 6. Analyzer Assembly

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Figure 7. Recorder Left Front Control Panel

ANALYTICAL LABORATORIES

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Title

ANION ANALYSIS ON DIONEX MODEL 2020i

Author: H. S. Rich 4

SUMMARY

Ion chromatography is used to determine common anions such as chloride, phosphate, nitrate, fluoride, nitrite, and sulfate quantitatively in a single instrumental technique. Anions of interest become separated by a strong basic anion exchanger and are directed to a strongly acidic cation exchanger where they are changed to a high conductive acid form. The anions that are separated in their acid form are changed to a weak acid with eluent and measured by a conductivity cell. This procedure describes the operation and the determination of anions on the Model 2020i Dionex Ion Chromatograph.

LIMITATIONS

Table I lists the anion concentrations used in calibration. Samples that have concentrations greater than the highest calibration standard, must be diluted with E2 eluent. The procedure is designed to give a precision of $\pm 10\%$ for each of the six anions. Samples that contain particles greater than 0.45 microns and reagents that contain particles greater than 0.20 microns require filtration to prevent damage to flow systems and columns. Interfering ions include sulfite, chromate, perchlorate, iodide, iodate, iron, aluminum, zirconium, arsenate, hydroxide, and several organic compounds. Nitrite interferes with system 2 analysis because it has the same retention time as phosphate. Interferences can be caused by substances with retention times that are similar to and overlap those of the anions of interest. Spiking the sample with a known amount of standard can identify the anions of interest thus eliminating any mis-identification of anions.

APPLICATIONS

Anions in waters from cooling basins, boilers, and other sources of demineralized water, industrial waters, and surface waters may be analyzed using this procedure.

When this procedure is used in analyzing unfamiliar samples for any of the anions, anion identification should be supported by the addition of a spike solution containing anions of known concentrations.

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SAFETY

- | The following safety concern is associated with this procedure.
- | Radioactive sample dilutions reading greater than 10 mRAD/hr should not be run on the ion chromatograph without special planning involving appropriate technical and supervisory personnel.

REAGENTS

- | Stock standards are stable for at least one month when stored at 4°C. Dilute working standards should be prepared weekly except those that contain nitrite and phosphate should be prepared fresh daily.

NOTE: It is, at times, desirable to vary the concentration of the eluent (see DISCUSSION for details). Changes in eluent concentration will not be made without first consulting the responsible scientist. Table I (Eluent Dilution Table) gives the dilution codes to be used when making up fresh eluent. These appropriate codes will be recorded in the log book when fresh eluent is made.

SYSTEM 1

- | E2 CONCENTRATE: 0.300 M Sodium Bicarbonate (MSDS #1480) and 0.240 M Sodium Carbonate. (MSDS #1484)

To prepare 0.300 M sodium bicarbonate and 0.240 M sodium carbonate, weigh out 50.40 g of sodium bicarbonate and 50.90 g of sodium carbonate and dissolve in a 2 liter volumetric flask containing 1500 mL of deionized water (high purity : 16 megohm). Bring to a total of 2 liter volume with deionized water. This solution must be stored in a plastic bottle and labeled as E2 Concentrate System 1. E2 Concentrate will be used in the preparation of E2 Eluent. The E2 concentrate will depreciate after two months from the time of preparation.

SYSTEM 1

- | E2 ELUENT: 0.003 M Sodium Bicarbonate and 0.0024 M Sodium Carbonate.
(Nominal Eluent Concentration, see Table II)

To prepare 0.003 M sodium bicarbonate and 0.0024 M sodium carbonate, add 200 mL (Nominal Eluent Concentration, see Table II) of E2 Concentrate to a 20 liter plastic reservoir. Bring solution to a total volume of 20 liters using deionized water (high purity : 16 megohm). Mix the solution on the Ultra-Turrax mixer for 8 - 10 minutes. Measure conductance of previous eluent against conductance of the new eluent using the conductivity meter. The measured conductivity of the new eluent must be within 5 uMHO of the previous eluent. Deionized water used in the preparation of the new eluent will be analyzed as a blank for quantifying any analyte concentration along with the new E2 Eluent prepared. The E2 Eluent will depreciate after two months from the time of preparation.

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SYSTEM 2

| E2 Concentrate: 0.600 M Sodium Carbonate and 0.200 M Sodium Hydroxide
(MSDS #1105)

| To prepare 0.600 M sodium carbonate and 0.200 M sodium hydroxide, dissolve 63.594 g of sodium carbonate and 8.0 g of sodium hydroxide in 500 mL of deionized water (high purity : 16 megohm) in a 1 liter volumetric flask. Bring to a total volume of 1 liter with the deionized water. This solution will be labeled as E2 Concentrate System 2 and will depreciate after two months from the time of preparation.

| E2 Eluent: 0.006 M Sodium Carbonate and 0.002 M Sodium Hydroxide.
(Nominal Eluent Concentration, see Table II)

| To prepare 0.006 M sodium carbonate and 0.002 M sodium hydroxide add 200 mL (Nominal Eluent Concentration, see Table I) of E2 Concentrate system 2 to a 20 liter plastic reservoir. Bring to 20 liters total volume with deionized water (high purity). Store the solution in the 20 liter reservoir labeled E2 Eluent System 2. The E2 Eluent will depreciate after two months from the time of preparation.

Regenerant Solutions:

SYSTEM 1

| Regenerant 1: 0.0125 M Sulfuric Acid (MSDS #1529)

| To prepare a 0.0125 M sulfuric acid for System 1, add 1 liter of 0.25 M sulfuric acid (prepared by Data Measurements and Control Section and stored in a 1 liter plastic bottle) to 19 liters of deionized water. Mix on the Ultra-Turrax for 8 - 10 minutes. Replenish the regenerant reservoir with this solution labeled 0.0125 M Sulfuric Acid System 1. The expiration date should be approximately two months.

SYSTEM 2

| Regenerant 2: 0.025 M Sulfuric Acid

| To prepare a 0.025 M sulfuric acid for System 2, add 1 liter of 0.25 M sulfuric acid (prepared by Data Measurements and Control Section and stored in a 1 liter plastic bottle) to 9 liters of deionized water. Mix on the Ultra-Turrax for 8 - 10 minutes. Replenish the regenerant reservoir with this solution labeled 0.025 M Sulfuric Acid System 2. The expiration date should be approximately two months.

COMPRESSED GAS:

Purified nitrogen (MSDS #1390) for both systems 1 and 2.

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CALIBRATION STOCK STANDARD SOLUTIONS:

NOTE: Good for one month. Store each solution separately in polyethylene bottle. Dry all powder chemicals overnight in 100-110 °C drying oven. High Purity reagents to be used are "Baker Analyzed".

| Chloride (Cl) 10,000 mg/L: (MSDS #1485)

Dissolve 0.6485 g of sodium chloride (NaCl) in Q-water in a 100 mL calibrated volumetric flask and stir at least 2 - 5 minutes. Dilute to 100 mL with Q-water.

| Phosphate (PO₄) 10,000 mg/L: (MSDS #2286)

Dissolve 0.7165 g potassium phosphate (KH₂PO₄) in Q-water in a 50 mL calibrated volumetric flask and stir at least 2 - 5 minutes. Dilute to 50 mL with Q-water.

| Nitrate (NO₃) 10,000 mg/L: (MSDS #1506) .

Dissolve 0.3427 g sodium nitrate (NaNO₃) in Q-water in a 25 mL calibrated volumetric flask and stir at least 2 - 5 minutes. Dilute 25 mL with Q-water.

| Sulfate (SO₄) 10,000 mg/L: (MSDS #1844)

Dissolve 0.4535 g potassium sulfate (K₂SO₄) in Q-water in a 25 mL calibrated volumetric flask and stir at least 2 - 5 minutes. Dilute 25 mL with Q-water.

| Fluoride (F) 10,000 mg/L: (MSDS #1491)

Dissolve 0.5525 g sodium fluoride (NaF) in Q-water in a 25 mL calibrated volumetric flask and stir at least 2 - 5 minutes. Dilute 25 mL with Q-water.

| Nitrite (NO₂) 10,000 mg/L: (MSDS #1495)

Dissolve 0.3749 g sodium nitrite (NaNO₂) in Q-water in a 25 mL calibrated volumetric flask and stir at least 2 - 5 minutes. Dilute 25 mL with Q-water.

CALIBRATION WORKING STANDARDS

NOTE: This standard is prepared by Data Measurements and Control Section with concentrations listed below and stored in a polyethylene bottle. Using the solutions from step 10, dilutings are made as listed using eluent to bring the mark of 100 mL calibrated volumetric flask. The working standard is in a clean matrix.

SOLUTION	CONCENTRATION (ppm)		mL NEEDED/100mL
NaF	(F ⁻)	50	5 mL
NaCl	(Cl ⁻)	60	6 mL
KH ₂ PO ₄	(PO ₄ ⁻)	500	5 mL
NaNO ₃	(NO ₃ ⁻)	500	5 mL
Na ₂ SO ₄	(SO ₄ ⁻²)	500	5 mL
NaNO ₂	(NO ₂ ⁻)	500	5 mL

NOTE: Nitrite is not included in the calibration standard for Dionex 2020i system 2.

EQUIPMENT

| Dionex Ion Chromatograph, Model 2020i; with two independent systems equipped with conductivity cells for detection, two pre-columns, two separator columns and two membrane suppressors.

Hewlett-Packard, 3390-A Integrators for systems 1 and 2.

| Milton-Roy pump for system 1.

Ultra-Turrax mixer; Janke and Kunkel.

Vials, polyethylene, 22 mL size, with screw caps, stock room part #57-9000-025.

Syringes, plastic disposable, 5 cc. and 10 cc, Luer-lok tip.

Dispenser, 1 liter with 10 mL dispensette.

Eppendorf pipets, sizes: 10/25/50/75 through 1000 uL with appropriate tips.

Carboys-plastic reservoirs with attached spigots. Two 20 liter sizes for eluent storage, and one 10 liter and one 20 liter size for regenerant reservoir.

Glass bottles 1 gallon size for waste effluent.

PROCEDURE

NOTE: The Dionex Model 2020i consists of two systems, each containing a pump, eluent, an injector, columns, a membrane suppressor, a detector and an integrator. (See Figures III to VII.) Each component is labeled as either "System 1" or "System 2". System 1 is set up for analysis of chloride, phosphate, nitrate, and sulfate. System 2 is set up for samples high in nitrate. The eluent complexed with regenerant screens out the nitrate concentration and permits the other anions to be examined without difficulty.

1. Determine use of systems 1 or 2.
2. Check to see if eluent reservoirs are full. If half full or less, fill with more eluent according to directions in Appendix I and Figure I.
3. Empty waste bottles.
4. For system 1 turn on gas (80 - 85 psi) and the Milton-Roy pump, located on the utility bench set, at the position of 70% maximum capacity (controls regenerant flow for system 1). For system 2, turn on gas only (regenerant is air pressure fed at 80 - 85 psi).
5. Turn on the power. See Figure III.
6. Turn off conductivity cells (systems 1 and 2). See Figure VI.
7. Select eluent 1 on pump-system 1. Select eluent 2 on pump-system 2. See Figure IV.
8. Check flows to see that they are set at 2.0 mL/min^{-1} and 2.5 mL/min^{-1} for systems 1 and 2 respectively. See Figure IV.
9. Set local/remote to local for the respective systems. See Figure V.
10. Press start on module 1 and/or 2. See Figure IV.
11. If system 2 is being operated, press B in the hood where the advanced chromatography module is located. See Figure VI.
12. When the ready light comes on and the pressure is stable at ± 10 psi (approximately 45 minutes), the instrument has equilibrated. If there is a pressure problem (i.e., pressure exceeds 1900, system 1 or 1000, system 2), turn the instrument off and contact the chemist in charge. See Figure IV.
13. Turn on the conductivity cell(s). See Figure V.

PROCEDURE (continued)

14. Set up the HP3390A integrator as follows:

- a. Verify that the green ready light is on. Power should be left on at all times. When power fails the integrator will need to be programmed.
- b. Press "LIST", "METHOD", and "ENTER". The integrator prints the parameters. The correct parameters are posted on the top of the integrator.
- c. Re-enter any parameters not matching those posted on the integrator (Figures II and VI).

1. Press "ZERO" on keyboard, then "0" and "ENTER".
2. Press "ATT^2", then "10" and "ENTER".
3. Press "CHTSP", then "1" and "ENTER" (system 1).
Press "CHTSP", then "0.4" and "ENTER" (system 2).
4. Press "PK WD", then "0.04" and "ENTER" (systems 1 and 2).
5. Press "THRSH", then "7" and "ENTER" (system 1).
Press "THRSH", then "8" and "ENTER" (system 2).
6. Press "AR REJ", then "300000" and "ENTER" (systems 1 and 2).
7. Press "OP()", then "4" and "ENTER" (systems 1 and 2). This changes the response from "NO" to "YES", for peak height mode.
8. Press "OP()", then "1" and "ENTER". The integrator responds with "M-D-Y" and "DATE".

M=Month, D=Day, Y=Year

Press N-month, N-day, N-year, then "ENTER". For example: if the date is March 4, 1987, press "03-04-87" and then press "ENTER".

9. The integrator responds with "H-M-S".

H=Hour, M=Minutes, S=Seconds

Press N-hour, N-minutes-, N-seconds, then "ENTER". For example: if the time is 8:30:40, press "08-30-40" and then "ENTER".

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PROCEDURE (continued)

10. Press "STOP" and "TIME", then the stop times for the respective systems. For example: press "10" after "STOP" and "TIME" for system 1 and "40" after "STOP" and "TIME" for system 2, then press "ENTER". For system 2, press "INTG#" and "6.0"; then "ENTER". This directs the integrator to initiate an integration at 6.0 minutes.
11. Press "LIST", "METHOD", and then "ENTER". Compare parameters with those listed on the integrator.
15. Turn on the auto offset on the detector module and observe the conductivity. If the value drifts from 0.00 to 0.10, then wait 5 minutes. Turn off auto offset.
16. Turn on the auto offset, and if the value doesn't drift, then proceed to step 17. Repeat step 15 again if the value drifts.
17. Verify settings on each module (Figure III, IV, V, and VI).
 - a. ANALYTICAL PUMP and CONDUCTIVITY DETECTOR C "ENTER"

1. SYSTEM 1	SETTING
LOCAL/REMOTE	LOCAL
CELL	ON
AUTO OFFSET	ON
OUTPUT RANGE	10 uS
TEMPERATURE COMPENSATION	1.7
FLOW	2 mL/min
PRESSURE LIMITS SELECT	19 x 100 psi
2. SYSTEM 2	SETTING
LOCAL/REMOTE	LOCAL
CELL	ON
AUTO OFFSET	ON
OUTPUT RANGE	10 uS
TEMPERATURE COMPENSATION	1.7
FLOW	2.5 mL/min
PRESSURE LIMITS SELECT	19 x 100 psi

PROCEDURE (continued)

b. ADVANCED CHROMATOGRAPHY

1. SYSTEM 1	SETTING
LOCAL/REMOTE	LOCAL
LOAD/INJECT	LOAD
A OFF/B OFF	A OFF/B OFF
2. SYSTEM 2	SETTING
LOCAL/REMOTE	LOCAL
LOAD/INJECT	LOAD
A OFF/B OFF	A OFF/B ON

18. Prepare to run: calibration standards (when calibrating the instrument), LMCS standards, QC standards, and samples. Make the necessary dilutions using Eppendorf pipets into 10 mL of E2 eluent and mix thoroughly. Highly radioactive samples must be treated according to the safety section of this procedure.
19. Fill a 5 cc(mL) syringe with 4 cc of sample and place the syringe such that it locks into the Luer adapter (sample port) with a small turn of the syringe.
20. Load the sample/standard into the sample port while the instrument is in the load mode, completely filling the sample loop. Since the sample loop holds only 50 uL, excess sample is shunted to waste. At the end of the day, deionized water may be loaded into the instrument to reduce the radioactivity accumulated during sample analyses.
21. After the sample/standards have been loaded and the auto offset is ON (conductance is 0.0), press the LOAD/INJECT mode into the INJECT setting on the advanced module and the START button on the 3390 A integrator simultaneously for the respective system in operation.
22. After the final peak has eluted and the integrator tick mark has occurred, the STOP button on the integrator may be pressed. (See Figures VII and VIII).
23. Repeat steps 18 through 22 for each new sample or standard.
24. Record in the Dionex 2020i log books, located in the laboratory, the number of the calibration used in the sample analyses, the serial number of the LMCS standard used for verification of the calibration, and percent recoveries for LMCS.

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CALIBRATION AND STANDARDIZATION

NOTE: Only the responsible scientist or a qualified technologist fully familiar with the calibration procedure will calibrate the instrument. A new calibration is required when one of the following is changed:

- 1) Pre-column or guard column
- 2) Separator column
- 3) Eluent

A. SYSTEM 1

1. Prepare a series of calibration dilutions using the mixed calibration standard prepared by Data Measurements and Control Section. Dispense 10 mL of E2 eluent system 1 into four (22 mL) polyethylene vials. To the successive vials add 25, 50, 150, 250, 350 uL of the mixed anion calibration standard. For the 350 uL dilution, fluoride and sulfate peak heights are not to be entered into the M600 computer. Mix dilutions thoroughly.

B. SYSTEM 2

1. Prepare a series of calibration dilutions using the mixed calibration standard prepared by Data Measurements and Control Section. Dispense 10 mL of E2 eluent system 2 into four (22 mL) plastic vials. To the successive vials add 100, 200, 300, 500, and 750 uL of the mixed anion calibration standard. Mix dilutions thoroughly.

C. SYSTEMS 1 & 2

1. Record peak heights and retention times for all the anions in the log book. Also record the % recoveries on the LMCS standards. LMCS standards will be analyzed prior to and following all sample runs and must fall within the 100 +/-10% control limits.

REFERENCES

1. Dionex 2020i Operator's Manual, Dionex Corporation, Sunnyvale, CA 1983.
2. Dionex Basic Ion Chromatography Training Course Manual, Dionex Corporation, Sunnyvale, CA 1983.
3. Greenberg, A., Trussell, R., and Clesceri, L. 1985. 429- Determination of Anions by Ion Chromatography with Conductivity Measurement. 483-487, Standard Methods- for the Examination of Water and Waste Water.
4. O'Dell, J., Pfaff, J., Gales, M., and McKee, G. Jan. 1984. Test Method- The Determination of Inorganic Anions in Water by Ion Chromatography Method 300.0. 300.0.1 - 300.0.5, Research and Development E.P.A.

APPENDIX I

COLLAPSIBLE PLASTIC RESERVOIR

Assembly of the reservoirs is shown in Figure I

1. Shut off faucet to stop liquid flow of the eluent reservoir to be replenished.
2. Remove the reservoir from the eluent rack with the faucet still attached.
3. Unscrew the faucet from the reservoir and fill to the top with the appropriate eluent.
4. Expel the air from the reservoir by pressing on the sides of the reservoir until most or all of the air has been released and the liquid appears at the top. Turn the reservoir up side down allowing air bubbles to move away from the faucet.
5. Place the faucet, still in the closed position, on the reservoir and tighten.
6. Place the reservoir in the eluent rack at the top of the instrument and turn the shut off valve to the open position so that the liquid may return to the instrument.

FIGURE I

FIGURE II

HEWLETT PACKARD 3390-A INTEGRATOR

System 1

RUN PRMTRS

ZERO = 0
 ATT2^ = 10
 CHT SP = 1.0
 PK WD = 0.04
 THRSH = 7
 AR REJ = 300000

RPRT OPTNS

2. RF UNC PKS = 0.0000E+00
 3. MUL FACTOR = 1.0000E+00
 4. PK HEIGHT MODE YES
 5. EXTEND RT NO
 6. RPRT UNC PKS NO

TIME TBL

10.00 STOP

CALIB TBL

EMPTY

System 2

RUN PRMTRS

ZERO = 0
 ATT 2^ = 10
 CHT SP = 0.4
 PK WD = 0.04
 THRSH = 8
 AR REJ = 300000

RPRT OPTNS

2. RF UNC PKS = 0.0000E+00
 3. MUL FACTOR = 1.0000E+00
 4. PK HEIGHT MODE YES
 5. EXTEND RT NO
 6. RPRT UNC PKS NO

TIME TBL

6.00 INTG # = 6
 40.0 STOP

CALIB TBL

EMPTY

TABLE I
ELUENT DILUTION TABLE

<u>Dilution Code</u>	<u>Vol. of Conc. Eluent (mL)</u>	<u>Total Vol. (L)</u>
A	220	20
B	210	20
C	200	20
D	190	20
E	180	20
F	170	20
G	160	20
H	150	20

FIGURE III

FIGURE IV

FIGURE V

CONDUCTIVITY DETECTOR

FIGURE VI

ADVANCED CHROMATOGRAPHY MODULE

FIGURE VII

3390 A INTEGRATOR

ANALYTICAL LABORATORIES

Issued By: T. A. Lane

Manager,
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Author: R. L. Wilson

Title
SAMPLE PREPARATION FOR X-RAY FLUORESCENCE

SUMMARY

This procedure covers the steps necessary for routine sample preparation for qualitative and semi-quantitative x-ray fluorescence analysis of solid samples. This procedure is to be used in conjunction with LA-507-131.

LIMITATIONS

This procedure is limited to solid samples. Personnel exposure will be the limiting factor for highly radioactive samples. All mounted samples must be nonsmearable.

APPLICATIONS

This procedure applies to solid samples, both radioactive and nonradioactive.

SAFETY

The provisions of "General Regulations and Practices for Radiation Work," RHO-GM-MA-2, Volume 6, Book 1, Standard Requirements and Procedures Section 61-02.5, and Radiation Work Permits SL-3 and SL-6 found in RHO-MA-172 apply to all work performed under this procedure and must be followed at all times.

EQUIPMENT

1. X-ray sample cups.
2. Krylon.
3. Mylar film.
4. Kapton film.
5. Polypropylene film.
6. Microporous film.
7. Boron carbide mortar and pestle.

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PROCEDURE STEPS

1. Poke a vent hole in the top of the sample cup.
2. Attach one piece of Kapton film onto the sample cup using the narrow ring.
3. If the sample is not a fine powder, then grind it in the boron carbide mortar and pestle.
4. Put about 1-2 mg of the sample onto the Kapton film.
5. Put 100 microliters of Krylon onto the sample.
6. With a small stir rod or similar device, smear the solid/liquid mixture around on the Kapton until you get a SMOOTH, THIN layer that completely covers the Kapton.
7. Let the smear air dry.
8. Cover the dry smear with a piece of Kapton, attaching with the wide ring.

NOTE: Typically, Kapton will be used to wrap samples. However, there are times when Mylar or polypropylene may be used, depending on the particular sample. The responsible scientist will decide which film is appropriate for a given situation.

9. For radioactive samples, you MUST perform the following additional six steps.
10. With 1/2 inch white tape, tape around the side of the sample cup.
11. Smear the sample cup to make sure it is nonsmearable.
12. If any smearable contamination is found, wipe the holder thoroughly with a Kimwipe dampened with ethanol.
13. "Bag" the sample cup up in a piece of the 6" Mylar.
14. Smear the "bagged" sample to make sure it is nonsmearable.
15. If the "bagged" sample has any smearable contamination, remove the Mylar bag and repeat Steps 11 - 14.

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DISCUSSION

Care must be taken when mounting samples for x-ray fluorescence analysis. The intensity of the x-rays that the detector will see depends not only on the concentration of a particular element in the sample but also on the area, thickness and particle size distribution of the sample. Thus, we want to be consistent in the way that each sample is mounted. Each sample must be a fine powder, about 1-2 mg, spread smoothly and thinly over the complete sample mount area.

REFERENCES

A. Procedures.

1. LA-507-131, "Qualitative Elemental Analysis Using the RigaKu S/Max."
2. LO-150-011, "Safe Operation of the X-Ray Laboratories."

B. Source Document.

Wilson, R. L., personal communication.

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ANALYTICAL LABORATORIES

Issued By:

T. A. Lane

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Author: R. L. Wilson

Title

OPERATION OF THE LINK XR300 FOR QUANTITATIVE
X-RAY FLUORESCENCE ANALYSIS

SUMMARY

This procedure covers the steps necessary for running a routine quantitative method on the Link XR300 energy dispersive x-ray fluorescence instrument.

LIMITATIONS

This procedure is limited to "quantitative methods" currently stored in the XR300 computer.

This procedure covers solid samples only. Liquids cannot be analyzed under vacuum.

Personnel exposure will be a limiting factor for highly radioactive samples.

All samples must be nonsmearable.

Only those personnel specifically qualified by the x-ray safety officer for operation of the Link XR300 may operate this instrument.

APPLICATIONS

This procedure applies to solid samples, both radioactive and nonradioactive.

This procedure describes the operation of the Link XR300 energy dispersive x-ray fluorescence instrument to obtain quantitative elemental analyses using stored methods. Each method will have a separate set of EDP Codes.

SAFETY

The provisions of "General Regulations and Practices for Radiation Work," RHO-GM-MA-2, Volume 6, Book 1, Standard Requirements and Procedures Section 61-02.5, and Radiation Work Permits SL-3 and SL-6 found in RHO-MA-172 and the Laboratory Operating Procedure LO-150-011 apply to all work performed under this procedure and must be followed at all times.

EQUIPMENT

Link XR300 spectrometer

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PROCEDURE STEPS

1. Open the sample chamber lid.
2. Check that the appropriate collimator is in place as posted on the instrument.
3. Load the standards and/or samples in the 16 position sample holder.
4. Close the lid.
5. Open the shutter.
6. Insert the XR300 key and turn it to the "x-rays on" position.
7. Start the vacuum.
8. If the computer hasn't already been booted up, turn on the printer, push CAPS LOCK and CRT buttons, then press AUTO LOAD.
9. Press ON-LINE, FF and then ON-LINE on the printer to advance the paper.
10. Check that the pulse processor range is set at the correct KeV as posted on the instrument.
11. Press the function keys in the following sequence: F8, F1 and then the BLUE key.
12. Select the appropriate method by moving the curser up or down until the method is highlighted.
13. Press the GREEN key.
14. Type in the filename (3 letter group name, date and batch letter - see the example posted on the instrument) and then press the RETURN key.
15. Press F1.
16. Press the DOWN ARROW then the GREEN key.
17. Type in the individual sample names as directed (position number first then the sample name).
18. Press F19.
19. Type in the root name - same as in Step 14.
20. Record the time, method name, root name and operator's name in the x-ray logbook.
21. While the x-rays are on, survey around the sample chamber and record the results in the survey logbook.

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PROCEDURE STEPS (continued)

22. When the analysis is finished, close the shutter, shut off the vacuum and open the sample chamber lid.
23. Remove the standards and/or samples and close the lid.
24. If no more analyses are to be run, turn the "x-rays on" key to the off position, remove and lock in the filing cabinet.
25. Record the time in the x-ray logbook.
26. Press F20, F3 then Y.
27. Shut off the CRT, CAPS LOCK and the printer.

DISCUSSION

This procedure covers the operation of the Link XR300 for routine quantitative analysis of solid samples using methods currently stored in the computer. It does not cover interpretation of the results.

The instrument is calibrated when the method is set-up. A CuO reference standard is always in position number one. It is checked at the beginning of each run and at every 5 sample intervals. Thus the energy and intensity calibration are updated on a regular basis.

An appropriate LMCS Standard must be analyzed with each batch of samples.

REFERENCES

1. Link operation manual.
2. LO-150-011, "Safe Operation of the X-Ray Laboratories."
3. Wilson, R. L., personal communication

ANALYTICAL LABORATORIES

Issued By:

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Title

OPERATION OF THE D/MAX DIFFRACTOMETER

SUMMARY

This procedure covers the steps necessary for start up and shut down of the D/MAX X-Ray Diffractometer, and running samples from the D/MAX controller or DEC 11/23 computer.

LIMITATIONS

Samples emitting alpha or beta radiation at any level will not interfere with the determination. Personnel exposure in this case will be the limiting factor. Gamma radiation may raise the background if it is of sufficient quantity and of a high enough energy. Higher backgrounds will increase the detection limit but otherwise will cause no problems. Personnel exposure may again be the limiting factor for how radioactive samples can be analyzed. Consult the responsible chemist before analyzing any radioactive samples. All radioactive samples MUST be non-smearable. Precision and accuracy are not applicable as this is a qualitative procedure only.

This instrument is to be operated only by qualified x-ray operators. A list of qualified operators is posted on the bulletin board on the west wall of the x-ray lab.

APPLICATIONS

This procedure applies to any solid samples either radioactive (non-smearable) or nonradioactive.

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SAFETY

The following safety precautions will be observed at all times for operation of the D/MAX x-ray diffractometer:

1. Keep the keys to the D/MAX locked in the file cabinet when the instrument is not in use.
2. Keep the safety shield doors closed at all times unless a sample is being loaded or unloaded.
3. Always check the position of the x-ray shutter before opening the doors. It should be closed except for special operations (e.g., surveying and aligning).
4. Survey inside the safety shield once each day of operation with the x-rays at normal operating power and with the shutter open.

Follow Laboratory Operating Procedure LO-150-011, "Safe Operation of the X-Ray Laboratories". The provisions of General Regulations and Practices for Radiation Work found in RHO-GM-MA-2, Volume 6, Book 1, Standard Requirements and Procedures, Section 61-02.5 and Radiation Work Permits SL-6 and SL-3 found in RHO-MA-172 apply to all work performed under this procedure and must be followed at all times.

PROCEDURE STEPS

I. STARTUP

1. If the OPERATE light on the front of the D/MAX is not on, contact the responsible chemist, otherwise continue. (See Figure 1a.)
2. Turn on the main power switch on the front of the D/MAX heat exchanger.
3. If both heat exchanger pump lights are not on, stop and contact the responsible chemist.
4. If any ALARM lights are on, stop and contact the responsible chemist. (See Figure 1b.)
5. Turn on the BUZZER switch located inside the right front panel of the D/MAX.
6. Open the front safety shield door.
7. Turn on the fluorescent light inside the enclosure.
8. Close all safety shield doors.
9. Insert the key into the lock labeled SESAME and open SESAME. (See Figure 1a.)

PROCEDURE STEPS (continued)

10. If the X-RAY READY light is not on, stop and contact the responsible chemist.
11. Open and close one of the radiation shield doors and watch the X-RAY READY light.
12. If the X-RAY READY light does not go off and on, stop and contact the responsible chemist.
13. Press the X-RAY ON button to turn on the x-rays. (See Figure 1b.)
14. Record the time, hour meter reading and your initials in the X-RAY LOG BOOK.

VERY IMPORTANT!

CAUTION: WHENEVER CHANGING THE CURRENT AND VOLTAGE, ALWAYS ALTERNATE BACK AND FORTH BETWEEN THE CURRENT AND VOLTAGE CONTROL KNOBS, AS DIRECTED IN STEPS 15-21. NEVER TURN ONE KNOB ALL THE WAY TO ITS OPERATING VALUE WITHOUT MOVING THE OTHER KNOB.

15. Increase the x-ray power to 50KV and 150mA, as follows. (See Figure 1c.)

VERY IMPORTANT!

CAUTION: In the following, wait 1/2-1 minute between EACH change in voltage and/or current.

CAUTION: Watch the vacuum gauge CAREFULLY while changing the kV and mA. If you see ANY fluctuations, keep the D/MAX AS IS and contact the responsible chemist. Do not increase the kV or mA.

Watch the mA meter as you increase the current to be sure that it is increasing with each step. If it does not increase, contact the responsible chemist.

16. Increase the voltage to 30 kV.
17. Increase the current in 10 mA steps (waiting 1/2 - 1 min. between steps) to 50 mA.
18. Increase the voltage to 40 kV.
19. Increase the current in 10 mA steps (waiting 1/2 - 1 min. between steps) to 100 mA.
20. Increase the voltage to 50 kV.

PROCEDURE STEPS (continued)

21. Increase the current in 10 mA steps (waiting 1/2 - 1 min. between steps) to 150 mA.
22. Insert the FS RELEASE key into the lock. (See Figure 1a.)

VERY IMPORTANT!

WARNING: ALWAYS CHECK THE STATUS OF THE SHUTTER BEFORE OPENING THE SAFETY SHIELD DOORS. IF THE SHUTTER LIGHT IS ON, THE SHUTTER IS OPEN.

23. Check the SHUTTER to make sure it is closed. (See Figure 1a.)
24. Perform the safety checks in Steps 25 to 50 each day the DMAX is to be used.
25. Release the safety shield doors with the FS RELEASE key.
26. Open the front safety shield door.
27. Survey around the shutter with a GM.
28. If any counts above background are detected, stop and contact the responsible chemist.
29. Record the survey result in the X-RAY SURVEY LOG BOOK.

VERY IMPORTANT!

WARNING: DO NOT CLOSE THE DOOR PAST THE MARKS ON THE SIDE OR ELSE THE X-RAYS WILL BE SHUT OFF. SHUTTING THE X-RAYS OFF IN THIS MANNER COULD DAMAGE THE INSTRUMENT.

30. Remove the sample compartment cover.
31. CAREFULLY close the safety shield door.
32. If the FS RELEASE light is still blinking, stop and contact the responsible chemist. (See Figure 1a.)
33. Switch the SHUTTER switch to OPEN. (See Figure 1a.)
34. If the shutter light comes on, stop and contact the responsible chemist.
35. Reset the shutter switch to CLOSE.
36. Release the safety shield doors with the FS RELEASE key.

PROCEDURE STEPS (continued)

37. Open the front safety shield door.

VERY IMPORTANT!

WARNING: DO NOT LET ANY PART OF THE BODY GO NEAR THE X-RAY BEAM PATH. ONLY THE SURVEY INSTRUMENT SHOULD COME NEAR ANY PART OF THE X-RAY BEAM PATH.

38. Using the D/MAX controller (figure 2a), press the DATUM key.
39. Press the START key on the controller.
40. Insert a glass slide into the sample holder.
41. Replace the sample compartment cover.
42. Open the x-ray shutter.
43. Survey around the divergence slit with a G.M. and a C.P. and record the results in the survey logbook.
44. Survey around the sample shield with a G.M. and a C.P. and record the results in the survey logbook.
45. CAREFULLY close the safety shield doors and survey around them with a G.M. and record the results in the survey logbook.
46. Close the x-ray shutter.
47. Release the safety shield doors with the FS RELEASE key.
48. Open the front safety shield door.
49. Remove the sample compartment cover.
50. Remove the glass slide from the sample compartment.
- NOTE: If you have a sample ready to run, you may skip to Section II, Step 5.
51. Replace the sample compartment cover.
52. CAREFULLY close the safety shield doors.

PROCEDURE STEPS (continued)

II. AUTOMATED SAMPLE ANALYSIS

1. Make sure the x-ray shutter is closed.
2. Release the safety shield doors with the FS RELEASE key.
3. Open the front safety shield door.
4. Remove the sample compartment cover.
5. Insert the sample to be analyzed.
6. Replace the sample compartment cover.
7. CAREFULLY close the safety shield door.
8. Set the shutter switch to EXT. (See Figure 1a.)

NOTE: The following is an example of the dialog used in running the program DMAX. All items in capital letters are typed by the computer. All underlined items are typed by the operator. <CR> = press the RETURN key.

9. Type RUN DMAX <CR>.
10. The computer now asks for a sample ID.

NOTE: The sample name may contain up to 40 characters and is divided into two parts: the first ten characters should contain the serial number of the sample, and the rest should contain sample analysis information such as voltage, current, and type of mount. Since the terminal stops for operator input on column 24, columns 24 to 33 should contain sample ID, and any additional information should be typed in columns 34 to 63. The current column number is displayed on the terminal.

11. Type in the sample ID, for example:
R0234 50 KV 150 MA glass slide <CR>
12. The terminal will respond with:
· USING SAME CONDITIONS AS LAST TIME (Y/N)?
13. If the conditions will be the same, type Y <CR>.
14. If the conditions will not be the same, skip to Step 30.

NOTE: The terminal will not print out the condition details, an estimated time for the scan, and ask if the entries are correct.

PROCEDURE STEPS (continued)

15. If the conditions are correct, type Y <CR>, if not, go to Step 28.

NOTE: The scan will now start and the printer will print out a filename to which the raw data will be written.

16. Record this file name in the XRD SAMPLE LOG BOOK.

NOTE: When the scan is finished, the computer will close the shutter.

17. When the scan is finished, press the DATUM key on the controller.

18. Press the START key on the controller.

19. Release the safety shield doors with the FS RELEASE key.

20. Open the front safety shield door.

21. Open the sample compartment cover.

22. Remove the sample from the sample compartment.

23. If more samples are to be analyzed, go to Step 5.

24. Once a week perform an alignment and intensity check by running the NBS SRMs 640 and 675 as posted on the LA-120. Enter the two theta values into LMCS.

25. If no more samples are to be analyzed, replace the sample compartment cover.

26. CAREFULLY close the safety shield door.

27. Go to the SHUTDOWN procedure.

28. If the conditions are not correct, type N <CR>.

29. The computer will again ask:

USING SAME CONDITIONS AS LAST TIME (Y/N)?

30. Type N <CR>.

31. The computer will ask:

ENTER STORED PROGRAM NUMBER (1-32):

32. Enter the correct program number. See list attached to the terminal.

33. The computer will again printout the measurement conditions. Go to Step 15.

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PROCEDURE STEPS (continued)

III. SHUTDOWN

VERY IMPORTANT!

CAUTION: WHENEVER CHANGING THE CURRENT AND VOLTAGE ALWAYS ALTERNATE BACK AND FORTH BETWEEN THE CURRENT AND VOLTAGE CONTROL KNOBS, AS DIRECTED IN STEPS 1-7. NEVER TURN ONE KNOB ALL THE WAY TO ITS OPERATING VALUE WITHOUT MOVING THE OTHER KNOB.

1. Slowly lower the KV and mA controls to their lowest values, as follows. (See Figure 1c.)
2. Decrease the current in 10 mA steps (waiting 15-30 seconds between steps) to 100 mA.
3. Decrease the voltage to 40 kV.
4. Decrease the current in 10 mA steps (waiting 15-30 seconds between steps) to 50 mA.
5. Decrease the voltage to 30 kV.
6. Decrease the current in 10 mA steps (waiting 15-30 seconds between steps) to 10 mA.
7. Decrease the voltage to 20 kV.
8. Push the X-RAY OFF button. (See Figure 1b.)
9. Record the time and Hour Meter reading in the X-RAY LOG BOOK.
10. Close SESAME and remove the key. (See Figure 1a.)
11. Remove the FS RELEASE key.
12. Lock the keys in the file cabinet.
13. Open the front safety shield door.
14. Turn off the fluorescent light inside the enclosure.
15. Close the front safety shield door.
16. Allow the instrument to cool down for at least 30 minutes before proceeding.

CAUTION: DAMAGE TO THE ANODE WILL RESULT IF IT IS NOT COOLED DOWN PROPERLY.

17. Turn off the BUZZER switch located inside the front right panel.

PROCEDURE STEPS (continued)

18. Turn off the power switch on the D/MAX heat exchanger.

NOTE: The D/MAX is now in it's normal shutdown mode. the vacuum pumps, however, are still on and some cooling water is still flowing. Only if the electrical power is going to be interrupted, or for some emergency or planned maintenance, do you continue with this procedure to turn the D/MAX all the way off.

NOTE: STOP HERE.

PROCEED ONLY WITH THE PERMISSION OF THE RESPONSIBLE CHEMIST.

19. Turn the VACUUM CONTROLLER knob to STOP. (See Figure 1a.)

20. Allow the D/MAX diffusion pump to cool for A MINIMUM OF TWENTY-FOUR (24) hours.

NOTE: Damage to the diffusion pump will result if it is not cooled down properly.

21. Turn off the cooling water (Neslab Coolflow unit) behind the D/MAX.

22. Shut off the switch labeled BREAKER inside the left front panel of the D/MAX.

REFERENCES

1. LO-150-011, "Safe Operation of the X-Ray Laboratories."
2. LA-507-150, "Startup and Shutdown of the PDP 11/23 Computer in 4-L."

FIGURE 1a
D/MAX Front Panel Controls

FIGURE 1b
D/MAX Front Panel Controls

FIGURE 1c
D/MAX Front Panel Controls

FIGURE 2a
D/MAX Console Controls

PROGRAM NO.	CONDITION NO.	ANGLE/CODE NO.	COUNT

☐ POWER |

☐ OPERATE |

☐ GONIO ERROR |

☐ DATUM |

☐ IATTACH ERROR |

☐ AUX. |

☐ I/O ERROR |

DATUM	PRINT
-------	-------

SLEW	SCAN
RM.	FT

PROG	REPEAT
------	--------

SAMPLE	POLE
CHANG	FIG

START	STOP
-------	------

7	8
4	5
1	2
0	-
19	6
.	CLEAR
ENTER	3

Rockwell Hanford Operations		ANALYTICAL LABORATORIES		
Issued By: A. F. Noonan Manager, Analytical Laboratory Author: S. A. Gower		Title PERCENT WATER IN TANK FARM SAMPLES AND PILOT EVAPORATORY SAMPLES Supercedes: AP-PWTF-01C		
<p><u>SUMMARY</u></p> <p>Percent water in tank farm samples is determined by heating a known weight of sample at 120° C for several hours, cooling the sample to room temperature and finally weighing the sample residue.</p> <p>Water is quantitatively lost from most simple inorganic salts present in tank farm samples. Sodium tetrahydroxyaluminate ($\text{Na}^+, \text{Al}[\text{OH}]_4^-$) loses water to form sodium aluminate ($\text{Na}^+, \text{AlO}_2^-$) below 120° C. (1) Water is lost from $\text{Na}_2\text{CO}_3 \cdot 10\text{H}_2\text{O}$ below 40° C to form anhydrous salts. Sodium phosphate dodecahydrate loses its water of crystallization at 100° C. Sodium nitrate and sodium nitrite do not ordinarily form crystal hydrates. Consequently, the major constituents (2) of tank farm samples dehydrate at the temperature of this determination.</p> <p><u>LIMITATIONS</u></p> <p>This procedure determines the total of all substances volatile at 120° C. Ordinarily, this will be water unless, for example, volatile organics are present. Since the water loss is not instantaneous, sufficient time should be allowed for dehydration to occur (see Discussion section).</p> <p>Sodium hydroxide absorbs water in the presence of moisture in air. The sample should be cooled in the absence of moisture. This can be accomplished with the cap tightly in place during the cooling process.</p> <p>Due to the limited size of the oven, new wet samples should not be placed in the oven with dried samples about to be removed.</p> <p>The sources of error in this method are primarily errors in weighing or in recording the weights. The accuracy of the method is 100.00% with a precision of $\pm 5\%$.</p> <p><u>APPLICATIONS</u></p> <p>This procedures is generally applicable for the determination of percent water in solutions and slurries.</p> <p><u>SAFETY</u></p> <p>Tank Farm samples may be highly radioactive. The provisions of General Regulations and Practices for Radiation Work (GEN-0) and Radiation Work Permit SL-3, found in RHO-MA-172, apply to all work performed under this procedure and must be followed at all times</p>				
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EQUIPMENT

15-mL glass vial (Store Storck 57-0345-015) and cap (56-5350-034).
Analytical balance, five-place; i.e., Mettler H-52
1-mL pipet (Store Stock 57-1730-1000) or transfer pipet (57-1815-100)
Drying oven and thermometer (0 to 150° C)
Marking pen, heat stable ink

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PROCEDURE

NOTE: The balance must be zeroed before each weighing.

1. Label a clean and dry 15-mL glass vial and cap with the analytical number. A felt tip pen can be used provided the ink is stable to 150 C. White tape must be used on the black cap to label.
2. Add a small wad of glass wool (about 0.5 g) to the vial.
3. Weigh the labeled vial and cap. Record the "tare weight", W_1 , on the analytical card.

NOTE: Do not mix caps and vials. The same cap and vial must be used throughout the procedure.

4. Pipet an aliquot of sample, usually one mL, into the tared vial. The volume does not have to be accurately measured and a transfer pipet can be used for samples containing solids. For highly radioactive samples, a smaller volume (400-500 uL) can be used provided weighings are made to five decimal places.
5. Place cap on vial.
6. Check capped vial for smearable contamination. The outside of the vial must be clean and non-smearable to prevent transferring contamination to the balance pan and subsequently to the oven.
7. Weigh the vial plus cap plus sample and record the gross weight, W_2 , on the analytical card.
8. Remove the vial cap.
9. Place cap on top of oven.

NOTE: Long forceps with Tygon tubing over the tips may be used for transferring the vials into or out of the oven.

10. Place sample vial inside oven at 120 C (+/- 3 C) and heat at this temperature for 18 +/- 3 hours.
11. Record time sample is placed in oven on the back of the analysis card.
12. Remove vial from oven using long forceps.
13. Cap vial tightly. Hold vial with long forceps and secure cap tightly to minimize reabsorption of water.

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14. Allow capped vial to cool to room temperature. A minimum cooling time of 15 minutes must be allowed for this step.

NOTE: Be sure to rezero the balance before weighing vial.

15. Weigh the cap plus vial plus cap plus residue and record this weight, W_3 , on the analytical card.
16. Calculate the weight percent water loss according to the Calculations section.
17. Remove cap.
18. Place cap on top of oven.
19. Place vial in oven.
20. Record time vial placed in oven.
21. Heat for at least one hour at 120 ± 3 C.
22. Remove vial from oven.
23. Place cap tightly on vial.
24. Cool for at least 15 minutes.
25. Weigh the vial plus cap and contents. Record the weight, W_4 , on the analytical card.
26. Calculate the difference between W_3 and W_4 according to the Calculation section. If these weights differ by more than $\pm 0.25\%$, repeat steps 16 through 25, until sequential weighings agree.

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Calculations

Sample Weight = $W_2 - W_1$ = Gross Weight - Tare Weight

Weight Loss = $W_2 - W_3$ = Gross Weight - Residue Weight

ZH_2O Weight Loss = $(W_2 - W_3) / W_2 - W_1 * 100.00$

% difference = $[(W_3 - W_4) / W_4] * 100.00$

Example:

22.3651	Tare plus Sample Weight (Gross Weight), W_2
<u>21.1067</u>	Tare Weight, W_1
1.2584	Sample Weight

22.3651	Gross Weight (Tare plus Sample Weight), W_2
<u>21.5995</u>	Residue Weight (Tare plus Residue Weight), W_3
0.7656	Net Residue Weight

ZH_2O Weight Loss = $[(0.7656) / (1.2584)] * 100.00 = 60.839\%$

21.5889 Residue weight after reheating, W_4

% Difference = $[(21.5995 - 21.5889) / 21.5889] * 100.00 = 0.0491\%$

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DISCUSSION

This procedure is straightforward and essentially the sources of error are errors in weighing or in recording the weights.

Any sample ingredient volatile at 120° C will be included in the weight loss.

The minimum time for water loss has not been determined and depends on sample volume and exposed sample surface area. However, the following results have been reported for the method:

<u>TIME</u>	<u>% H₂O FOUND</u>	<u>% RECOVERY</u>
2 Hours	60.84	89.35
	61.13	89.79
	60.97	89.55
	61.25	89.95
	61.00	89.59
18 Hours	68.38	100.42
	68.13	100.06
	68.46	100.54
	68.47	100.55
	68.40	100.45
66 Hours	68.80	101.04
	68.81	101.06
	68.71	100.91
	68.45	100.53
	68.71	100.91

A rush sample analysis requiring a "short" analysis time may be heated for a shorter period of time (4 hours), weighed, reheated for an additional hour, and reweighed. The difference in these sequential weighings should be less than twice the apparent precision of the method (+/- .25%).

REFERENCE

ARH-ST-133, (unclassified), January 1976, G. Scott Barney, "Vapor-Liquid Solid Phase Equilibrium of Radiactive Sodium Salt Wastes at Hanford."

ANALYTICAL LABORATORIES

Issued By:

T. A. Lane

Manager,

Analytical Laboratory

Author: S. P. Juracich

Title

DETERMINATION OF PERCENT WATER BY
THERMOGRAVIMETRIC ANALYSIS

SUMMARY

This procedure is designed to quantitatively determine percent water in a variety of sample types. The samples are heated from ambient temperature to 400°C for determining "free" water to 1000°C for determining "bound" water and the weight loss is recorded by means of a DuPont 1090 Thermal Analyzer and a DuPont 951 Thermogravimetric Analyzer.

LIMITATIONS

The maximum sample size is approximately 350 mg and must not be exceeded because damage to the balance mechanism could result.

No precision and accuracy statements are available at this time.

APPLICATIONS

This procedure is applicable to both liquid and solid tank farm, evaporator, and tank core samples.

SAFETY

The provisions of "General Regulations and Practices for Radiation Work", RHO-GM-MA-2, Volume 6, Book 1, Standard Requirements and Procedures Section 61-02.5, and Radiation Work Permit SL-3 found in RHO-MA-172 apply to all work performed under this procedure and must be followed at all times.

The samples can be very radioactive and frequent monitoring is necessary to prevent contamination of the furnace assembly and hood. Finger rings should be utilized to monitor extremity dose when appropriate. The fan switch should be left on during a run to assure that the outside of the furnace is cooled. The furnace tube should not be removed until the temperature is below 500°C. The furnace tube/sample pans will become extremely hot and will require time for cooling to insure safe handling.

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Expires

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EQUIPMENT

1. DuPont 1090 Thermal Analyzer and DuPont 951 Thermogravimetric Analyzer.
2. Sample pans: Platinum, as received; Quartz, shop made.
3. Microliter pipet, 50 uL Eppendorf.
4. Spatula, stainless steel (#57-7930-006).
5. Tweezers.

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PROCEDURE STEPS

NOTE: Training will be done by authorized chemists only. There will be absolutely no cross training by chemical technologists.

NOTE: Purging of system must be done for all samples. Start purge operation prior to procedure steps.

1. Turn on main supply tank for appropriate purge gas.
 - a. Air for normal samples.
 - b. N₂ for special requests.
2. Check pressure of tank to insure setting is between 10 and 20 PSI.
3. Turn switching accessory to appropriate gas.

NOTE: If a hissing sound is heard you are in the wrong mode.

4. Switch valve to proper module (DSC/TGA).
5. Adjust air flow to 25 cc/min using the needle valve.
6. Once procedure is finished turn off main gas valve and press switching accessory to vent off all excess gas.

A hissing sound should occur for 1 - 5 seconds.

A. Instrument Set-Up

1. Turn the knob on the Module Switching Accessory to position 2 labeled TGA.

NOTE: In the following procedure steps, the 1090 system will ask a series of questions where the proper response is initiated by a single or a series of key strokes.

2. 1090; "Is date/time correct?".

Response: "Yes".

3. 1090; "Module type".

Response: "7, enter".

4. 1090; "TGA Signal-A Units 2".

Response: "Place floppy disk titled 'TGA' into disk drive".

5. Press "Recall parameters". File section.

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PROCEDURE STEPS (continued)

6. 1090; "Enter drive number 1".

Response: "Enter".

7. 1090; "Recall complete".

8. Press "New File". File section.

9. 1090; "New data file name?".

Using the alpha and numeric keys, type in serial number and at the end of the number, add ".01".

10. Press; "Enter".

11. Press; "Sample ID". Set params section.

1090; "Sample".

Response: Enter sample point listed on analytical card.

NOTE: The 1090 will automatically enter a sample weight when the sample run is initiated and will skip the sample weight and go to rate.

1090; "Rate".

Response: "20 deg/min, Enter".

1090; "Operator".

Response: "Technologist's payroll number, Enter".

12. Press; "Stand-by". Operate section.

NOTE: If the screen reads "STAN", go to step 16.

13. Press; "Store data". Operate section.

14. Press; "Auto analyze". Operate section.

NOTE: Screen should read "STAN" in the lower right hand corner. If it reads only analyze, press store data again. If it reads only store, press auto analyze. If it shows neither store or analyze, press both keys.

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PROCEDURE STEPS (continued)

15. Press; "Method". Set Params section.

NOTE: If running a % Free Water determination with platinum pans, press "1, Enter".

If running, a % Free Water determination with quartz pans, press "9, Enter".

If running a % Bound Water determination, press "2, Enter".

16. Complete Section B (Zeroing the Balance) and Section C (Loading the Sample) before proceeding to step 17.

17. Press; "Set-up". Operate section.

18. Press; "Start, start". Operate section.

19. The run will be complete when the lower right hand corner displays CMLPT.

20. Proceed to Section D, Clean Up, and to the ANALYSIS Section when the run is complete.

B. Zeroing the Balance.

1. Unscrew the furnace tube retaining ring and slide the balance assembly from the furnace tube. The furnace will support the furnace tube.

NOTE: The quartz rod is very delicate and extreme care must be exercised when placing the sample pan on the quartz rod. If the quartz rod is broken in the attempt to place the sample pan on the rod, contact the chemist in charge for replacement.

2. Hang a sample pan in the groove on the quartz rod using the tweezers.

NOTE: If the quartz rod is broken in the attempt to place the sample pan on the quartz rod, contact the chemist in charge for replacement.

3. Slide the balance assembly into the furnace tube.

4. Tighten the furnace tube retaining ring finger-tight.

5. Press "Signal Zero". Axis section.

6. 1090; "Auto-zero".

Response: "Enter".

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PROCEDURE STEPS (continued)

7. Press "Display Axis". List section.

NOTE: The weight display in the lower left hand corner should read 0.000 +/- 0.005 mg. If not, repeat steps 5 through 7. If the balance will not zero, contact the chemist.

8. When the balance is zeroed, proceed to step 1, Section C, Loading the Sample.

C. Loading the Sample.

1. Unscrew the furnace tube retaining ring and slide the balance assembly from the furnace tube. The furnace will support the furnace tube.

CAUTION: Samples may be very radioactive. Use extension devices when possible when handling samples. Survey frequently and thoroughly.

2. If the sample is a solid, load approximately 30 mg of sample into the sample pan using a microspatula. Go to step 4.
3. If the sample is a liquid, load approximately 70 mg of sample into the sample pan using a 50 uL Eppendorf pipet.
4. Adjust the sample thermocouple so that it is outside and along side the sample pan.
5. Carefully slide the balance assembly into the furnace tube.
6. Tighten the furnace tube retaining ring finger-tight.
7. Push the RESET derivative toggle switch.
8. Push the fan switch to the ON position.
9. Proceed to step 17, Section A, Instrument Set-Up.

D. Clean-Up.

NOTE: Be careful not to touch the furnace tube when removing it from the furnace because severe burns could result.

1. After CMPLT shows in the lower right hand, slide the entire balance assembly, including the furnace tube, out of the furnace.
2. Allow approximately 40 minutes for the furnace to cool to room temperature.
3. Slide the balance assembly back into the furnace.
4. Unscrew the furnace tube retaining ring.

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PROCEDURE STEPS (continued)

5. Slide the balance assembly out of the furnace tube.
6. Remove the sample pan.

NOTE: Platinum sample pans are very expensive and should be recycled for future use. Quartz pans are to be discarded to radioactive waste.
DO NOT REUSE!

7. Place the used sample pan in the jar of 6 M HCl located in the hood. After soaking for a few hours, the sample pans should be rinsed with water and flamed to remove any contaminants.
8. Slide the balance assembly into the furnace tube.
9. Tighten the furnace tube retaining tube finger-tight.
10. After the temperature reaches room temperature, another run may be initiated by returning to step 1, Section A, Instrument Set-Up.

ANALYSIS

1. Press; "Set-Up". Data analysis section.
2. 1090; "Enter drive number 1" or "Change current program?".
If "Enter drive number 1", go to step 3.
If "Change current program?", press "Yes", and go to step 3.
3. Place TGA Data Analysis Program disk into drive.
4. Press; "Enter".
5. 1090; "TGA.02".
6. 1090; "Enter data file name".

Response: Using the alpha and numeric keys, type file name from step 9 of the Instrument Set-Up Section.

7. Remove TGA Data Analysis Program disk and insert TGA disk back into drive.
8. Press; "Enter".
9. 1090; "Weight units: 2".

Response: "2, Enter".

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PROCEDURE STEPS (continued)

10. 1090; "Data sampling interval".

Response; "3.0, Enter".

11. 1090; "Limit option".

Response: "0, Enter".

12. 1090; "X-Axis".

Response: "2, Enter".

1090; "Curve 1".

Response: "3, Enter".

1090; "Curve 2".

Response: "0, Enter".

13. 1090; "Auto-scale? - Yes".

Response: "Enter".

14. 1090; "Auto-scale? - Yes".

Response: "Enter".

15. Place chart paper and pen on chart recorder. Push chart load button so the red light is off.

16. 1090; "Ready to Plot? - Yes".

17. Press; "Enter".

After the 1090 has plotted the data, the data analysis program will proceed to the Data Analysis Section of the program where the transition will be analyzed.

18. 1090; "Option".

Response: "1, Enter".

NOTE: See Figure 1 in the DISCUSSION for a typical sample run and a discussion on setting transition limits.

19. 1090; "Start Temp:".

Response: "25, Enter".

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PROCEDURE STEPS (continued)

20. 1090; "Stop Temp:".

Response: "300, Enter".

21. 1090; "Limits OK?".

Response: "Yes, Enter".

22. 1090, "Label:".

Response: "Water, Enter".

23. 1090; "Calculating Transition".

NOTE: Wait for the 1090 to calculate and plot the transition before going to step 24.

24. 1090; "Save results?".

Response: "No, Enter".

25. Press the chart load button so that the red light is on.

26. Remove chart.

27. Take out pen and recap.

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DISCUSSION

The 951 Thermogravimetric Analyzer (TGA) is used mainly to determine percent water in a variety of samples. The term "Free Water" refers to water that is physically absorbed in the sample and waters of hydration. The term "Bound Water" is usually associated with chemically bound water.

The 951 Thermogravimetric Analyzer operates on a null-balance principle. Physically attached to a taut-band meter movement, the balance beam is maintained in a horizontal reference position by an optically actuated servo loop. Attached to the control end of the balance beam is a light shutter; a constant intensity lamp is focused through an aperture slit in the shutter to strike two vertically mounted photodiodes. When the balance beam is in a null position, the focused light strikes both photodiodes equally. As sample weight is lost or gained, however, the beam becomes unbalanced and moves from the null position, causing more light to strike one photodiode than the other. The voltage output from the photodiode receiving the most light increases and unbalances the photodiode than the other. The voltage output from the photodiode amplifier, producing a current flow in the taut-band meter which acts as a restoring force on the balance beam, driving it back to its null position. The magnitude of the restoring current flow is directly proportional to the sample weight lost or gained.⁽¹⁾

Figure 1 shows a typical TGA data plot. The chart usually consists of weight change on the y-axis and temperature on the x-axis. One of the more difficult items concerning TGA plots is deciding where to establish the transition limits. The first transition temperature is usually the starting temperature of the TGA run. The final temperature transition occurs where the weight percent change levels off to form a plateau. In the example, the transition limits were set at 25°C and 270°C.

The use of platinum pans is recommended for routine use and will withstand a temperature of more than 1000°C. The platinum pans should be saved for cleaning and future use.

Quartz sample pans have been designed by K. A. Norton and B. Watts for use with liquid samples for the TGA. It has been determined that there is no statistical difference in data generated from standards between the platinum and quartz pans. Note that quartz pans are for one-time use ONLY! Do not attempt to clean and reuse them.

REFERENCES

1. 1090 Thermal Analysis System Operator's Manual, DuPont Company, Wilmington DE, May 1982.
2. 951 TGA Thermogravimetric Analyzer Operator's Manual, DuPont Company, Wilmington DE, September 1983.

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Typical Thermogravimetric Analysis Plot

Sample: TERLIQ.01 11C11K
 Size: 12.37 mg
 Rate: 20 DEG/MIN
 Program: TGA Analysis V2.0
 Date: 29-Feb-84 Time: 15:22:51
 File: TERLIQ.02 TGA.01
 Operator: 89750
 Plotted: 1-Mar-84 13:20:30

TGA

FIGURE 1

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Rockwell Hanford Operations		ANALYTICAL LABORATORIES	
Issued By: A. F. Noonan Manager, Analytical Laboratory Author: R. G. Marx		Title: Specific Gravity of High Beta-Gamma Caustic Samples	
<p><u>SUMMARY</u></p> <p>Specific gravity of a substance is defined as its weight per unit volume (density) compared to that of water at 3.98°C. A known volume of liquid sample is pipetted into a preweighed clear-site (T-9) vial. The difference in weight of the vial plus solution and the empty vial is the weight of the solution. The density is then calculated by dividing weight by volume and specific gravity determined by the ratio of its density as compared to water's density at specified temperatures.</p> <p><u>LIMITATIONS</u></p> <p>This method of determining specific gravity is limited to nonviscous liquid. Errors in weighing and volume measurement limit the accuracy and precision of the method. Depending on the radioactivity of the sample, very small sample sizes (100 uL) must be used. The resulting small difference in weight greatly increases the percent error.</p> <p>This procedure must not be used where an extremely accurate analysis of specific gravity is needed or where the specific gravity is a critical criterion for the process being monitored. Studies made shows a low bias of about 1% with respect to the submarine method² and a relative precision of +/- 0.5% (95% C.L.).</p> <p>A more detailed treatment of errors may be found in the "Discussion" section.</p> <p>A number of solutions may react with the plastic vials (e.g. acetone) or the cotton (concentrated nitric acid), and should not be run by this method. If there is any doubt about a sample, check with supervision.</p>			
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SAFETY

The provisions of General Regulations and Practices for Radiation Work (GEN-0) and Radiation Work Permit (SL-3) found in RHO-MA-172, shall apply to all work performed under this procedure.

Each vial must be carefully surveyed for radiation exposure and smearable contamination before weighing the sample. Metal forceps may be used to transfer vials to the balance pan to reduce exposure.

REAGENT

Ethanol (for rinsing the vials), 95% or equivalent.

EQUIPMENT

Five-place analytical balance (Mettler Model H18 or equivalent).

Pipets 200uL, 100uL, ASTM Certified +/- 0.37%

Clear-site plastic vials and caps, store stock #57-8900-300.

Cotton dental rolls (or cotton balls), store stock #57-5455-375.

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PROCEDURE

1. Rinse each vial and cap with ethanol and air dry for at least 15 minutes. DO NOT USE ACETONE.
2. Identify the cap and vial section of the three clear-site vials so each cap is associated with its respective vial.

NOTE Do not mix caps of one vial with the cap of another vial or the tare weights of the vials will change.

3. Place a dental roll (or cotton ball) in each vial.

NOTE All identifying marks must be made before weighing.

4. Record the weight of the cap, vial, and dental roll to the nearest 0.01 mg on sample card.

CAUTION Sample may be highly radioactive. Check dose rate throughout the procedure. Use shielded control when pipetting sample and shielded forceps when transferring vials.

5. Pipet sample slowly and accurately onto dental roll in preweighed vial. Be sure all liquid is removed from the tip and do not rinse pipet.
6. Record pipet volume on sample card.
7. Place the respective caps on the vials and survey for radiation dose rate and smearable contamination.
8. Record total weight of cap, vial, dental roll, and sample to the nearest 0.01 mg on sample card.
9. After vials have been properly weighed and recorded, dispose of in waste carton and then transfer to high-level waste immediately.

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CALCULATIONS

$$\text{Specific Gravity (SPG)} = \frac{\text{Substance Density (g/mL)}}{1.000 \text{ g/mL}}$$

* The density of water at 3.98°C

$$\text{Substance Density} = \frac{\text{Wt. of solution}}{\text{Vol. of solution}}$$

$$\text{Wt. of solution} = A - B$$

Where;

$$\begin{aligned} A &= (\text{Wt. of vial} + \text{cap} + \text{cotton} + \text{solution}) \\ B &= (\text{Wt. of vial} + \text{cap} + \text{cotton}) \end{aligned}$$

$$\text{Vol. of solution} = (\text{Volume of pipet in uL})$$

$$\text{SPG} = \frac{(A-B) \times (1000 \text{ uL/mL})}{(\text{Vol. of solution uL}) \times (1.000 \text{ g/mL})}$$

EXAMPLE

$$A = 44.12230 \text{ g}$$

$$B = 44.00000 \text{ g}$$

$$\text{Vol. of solution} = 100 \text{ uL}$$

$$\text{SPG} = \frac{(44.12230 - 44.00000) \times (1000 \text{ uL/mL})}{(100 \text{ uL}) \times (1.000 \text{ g/mL})} = 1.1223$$

Report results to 3 figures past the decimal.

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DISCUSSION

A. Specific Gravity Methods

The specific gravity (SpG) of liquid samples and solutions may be accurately determined by using a calibrated pycnometer³. This method, however, is limited to cold samples, or samples with fairly low-level beta-gamma activity, as it requires a relatively large volume of sample (typically, 15 ml or more).

In the case of highly radioactive aqueous solutions, the falling drop method is most desirable, since it requires a minimum amount of sample (about 5 microliters). However, this method works only for solutions which are neutral to acid (10M HNO₃). It is not satisfactory for:

1. Caustic solutions. They lower the interfacial tension between the aqueous drop and the organic medium through which it falls, thus giving erroneous results. In addition, the caustic drops sitting in the bottom of the tube cause faster deterioration of the medium, necessitating early replacement and recalibration of the tube.
2. Samples containing water-soluble organic (acetone, alcohol, etc.). This will bias the method, since part of the drop will mix with the medium, and its weight will change as it falls. This will also change the SpG of the medium, and again cause early replacement and recalibration.
3. Organic samples, or any sample which is partially or completely miscible with the media used (see Item 2 above).

For these reasons, the falling drop method is not satisfactory for determining the SpG of the many highly radioactive, caustic waste solutions. In contrast, practically any solution may be analyzed by this method using a plastic vial, providing the liquid does not react with the vial or the cotton. See LIMITATIONS.

B. ERRORS

There are several sources of error in this method. In addition to the random errors inherent in any procedure, the following errors may be introduced:

1. Accuracy of the pipet. More accurate analysis may be possible with calibrated pipets, and it is required that these be used.

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DISCUSSION (CONTINUED)

B. ERRORS (Continued)

2. Accuracy of the balance. Changes in temperature may affect the accuracy and reproducibility of the balance. The balance should be carefully zeroed before all weightings. See Item 4 in this list.
3. Dispensing of solution from pipet. A certain negative error will be introduced in dispensing the solution, since any liquid remaining on the walls of the pipet will not be weighed. Since the procedure assumes an exact amount is dispensed, the calculated weight/volume will always be low. To minimize this error, the pipet must be scrupulously clean and free of all grease.
4. Temperature effects. A given amount of solution will change volume with a variance in temperature. No correction for any change in temperature is made in this procedure, but the error may be minimized by keeping the hood, balance, and samples as close to room (ambient) temperature as practicable.
5. The vials used in this procedure are plastic, and as such have a tendency to pick up a static charge and attract dust, thus changing the apparent weight of the vials. The amount of dust picked up can also change between weightings for the same vial. This problem can't be completely eliminated, but it can be minimized by holding the handling of the vials to a minimum, and then only with metal tweezers.

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ANALYTICAL LABORATORIES

Issued By:

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Title

PERCENT WATER, BULK DENSITY AND PARTICLE
DENSITY OF WASTE TANK SAMPLES

Author: R. E. Brandt

SUMMARY

This analysis determines the water content, bulk density and particle density on the same sample of waste tank salt cake. The sample is centrifuged and the separated water, assumed to represent the tank supernate, is removed before the analysis is started.

After centrifuging in a tared, graduated cone the sample is weighed and the volume of the cake is measured. From these figures the bulk density is calculated.

The sample is then heated for 18 hours (overnight) at 120° C and the weight loss determined. This treatment removes the remaining interstitial water as well as water of hydration of such salts as $\text{Na}_2\text{CO}_3 \cdot 10\text{H}_2\text{O}$, $\text{Na}_2\text{SO}_4 \cdot 7\text{H}_2\text{O}$ and $\text{Na}_3\text{PO}_4 \cdot 12\text{H}_2\text{O}$. Hydrated sodium aluminate is converted to NaAlO_2 . The weight loss is reported as percent water.

A known volume of normal paraffin hydrocarbon (NPH) is added to the dried sample residue and it is again centrifuged. The volume of the dried sample is determined by subtracting the volume of the NPH from the total volume in the cone. Particle density is then calculated from this volume and the residue weight.

LIMITATIONS

The percent water part of this procedure determines the total of all substances volatile at 120° C. Ordinarily this will be water unless, for example, volatile organics are present. Due to the compact nature of the solid after centrifugation a relatively long heating period is required for the removal of all the water.

Sodium hydroxide deliquesces in the presence of moisture. The tube should be tightly stoppered during the cooling step to prevent the absorption of atmospheric moisture.

The determinations of bulk density and particle density are straightforward and relate the appropriate values of weight and volume. Bulk density is the weight per unit volume of the compacted but wet cake. Particle density is determined on the dried sample and is more nearly the true density of the sample material.

Since it is improbable that the waste tank contents are uniform throughout, the results on any one sample should not be assumed to represent the entire tank.

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APPLICATIONS

This is an empirical test rather than a precise chemical analysis. It is designed for use only on waste tank salt cake samples.

Only the percent water part of the procedure is monitored by the LSR program. Standard results indicate an accuracy and precision of $99.95 \pm 2.42\%$ for the weight loss during the heating step. There may also be some undetermined variability due to the centrifugation and water removal steps.

SAFETY

Tank farm samples may be highly radioactive. When working with instruments in any radiation zone, the appropriate provisions of 61-02.5 through 61-02.5.5, Standard Requirements and Procedures/Safety and Environment (RHO-GM-MA-2, Volume 6, Book 1) apply. In addition, specific building radiation work permit SL-3 found in RHO-MA-172 also applies.

Radiation Monitoring must be present during the handling of any sample with a field reading greater than 100 mrad/hour at the surface. Shielding and tools for remote handling must be used whenever possible. Finger ring dosimeter must be worn.

Care must be used in working around the oven. Serious burns can be sustained at 120°C . Tongs or leather gloves over surgeon's gloves should be used for removing samples from the oven.

The centrifuge cover must be closed before the centrifuge is turned on and must remain closed until the rotor has come to a full stop. The sample must always be adequately counterbalanced.

REAGENTS

1. NPH - Normal paraffin hydrocarbon.
2. Method Standard - Sodium tartrate dihydrate, $\text{Na}_2\text{C}_4\text{O}_6 \cdot 2\text{H}_2\text{O}$, Analytical Reagent Grade. This compound contains 15.66% water of hydration which is completely driven off at 120°C . This standard should be protected from atmospheric moisture, preferably by storing in a desiccator. It will not lose its water of hydration unless heated to 57°C or greater.

EQUIPMENT

1. Centrifuge.
2. Centrifuge tubes - 15 ml, graduated, (store stock no. 57-3705-015).
3. Cork stoppers - to fit centrifuge tubes.
4. Analytical Balance - 4 or 5 place.
5. Drying oven and thermometer - 0 to 150° C.
6. Marking Pen - with heat stable ink, e.g., Sharpie pen.

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PROCEDURE

1. Take a CP reading at the surface of the sample. Call RM if the reading is 100 mrad/hour or greater.
2. Label a clean, dry centrifuge tube and cork stopper with the sample number.
3. If a standard is to be run prepare a similar tube and stopper for the Method Standard. The standard should be carried through Steps 4, 5, 9 and 11 through 16 of the procedure.
4. Weigh the labeled tube and stopper and record the tare weight as W(1). The same stopper must be used with the same tube for each weighing.
5. To the sample tube add 1 to 2 grams of sample. For highly radioactive samples the sample size should be held to about 1 g. Clean inside top of tube with dental wipe on forceps or cotton applicator. Insert mating stopper or cork.
6. Check the outside of the stoppered tube for smearable contamination. If it is contaminated, clean the tube or start over with a clean tube.
7. Centrifuge the sample for 10 minutes at maximum speed. Be sure that the centrifuge cover is closed while the rotor is in motion and that the rotor is properly balanced. See LO-161-002, "Sample Centrifugation."
8. Remove the stopper and decant the supernate into a waste container. Using a cotton tipped applicator remove any drops which adhere to the walls of the tube. Clean inside top as in Step 5 before inserting stopper.
9. Replace the stopper and weigh the tube. Record the gross weight as W(2).
10. Record the volume of the cake in the centrifuge tube as V(1).

CAUTION: Stopper must be removed before tube is placed in oven to prevent pressurization and possible explosion of the tube.

11. Remove the stopper and place the tube in an oven at 120° C for 18 hours (overnight). DO NOT place the stoppers in the oven, but save them to use in the final weighing.

CAUTION: The stoppers may be contaminated.

12. Remove the tube from the oven. Check outside of tube for contamination as in Step 6 and clean if necessary. Stopper tightly, making sure each tube has the right stopper. Use tongs or leather gloves over surgeon's gloves to remove samples from oven. Cool to room temperature - a minimum of 15 minutes.

PROCEDURE (continued)

13. Weigh the centrifuge tube and stopper and record the weight of tube and residue.

CAUTION: Stopper must be removed before tube is placed in oven to prevent pressurization and possible explosion of the tube.

14. Remove the stopper and again place sample tube in the oven. Allow to remain for one hour.
15. Repeat Steps 12 and 13.
16. Repeat this process until the latest weight of tube and residue differs from the previous figure by no more than 10 mg. Record this weight as W(3).
17. Pipet 3.00 ml of NPH into the centrifuge tube. Stopper the tube and again centrifuge for 10 minutes. (See precautions in Step 7.)
18. Read the total volume in the tube (meniscus at top of NPH layer). Record this volume as V(2).

CALCULATIONS

Bulk Density

$$\begin{aligned}\text{Sample Weight} &= W(2) - W(1) \\ \text{Cake Volume} &= V(1) \\ \text{Bulk Density} &= \frac{W(2) - W(1)}{V(1)}\end{aligned}$$

Percent Water

$$\begin{aligned}\text{Sample Weight} &= W(2) - W(1) \\ \text{Weight Loss} &= W(2) - W(3) \\ \text{Percent Water} &= \frac{W(2) - W(3)}{W(2) - W(1)} \times 100\end{aligned}$$

Particle Density

$$\begin{aligned}\text{Dried Sample Weight} &= W(3) - W(1) \\ \text{Vol., Dried Sample + NPH} &= V(2) \\ \text{Particle Density} &= \frac{W(3) - W(1)}{V(2) - 3}\end{aligned}$$

Example of Calculations

$$\begin{aligned}W(1) &= 21.1067 \text{ g} \\ W(2) &= 22.3651 \text{ g} \\ W(3) &= 21.5995 \text{ g} \\ V(1) &= 0.67 \text{ ml} \\ V(2) &= 3.21 \text{ ml}\end{aligned}$$

$$\text{Bulk Density} = \frac{22.3651 - 21.1067}{.67} = 1.88 \text{ g/ml}$$

$$\text{Percent Water} = \frac{22.3651 - 21.5995}{22.3651 - 21.1067} \times 100 = 60.84\%$$

$$\text{Particle Density} = \frac{21.5995 - 21.1067}{3.21 - 3} = 2.35 \text{ g/ml}$$

DISCUSSION

This procedure is straightforward and the accuracy depends, to a large extent, on the care used in weighing and recording the weights and volumes.

Bulk density is an empirical figure whose accuracy and precision are limited by the accuracy with which the volume can be read using the centrifuge tube graduations.

Any sample ingredient volatile at 120° C will be included in the weight loss and reported as water.

The centrifugation compacts the sample considerably and this, along with the small surface area, makes a long heating period necessary. Since sample characteristics may vary, the samples are subjected to one or more short heating periods after the first long heating period until the weight loss is essentially constant.

The volume for the particle density can be read somewhat more precisely than in the case of the bulk density since it is being read to a liquid meniscus. The centrifugation with NPH is necessary to fill the voids in the cake created by the removal of water.

REFERENCES

1. LA-564-101, "Percent Water in Tank Farm Samples and Pilot Evaporatory Samples."
2. LO-161-002, "Sample Centrifugation."
3. Internal Letter 65124-80-047, M. E. Mitchell to W. H. Sant, January 3, 1980.
4. Internal Letter 65124-80-072, M. E. Mitchell to W. H. Sant, January 29, 1980.

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Rockwell Hanford Operations		ANALYTICAL LABORATORIES	
Issued By: T. A. Lane Manager, Analytical Laboratory Author: R. G. Marx		Title SOFTENING POINT DETERMINATION BY DSC	
<p><u>SUMMARY</u></p> <p>The softening point of a waste tank sample can be determined by use of a Differential Scanning Calorimeter. The samples are heated from ambient temperature to 350°C at a rate of 10°C/min. The softening point appears as an endotherm on the thermogram. A Du Pont 1090 Thermal Analyzer and a Du Pont 910 Differential Scanning Calorimeter are used for the determination.</p> <p><u>LIMITATIONS</u></p> <p>Due to the small sample size required for this procedure, weighing errors will have a direct influence on the precision and accuracy.</p> <p>The precision as determined from repeated melting of a polyethylene powder, gave an average melting point of 102.04°C +/- 0.3°C at the 95% confidence level.</p> <p><u>APPLICATIONS</u></p> <p>This procedure is applicable to Waste Tank Samples.</p> <p><u>SAFETY</u></p> <p>Provisions of General Regulations and Practices for Radiation Work (GEN-0) and Radiation Work Permit SL-3 as found in RHO-MA-172 shall apply to all work performed under this procedure.</p> <p>The samples can be very radioactive. SWP's and surgeon's gloves are needed in this procedure. Frequent monitoring is necessary to prevent contamination of the cell/furnace assembly and hood.</p>			
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SAFETY (CONTINUED)

After the samples are dried, the potential for airborne release or of smearable contamination becomes extremely high. Samples must be carefully monitored, and any excessive handling of sample cells must be avoided.

Care must be used in handling the sample pans within the furnace. The furnace must be allowed to cool before placement or removal of the pans. The sample pans will become extremely hot and require time for cooling to ensure safe handling..

To avoid smearable alpha contamination, samples with greater than 5000 dpm/mL are not to be analyzed by this procedure. Beta-gamma emitters may be analyzed as long as dosage at the hood face does not exceed 10 mrad/hr.

EQUIPMENT

1. Du Pont 1090 Thermal Analyzer and a Du Pont 910 Differential Scanning Calorimeter.
2. Sample pans, stainless steel, or platinum depending on sample.
3. Tweezers.
4. Encapsulation tool

PROCEDURE STEPS

- NOTE: Turn the knob on the Module Switching Accessory to position 1 labeled DSC.
- NOTE: If a Specific Heat and/or Heat Capacity is not requested, do not proceed with the weighing or drying steps.
- NOTE: Purging of system must be done for all samples. Start purge operation prior to procedure steps.

1. Turn on main air tank for appropriate purge gas.
 - A. Air for normal samples.
 - B. N₂ for special requests.
2. Check pressure of tank to insure setting is between 10 and 20 PSI.
3. Turn air switching accessory to appropriate gas.

NOTE: If a hissing sound is heard you are in the wrong mode.

4. Switch valve to proper module (DSC/TGA).
5. Adjust air flow to 25 cc/min using the needle valve.
6. Once procedure is finished, turn off main gas valve and press air switching accessory to vent off all excess air.

A hissing sound should occur for 1 - 5 seconds.

Sample Preparation Liquid

1. Weigh a clean empty sample pan with cover using an analytical balance to the nearest 0.1 milligrams and record weight on analytical card.
2. Transfer 10 uL of sample directly into the center of the sample pan.
3. Place cover on sample pan.
4. Reweigh sample pan and record total weight on analytical card.

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PROCEDURE STEPS (CONTINUED)

WARNING: The beta radiation level can increase dramatically as water is lost by evaporation. Careful monitoring must be practiced. Special caution must be taken to limit extremity exposure.

5. Dry sample under heat lamp. Only dry sample until the first crystals appear, then turn off heat lamp. DO NOT BAKE SAMPLE.

Sample Preparation Solid Sample

1. Weigh a clean empty sample pan with cover using an analytical balance to the nearest 0.1 milligrams and record weight on analytical card.

WARNING: High extremity exposure is possible with solid samples when loading, care must be employed at all times to limit exposure.

2. Place sample in weighed pan.
3. Place cover on sample pan.
4. Reweigh sample pan and record total weight on analytical card.

Loading Sample

1. Place empty covered reference pan on rear sensor using tweezers.
2. Place sample pan on front sensor.
3. Place cover on furnace.
4. Place lid on furnace.
5. Place glass dome over furnace.

Instrument Set-up

NOTE: In the following procedure steps, the 1090 system will ask a series of questions where the proper response is initiated by a single or a series of key strokes.

PROCEDURE STEPS (CONTINUED)

1. 1090; " Is date/time correct? "
Response; " Yes."
2. 1090; " Module type."
Response; " 1, enter."
3. 1090; " Sampling interval "
Response; Place floppy disk titled " SOFT POINT " into disk drive.
4. Press " Recall parameters." File section.
5. 1090; " Enter drive number 1."
Response; " Enter."
6. 1090; " Recall complete."
7. Press; " New file." File section.
8. 1090; " New data file name?"
Using alpha and number keys, type in sample number and at the end the number " .01 "
9. Press; " Enter."
10. Press; " Sample ID." Set params section.
1090; " Sample "
Response; Enter sample number entered in step 9. "Enter."
1090; " Size."
Response; " Weight of sample." The weight is calculated by subtracting the empty sample pan weight from the total weight. See Calculation Section for example.
1090; " Rate."
Response; " 10 deg/min, Enter."

PROCEDURE STEPS (CONTINUED)

1090; " Operator "

Response; " Your payroll number, Enter."

11. Press; " Stand-by." Operate section.

12. Press; " Store data." Operate section.

13. Press; " Auto analyze." Operate section.

NOTE: Screen should read "STAN". If it reads only "analyze", press "store data" again. If it reads only "store", press "analyze". If it shows neither "store" or "analyze", press both keys.

14. Press; " Method." Set params section.

15. 1090; " Initial method."

Response; " 1, Enter."

16. Press; " Set-up." Operate section.

17. Press; "Start, start." Operate section.

18. Wait until the 1090 says complete in lower right hand corner before starting step 19.

19. Turn on vacuum line and cool furnace.

20. Press; " Set-up." Data analysis section.

21. 1090; " Enter drive number 1." or " Change current program?"

If " Enter drive number 1." go to step 22.

If " Change current program." press " Yes.", and go to step 22.

22. Place Extended Playback disk into drive.

23. Press; " Enter."

PROCEDURE STEPS (CONTINUED)

24. 1090; " Playback.03."

Response; " Enter."

25. 1090; " Enter data file name."

Response; Using the alpha keys and numbers type file name from step 9. of the instrument set-up section.

26. Place SOFT POINT disk back into drive.

27. Press; " Enter."

28. 1090; " Data sampling interval."

Response; " Enter."

29. 1090; " Type of axis."

Response; " Enter."

30. 1090; " Limit option."

Response; " 0, Enter."

31. 1090; " X-Axis."

Response; " 2, Enter."

1090; " Curve 1."

Response; " 3, Enter."

1090; " Curve 2."

Response; " 0, Enter."

1090; " Curve 3."

Response; " 0, Enter."

32. 1090; " Auto-scale? - yes"

Response; " Enter."

PROCEDURE STEPS (CONTINUED)

33. 1090; " Auto-scale? - yes"
Response; " Enter."
34. 1090; " Ready to plot?"
35. Place chart paper and pen on chart recorder. Push chart load button so red light is off.
36. Press; " Enter."
37. After chart is finished, press chart load button so that the red light is on.
38. Remove chart.
39. Turn off vacuum once temperature display reads between 45 and 50°C then go to step 40.
40. Press; " New file." File section.
41. 1090; " New data file name?"
Using alpha and number keys, type in sample number and at the end the number " .02 ".
42. Press; " Enter."
43. Press; " Sample ID." Set params section.
1090; " Sample "
Response; Enter sample number entered in step 41. "Enter."
1090; " Size."
Response; " Weight of sample." The weight is calculated by subtracting the empty sample pan weight from the total weight. See Calculation Section for example.
1090; " Rate."
Response; " 10 deg/min, Enter."
1090; " Operator "
Response; " Your payroll number, Enter."

PROCEDURE STEPS (CONTINUED)

44. Press; " Stand-by." Operate section.
45. Press; " Method." Set params section.
46. 1090; " Initial method."
Response; " 5, Enter."
47. Press; " Set-up." Operate section.
48. Press; "Start, start." Operate section.
49. Place chart paper on chart recorder. Push chart load button so red light is off.
50. After chart is finished, push button so red light is on and remove chart.
51. Remove pen and cap.
52. Turn in both thermograms to chemist-in-charge or designate for interpretation of data.

Calibration Standard Procedure

1. Load polyethylene standard into cell following procedure steps 1 - 17, changing only step 15 to use method 3 instead of 1. This standard is preweighed and encapsulated.
2. After sample is complete, remove and save standard. This standard will be used over again since it degrades slowly.
3. Turn in thermogram to chemist along with samples when complete.

CLEAN-UP

1. Once temperature reading reaches room temperature,
 - a. Remove dome lid.
 - b. Remove lid.
 - c. Remove cover.

PROCEDURE STEPS (CONTINUED)

2. Remove sample and reference pans from furnace. Ensure not to damage cell base.

NOTE: Sample pans are very expensive, save for cleaning and future use. See procedure LA-560-121, D. Clean-Up, for proper cleaning instructions.

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CALCULATIONS

To determine the weight of a sample (S), subtract the sample pan weight (SP) from the sample pan and sample weight (SP+S).

EXAMPLE:

SP	=	25.0230 g
SP+S	=	25.0640 g
S	=	25.0640 - 25.0230
S	=	0.0410 g

DISCUSSION

Differential Scanning Calorimetry (DSC) can be used in softening point determination. Its dual heater system heats sample and reference in the cell separately at a controlled predetermined rate. Any difference in temperature (ΔT) produced through endothermic or exothermic activity is determined by a thermocouple so the heater can continuously and automatically adjust the temperature. This differential (dh/dt) heat flow between the sample and reference is fed to a recorder and plotted against time. The DuPont 1090 system records the heating difference as a milliwatt change which allows easy conversion to joules.

When using DSC in softening point determination it is a matter of interpreting the thermogram at the melting point of the crystalline sample. By integrating between the pre and post transitions of the derivative curve of the thermogram, the onset temperature of the melting point can be determined and reported as the softening point.

Determination of softening point is not straightforward. Fairly complex systems with overlapping peaks can generate problems when measuring heat capacity, enthalpy, and the softening point at the transition temperature. Further information on interpretation of thermograms is covered in the INTERPRETATION section.

INTERPRETATIONS

The Thermogram

Determining the softening point of a sample is not straightforward. In this discussion, we will determine what a softening point is, look at some basic examples, learn how to interpret a thermogram, and finally interpret a complex thermogram for its softening point.

What is a softening point? It is the temperature at which a discontinuity in heat capacity/specific heat and coefficient of volume expansion is observed. Or more simply, the temperature where a solid sample would become amorphous and start to flow.

The simplest softening point to determine is one of a pure metal. Tin is a good example (FIGURE 1). In a metal, the softening point is the melting point. FIGURE 2 (an expanded view of FIGURE 1) shows an onset temperature of 231°C , which is the melting point of tin.

With real-life samples, analysis is not so easy. Samples will be composed of salts of many origins and different concentrations. As a first salt example, let's look at NaNO_3 (FIGURE 3). Note the onset at 300.7°C , this is almost the melting point of the pure salt (306.8°C). But there is also a smaller secondary peak just before it with an onset point of 262.0°C . This corresponds to the melting point of NaNO_2 (271°C), which one would expect in a NaNO_3 solution.

These results are not "perfect" as in the tin example, but there can be many reasons for this. The first is contamination of the sample, since we had a mixture of salts a melting point depression is observed. Also, there is a time lag due to the thermal conductivity of the material if a sample is thick: the bottom next to the heater will be hotter than the top exposed to air resulting in a broadening of the peak. The rate of heating is a third possibility. A thermogram determined at $1^{\circ}\text{C}/\text{min}$ will look different than one produced at $25^{\circ}\text{C}/\text{min}$. There are other reasons for the slight differences observed and one can consult the references for further information.

Now let's look at FIGURES 4 & 5. Here are two interesting thermograms, one with 2 peaks and the other with 3. At first glance, we would expect the softening point to be the first peak on each thermogram, but this is fallacious. Our 2 examples are KNO_3 (#4) and NH_4NO_3 (#5), both have polymorphic transitions before the melting point. This tells us the softening point of these 2 are 329.2°C and 169.1°C resp.

INTERPRETATIONS (CONTINUED)

This brings us to another point of discussion. Before you can interpret a softening point, you must KNOW THEIR SAMPLE. If you can look at a complete analysis of the sample, you can determine what concentration of salts could exist and find their melting and polymorphic transition points. By comparing this with a thermogram an accurate determination of the softening point should be possible.

Now comes the hard part, what happens if we don't have salts that just melt. Look at FIGURE 6. Here we have a mixture of NaHCO_3 and NaNO_3 , a real mess. There are numerous peaks and if we didn't already know what the mixture was, we might say the softening point was somewhere around 120°C . However, by adding the additional step of reheating the sample after cooling, a beautiful thermogram like FIGURE 7 can be produced. What has happened is the volatiles in the sample have disappeared leaving just the solid NaNO_3 to melt (the NaNO_2 is also present). This is why a second heating is performed on all softening point determinations. This reheating modifies our basic sample and gives us a loss of features from our first trace. These losses are due to: evaporation and deposition of some of the melt onto positions inside the sample pan which have a lower temperature producing a temperature gradient in the cell or decomposition of the sample.

Before we go on to interpret an unknown sample, there is one more helpful item we can employ: the derivative. The 1090 thermal analyzer can plot the derivative of the curve if desired (that is the dot-dashed line on some of the thermograms see so far). By choosing any 2 points on the derivative curve which are on the baseline (zero) that surrounds the peak in question, an accurate onset temperature can be determined. The ideal place would be where the curve starts to displace from the baseline because if a specific heat is required only the area under the curve needs to be counted.

INTERPRETATIONS (CONTINUED)

With all our new knowledge, let's try a real sample. Our examples are shown in FIGURES 8, 9 and 10. Eight shows us the first complete run of the sample which yields so many peaks interpretation would be difficult. FIGURE 9 is the second run, showing 2 peaks and a constant baseline. At this point we must determine which of the two endotherms is the real softening point. Looking back to the analysis, we find potassium and nitrate in our sample. This tells us that the first peak is the polymorphic transition of KNO_3 and not the true softening point. The second peak is our softening point, so now the onset temperature needs to be determined. FIGURE 10 shows the plot with the onset of 219.3°C . 200 and 250 degrees were used as the 2 points on the derivative curve. The calculation for the onset was done by the 1090 using the General Analysis Utility Data Analysis Program (GAUDAP). The procedure for using that program is in the following section.

Specific Heat

A Specific Heat (at the melting point S) can be calculated using the GAUDAP. Once an onset point is determined, the 1090 also displays an enthalpy (H) in Joules/gram. The Specific Heat is calculated by dividing the temperature range into the enthalpy.

$$S_m = \frac{H}{T_1 - T_2}$$

Where T_1 = The point where the thermogram returns to the baseline (final temperature).

T_2 = The point where the thermogram deviates from the baseline (onset point).

Taking the KNO_3 example we used before, we can expand the thermogram around the peak and determine the specific heat. Example 11 shows an H of 88.7 J/g over a temperature range of 10°C . The Specific Heat is then,

$$\frac{88.7 \text{ J/g}}{328.4 - 338^\circ\text{C}} = S_m = 9.2 \text{ J/g}^\circ\text{C}.$$

INTERPRETATIONS (SPECIFIC HEAT) (CONTINUED)

The known value of KNO_3 is $9.944 \text{ J/g}^\circ\text{C}$, so our result is 92.9%.

Follow this procedure for determining the Specific Heat.

1. Press; " Set-up." Data analysis section.
2. 1090; " Enter drive number 1." or " Change current program?"

If " Enter drive number 1." go to step 3.
If " Change current program." Press " Yes.", and go to step 3.
3. Place General Analysis Utility Data Analysis Program (GAUDAP) disk into drive.
4. Press; " Enter."
5. 1090; " General.01."

Response; " Enter."
6. 1090; " Enter data file name."

Response; Using the alpha keys and numbers, type file name from step 41. of the instrument set-up section.
7. Place SOFT POINT disk back into drive.
8. Press; " Enter."
9. 1090; " Error."

Response; " Place GAUDAP back into drive."
10. Press: " Enter."
11. 1090; " Sample size."

Response; " Enter."
12. 1090; " Cell constant."

Response; " Enter."

INTERPRETATIONS (SPECIFIC HEAT) (CONTINUED)

13. 1090; " Data sampling interval."

Response: " Enter."

14. 1090; " Type of labels."

Response; " Enter."

15. 1090; " Limit option."

Response; " 2, enter."

16. 1090; " Start temperature."

Response; " Initial temperature on the left hand side of the peak in question, enter."

1090; " Stop temperature."

Response; " Final temperature on the right hand side of the peak in question, enter."

1090; " Delay time."

Response; " Enter."

1090; " Limits okay."

Response; " Replace softening point data disk back into drive."

17. Press; " Enter."

18. 1090; " Scanning data file."

INTERPRETATIONS (SPECIFIC HEAT) (CONTINUED)

19. 1090; " X-Axis."
Response; " 2, enter."
1090; " Curve 1."
Response; " 3, enter."
1090; " Curve 2."
Response; " 0, enter."
1090; " Curve 3."
Response; " 4, enter."
20. 1090; " Auto-scale? - yes."
Response; " Enter."
21. 1090; " Auto-scale? - yes."
Response; " Enter."
22. 1090; " Auto-scale? - yes."
Response; " Enter."
23. 1090; " Ready to plot?"
24. Place chart paper and pen on chart recorder. Push chart load button so red light is off.
25. Press; " Enter."
26. Once chart has finished replace GAUDAP in drive.
27. 1090; " Option."
Response; " 1, enter."
28. 1090; " Analysis option."
Response; " 1, enter."

INTERPRETATIONS (SPECIFIC HEAT) (CONTINUED)

29. 1090; " Curve to analyze."
Response " 1, enter."
30. 1090; " Partical area."
Response; " No."
31. 1090; " Special calculation."
Response; " No."
32. 1090; " Start temperature."
Response; " T2."
1090; " Stop temperature."
Response; " T1."
1090; " Limits okay."
Response; " Enter."
33. 1090; " Error."
Response; Replace softening point data disk back into drive, " enter."
34. 1090; " Save results."
Response; " No."
35. After chart is finished, push button so red light is on and remove chart.
36. Remove pen and cap.

INTERPRETATIONS (CONTINUED)

Heat Capacity

The Heat Capacity of the sample can be calculated by comparing it to sapphire's Heat Capacity. The sapphire must be heated in the same or identical pan at the same rate and sensitivity through the temperatures desired. A cell constant is then calculated at that temperature and the Cp of the sample determined.

Using the following equation,

$$C_p = [60 \times E \times q_s/Hr](\Delta y/m),$$

and the known Cp of sapphire, the cell constant (A), can be determined.

$$A = [60 \times E \times q_s/Hr],$$

EXAMPLE

The Cp of a sapphire at 430 K is .997 J/g°.

If a .06012 g sample had a Δy from the baseline of 5.2 cm, the the cell constant is;

$$A = (0.997)(.06012)/5.2$$
$$A = 0.0113 \text{ at } 430 \text{ K}$$

Having calculated the cell constant (A), the heat capacity of any material can be easily determined if the sample is run under identical experimental conditions. The Heat Capacity Cp of the sample can be calculated from,

$$C_p = (A)(\Delta y/m).$$

INTERPRETATIONS (CONTINUED)

EXAMPLE

A sample run was determined to have a Δy from the baseline of 6.2 cm at 160°C. A sapphire run under identical conditions had a Δy of 7.3 cm at the same temperature. The known Cp of sapphire at 160°C is 100 J/deg M. The sample mass is 20 mg and the sapphire mass of 60 mg.

$$100 = (A)(7.3/.060)$$
$$.82 = A$$

$$Cp \text{ sample} = (.82)(6.2/.02)$$
$$Cp \text{ sample} = 254 \text{ J/deg M.}$$

REFERENCES

Section A - Procedures

LA-560-121, "Determination of Percent Water by Thermogravimetric Analysis."

Section B - Source Documents

1. 1090 Thermal Analysis System Operator's Manual, Du Pont Company, Wilmington DE, May 1982.
2. 910 DSC Differential Scanning Calorimeter Operator's Manual, Du Pont Company, Wilmington DE, July 1983.
3. Differential Scanning Calorimetry, J. L. McNaughton and C. T. Mortimer, Perkin and Elmer Corporation, Norwalk, Connecticut 06856.
4. Determination Of The Softening Point And Specific Heat Of Hanford Defense Wastes By Differential Scanning Calorimetry, T. V. Rebagay, Sept. 1984.
5. Analytical Calorimetry, Roger S. Porter and Julian F. Johnson, Plenum Press, New York, 1968.
6. Thermal Properties of Aluminum Oxide From 0° to 1200°K, G. T. Furukawa, T. B. Douglas, R. E. McCoskey, and D. C. Ginnings. J. Res. Natl. Bureau of Std. 57 p 67, 1956

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Sample: TIN
Size: 29.13 MG
Rate: 10 DEG/MIN

DSC

Date: 3-Oct-84 Time: 7:33:35
File: SN.01 SOFT POINT
Operator: 69756

FIGURE 1

DuPont 1090

Sample: TIN
Size: 29.13 MG
Rate: 10 DEG/MIN
Program: General Analysis V1.0

DSC

Date: 3-Oct-84 Time: 7:33:35
File: SN.01 SOFT POINT
Operator: 69756
Plotted: 17-Jan-85 8:27:52

FIGURE 2

Sample: NANO3

Size: 5

Rate: 10 DEG/MIN

Program: General Analysis V1.0

DSC

Date: 28-Aug-84 Time: 11:18:31

File: NANO3.01 SOFT POINT

Operator: 69756

Plotted: 17-Jan-85 8:36:06

FIGURE 3

Sample: POTASSIUM NITRATE
Size: 11.45 MG
Rate: 10 DEG/MIN

DSC

Date: 10-Oct-84 Time: 7:46:19
File: KN03.01 SOFT POINT
Operator: 69756

FIGURE 4

Sample: NH4NO3

Size: 3

Rate: 10 DEG/MIN

DSC

Date: 27-Aug-84 Time: 14:42:03

File: NH4NO3.01 SOFT POINT

Operator: 69756

FIGURE 5

[—] Heat Flow (mW)

[---] Derivative (mW/min)

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Sample: NAHCO3 + NAN03

Size:

Rate: 10 DEG/MIN

DSC

Date: 11-Oct-84 Time: 10:39:11

File: MIX.02 SOFT POINT

Operator: 69756

FIGURE 6

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Sample: NAHCO3 + NAN03
Size:
Rate: 10 DEG/MIN

DSC

Date: 11-Oct-84 Time: 14:04:16
File: MIX.03 SOFT POINT
Operator: 69756

FIGURE 7

Sample: TRAINING SOLID STD

Size:

Rate: 10 DEG/MIN

DSC

Date: 17-Oct-84 Time: 11:02:04

File: SKS.05 SOFT POINT

Operator: 6A054

FIGURE 8

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Sample: TRAINING SOLID STD

Size:

Rate: 10 DEG/MIN

DSC

Date: 17-Oct-84 Timer 12:50:30

File: SKS.06 SOFT POINT

Operator: 6A054

FIGURE 9

[—] Heat Flow (mW)

[---] Derivative (mW/min)

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Sample: TRAINING SOLID STD

Size:

Rate: 10 DEG/MIN

Program: General Analysis V1.0

Date: 17-Oct-84 Time: 12:50:30

File: SKS.06 SOFT POINT

Operator: 6A054

Plotted: 17-Jan-85 10:50:00

DSC

FIGURE 10

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Sample: POTASSIUM NITRATE

Size: 11.45 MG

Rate: 10 DEG/MIN

Program: General Analysis V1.0

DSC

Date: 10-Oct-84 Time: 10:03:22

File: KN03.02 SOFT POINT

Operator: 69756

Plotted: 17-Jan-85 11:12:22

[—] Heat Flow (mW)

329.2°C

88.7 J/g

332.2°C

[—] Derivative (mW/min)

Temperature (°C)

DuPont 1090

FIGURE 11

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TABLE I

TABLE 2. Thermodynamic properties of methanone oxide at
1 atm pressure
(K = 0 to 2500)

T	C_p	$H_f - H_{f,0}$	$S_f - S_{f,0}$	$-G_f - H_{f,0}$
K	cal deg ⁻¹ mole ⁻¹	cal / mole	cal deg ⁻¹ mole ⁻¹	cal / mole
0	10.00	0.00	0.00	0.00
100	10.00	0.00	0.00	0.00
200	10.00	0.00	0.00	0.00
300	10.00	0.00	0.00	0.00
400	10.00	0.00	0.00	0.00
500	10.00	0.00	0.00	0.00
600	10.00	0.00	0.00	0.00
700	10.00	0.00	0.00	0.00
800	10.00	0.00	0.00	0.00
900	10.00	0.00	0.00	0.00
1000	10.00	0.00	0.00	0.00
1100	10.00	0.00	0.00	0.00
1200	10.00	0.00	0.00	0.00
1300	10.00	0.00	0.00	0.00
1400	10.00	0.00	0.00	0.00
1500	10.00	0.00	0.00	0.00
1600	10.00	0.00	0.00	0.00
1700	10.00	0.00	0.00	0.00
1800	10.00	0.00	0.00	0.00
1900	10.00	0.00	0.00	0.00
2000	10.00	0.00	0.00	0.00
2100	10.00	0.00	0.00	0.00
2200	10.00	0.00	0.00	0.00
2300	10.00	0.00	0.00	0.00
2400	10.00	0.00	0.00	0.00
2500	10.00	0.00	0.00	0.00

TABLE 3. Thermodynamic properties of methanone oxide at
1 atm pressure (Continued)
(K = 0 to 2500) (Continued)

T	C_p	$H_f - H_{f,0}$	$S_f - S_{f,0}$	$-G_f - H_{f,0}$
K	cal deg ⁻¹ mole ⁻¹	cal / mole	cal deg ⁻¹ mole ⁻¹	cal / mole
2600	10.00	0.00	0.00	0.00
2700	10.00	0.00	0.00	0.00
2800	10.00	0.00	0.00	0.00
2900	10.00	0.00	0.00	0.00
3000	10.00	0.00	0.00	0.00
3100	10.00	0.00	0.00	0.00
3200	10.00	0.00	0.00	0.00
3300	10.00	0.00	0.00	0.00
3400	10.00	0.00	0.00	0.00
3500	10.00	0.00	0.00	0.00
3600	10.00	0.00	0.00	0.00
3700	10.00	0.00	0.00	0.00
3800	10.00	0.00	0.00	0.00
3900	10.00	0.00	0.00	0.00
4000	10.00	0.00	0.00	0.00
4100	10.00	0.00	0.00	0.00
4200	10.00	0.00	0.00	0.00
4300	10.00	0.00	0.00	0.00
4400	10.00	0.00	0.00	0.00
4500	10.00	0.00	0.00	0.00
4600	10.00	0.00	0.00	0.00
4700	10.00	0.00	0.00	0.00
4800	10.00	0.00	0.00	0.00
4900	10.00	0.00	0.00	0.00
5000	10.00	0.00	0.00	0.00

Molecular weight, 44.013

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REAGENTS

1. Reference alumina (Al_2O_3) or glass beads.
2. Synthetic DTA LSR Standard:
CSAL Spec. No. 56C3-8: 1.4 M NaOH, 0.5 M NaAlO_2 , 0.7 M NaNO_3 , 0.3 M NaNO_2 , 0.1 M HEDTA sodium salt: can be prepared by the addition of HEDTA to internal tank solution.
3. 4.0M KNO_3 prepared by Standards Preparation Unit.
4. Compressed air.

EQUIPMENT

Du Pont 1090 Analyzer and the 910 Du Pont Differential Scanning Calorimeter.

Stainless steel sample pans prepared by the scientist in charge.

Eppendorf pipet, 10 uL size.

Stainless steel micro spatula (Pn#21-401-25A).

Extra long and curved forceps.

Small forceps.

PROCEDURE

A. SAMPLE LOADING

1. Using the micro spatula, place a thin layer of glass beads across the bottom of the two stainless steel pans.

NOTE: Assure the temperature of the cell is cool before proceeding.

2. Using the curved forceps, place one of the pans in the sample chamber on the reference sample platform (rear elevated portion of the grid). See Figure I.
3. In the other pan, pipet 10 uL of the sample onto the glass beads.
4. Carefully place the sample in the sample chamber on the sample platform (front elevated portion of the grid).
5. Place the platinum lid on top of the sample chamber using the extra long forceps.
6. Place the cover on top of the lid using the extra long forceps.
7. Place the bell jar over the furnace assembly. Proceed to instrument set-up.

B. INSTRUMENT SET-UP

NOTE: The 1090 Thermal Analyzer is a microcomputer-based system that is able to perform an analysis, collect and analyze data, and display results automatically. The power should be left on at all times (for disc drives and the analyzer). See Figure IV.

1. The 1090 Thermal Analyzer is used with a Differential Scanning Calorimeter (DSC) module switching accessory located on the right side of the analyzer.
2. Turn the module switch to the "DSC" position on the module.
3. Turn on the air tank for the appropriate gas. Normally compressed air is used; however, special samples may require N₂ gas.
4. Check the flow regulator on the air line to insure that the flow is between 10 and 20 psi.
5. Turn the air switching accessory to the appropriate gas.

NOTE: If a hissing sound is heard, the system is in the wrong mode.

6. Switch the valve to the proper analysis on the gas line (DSC).

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PROCEDURE (continued)

7. Adjust the air flow to 20 psi using the needle valve on the flow regulator.

NOTE: Under the plotter board is a display screen, and below the screen is a keyboard containing several groups of keys that will be used to control the operation of the 1090 Thermal Analyzer.

8. Insert the correct floppy disc (DTA/DSC) into drive #1 located below the keyboard such that the front top of the disc is facing upward and the printing on the label faces the drive unit.
9. The display screen will appear as follows:

1090 THERMAL ANALYZER TEMP
COPYRIGHT 1981 DU PONT CO. NN.N

(CORRECT DATE)
(TIME OF DAY)

IS DATE/TIME CORRECT? XXX
 STDBY

10. If the date and time are not correct, then press the "NO" key and key in the correct date and time when the screen displays entry for this information respectively. After each entry press the "ENTER" key.
11. If the date and time are correct, then press the "YES" key.

NOTE: If at any time the 1090 Analyzer does not act out a function, press "RESET" and begin the set-up procedure again. Sometimes the mother board will not accept the proper information due to room temperature changes or power surges; therefore, pressing the "RESET" button will clear the interferences.

12. The 1090 will respond with: "MODULE TYPE". Press "1 and ENTER" for DSC.
13. The 1090 will respond with: "SAMPLING INTERVAL". Press "RECALL PARAMETERS" in the file section.
14. The 1090 will respond with: "ENTER DRIVE NUMBER 1". Press "1 and ENTER".
15. The 1090 responds with: "RECALL COMPLETE". Press "NEW FILE" in the file section.

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PROCEDURE (continued)

16. The 1090 responds with: "NEW DATA FILE NAME?". Press the sample number and include a ".01" at the end of the number using the alphanumeric keyboard. Then, press "ENTER".
17. Press "SAMPLE ID" in the set params section. The 1090 will respond with: "sample". Press the same number used in step 16.
18. The cursor will automatically move down to the next step, "SIZE". Press "10 uL" and then "ENTER".
19. The cursor will automatically move down to "RATE". Press "10 deg/min" and then "ENTER".
20. The cursor will automatically move down to "OPERATOR". Press the operator's payroll number and then "ENTER".
21. Press "STAN-BY" in the operate section.
22. Press "STORE DATA" in the operate section.
23. Press "AUTO ANALYZE" in the operate section.

NOTE: "STAN" should be seen in the lower right hand corner of the screen at this time. If only "ANALYZE" is seen, then press "STORE DATA". If "STAN" or "ANALYZE" are not seen, then repeat steps 17 and 18.

24. Press "METHOD" in the set params section.
25. The 1090 responds with: "INITIAL METHOD 1-9". Press "1 and ENTER".
26. The 1090 responds with:

METHOD 1

INITIAL TEMP: 25.0

PROGRAM RATE: 10.0

FINAL TEMP: 102.0

ISO MINUTES: 10.0

NEXT METHOD: 2

NOTE: When the "ENTER" key is pressed, the cursor moves throughout method 1 and into method 2. In order to verify that the methods are correct, the next method should be reviewed prior to an analysis. This is done by pressing "ENTER" five times.

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PROCEDURE (continued)

27. The 1090 responds with:

METHOD 2

INITIAL TEMP: 102.0

PROGRAM RATE: 10.0

FINAL TEMP: 400.0

ISO MINUTES: 0.0

NEXT METHOD: 0

28. Press "SET-UP" in the operate section.

29. Press "START, START" in the operate section.

30. Do not disturb the analyzer during the operation. The word "GO" will appear at the lower right corner of the screen until the initial temperature has been reached and then the word "HOT" will appear.

31. The analysis is complete when the word "COMPLT" appears on the screen in the lower right corner.

32. If no additional samples are to be analyzed, turn off the main gas valve and press the air switching accessory to vent off the excess air. A hissing sound is heard for approximately 1-5 seconds.

33. If more samples are to be analyzed, do not turn the gas off and allow the furnace to cool down before beginning a new sample. The temperature may be observed in the upper right corner of the screen on the 1090 Analyzer.

34. Proceed to C. DATA ANALYSIS after each standard/sample is complete.

35. When analyzing a new sample and the furnace has cooled down to about 25 degrees C, press "NEW FILE" in the file section and follow procedure steps 16-34.

36. A synthetic DTA LSR standard prepared by Standards Preparation Unit (LMCS) must be analyzed (routinely as set forth by LMCS) to insure that the instrument is functioning properly. The synthetic DTA LSR standard must be run whenever the instrument's operation is questionable.

PROCEDURE (continued)

C. DATA ANALYSIS

1. Place the EXTENDED PLAYBACK disc into drive #2.
2. Press "SET-UP" in the data analysis section.
3. The 1090 Analyzer responds with: "ENTER DRIVE NUMBER" or "CHANGE CURRENT PROGRAM?".
4. If "ENTER DRIVE NUMBER", then press "2 and ENTER".
5. If "CHANGE CURRENT PROGRAM?", then press "YES and ENTER".
6. The 1090 responds with "PLAYBACK .03". Press "ENTER and ENTER" again.
7. The 1090 responds with: "ENTER DATA FILE NAME".
8. Using the alpha numeric keys and numbers, type in the file name used in step 16 of B. INSTRUMENT SET-UP and press "ENTER".
9. The 1090 responds with: "DATA SAMPLING INTERVAL".

ACQUIRED AT : 1.0

PLAYBACK AT : 1.0

SECONDS/POINT

10. Press "ENTER".
11. The 1090 responds with: "TYPE OF AXIS".

1 - NORMAL

2 - FAST

12. Press "1 and ENTER".
13. The 1090 responds with "LIMIT OPTION".

0 - NO LIMITS

1 - TIME LIMITS

2 - TEMPERATURE LIMITS

14. Press "0 and ENTER".

PROCEDURE (continued)

15. The 1090 responds with: "X-AXIS". Press "2 and ENTER".
16. The cursor moves down to "CURVE 1". Press "3 and ENTER".
17. The cursor moves down to "CURVE 2". Press "0 and ENTER".
18. The cursor moves down to "CURVE 3". Press "0 and ENTER".
19. The 1090 responds with:

X-AXIS TEMPERATURE

MINIMUM NN.N DEG

MAXIMUM NNN.N DEG

AUTO-SCALE? YES

RANGE: NN.N DEG/CM

START: N.NN DEG

20. Press "ENTER" and the 1090 responds with: "AUTO-SCALE? YES".

CURVE I HEAT FLOW

MINIMUM: NN.N MW

MAXIMUM: N.NN MW

RANGE: NN.N MW/CM

START: NN.N MW

21. Press "ENTER", and the 1090 responds with "READY TO PLOT? YES".
22. Push the chart load key located near the push button controls. When pressed, the red pilot light ignites and the electrostatic force is removed. Place the chart paper on the plotter board. When the chart load key is pushed again, the pilot light goes out and the chart paper is held in place.
23. Place the recorder pen in the pen holder carefully holding the holder such that the tip of the pen does not get damaged when attaching it to the holder.
24. Press the "ENTER" key and the 1090 will plot the thermogram.

PROCEDURE (continued)

25. After the thermogram has been plotted, remove and recap the pen. See Figures II and III for thermograms that represent a standard/sample with an exothermic reaction and a sample that does not have an exothermic reaction.
26. Take out the discs when the analysis is complete and place them in the storage box in their respective envelopes. If additional analyses are required, continue by starting with steps 1-7 of the SAMPLE LOADING section and steps 16-34 of INSTRUMENT SET-UP section of the procedure.
27. After the furnace has cooled down and no additional samples are to be analyzed, the sample pans must be discarded in the waste carton located near the instrument in the hood.
28. Turn off the gas at the regulator.
29. Reset the 1090 Analyzer by pressing the reset button located near the push button controls.
30. Clean work area and log in the condition of the instrument and the LMCS standard analysis.

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CALCULATIONS

The Differential Thermal Analysis is a qualitative analysis and therefore does not require any calculations.

CALIBRATION

A synthetic DTA LSR standard must be analyzed prior to all analysis. This assures that the instrument is operating properly.

DISCUSSION

The Differential Scanning Calorimeter's measuring device is a cell that is plugged into the 910 instrument and is used to measure the differential heat flow of a sample. The sample and reference pan are placed on a raised platform within the cell. The raised platform contains a constantan disc that has heat transferred through it to the sample and the reference pans. Differential heat flow of the sample is monitored by thermocouples located below the constantan disc. Any temperature changes in the sample relative to the reference are due to phase transitions or chemical reactions and are directed as a dip (endothermic) or a peak (exothermic) in an otherwise straight line. Synthetic DTA LSR standard is used to represent thermal characteristics as similar as possible to those of a sample (waste tank solution). The rates of heating must be so chosen to insure the sample being essentially in equilibrium condition throughout the test. Rates that are too fast may result in fictitious temperatures of transformations, and double points on curves due to an incomplete reaction at that temperature.

The temperatures at which these heat effects occur and their relative intensities are characteristic of the material being analyzed. Therefore, an exothermic detection occurs between the ambient to 400 degrees C temperature range with a heating rate of 10 degrees C/min.

The shape of the DTA curve and the assignment of transition temperature, are dependent on where the temperatures are measured and the heat flow rates. A change in the rate of heating shifts the position of a peak maximum.

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REFERENCES

Section A - Procedures

1. LA-514-112, "Differential Thermal Analysis of Caustic Samples."

Section B - Source Documents

1. 1090 Thermal Analysis System Operator's Manual, Du Pont Company, Wilmington, De., May 1982.
2. 910 DSC Differential Scanning Calorimeter Operator's Manual, Du Pont Company, Wilmington, De., July 1983.
3. Kirk, Othmer, Encyclopedia of Chemical Technology, Vol. 2. 610-612.
4. Smothers, W. J., Chaing, Y. 1958, Differential Thermal Analysis: Theory and Practice, 9-65.

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FIGURE I

Cross Section, DSC Cell

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FIGURE II

A THERMOGRAM OF A STANDARD/SAMPLE WITH AN EXOTHERMIC REACTION

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FIGURE III

A THERMOGRAM OF A SAMPLE WITHOUT AN EXOTHERMIC REACTION

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FIGURE IV
THE 1090 THERMAL ANALYZER

Rockwell Hanford Operations**ANALYTICAL LABORATORIES**

Issued By: T. A. Lane

Title

PERCENT SOLIDS BY CENTRIFUGE

Manager,

Analytical Laboratory

Author: R. N. Diebel

SUMMARY

Many samples generated at B-Plant and at the tank farm have solids present. Often the significant elements in the sample are found to be present in the solids as well as the liquid phase. Because of the presence of these solids, the percent centrifuged solids is often requested by process.

LIMITATIONS

Accuracy is largely dependent upon sample size. If the sample size is 5 mL and the smallest increment measured on a graduated cone is 0.1 mL, the minimum detection limit (MDL) is 2%. If solids are visible, but less than 0.1 mL in volume, then we can accurately state nothing more than "solids present at less than 2%."

The particle sizes of solids may, in some cases, be so small that they will not settle to the bottom of the cone, but will cause the sample to be cloudy. This circumstance should be reported to the shift supervisor and process so that a determination of process needs such as filtering, etc., can be made.

SAFETY

Refer to procedure LO-080-112 to determine how the samples can be handled (hood or hot cell). Follow the appropriate provisions of 61-02.5 through 61-02.5.5, Standard Requirements and Procedures/Safety and Environment (RHO-GM-MA-2, Volume 6, Book 1). In addition, building radiation work permit SL-3 found in RHO-MA-172 also applies.

REAGENTS

Not applicable.

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EQUIPMENT

1. Centrifuge cone, graduated, 50 mL, order #VWR 21092-007.
2. Centrifuge cone, graduated, 15 mL Store Stock #57-3705-015.
3. Centrifuge cone, graduated, 10 mL, order Kimble 45180.
4. Centrifuge cone, Bauer-Schneck, order #VWR 21074-005.
5. Beaker, 150 mL, Store Stock #57-0225-150.
6. Centrifuge, clinical.

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PROCEDURE

1. Load sample into cubicle following procedure LO-161-101 for 1-F cubicle or procedure LO-161-141 for 1-E1 cubicle.

2. Record estimated total sample volume.

3. Determine type of centrifuge cone to be used from Table 1.

NOTE: For small trombone type samples, sparge the sample so that it is homogeneous and then transfer.

4. Transfer sample to appropriate size cone.

5. Rinse sample vial using the sample's own supernate.

6. Transfer the liquid to the cone when rinsing is finished.

7. Repeat as many times as necessary to ensure that all solids are transferred to the cone.

8. Follow Step 9 if the sample volume is larger than the selected cone, or the amount of solids is small in comparison to the total volume. If not, follow Step 17.

9. Transfer first increment to the cone.

10. Centrifuge for 20 to 25 minutes.

11. Record supernate volume and solids volume.

12. Transfer supernate to clean 150 mL beaker.

13. Transfer more sample with remaining solids to cone.

14. Centrifuge for 20 to 25 minutes.

15. Record total supernate volume and total solids volume.

16. Repeat Steps 13 - 15 as many times as necessary until all solids are transferred.

17. Centrifuge for 10 +/- 10 minutes.

18. Record total sample volume and total solids volume.

19. If solids are to be analyzed, refer to procedure LA-549-132.

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LA-519-132 (N-2-71)

CALCULATIONS

A. $\text{Volume \% Solids} = \frac{\text{Total Solids Volume} \times 100}{\text{Total Sample Volume}}$

Example:

Total Solids Volume from Step 18 = 2.4 mL

Total Sample Volume from Step 18 = 10.0 mL

$$\text{Volume \% Solids} = \frac{2.4 \text{ mL} \times 100}{10 \text{ mL}} = 24 \% \text{ Solids}$$

B. Volume % solids by the increment method:

1. Total Supernate Volume = Sum of Supernate Volumes from Step 15.

2. Total Solids Volume = Final Solids Volumes from Step 18.

3. Total Sample Volume = Total Supernate Volume + Total Solids Volume.

$$\text{Volume \% Solids} = \frac{\text{Total Solids Volume} \times 100}{\text{Total Sample Volume}}$$

Example: Supernate Volume 1 = 8.0 mL

Supernate Volume 2 = 7.5 mL

Supernate Volume 3 = 6.5 mL

Total Supernate Volume = 22 mL

Total Solids Volume = 4 mL

Total Sample Volume = 22 + 4 = 26 mL

$$\text{Volume \% Solids} = \frac{4 \text{ mL} \times 100}{26 \text{ mL}} = 15\% \text{ Solids}$$

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DISCUSSION

The centrifuge inside the cubicle will deliver approximately 200 gravities of force at a maximum power setting. This force must be applied to the sample for at least one hour to ensure that all visible solids are packed into the bottom of the cone.

There are several types and sizes of graduated cones available for this procedure. Because of the expense involved in some of these cones, determination must be made of the accuracy and needs of process. If a very high degree of accuracy is needed in a sample that is supposedly free of solids and is small in volume, then the Bauer-Schenck cone should be used. However, if the sample size is large (more than 15 mL) and there are significant solids present, then the 50 mL cone should be used.

Normally, the sample will be a 5 mL filtrate and the purpose will be to quantitatively determine that no solids are present. The 25 mL graduated cone or the 10 mL narrow bottom cone will be suitable for this purpose. Table I provides the type of cones available and their intended use.

There may be cases where the sample volume may be larger than the indicated cone; or where the amount of solids present is very small in comparison to the sample size thereby requiring the use of a smaller cone; in cases such as this, an increment method of centrifuging is necessary. Step 9 of this procedure provides a suitable increment method.

REFERENCES

1. LO-080-112 (unclassified), "Sample Pig Handling."
2. LO-161-101 (unclassified), "1-F Cubicle Operations, 222-S Building."
3. LO-161-141 (unclassified), "1-E1 Cubicle Operations, 222-S Building."
4. LA-549-132 (unclassified), "KOH Fusion Cubicle."

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TABLE 1
TYPES AND SIZES OF CENTRIFUGE CONES

A. 50 mL graduated cone	Sample volume is between 12 and 50 mL. If solids are present, they are at least five percent of minimum volume. Accuracy of cone is $\pm 1\%$.
B. 15 mL graduated cone	Sample volume is between 3 mL and 12 mL. If solids are present, they are at least 6% of minimum volume. Accuracy of cone is $\pm 0.35\%$.
C. 10 mL graduated round bottom cone	Sample volume is between 3 mL and 10 mL. If solids are present, they are at least 4% of minimum volume. Accuracy of cone is $\pm 0.35\%$.
D. 3 mL high accuracy Bauer-Schenck cone	Sample volume is between 0.4 mL and 3 mL. Solids are only minutely present, if at all. This cone should be used only in cases where it is critical to show with a high degree of accuracy that no solids are present or that a trace amount exists not more than 10% of maximum volume.

ANALYTICAL LABORATORIES

Issued By:

T. A. Lane

Manager,

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Author: S. A. Jones

Title

SPECTROPHOTOMETRIC DETERMINATION OF THORIUM
WITH ARSENAZO IIISUMMARY

After separation from interfering ions, thorium is determined by measuring the absorption of 660-665 nm light by the thorium complex of Arsenazo III (1,8-dihydroxynaphthalene-3,6-disulfonic acid-bis[(azo-2)-phenylarsonic acid]).

LIMITATIONS

Arsenazo III forms colored complexes with many metals. However, in 5-9 M HCl only Th, Zr, Hf, U(IV), Pu(IV), and Np(IV) form colored compounds. With the exception of Th, these metals are all extracted by TIOA from 7-9 M HCl, making the method very specific for thorium.

Arsenazo III is destroyed by oxidizing or reducing agents. These must not be present during the color formation or measurement.

If the Pu/Th ratio is greater than about 500, a third TIOA extraction may be necessary.

There are not sufficient data available to make an accuracy and precision statement.

APPLICATIONS

About 1 microgram of thorium in 10 mL of solution may be detected by this method. The best working range is 2-20 micrograms/10 mL.

SAFETY

The provisions of "General Regulations and Practices for Radiation Work," RHO-GM-MA-2, Volume 6, Book 1, Standard Requirements and Procedures Section 61-02.5 and Radiation Work Permit SL-3 found in RHO-MA-172 apply to all work performed under this procedure and must be followed at all times. All work with chemical reagents will conform to RHO-MA-221. Observe the Material Safety Data Sheets (MSDS's) for hydrogen chloride (1254) and sulfamic acid (1623 and 1623a) found in the 222-S shift managers' office.

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REAGENTS

All reagents are labeled according to the provisions found in LO-120-001.

Hydrochloric Acid

Concentrated, 37 percent, Reagent Grade or better.

Hydrochloric Acid, 7 M

Dilute 575 mL of concentrated acid to 1 liter and mix thoroughly.
Replace every 12 months.

Sodium Nitrite, 1.5 M

Dissolve 10.4 grams of NaNO_2 in deionized water and dilute to 100 mL.
Store in a brown bottle and do not use more than 1 month after makeup.
Replace if solution turns yellow.

TIOA, 10 percent (v/v)

Add 50 mL of tri-iso-octylamine to 450 mL of xylene and mix thoroughly.
Store in a dark bottle and replace every 3 months.

Arsenazo III, 0.05 percent

Dissolve 0.05 g of the compound in 100 mL of water. This reagent dissolves slowly. At least one hour of stirring should be allowed for the dissolution. The solution is stable and does not deteriorate with time. A new calibration should be made whenever a new Arsenazo solution is put to use.

Sulfamic Acid, 100 g/L

Dissolve 10 g of sulfamic acid in water and dilute to 100 mL. Replace solution every 6 months.

Thorium Standard

Standardize a 0.01 M thorium nitrate solution in 0.5 M HNO_3 to give a concentration of about 15 ug Th/mL.

EQUIPMENT

15-mL glass vials.

Glass-covered stir bars.

Spectrophotometer equipped with 1 cm cells and capable of operating at 660-665 nm.

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PROCEDURE

1. Pipet 5.00 mL of 7 M HCl into a 15 mL glass vial.
2. Pipet sample containing 2-20 ug of thorium into the vial and rinse with the liquid in the vial.
3. Add a glass covered stir bar.
4. Start a reagent blank (5.00 mL 7 M HCl) and carry through all steps of the procedure.
5. While stirring the contents of the vial, add 500 uL of 1.5 M NaNO₂.
6. Add about 5 mL of 10 percent TIOA in xylene and stir to an emulsion for at least 5 minutes.

NOTE: A separate waste bottle is required for the organic solution disposal. The organic solution may not be added to the aqueous trap bottle.

7. Remove from stirrer and allow phases to separate, then (using a transfer pipet) slurp off as much of the organic (top) layer as possible.

8. Repeat Steps 6 and 7 with a new portion of TIOA.

NOTE: If the Pu/Th ratio is greater than 500, Steps 6 and 7 will need to be repeated for a third time.

9. Transfer exactly 4.00 mL of the aqueous solution to a clean 10 mL volumetric flask.
10. Add 2 mL of concentrated HCl and swirl flask to mix.
11. Add three or four drops of sulfamic acid and mix.

NOTE: Steps 12-15 must be done separately for each sample because the colored complex is stable for no longer than 8 minutes. The reagent blank must be run first in order to zero the spectrophotometer and have a reference solution against which to measure the sample absorbance.

12. Add 1.00 mL of 0.05 percent Arsenazo III and swirl to mix.

NOTE: For this procedure, the solution should be a violet red to purple color. If the solution is blue to green, then the thorium concentration is too high and a new dilution will have to be taken through the procedure.

13. Dilute to the mark with deionized water and add a glass covered stir bar. Stir until thoroughly mixed.

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PROCEDURE (continued)

14. Transfer a portion of the solution to a 1 cm spectrophotometer cell.
15. Set up the spectrophotometer according to the operating procedure.
16. Measure the absorbance spectrum at 660 nm against the reagent blank.

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CALIBRATION

1. Pipet the following amounts of thorium standard into a series of 10 mL volumetric flasks:

<u>Volumetric</u>	<u>Pipet size (uL)</u>
1	100
2	250
3	500
4	750
5	1000

2. Use another flask as the reference blank and include all reagents except the thorium.
3. Rinse the pipet twice with water adding the washes to the flask.
4. Add 4 drops of sulfamic acid to each flask.
5. Add 4 mL of concentrated HCl and enough water to make the volume of liquid about 8 mL.
6. Mix by swirling.
7. Allow solution to cool to room temperature.
8. Finish the calibration by following Steps 12 through 16 of the sample procedure.

CALCULATIONS

C = Thorium standard concentration (ug/mL)
S = Sample size (mL)
T = Thorium concentration (g/L)

MF = Method Factor = $\frac{5.5 + S}{4}$

DF = Dilution Factor = $1/S$
A = Sample absorbance
a = Intercept of calibration curve
b = Slope of calibration curve

CALCULATIONS (continued)

1. Calibration curve parameters

a) Th concentration

$$T = (C)(S)(10^{-3} \text{ mg/ug})$$

Example:

$$\begin{aligned} T &= (14.993 \text{ ug/mL})(0.500 \text{ mL})(10^{-3} \text{ mg/ug}) \\ &= 7.497 \times 10^{-3} \text{ mg} \end{aligned}$$

b) Sample absorbance

c) To calculate the calibration curve a linear regression analysis is used to determine the slope (b) and y-intercept (a) of the line given by the equation:

$$y = bx + a$$

where: x = mg Th

$$y = A = \text{absorbance}$$

The HP-67 or HP-97 program "Curve Fitting" is used for this calculation.

d) Percent Recovery of calibration curve standards

$$\% \text{ recovery} = \frac{(A-a)}{(b)(x)}(100)$$

Example:

$$\% \text{ recovery} = \frac{(0.407 + 0.0067)}{(56.87)(7.497 \times 10^{-3})}(100)$$

$$\% \text{ recovery} = 98.2\%$$

2. Sample concentrations

a) Thorium concentration

$$T = \frac{(A-a)}{(b)} (MF)(DF) = \frac{(A-a)(5.5 + S)}{(b)(4)} (DF)$$

$$T = \frac{(0.296 + 0.067)(5.5 + 0.5)}{(b)(4)} (202)$$

$$T = 1.6 \text{ g/L Th}$$

CALCULATIONS (continued)

If a dilution has to be made before the sample is run then DF is replaced by the "dilution factor" for this dilution.

For example:

For a 100-10-50 dilution

$$DF = \frac{1 \text{ mL}}{0.100 \text{ mL}} \times \frac{10.00 \text{ mL} + 0.100 \text{ mL}}{1 \text{ mL}} \times \frac{1 \text{ mL}}{0.500 \text{ mL}}$$

- b) QA standard recovery - Calculate the same way as the thorium concentration in 2.a above and then divide by the value for the QA standard.

Example:

$$\% \text{ recovery} = \frac{(0.230 + 0.067)(5.5 + 0.5)}{(76)(74)} (202) \frac{(100)}{1.320 \text{ g/L}}$$

$$\% \text{ recovery} = 95.5\%$$

DISCUSSION

Arsenazo III, 1,8-dihydroxynaphthalene-3,6-disulfonic acid-2,7-bis[(azo-2)-phenylarsonic acid], forms colored complexes with many metals under various conditions. However, in 4-9 M HCl only a few tetravalent metals react to form these complexes. These metals include: Th, Zr, Hf, U(IV), Pu(IV), and Np(IV). With the exception of thorium, all these metals are extractable with TIOA in xylene from 7-9 M HCl. This makes the procedure very specific for thorium.

The reported value of 130,000 for the molar absorptivity of the Th-Arsenazo III complex (Ref. 1) was confirmed in this work. However, a difference was found between different solutions of Arsenazo III. The difference was small but significant. Therefore, it is necessary that a new calibration be made for each Arsenazo III solution. This is no great hardship since the solution is stable under storage and sufficient solution can be prepared to last several months.

The colored complex formed and the Arsenazo III itself are sensitive to both oxidizing and reducing agents. In working with plutonium containing samples it is necessary to use sodium nitrite to ensure the proper valence (+4) for the TIOA extraction. The excess nitrite must be destroyed by the addition of sulfamic acid or hydrazine before the addition of the Arsenazo III.

High molecular weight amines, including TIOA, have been called liquid ion exchangers since they extract metals only under conditions where the metals form anionic complexes. This offers a very convenient scheme of separation since the interfering ions form anionic chloride complexes, but thorium does not.

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DISCUSSION

For samples containing small amounts of thorium and large amounts of interfering ions, two or more extractions are necessary. For Pu/Th ratios of up to 500, two extractions were found to be sufficient. For higher ratios, a third extraction is recommended.

The thorium-Arsenazo III complex form almost immediately but fades somewhat with time. Residual nitrite, which could gradually destroy the Arsenazo III, is eliminated by the addition of sulfamic acid.

REFERENCES

1. S. B. Savvin, Analytical Uses of Arsenazo III, *Talanta*, **8**, 673 (1961).
2. F. L. Moore, Liquid-Liquid Extraction with High Molecular Weight Amines, Nat. Acad. Sci., NRC, NAS-NS-3101 (1960).
3. F. L. Moore, *Anal. Chem.*, **10**, 908 (1958).
4. H. Onishi and K. Sekine, *Talanta*, **19**, 473 (1972).
5. J. E. Grindler, The Radiochemistry of Uranium, Nat. Acad. Sci., NRC, NAS-NS-3050, (1961).
6. LO-120-001, "Labeling of Standards and Reagents."

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ANALYTICAL LABORATORIES

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Title

SPECTROPHOTOMETRIC DETERMINATION OF NITRITE

SUMMARY

Nitrous acid reacts with organic amino compounds to produce diazonium salts, which can then be coupled with certain other organic amines to produce azo dyes. This method employs first sulfanilic acid and subsequently 1-naphthylamine-7-sulfonic acid to yield an intense pink color. A UV-visible spectrophotometer is used to measure the absorbance at 525 nm.

LIMITATIONS

The reaction is specific for nitrite. Orange, red, or yellow substances will interfere with the colorimetric determination. Intense interfering colors require consultation with the chemist in charge.

Routine standard analysis of 145 standards resulted in an average recovery of 98.9% with a standard deviation of 3.6%.

The detection limit for this procedure is approximately 1×10^{-6} M nitrite.

APPLICATIONS

This procedure is applicable to all types of samples. Care must be taken in samples that contain high levels (> 1 M) of nitrite because of the large dilutions required.

SAFETY

When working with instruments in any radiation zone, the appropriate provisions of 61-02.5 through 61-02.5.5, Standard Requirements and Procedures/Safety and Environment (RHO-GM-MA-2, Volume 6, Book 1) apply. In addition, specific building radiation work permits (AL-1, SL-3, Z-3) found in RHO-MA-172 also apply.

EQUIPMENT

Disposable glass vials, 15 mL with poly seal caps

Disposable or glass cuvettes

Spectrophotometer capable of absorption measurements at 525 nm

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REAGENTS

NOTE: Use analytical reagent grade chemicals for all solutions whenever possible.

1. 6 g/L sulphanilic acid in 50% acetic acid. Dissolve 1.5 g of sulphanilic acid in 125 mL boiling water and cool. Add 125 mL concentrated glacial acetic acid. Store in a dark brown bottle. Replace hood supply every month. Label with preparation and expiration dates.
2. 0.6 g/L 1-naphthylamine-7-sulfonic acid in 50% acetic acid. Dissolve 150 mg of 1-naphthylamine-7-sulfonic acid in 125 mL boiling water and cool. Add 125 mL concentrated glacial acetic acid. Store in a dark brown bottle in a refrigerator until dispensed. Replace hood supply every month. Label with preparation and expiration dates.
3. 0.67 M NH_4OH buffer. Add 3.6 g NH_4Cl and 4 mL NH_4OH (conc.) to a 100 mL volumetric flask and dilute to volume with water. Stable indefinitely.
4. Stock nitrite Calibration Standard, 2×10^{-2} M. Weigh out 0.0690 g NaNO_2 to make 50 mL of solution. Add 2.5 mL of buffer (reagent 3) and dilute to 50 mL with water. Stable for 2 weeks. Label with preparation and expiration dates.
5. Nitrite calibration standard, 2×10^{-4} M. Prepare 100 mL by a 100-fold dilution of the stock nitrite calibration standard (reagent 4). Store in glass. This calibration stand should be prepared just prior to running the calibration. DO NOT STORE.

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PROCEDURE STEPS

A. Calibration

NOTE: A calibration should be run whenever the percent recovery for the NOX standard fall outside the 95 to 105% range, or when the chemist decides it is necessary due to obtaining fresh chemicals or changing instrument parameters.

1. Dispense exactly 6 mL of Q-water into each of four 15 mL disposable vials. Pipet the following amounts of Nitrite Calibration Standard into the separate vials: 50, 100, 500, 1000, 1500, 2000 and 2500.
2. Carry the calibration standards through the procedure starting with Step 4. Be sure to include a blank and a standard.
3. The slope and intercept are obtained by entering the calibration data into the "Generic Calibration" program on the HP-97. See Appendix A for further details.

B. Sample Preparation and Measurement

NOTE: Carry a reagent blank and QC standard through the procedure with every batch of samples.

1. Dispense exactly 6 mL of Q-water into a disposable vial containing a glass covered stir bar.
2. Pipet sample into the Q-water in the vial.
3. Record dilution size if used.

NOTE: The following two reagents (Steps 4 and 5) must be added in the order listed, otherwise an incorrect result will be reported for the sample.

4. Dispense 2 mL of 6 g/L sulfanilic acid in 50% acetic acid (reagent #1). Allow at least 30 seconds before next step.
5. Dispense 2 mL of 0.6 g/L 1-naphthylamine-7-sulfonic acid in 50% acetic acid. Mix by stirring.

NOTE: If the mixture turns dark red, orange, red or yellow, the sample is too concentrated and a larger dilution and/or larger sample size is needed.

6. Cap the vial and stir the mixture for 5 minutes.
7. Wait for at least 45 minutes but not more than 6 hours.

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PROCEDURE STEPS (continued)

8. Transfer a portion of each sample to a cuvette and measure the absorbance at 525 nm. Use the reagent blank to zero the instrument.
9. Slurp the solution from the cuvettes and vials, dispose of the disposable cells and vials. If glass cuvettes are used, rinse the cells with Q-water and ethanol.

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CALCULATIONS

A. Standard and sample concentrations may be calculated by hand as listed below:

1. The slope and y-intercept are obtained according to the CALIBRATION section of this procedure.
2. The concentration of nitrite is calculated using the following expression:

$$[\text{NO}_2^-] = \frac{\text{Abs. at 525 nm} - \text{y-intercept}}{\text{Slope}} \times \text{DF}$$

DF = dilution factor

3. The standard recovery is calculated as follows:

$$\text{Standard recovery} = \frac{[\text{NO}_2^-]_{\text{observed}}}{\text{standard value}} \times 100\%$$

4. Enter the calibration data in the instrument log book and the calibration log book in the lab leader's office.

Example:

A standard was run using a 50-10-100 dilution:

The absorbance was 1.385 at 525 nm
the slope was 45358.91 a.u.
the y-intercept was .005 a.u.
the true concentration of the standard is 0.5999 M NO_2^-

$$\text{DF} = 10.05/.05 \times 10.1/.1 = 20301$$

$$\begin{aligned} [\text{NO}_2^-] &= 1.385 - .005 / 45358.91 \times 20301 \\ &= .6176 \text{ M} \end{aligned}$$

$$\text{standard recovery} = .6178/.5999 \times 100\% = 103.0\%$$

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CALCULATIONS (continued)

- B. The concentration may also be calculated using the "Spectrophotometer" program on the HP-97 calculator by following this sequence:
1. Turn on the calculator.
 2. Find the magnetic card labelled "Spectrophotometer."
 3. Load the program into the calculator by passing the card through the reader slot on side 1 and side 2.
 4. Key in the predilution factor and press [E].
 5. Key in the sample volume in mL and press [D].
 6. Key in the sample absorbance and press [A]. The calculator will print the sample concentration.

Example:

A standard was run using a 50-10-100 dilution:

The absorbance was 1.385 at 525 nm
the slope was 45358.91 a.u.
the y-intercept was .005 a.u.
the true concentration of the standard is 0.5999 M NO₂⁻

The slope and intercept should be stored on the magnetic strip of the program "Spectrophotometer." If a new calibration has been run, the slope and intercept may be stored on the program card as follows:

- a. Load the program as in steps B. 1-3 above.
- b. Key in the intercept and press [Enter].
- c. Key in the slope and press [f] [a].
- d. The calculator will display Crd. Run side 2 of the program card through the card reader and the calibration data will be stored on the magnetic card.

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CALCULATIONS (continued)

Calculate the standard concentration as follows:

1. Key in 101 and press [E] (this is the predilution factor for a 100-10-50 sample).
2. Key in .05 and press [D] (this is the sample size in mL for a 100-10-50 sample).
3. Key in 1.385 and press [A] (this was the absorbance in the example). The calculator will print out 6.176 -01. This is the concentration of the sample in molarity.

DISCUSSION

This procedure follows the modified Greiss method of analysis for nitrite. Two reaction stages are involved. The initial stage of the reaction is called diazotization. A nitrous acid is formed by acidifying a solution containing a primary aromatic amine/acid (sulfanilic acid). The acid concentration is maintained high enough to cause diazotization but not so high as to interfere with the second stage. This requirement is taken care of by using a matrix of acetic acid.

The product of this reaction is unstable. It is immediately coupled with an aromatic amine (1-naphthylamine-7-sulfonic acid). The para position reacts forming an azo dye.

DISCUSSION (continued)

The absorption maximum for this pink azo dye is in the region 520-530 nm. The molar absorptivity is about 53,000.

The sample size selected should contain 4×10^{-5} to 4×10^{-4} millimoles/mL (or 1.8 to 18 ug/mL) of NO_2 .

Samples with interfering colors are not usually a problem due to the extreme sensitivity of the method and the large dilutions required. Samples with intense interfering colors can be measured by using a portion of the sample as a blank without adding the reagents to it.

Most of the difficulties that arise in this procedure are due to inadequate cleaning of glassware. Only Q-water should be used for rinsing glassware. DO NOT use nitric acid in the hood in which this procedure is performed.

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APPENDIX

CALIBRATION PROGRAM

These are instructions for using the HP-97 calculator to evaluate the calibration curve data and obtain the slope intercept and r^2 values necessary to calculate the concentration of nitrite in samples.

1. Turn on the HP-97 calculator.
2. Find the Magnetic card labelled "Generic Calibration."
3. Read the card into the calculator by passing it through the card reader slot.
4. Enter the NO_2^- concentration of the calibration standard and depress [f] then [A]. This step will initialize the calculator, store the standard concentration and print the standard concentration.
5. Enter the dilution volume (10 mL) and depress [f] then [B]. This will be used to calculate the dilution concentrations used in the calibration.
6. Key in the sample size for the first calibration solution, in mL, and press [ENTER].
7. Key in the absorbance value for this calibration solution then press [A]. The concentration of the solution and the absorbance values will be printed.
8. If an incorrect data set is entered and the [A] has been pressed, re-enter the same (wrong) data set and press [B]. This will delete the data set.
9. Repeat steps 6 and 7 for all calibration data sets.
10. To calculate the r^2 value, the intercept, and the slope, press [C]. These values will be printed out.

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APPENDIX - CALIBRATION PROGRAM
(continued)

Example data and resulting printout:

Concentration of NO_2^- in calibration solution: 0.0002 M

mL Calibration solution	Absorbance
0.050	0.054
0.100	0.101
0.200	0.203
0.300	0.294
0.500	0.482
0.750	0.700
1.000	0.898
1.500	1.294
2.000	1.637
2.500	1.957

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Rockwell Hanford Operations**ANALYTICAL LABORATORIES**

Issued By:

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Title

DETERMINATION OF HYDROXIDE ION IN SOLUTIONS
CONTAINING HYDROLYZABLE ANIONS BY POTENTIOMETRIC
TITRATION (AUTOMATIC)**SUMMARY**

Hydroxide ion concentration is determined by titrating an aliquot of sample with nitric acid to a potentiometric endpoint, using a combination pH electrode as an indicator. Interfering basic anions, mainly carbonate, are precipitated with barium chloride prior to titrating.

A differential titrator dispenses the titrant and plots the first derivative of pH versus volume (dpH/dV). The endpoint of the titration is determined by the location of the differential peak.

LIMITATIONS

Hydrolyzable anions (e.g., carbonate, aluminate, phosphate) if present, will bias the results high. Chromate ion will also cause high results. Some of these anions may be removed from solution by precipitation with barium chloride. Even then, however, these anions will cause a high bias above certain limits. Interfering anions most likely found in Hanford waste solutions have been studied and are listed in Table I (also see DISCUSSION).

Ammonia (NH_3) will titrate as hydroxide (OH^-). If a separate analysis for NH_3 is done, the NH_3 M should be subtracted from the OH^- M.

The hydroxide endpoint usually occurs between pH 8 and 10, depending on the content of hydrolyzable anions in the sample. The presence of barium salts usually does not interfere with this endpoint, as they dissolve only after the pH drops below 7.

Ions of other weak acids (e.g., cyanide, borate) may also interfere and must be absent (mole ratio of anion to $\text{OH}^- < 0.001$).

Table I - Maximum Limits for Some Anions

<u>Anion</u>	<u>MTR*</u>	<u>Reference</u>
$\text{Al}(\text{OH})_4^-$	0.5	1
CO_3^{2-}	2.5	1
PO_4^{3-}	0.6	1
NO_2^-	No Interference**

*Maximum Tolerable Ratio, expressed as mole ratio of anion/ OH^- ion.

**Nitrite ion does not interfere at the levels commonly encountered.

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APPLICATIONS

This method has been used to determine free hydroxide ion concentrations in a number of synthetic and actual waste samples containing one or more of the hydrolyzable anions studied. A relative standard deviation (95% C.L.) of ± 9 percent should be obtained on synthetic waste solution (ITS-OH, 9C11). Samples will of course give a wider variation.

SAFETY

Samples may be radioactive, thus provisions of General Regulations and Practices of Radiation Work as found in RHO-GM-MA-2 (SRP 61-02.5.2), and applicable Radiation Work Permits shall apply to all work performed under this procedure. The applicable RWP, found in RHO-MA-172, is SL-3 for work performed at the 222-S Laboratory.

All work with chemical reagents shall conform to RHO-MA-221. MSDS No. 80 - "Nitric Acid" and #226 - "Sodium Hydroxide" should be followed.

REAGENTS (See Labelling Procedure LO-120-001)

1. Nitric Acid (HNO_3), Standardized, $0.2000 \pm 0.02 \text{ M}$.

Add $12.8 \pm 0.1 \text{ mL}$ of concentrated (15.6 M) HNO_3 to Q-water and dilute to $1 \pm .01$ liter. Must be standardized against a known standardized base to 0.0001 M . This reagent must be labeled with preparation date, with a discard date of one year after the preparation date, and with the exact concentration of the acid. Store in a glass bottle, tightly capped when not in use. The shelf life is six weeks after the bottle is opened.

2. Barium Chloride $1.0 \pm 0.01 \text{ M}$.

Dissolve 244.2 ± 2 grams of barium chloride dihydrate ($\text{BaCl}_2 \cdot 2\text{H}_2\text{O}$) in deionized water and dilute to one liter. This reagent does not require standardization. The reagent must be labeled with the preparation date and a discard date of one year after the preparation date.

3. Buffer for pH 7 and pH 10.
4. Electrode storage solution, Beckman-Altex no. 531056.

EQUIPMENT

1. Magnetic stirrer.
2. Differential titrator.
3. Titrating beakers, 15 ml disposable plastic.

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PROCEDURE

NOTE: Set up titrator as described in appropriate procedure.

1. Check that electrode is calibrated appropriately and gives a stable reading.
2. Place the electrode tip in the solution so that the junction is completely immersed and will be at side opposite the buret tip.
3. Dropwise and slowly add 500 μ l of 1.0 M BaCl_2 to the beaker.
4. Place the buret tip in the solution mid-way between the vortex of the solution and the side of the beaker.
5. Titrate the sample as described in the appropriate instrument operating procedure.
6. Record the following information on the chart paper:
 - a. sample number
 - b. sample size
 - c. initial pH of the solution
 - d. molarity of nitric acid being used
7. Vacuum transfer any radioactive solutions to waste.
8. Dispose of plastic beakers and sample vials.
9. Clean work station thoroughly before leaving.

CALCULATIONS

NOTE: μ l = microliter (formerly lambda) = 1/1000 ml

$$\text{OH}^- \text{ M} = \frac{(\mu\text{l HNO}_3)(\text{M HNO}_3)}{\mu\text{l sample}}$$

Example: For a 25 μ l sample titrated with 0.1865 M HNO_3 .

$$\text{OH}^- \text{ M} = \frac{(25 \mu\text{l HNO}_3)(0.1865 \text{ M HNO}_3)}{25 \mu\text{l sample}} = 1.86 \text{ M}$$

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DISCUSSION

A. Interferences

The determination of hydroxide ion by titration with standard acid is basically quite simple and reliable. However, the method is not selective, and certain other anions also consume acid, thus giving high results. The anions most commonly encountered as troublesome include aluminate $[Al(OH)_4]^-$, carbonate (CO_3^{2-}) and phosphate (PO_4^{3-}). These all consume acid, presumably in steps as follows:

Equation				pH Range of Break
$Al(OH)_4^-$	$+ H^+$	$Al(OH)_3(s)$	$+ H_2O$	6-7
$Al(OH)_3(s)$	$+ H^+$	$Al(OH)_2^+$	$+ H_2O^*$	
$Al(OH)_2^+$	$+ H^+$	$AlOH^{2+}$	$+ H_2O^*$	
$AlOH^{2+}$	$+ H^+$	Al^{3+}	$+ H_2O^*$	
CO_3^{2-}	$+ H^+$	HCO_3^-		8-9
HCO_3^-	$+ H^+$	H_2CO_3		4-5
PO_4^{3-}	$+ H^+$	HPO_4^{2-}		12-13
HPO_4^{2-}	$+ H^+$	$H_2PO_4^-$		8-9
$H_2PO_4^-$	$+ H^+$	H_3PO_4		4-5

*These three steps may occur together, since $Al(OH)_3$ is a precipitate.

Chromate ion also consumes acid on a 1:1 basis. The ion dimerizes as the pH is lowered further:

In this method, the hydroxide concentration is determined by titrating to a differential endpoint. The major anions present ($>0.1M$) in a typical Hanford caustic waste sample are hydroxide, aluminate, nitrate and nitrite, which can vary widely in concentration between samples. In addition, smaller amounts of sulfate, carbonate, phosphate and chromate may be present.

DISCUSSION (continued)

The hydroxide differential peak is one of several peaks that occurs when one of these waste samples is titrated. A study has shown that, in a tank farm matrix, the first differential peak (pH 8-10) occurs at the endpoint of the free hydroxide.² However, if carbonate is present, as often occurs, the hydroxide differential peak can be displaced as well as suppressed. If barium ion is added to a dilute sample prior to titration, the carbonate interference will be removed as barium carbonate precipitate. Precipitation with barium will also remove sulfate, chromate, and some phosphate:

Where A^{2-} = carbonate, sulfate, chromate, and phosphate

This operation may cause a slight low bias in the results, due to occlusion of hydroxide in the precipitate, particularly if sulfate is present.³

Another study was made using a synthetic tank farm sample solution of the following composition:

NaOH	5.0 M
NaAl(OH) ₄	2.0
NaNO ₃	2.5
NaNO ₂	1.0

Various sample aliquots were made to which different amounts of sodium carbonate were added.⁴ Carbonate-to-hydroxide mole ratios ranged from 0.41 to 1.22. Titrations were made with and without barium chloride being added and the results compared. It was found for approximately every milli-equivalent (meq) of carbonate added, there was an additional meq of acid required to reach the endpoint. This suggests, at least around the concentration range considered, that this procedure can be used to check carbonate results obtained by other methods. Taking the difference between the volume of acid to titrate a sample without barium chloride added and the volume of acid to titrate a sample with barium chloride added (V_a) approximates the volume of acid required to titrate an equivalent amount of carbonate. Therefore, the approximate concentration of carbonate can be determined from the following equation:

$$\text{CO}_3^{2-} \text{ (M)} = \frac{(V) \text{ (M HNO}_3\text{)}}{\text{Sample Vol (uL)}}$$

NOTE: The sample sizes for both titration (with and without BaCl_2) must remain the same.

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DISCUSSION (continued)

A third study¹ was made for phosphate interference, using standard sodium hydroxide and various spike addition of trisodium phosphate. It was found that precipitation with barium ion did not remove all the phosphate and that high recoveries were observed above a phosphate-to-hydroxide mole ratio of 0.6 (Table II).

Table II - Results of Phosphate Interference Study

<u>Mole Ratio*, PO₄³⁻/OH⁻</u>	<u>Percent Recovery</u>
0.3	103.0
0.6	102.0
0.6	102.0
1.2	107.8
1.2	111.7
3.0	123.4
3.0	127.2

To test for problems a sample can be titrated with three or four different sample volumes. Plot the end point volumes versus sample volume and extrapolate to zero sample size. This intercept should be close to zero and all points on a straightline. Consult with chemist for interpretation and guidance.

REFERENCES

A. Procedures

1. LA-212-101 (Unclassified), "Set Up and Standardization of pH Meter and Glass Electrode."
2. Current Differential Titrator Operating Method such as LA-211-101 or other appropriate procedures.

B. Source Documents

1. B. H. Nicholson, Laboratory Notes, ARH-N-363, pp. 68-69.
2. Letter, May 2, 1972, A. H. Case to J. S. Buckingham, "Determination of NaOH in ITS Recycle Waste Solution."
3. H. A. Laitman, Chemical Analysis, McGraw-Hill, Inc., New York, 1960, pp. 96-97.

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4. Letter, July 25, 1972, V. W. Hall To W. H. Sant, "Development of an Analytical Procedure for Determining NaOH in ITS Caustic Waste Solutions."
5. Letter, April 6, 1973, A. H. Case to J. S. Buckingham, "Determination of NaOH in Spray Dry Solids."
6. R. A. Day, Jr. and M. H. Underwood, Quantitative Analysis, Prentice-Hall, Inc., Englewood Cliff, N. J., 1962, pp. 78, 80, 299, and 300.

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ANALYTICAL LABORATORIES

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Title

DETERMINATION OF CARBON IN SOLUTIONS BY
COMBUSTION AND COULOMETRY

SUMMARY

Liquid samples are introduced into an 850-900°C furnace through which a stream of oxygen flows (see Figure 1 and 2). Carbon present in sample aliquots is converted to carbon dioxide which is carried through purifying traps. The carbon dioxide is collected and quantitatively measured with a coulometer which generates base to automatically titrate carbonic acid.

LIMITATIONS

This analytical procedure includes steps for analyzing liquid samples for total carbon. In addition, organic carbon may be determined by pretreating liquid samples with acid to remove mineral carbonates prior to injecting samples into the combustion furnace. Results are for total carbon unless the carbonate is removed.

Potential chemical interferences are sulfur oxides, hydrogen halides, and oxides of nitrogen, all of which may be evolved from acids or their salts. Chemical scrubbers are included in the gas train to remove these interferences. Interferents in the coulometer cell are indicated by continual or late coulometer integration, perhaps for fog forming above the coulometer solution and by high blanks indicative that scrubbers are spent.

Levels of sodium greater than 1 M are detrimental to the quartz combustion tube. These should be analyzed by using smaller injection volumes.

Removal of carbonate carbon may result in the loss of volatile organic compounds. If such compounds are present in samples and are of interest, the total organic carbon content should be determined by the difference between total carbon and carbonate carbon.

The average percent recovery of seven replicate 2.0 g/L (0.17 M) carbon standards was 100.19% with a standard deviation of $\pm 0.37\%$. The precision of the method at the 95% confidence level is $\pm 0.72\%$.

APPLICATIONS

This procedure and the coulometrics instrumentation may be applied to both radioactive and nonradioactive samples, which are liquid. With careful monitoring of the blank, a lower detection limit of 1 μg of carbon in 200 μL of diluted sample is observed. This is equivalent to 55 mg of carbon per liter, or 55 ppm. For TOC by difference with undiluted samples the limit is about 10 ppm.

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APPLICATIONS (Continued)

Recovery obtained on standards is kept within 90 to 110%. It is often possible to keep recovery on standards within 95 to 105%, and the scientist should be notified when standards are consistently outside this narrower range.

SAFETY

This procedure has the following unique safety concerns:

- o Standard practices to contain radioactive substances and limit personnel exposure must be followed.
- o Always survey hood and its contents for smearable contamination and clean up any contamination found.
- o Always do a radiation survey inside hood with CP and remove or shield all sources so that self-survey limit of 100 mRad cannot be exceeded. Notify management if any shielded source exceeds 500 mRad inside the shield so that steps can be taken to assure that no unusual exposure will occur.
- o Be especially aware that radioactivity from samples accumulates in the furnace. Therefore, observe this:

WARNING: DO NOT MOVE FURNACE OR BRASS INLET FITTING. DO NOT LIFT THE PLATFORM OF INSTRUMENT.

- o BREAKAGE OF FURNACE TUBE IS A SERIOUS HAZARD--CALL for assistance and get out of the hood with as little spread of contamination as possible. Consult with management and radiation protection technologist about next action.
- o If the combustion tube cracks, lower the temperature control by two whole numbers and notify supervision. In the event the tube-end plug at furnace outlet (left end) shoots off, a pressure build-up in the tube or a blockage in trap lines is indicated, or more quartz wool is needed. Notify supervision of the problem.
- o Samples from PUREX may be a special radiation hazard when recent fission products are present. The ruthenium forms a volatile oxide which passes through the furnace and reacts with the rubber and plastic. This ruthenium tetroxide, RuO_4 , boils at about 40°C and will be partly trapped on the tin scrubber with the remainder condensing in the water scrubber and on the DRIERITE.

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SAFETY (Continued)

- o Pressure and Vacuum. Use great care to avoid changes of pressure or development of a vacuum in the apparatus. Otherwise, the water may move into the furnace tube and coulometer solution pulled into the acid scrubber tube when room temperature decreases at night, or if furnace goes off.
- o Injection Syringe. Keep fingers away from the injection button on the syringe when handling syringe prior to sample injection. Although the sample volumes used are very small, the instrument could become contaminated by inadvertently pushing the injection button prematurely. Keep the syringe pointed into the hood at all times. (See Figure 7.)
- o High Temperature. Although the furnace is well insulated and shielded, keep all paper, organic materials, and hands away from heated portions of the furnace and combustion tube. DO NOT OPEN THE FURNACE AT ANY TIME unless power is disconnected and temperature is less than 100°C.
- o TO MINIMIZE THE POTENTIAL FOR AN EXPLOSION, INJECTION VOLUMES MUST NOT INITIALLY EXCEED 200 uL FOR LIQUID SAMPLES. In the presence of pure oxygen, samples containing 10 mg or more of carbon may explode. The injection of 200 uL of water generates a large pressure pulse when no quartz wool is present and may crack the furnace tube.
- o The traps prevent any radioactivity which may be volatilized from being carried out of the hood and into the coulometer.
- o Oxidizing Agents. The gas scrubbers use one reagent, acid dichromate, which is a strong oxidizing agent. This reagent must be well diluted with water before going into waste bottles. The solids remaining after water wash of the acid dichromate may go into the solid waste carton.

REAGENTS

| Oxygen (O₂) (MSDS #1406)

Stores Stock 21-3500-035 with pressure regulator and a gauge so pressure can be kept at 8 to 12 psi.

| DRIERITE with Indicator (MSDS #14876) (CaSO₄) (MSDS 1090)

Anhydrous, granular, calcium sulfate, 20-30 mesh. The DRIERITE used with the TOC scrubber must be discarded to solid contaminated waste.

| Acid Dichromate (MSDS #2064)

On Silocel, Coulometrics Part No. 300-008. Used to remove nitrogen oxides, NO_x, and sulfur oxides. Store in a desiccator. Good until it becomes wet or loses yellow tint.

| Tin, granular metal (MSDS #2064)

20 mesh, reagent grade. Used in line following the TOC furnace to remove acid vapors, and to reduce nitrogen oxides, sulfur oxides and chlorine, and ruthenium vapors.

| Carbonate Free Deionized Water (MSDS #N/A)

Get water from deionizer in 1J having an organic removal cartridge or boil 3.5 L of distilled water with 10 g of potassium persulfate in a covered beaker. Allow it to cool to about 60°C. Pour into a clean glass gallon bottle. Stopper it with a dispensing apparatus which uses an Ascarite tube to prevent carbon dioxide from reaching the water. Shelf life is one year.

| Dilution Acid, 0.5m Sulfuric Acid, organic free (MSDS #1529)

The Standards Laboratory is responsible for the preparation of this acid.

| Coulometer Solutions (MSDS #N/A) KI (MSDS #1475)

Proprietary solution produced by Coulometrics, Inc., Cat. No. 101-040, which includes the anode solution and potassium iodide (KI). Store in gallon bottles in yellow cabinet for flammable solvents. Bench top quantity should not exceed 1000 mL.

| Potassium Hydroxide (KOH) Scrubbing Solution (MSDS #1442)

Dissolve 45 g of KOH and dilute to 100 mL with Q-water. Use CAUTION when adding water to the solid KOH as it is a very exothermic reaction.

EQUIPMENT

Syringes, metal, 50 and 200 mL Hamilton models CR-700-050, CR-700-200, (See Figure 7).

Coulometrics, Inc., total carbon analysis instrumentation with carbonate purging accessory, panel of gas purifying scrubbers, quartz combustion tube, and an oxygen cylinder with two stage pressure regulatory of 8 to 12 psi.

Vials, glass, 2 dram for dilution, rinsed to remove dust.

Dispenser pipet, Eppendorf type, 200 uL accurate to $\pm$ uL. Used for diluting samples. Calibration to be checked at lease every 3 months.

Reagent dispenser, 2.00 mL $\pm$ 0.02 mL. For use with the 0.5 M sulfuric acid in diluting and sparging samples.

Furnace, replacement for Coulometrics equipment, compact split tube, low density ceramic insulation, such as Lindberg 55035.

Furnace combustion tubes, packed according to Procedure LA-344-103, or prepacked by Coulometrics (UIC). Tubes are to be changed using Procedure LA-344-104. (See Figure 6.)

PROCEDURE STEPS

NOTE: To observe the following technical details:

- a. Any organic material from skin, surgeon's gloves, acetone, dilution water, and glass sample vials will affect analytical results.
- b. Glass should be cleaned with sulfuric acid dichromate before use if carbon content of less than 1 ug is to be measured.
- c. Plasticware, especially, must be avoided such as plastic beakers, bottles, while pipet tips may need to be rinsed twice with water before pipetting samples.
- e. Significant amounts of volatile organic compounds may be lost in carbonate removal during the sparging process, for example, acetic acid and acetone.

I. COULOMETER CELL SETUP

1. Pour 75 to 100 mL of coulometer solution into the 200 mL coulometer beaker containing a one-inch Teflon stir bar. (See Figure 4.)

NOTE: While filling both coulometer cells, keep inside tip portion of beakers and rubber stopper dry and free of acid and coulometer solution.

WARNING: DO NOT BEND PLATINUM WIRE NEXT TO GLASS ELECTRODE SINCE THE GLASS WILL LIKELY BREAK.

2. Contact scientist/manager if platinum wire needs to be reshaped.
3. Insert the rubber stopper cell top with the position of the platinum electrode on the opposite side from the side arm.
4. Add solid potassium iodide (KI) to a depth of 1/4-inch into the bottom of the side arm (anode compartment).
5. Fill the side arm with 10 to 12 mL of anode solution (keep solution level slightly below coulometer solution level).
6. Place the silver electrode into the anode compartment. The silver should reach almost to the bottom of the compartment but must not touch the KI salt. If not proper depth, adjust the electrode within the rubber stopper after removal of the stopper from the compartment.
7. Adjust position of bubbler tube to reach bottom of beaker at the rear of beaker and so bubbles will not pass through light beam.

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PROCEDURE STEPS (Continued)

8. Place coulometer cell into cell holder by sliding cell vertically from top to bottom of holder with the side arm extending out the front of holder and the platinum electrode toward back of holder.

II. COULOMETER STARTUP

1. Turn on the coulometer Power Switch (Figure 3).
2. Rotate cell in its holder until a maximum Percent Transmission (%T) is noted on the digital display.
3. Adjust the %T Knob until the %T Meter indicates a 100%T reading.
4. Remove the electrode shorting strap.
5. Connect the electrode leads to coulometer as follows:
 - a. Connect silver anode electrode to red.
 - b. Connect platinum cathode electrode to black.
6. Turn on the Cell Current Switch.
7. Observe coulometer solution.
 - a. Color becomes blue.
 - b. %T Meter reading becomes 29.
8. Set upper Select Lever to RUN position.
9. Set lower Select Lever to COUNT position.
10. Set Time Selection Thumbwheel to 1.0 minute for computer usage or 4.0 for manual operation.
11. Set Mode Selection Thumbwheel to 1 position for ug.
12. Reset the coulometer by pushing Reset Button.

III. CARBON ANALYZER START-UP

1. Remove the connecting bypass tubing between the inlet (green) and exhaust (yellow) lines.
2. Connect the gas lines to coulometer as follows:
 - a. Connect the green coulometer gas lead labeled "TOC" to the corresponding green beaker inlet.

PROCEDURAL STEPS (Continued)

- b. Connect the yellow beaker exhaust lead labeled "TOC" to the corresponding yellow return exhaust line.
 - c. Adjust position of bubbler tube to reach bottom of beaker so bubbles will not pass through light beam. There should be no variation in light transmittance when bubbling starts or stops.
- | 3. Set the oxygen regulatory to 10-11 psi.
- | 4. Turn on the oxygen carrier gas Flow Meter (the flow meter on the left) counterclockwise to 100 cc/min.
- | 5. Change the KOH Scrubber solution every two weeks or when foamy. Note in log book.
- a. Disconnect the Teflon tubing from the scrubber top.
 - b. Turn black cap counterclockwise on top of scrubber to access KOH solution.
- | NOTE: Do not rinse KOH scrubber with acetone, alcohol, or other organic solvents. Vapors from such solvents can be sprayed into combustion tube and explosively destroy tube and scrubber.
- c. Slurp the old KOH solution to waste bottle.
 - d. Add 15-20 mL of 45% KOH solution using a 30 mL beaker.
 - e. Turn black cap clockwise on scrubber top to secure to system.
 - f. Reconnect the Teflon tubing to the scrubber top.
- | 6. Empty the water trap when condensed water accumulates. (See Figure 5.)
- a. Remove clamp on water drain line.
 - b. Slurp the condensed water to waste bottle.
 - c. Replace clamp in drain line.
 - d. Replace water trap if internal filter becomes saturated.

PROCEDURAL STEPS (continued)

- | 7. Change the tin scrubber when discoloration appears. (See Figure 5.)
 - a. Disconnect both top and bottom tube fittings from the scrubber tube.
 - b. Discard the old scrubber tube into waste carton.
 - c. Place a small plug of quartz wool into one end of a new tube.
 - d. Fill the tube with fresh granular tin.
 - e. Secure the tin in the tube with another small plug of quartz wool.
 - f. Reconnect both top and bottom tube fittings to the scrubber tube.
- | 8. Change the DRIERITE scrubber when the majority of the contents are pink or white. (See Figure 5.)
 - a. Disconnect both top and bottom tube fittings from the scrubber tube.
 - b. Discard the old scrubber tube into waste carton.
 - c. Place a small plug of quartz wool into one end of a new tube.
 - d. Fill the tube with fresh DRIERITE.
 - e. Secure the DRIERITE in the tube with another small plug of quartz wool.
 - f. Reconnect both top and bottom tube fittings to the scrubber tube.
- | 9. Change the NO_x scrubber when it becomes wet or grayish-brown or green in color. (See Figure 5.)
 - a. Disconnect both top and bottom tube fittings from the scrubber tube.
 - b. Discard the old scrubber tube into waste carton.
 - c. Place a small plug of quartz wool into one end of a new tube.
 - d. Fill 2/3 of the tube with acid dichromate.
 - e. Secure the dichromate with another small plug of quartz wool.
 - f. Fill the remaining 1/3 of the tube with manganese dioxide (MnO₂).

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PROCEDURAL STEPS (Continued)

- g. Secure the MnO_2 in the tube with another small plug of quartz wool.
 - h. Reconnect both top and bottom tube fittings to the scrubber tube.
10. Purge apparatus for 10-30 minutes.

IV. COMPUTER SETUP

NOTE: This section is to be used when a desktop computer is utilized with the coulometer.

1. Turn on main Power Switch for all computer components.
2. Select desired analytical program from menu.
 - a. Computer monitor and print-out will list 11 prompts.*
 1. Enter the analysis ID; T=TOC,C-CO3 [T]
 2. Enter the sample ID: []
 3. Do you wish to run a blank: (Y/N) [N]
 4. Enter the blank value: [0]
 5. Enter your payroll number: []
 6. Enter the sample size in uL: [200]
 7. Enter the dilution factor: [11]
 8. Enter the minimum number of readings: [4]
 9. Enter the maximum number of readings: [10]
 10. Enter the % difference value: [10]
 11. Enter # to edit, Q=quit, or R=Run: [R]

* [] = Default Values

V. INSTRUMENT BLANK MEASUREMENT

NOTE: Coulometer is set for a minimum of four one-minute accumulative readings as ug carbon for each analysis.

1. Press "R" on computer keyboard or press Reset button on coulometer without computer.
2. Repeat instrument blanks until (1) the background readings stabilize to ± 1.0 ug of the previous value or (2) the background with gas flow is less than 1.5 ug carbon accumulated for each minute.

PROCEDURE STEPS (Continued)

VI. ACID OR WATER BLANK MEASUREMENT

NOTE: Samples for Total Carbon (TC) analysis are either injected undiluted or are diluted with distilled water prior to sample injection.

Do not use injection syringe for diluting hot samples since they accumulate radioactive contamination on the metal.

Move syringe plunger slowly upward to reduce formation of bubbles. Bubbles will also form if needle is becoming plugged or if plunger is loose in barrel.

1. Prepare to measure blanks by filling 200 uL syringe with (1) distilled water when analyzing samples for Total Carbon (TC) or (2) 0.5 M sulfuric acid (H_2SO_4) when analyzing samples for Total Organic Carbon (TOC), and inject to waste.

2. Repeat previous step twice more to rinse out syringe.

3. Pull out furnace stopper in sample introduction port using forceps.

NOTE: Check the syringe setting periodically to ensure that syringe is delivering 200 uL.

4. Draw up 200 uL of solution into syringe and insert syringe at introduction port with a slight twist.

5. Allow 1-2 minutes for the system to purge itself of any CO_2 which may have entered the system while the injection port was open.

6. Press "R" on computer or press Reset Button on coulometer without computer.

NOTE: Do not remove syringe from introduction port at this time.

7. Inject the sample by pressing the side button on syringe.

8. Record the blank value in ug on the analytical card or the computer after a minimum of 4 minutes.

9. Attach the computer printout blank value to the analytical card.

10. Repeat blanks until the background readings stabilize to ± 1.0 ug of the previous value before proceeding to do samples.

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PROCEDURE STEPS (Continued)

VII. DETERMINATION OF TC/TOC IN LIQUID SAMPLES

NOTE: Verify instrument operation with an independently prepared check standard every 15 samples.

NOTE: Run one spike duplicate sample for every 10 samples. A duplicate sample is a sample brought through the whole sample preparation process.

1. FOR TOC ANALYSIS ONLY

- a. Pipet sample indicated on analytical card into 2 mL of 0.5 M H_2SO_4 in a 2 dram vial.
- b. Place parafilm over top of vial containing diluted sample only for delayed analyses for 2 to 8 hours.
- c. Install clean capillary tubes in the Tygon tubing leading from the manifold to purge samples.
- d. Turn on oxygen purge gas flow meter (flow meter on the right) counterclockwise to 200 cc/min.
- e. Insert capillary tube into acidified sample by puncturing the parafilm at edge of vial top.

NOTE: Never leave the capillary tube in any solution unless the purge gas is flowing.

- f. Position the tube so that the gas flow has a stirring effect on the solution and purge sample for 6 minutes.

WARNING: EXTENDED PURGE WILL CONCENTRATE SAMPLE AND CAUSE ERRONEOUS RESULTS.

NOTE: Keep sparge gas flowing until capillaries are removed from samples.

- g. Remove capillary tube from samples using forceps.
- h. Turn off oxygen purge gas flow meter clockwise to 0 cc/min.

2. FOR TC ANALYSIS

- a. Rinse syringe twice with water.
- b. Dispense an aliquot of direct sample into a 2 dram vial.

3. Repeat Steps 3 through 8 under Section VII, ACID OR WATER BLANK MEASUREMENT, for all standards and sample to be analyzed.

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PROCEDURE STEPS (Continued)

NOTE: When net carbon is less than 10 ug, determine TOC by difference (TC minus carbonate).

- | 4. Agreement between sample injections must be within the larger of 4% of the result or 3 ug. If not, make another injection of appropriate sample size.
- | 5. Record the results of carbonate measurement on each card or computer. The value of background or blank shall be put on each sample card.
- | 6. Calculate recovery on standards before doing samples.

NOTE: Leave warning message for scientist if standards are consistently outside of 95 to 105% recovery.

Do not run any samples if standard is outside of 90 to 110%, unless the recovery is reproducible at the low value and the sample result is corrected for recovery. Make sure management approves this action and that scientist gets the message that recovery is out of bounds.

VIII. CARBON ANALYZER SHUTDOWN

1. Turn down the oxygen carrier gas flow meter (the flow meter on the left) clockwise to 10-20 cc/min.
2. Disconnect the gas lines to the coulometer; ie., both the inlet (green) and exhaust (yellow) lines.
- | 3. Connect bypass tubing between inlet (green) and exhaust (yellow) lines to allow purging oxygen gas flow back into hood.
- | 4. Do not lower the furnace temperature below 900°C except prior to combustion tube replacement.

IX. COULOMETER SHUTDOWN

1. Turn off the Cell Current Switch.
2. Disconnect the electrode leads to coulometer as follows:
 - a. Disconnect red silver anode electrode.
 - b. Disconnect black platinum cathode electrode.
3. Insert the electrode shorting strap between the cell current outlet terminals to protect them while the coulometer is not in use.
4. Turn off the coulometer Power Switch.

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| X. COMPUTER SHUTDOWN

- | 1. Turn off the main Power Switch for all the computer components.

| XI. COULOMETER CLEANUP

WARNING: DO NOT LEAVE THE COULOMETER CELL IN PLACE WITH THE ANODE COMPARTMENT FILLED FOR MORE THAN 16 HOURS. THE ANODE SOLUTION SLOWLY LEAKS INTO THE COULOMETER SOLUTION RESULTING IN SILVER DEPOSITS ON THE PLATINUM AND INCREASE IN THE BLANKS DUE TO IODIDE BEING OXIDIZED TO IODINE. THE PLATINUM ELECTRODE AND THE FRIT BECOME DISCOLORED AND REQUIRE CLEANING AFTER EXTENDED USE.

1. Remove coulometer cell from cell holder by lifting cell vertically from bottom to top of holder until free.
2. Remove the two rubber stopper cell cap assemblies and set aside.
3. Pour both the used cathode and anode coulometer solution into the organic waste storage bottle using a large funnel which is on the bench next to the TOC hood. Dispose of full waste bottles as per the procedure for handling of organic wastes.
4. Rinse both cells including precipitates and salts into the funnel using Q-water.
5. Rinse the silver electrode, the beaker, and platinum electrode with deionized water. If silver electrode is corroded, use fine steel wool to clean.
6. Rinse the anode compartment with water. If the anode compartment is discolored or the platinum electrode is not shiny, then soak them in 6 M nitric acid until clean. Be sure to thoroughly rinse off all acid. Also, rinse the rubber stopper and other parts so no acid gets into the cell.
7. Rinse off water with alcohol or ethanol and then draw alcohol through the frit using vacuum.
8. Make a final rinse of all components with Q-water and dry.
9. Store cleaned coulometer cell with electrodes installed in the cell holder to avoid breakage of the cell components.

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CALCULATIONS

The following makes it possible to calculate the carbon result by a manual calculation in event the computer is inoperative. The computer program is designed to guide the operator through each step of data collection needed to compute the carbon result. A tape printout is made for each calculation. This printout can be taped to the analytical card and becomes a permanent record.

1. Calculate the total organic carbon (TOC) in acidified liquid samples in the units grams of organic carbon per liter of solution:

- a. $\text{g/L TOC} = \frac{(\text{ug C} - \text{ug blank}) \times \text{D.F.}}{\text{uL of sample injected}}$

- b. Example: Sample diluted 200-2 [DF = 11] yielded 21.2 ug TOC reading and 1.2 ug blank from 200 uL injections.

$$\text{g/L TOC} = \frac{(21.2 - 1.2) \times 11}{200} = 1.10 \text{ g/L TOC}$$

2. Calculate the total organic carbon (TOC) in acidified liquid samples in the units of moles TOC per liter of solution:

- a. $\text{M TOC} = \frac{(\text{ug C} - \text{ug blank}) \times \text{D.F.}}{12 \times \text{uL of sample injected}}$

where 12 represents the atomic weight of carbon

- b. Example: Using the same data as in Step 1.b above:

$$\text{M TOC} = \frac{(21.2 - 1.2) \times 11}{12 \times 200} = 0.092 \text{ M TOC}$$

3. Calculate the total carbon (TC) in liquid samples.

- a. Use equation in 1.a or 2.a for reporting results in units of grams TC per liter of solution or mole TC per liter of solution respectively.

CALCULATIONS (Continued)

4. Calculate total organic carbon (TOC) by difference (carbonate correction).

NOTE: When carbonated has not been removed from liquid samples by acid purging, TOC may be determined by difference.

- a. Determine the total carbon content (TC) of liquid sample.
- b. Determine the carbonate content per Procedure LA-622-101 for samples.
- c. Calculate TOC by the appropriate equation below:

(1) Solutions:

$$\text{g/L TOC} = \frac{(\text{ug TC} - \text{ug blank}) \times \text{D. F.}}{\text{uL sample}} - \frac{\text{g.K. /CO}_3}{\text{g/L CO}_3}$$

NOTE: $\text{g/L CO}_3 = 12.01 \times \text{mol/L of CO}_3$

- d. Examples: A liquid sample diluted 200-2 gave a 110.3 TC reading from a 200 uL injection. The blank read 5.3 ug. A 50 uL aliquot of sample was injected into the carbonate apparatus yielding 1.2 g/L of CO₃ carbon. Determine TOC.

Solving:

$$\text{g/L TOC} = \frac{(110.3 - 5.3) \times 11}{200} - \frac{1.2 \times 1}{1} = 4.575 \text{ g/L TOC}$$

DISCUSSION

Carbon dioxide and interfering gases are produced from combustion of the sample at 850°C. Barium chromate in the combustion tube oxidizes uncombusted organic compounds and reacts with sulfur oxides to form barium chromite and sulfate. Hydrogen halides and phosphorous oxides (from thermal decomposition of phosphates) are removed by the silver metal on silica gel and the granular tin. This wet tin reacts with acids and reduces part of the oxides of nitrogen and sulfur. The remaining oxides of nitrogen and sulfur are efficiently removed from the gas stream by the granular acid dichromate. The gas must be dried before reaching the acid dichromate (to avoid diluting the concentrated sulfuric acid). This drying is done with DRIERITE (anhydrous calcium sulfate). The dichromate agent can absorb relatively large volumes of NO_x . This scrubbing agent is expensive and should be conserved.

Sodium in solutions injected into the combustion tube reacts with quartz to form sodium silicates, which have high coefficients of expansion. A tube with just a few milligrams of sodium in it and no quartz wool will probably break on cooling. The sodium problem can be reduced by adding extra quartz wool and by coating the quartz wool with tungsten trioxide. The tungsten oxide reacts with sodium to form sodium tungstate. It is possible to prolong the tube life by adding more quartz wool with tungsten trioxide when the initial loading has reacted. Another beneficial effect of tungstate is its reaction with strontium and barium carbonates to release the carbonate and form the more stable metal tungstates.

Barium tungstate is more stable than barium chromate. There must be a buffer length of about 1 inch of quartz wool between the tungstic oxide and the barium chromate to prevent their reacting in the furnace tube.

FIGURE 1.

COULOMETER AND TOC ANALYZERS

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FIGURE 2
TOC ANALYZER

FIGURE 3
CO₂ COULOMETER

FIGURE 4

COULOMETER CELL WITH TOP VIEW OF ALIGNMENT

FIGURE 5
POST COMBUSTION SCRUBBER MODULE

- A. Balston Filter
- B. Drierite Scrubber
- C. NO_x Scrubber
- D. Acid Dichromate on Silocel
- E. Manganese Dioxide
- F. Tin Scrubber

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FIGURE 6
COMBUSTION TUBES

SYRINGE COMBUSTION TUBE

- A. Barium Chromate Combustion Catalyst (140mm)
- B. Reduced Silver (30mm)
- C. Quartz Wool
- D. Loose-pack Quartz Wool w/ Tungsten Trioxide (20mm)
- E. Air Space (70mm)

PRECOMBUSTION TUBE

- A. Barium Chromate Combustion Catalyst
- B. Quartz Wool

FIGURE 7
METAL SYRINGE

ANALYTICAL LABORATORIES

Issued By:

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Title

AMMONIA BY KJELDAHL

SUMMARY

Ammonia is a weak base which is volatile. Therefore, if an excess of a strong base is added to a solution of an ammonium salt and the mixture distilled, the ammonia will be quantitatively expelled. Note References 1 and 2. This distillate is received in a boric acid solution which is titrated with standardized hydrochloric acid using bromcresol green as an indicator.

LIMITATIONS

The boric acid catch solution (20 mL of 0.1M H_3BO_3), has a neutralizing capacity of two millimoles of ammonia. If these quantities of ammonia are exceeded, the concentration of both the catch solution and the hydrochloric acid titrant must be increased. No less than the lower detection limit of 5×10^{-6} moles of ammonia should be determined by this method. The accuracy at levels higher than the lower detection limit should be better than $\pm 10\%$ at the 95% confidence level.

APPLICATIONS

Any type of sample may be run since there is no interference due to the presence of common process metal ions at typical concentrations. A spike of about 50 to 100 percent of the sample concentration should be run with every nonroutine sample. The spike is used only to determine matrix interferences, thus no spike corrections are necessary. If extreme spike recoveries are found (outside 90 - 110%), sample and sample + spike should be rerun. If after rerunning, the spike is still outside the limits (90 - 110%) contact the scientist in charge.

SAFETY

All work with chemical reagents will conform to WHC-CM-4-3, Industrial Safety Manual - Safety Standards, Safety Guides and Respiratory Protection; and Material Safety Data Sheets 1759 - ammonium chloride, 1498 - sodium hydroxide, and 1250 - hydrochloric acid. Particular attention should be given to the use of strong bases. No mechanical or thermal strains should be applied to the glass apparatus which would result in breakage and possible personal injury. No flammable vapors or liquids should be near the still. When replacing glassware, leather gloves must be worn.

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REAGENTS

Label reagents in accordance with procedure LO-120-001.

Boric Acid - 0.1 M

Dissolve 6.18 grams of H_3BO_3 crystals (reagent grade) in approximately 700 mL deionized water and dilute to one liter.

Bromcresol Green Indicator - 0.1 percent

Dissolve 0.1 gram in 14 mL of 0.01 M NaOH and dilute to 100 mL with deionized water.

Sodium Hydroxide - 1.0 M

Dissolve 40.0 grams of NaOH pellets (reagent grade) in approximately 700 mL deionized water and dilute to one liter.

Hydrochloric Acid - 0.1000 M (Standardized)

Obtain from Standards Preparation Unit.

Phenolphthalein Indicator - 0.05 percent

Dissolve 0.05 gram of phenolphthalein in 50 mL of ethanol and add 50 mL deionized water.

Ammonium Chloride - 0.0500 M (Standard)

Obtain from Standards Preparation Unit.

EQUIPMENT

Kjeldahl apparatus (250 mL)

Heating mantle (250 mL)

Manostat or digital buret

Magnetic stirrer

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PROCEDURE

A. Routine Samples

NOTE: For all samples except 242-A Evaporator bubbler samples.

NOTE: Prior to running each sample batch by this method, the NH_4 standard should be run.

1. Rinse the funnel and boiling flask by opening stopcock on funnel and rinsing with deionized water from a squirt bottle.
2. Slurp the water by closing the funnel stopcock and opening the stopcock to the flask drain. Close stopcock when complete.
3. To two 50 mL beakers, add $20 \text{ mL} \pm 1 \text{ mL}$ of 0.1 M boric acid (H_3BO_3). The second beaker is for a reagent blank.
4. Place the beaker of boric acid on the receiver tray and position the condenser receiver tip one-quarter inch below the surface of the boric acid.

CAUTION: If sample or hood dose rate is above 10 mRad/hr at open face of hood, call radiation protection technician for survey check.

5. With the funnel stopcock in the "off" position, add 15 mL of water and the specified sample into the funnel. Rinse pipet three times with water.
6. Add two drops of phenolphthalein indicator to the funnel.
7. Make sure the stopcock on the flask slurp tube is turned off.
8. Open stopcock to drain the contents of the funnel into the flask. Rinse with distilled water to ensure all the sample is inside the flask before the NaOH is added. Close stopcock when completed.

NOTE: Be sure to close stopcock before last of NaOH drains out to prevent venting loss of NH_3 from sample.

9. From a squirt bottle add 5 mL of 1.0 M NaOH into the funnel. Open stopcock to add NaOH to flask.
10. Rinse the caustic from the funnel with 5 mL of water.
11. Again be sure to close stopcock just as the last of the water drains out to prevent possible loss of NH_3 .

NOTE: The final solution should be pink in color. If final solution is not pink, add additional NaOH until pink and repeat rinsing Steps 10 and 11.

12. Turn on the condenser cooling water. Then turn on the heater to 100 V.

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PROCEDURE (continued)

13. Allow the flask to boil until about 30 mL $\pm$ 2 mL total liquid volume is in the receiver beaker. This should require about 15 $\pm$ 5 minutes.

NOTE: Step 14 is needed to prevent suck back of sample. The new beaker is only to catch drips.

14. Remove the beaker immediately from under the receiver tip and replace it with empty beaker.
15. Turn off the heater.
16. Turn off condenser water.
17. Open funnel stopcock and the stopcock to the drain and drain the liquid. Keeping the stopcocks open, allow air to flow through the boiling flask for 10 minutes or until the flask is cool to the touch.
18. Add distilled water to the blank until it is the same volume as the distillate sample beaker from Step 14.
19. Add three drops of 0.1 percent bromcresol green indicator to both beakers.
20. Titrate (see LA-501-206, if applicable) the blank with 0.1 M HCl (standardized) to the first permanent yellow color. Record as Volume HCl (mL) required for blank.
21. Titrate the sample distillate from Step 14 to the same yellow endpoint. Record as Volume HCl (mL) required for sample.
22. Survey the boiling flask. If a dose rate is detected, flush the apparatus with sufficient water to reduce the readings. In the event this equipment cannot be cleaned by flushing, remove the apparatus and take it to decon for cleaning, or flush with nitric acid in the decon hood.
23. Complete calculations (see Calculations Section).
24. If requested by manager, rerun Steps 1 - 14 with an identical sample plus an appropriate NH_4 spike. Spikes only need to be run on new sample points of nonroutine samples to check recovery.

B. Evaporator 242-A Bubbler Samples

1. To two 50-mL beakers, add 1 mL of 0.1 M boric acid (H_3BO_3). The second beaker is for a reagent blank.
2. Pipet the sample containing ammonia into the first 50-mL beaker.
3. Add distilled water to the blank beaker until it is the same volume as the sample beaker from Step 2.

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PROCEDURE (continued)

4. Add three drops of 0.1 percent bromcresol green indicator to both beakers.
5. Titrate (see LA-501-206, if applicable) the blank with 0.1 M HCl (standardized) to the first permanent yellow color. Record as Volume HCl (mL) required for blank.
6. Titrate the sample from Step 1 to the same yellow endpoint. Record as Volume HCl (mL) required for sample.
7. Complete calculations (see Calculations Section).
8. If requested by manager, rerun Steps 1 - 5 with an identical sample plus an appropriate NH_4 spike. Spikes only need to be run on new sample points or nonroutine samples to check recovery.

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CALCULATIONS

A. Sample

A quantity of acid is needed to titrate the indicator blank to the yellow endpoint. This volume is subtracted from the volume used to titrate the sample as:

$$\text{Net Volume HCl (uL)} = \text{Sample Volume (uL)} - \text{Blank Volume (uL)}$$

Sample concentration of NH_4^+ is calculated as follows:

Concentration of NH_4^+ in M =

$$\frac{(\text{Net Volume HCl in uL})(\text{Concentration of HCl in M})}{\text{Sample Volume in uL}}$$

Example:

Titration for 2 mL samples is 325 uL of 0.1000 M HCl, for blank 15 uL

$$\text{Net Volume 0.1000 M HCl} = 325 \text{ uL} - 15 \text{ uL} = 310 \text{ uL}$$

$$\begin{aligned} \text{Concentration of } \text{NH}_4^+ \text{ in M} &= \frac{(310 \text{ uL})(0.1000 \text{ M})}{2000 \text{ uL}} \\ &= 1.55 \times 10^{-2} \text{ M} \end{aligned}$$

B. Sample Plus Spike

Spike Recovery is calculated as follows:

$$\begin{aligned} \text{Spike Recovery} &= \frac{[(\text{Net Volume HCl in uL of Sample} + \text{Spike})(\text{M HCl})] \\ &\quad - (\text{Net Volume HCl in uL of Sample})(\text{M HCl})}{(\text{Concentration of Spike } \text{NH}_4^+ \text{ in M})(\text{Spike Volume in uL})} \times 100 \end{aligned}$$

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CALCULATIONS (continued)

Example:

For sample in the above example spike was 250 uL of 0.1000 M NH_4^+

Sample plus spike titration was 585 uL

Blank titration was 15 uL

Net Sample + Spike Volume HCl (uL) = 585 uL - 15 uL = 570 uL

Net Sample Volume HCl (uL) = 325 uL - 15 uL = 310 uL

Spike Recovery =

$$\frac{[(570 \text{ uL})(0.1000 \text{ M HCl}) - (310 \text{ uL})(0.1000 \text{ M HCl})] \times 100}{(0.1000 \text{ M NH}_4^+)(250 \text{ uL})}$$

= 104%

DISCUSSION

The following reactions summarize the method: In the distillation flask on the addition of the base to the ammonium salt,

In the boric acid catch solution the ammonia is neutralized,

On titration with hydrochloric acid,

The original pH of the solution is achieved and the indicator changes color.

It should be noted that ammonia is volatile in strongly basic solutions. In some basic samples the ammonia analysis may be unnecessary, or not representative of the quantity of ammonia present in the sample at the time it was taken. Any caustic (NaOH) which may be burped or sprayed out of the reaction vessel into the catch solution would give high results. Boiling chips and/or a spray trap prevent this. Note Reference 2. Current equipment design is adequate to prevent spraying problems (see Figure 1).

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DISCUSSION (continued)

If the boric acid reagent blank is titrated ahead of the sample and has been properly diluted to the same volume, it can serve as a color reference of the endpoint. The sample can be taken to the same endpoint (first "permanent" yellow color). Since the blank is subtracted from the sample, it also corrects for any ammonia or caustic which may be present in the boric acid used. This is actually only a partial reagent blank, however. A true blank would be the total run through the procedure omitting only the sample. This should be done to check on possible bad reagents or equipment whenever a standard result is outside of the control limits for no known reason. (Correct the problem and rerun the standard successfully before attempting samples.) A true blank should also be run and subtracted from the sample results whenever highly accurate results are needed. This is not required for routine process control samples, however.

Boric acid is used as an absorbing solution because it is a very weak acid and reduces the volatility of the ammonia from what it would be in a strong acid solution (such as 0.1 HCl). Note Reference 2.

Bromcresol green is used as the indicator in the titration because it has a more easily seen, "sharper" endpoint than methyl red. Bromcresol green changes from blue on the alkaline side to yellow on the acid side in the pH range 4.0 to 5.6. Note Reference 3. While the bromcresol green is made up in an alkaline solution, this will not normally affect the results because it is only three drops of 1.4×10^{-3} moles/liter or about 2.1×10^{-7} moles of NaOH (5% of our lower detection limit). The intensity of the color may be affected and make color comparison difficult, however, if the same amount of indicator is not added to both sample and blank.

Phenolphthalein is used in the reaction flask to give a visual indication of basicity and ensure that excess NaOH was added beyond that required to neutralize the sample. Phenolphthalein changes from colorless on the acid side to red on the alkaline side in the pH range 8.0 to 10.0. Note Reference 3.

The procedure section has been divided into two sections: (1) Routine Samples and (2) Evaporator Samples. For routine samples the digestion and distillation steps are required for ammonia volatilization and collection prior to the titrimetric determination of ammonia using bromocresol green as indicator. Since the evaporator samples already contain the ammonia content in 0.1 M boric acid, the digestion - distillation steps are omitted and a direct colorimetric titration of ammonia is permitted. However, since occasionally the boric acid evaporator samples are near the saturation point with ammonia, the addition of an excess of boric acid prior to the determination will prevent any ammonia loss due to evaporation while stirring.

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2. J. Kjeldahl, Z. Anal. Chem. 22, 1883, Page 366.
3. N. A. Lange, Handbook of Chemistry, 1952, Page 942.
4. LA-501-206, "Operating Procedure for Metrohm 665 Digital Buret."
5. LO-120-001, "Labeling Standards and Reagents."

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Figure 1
KJELDAHL APPARATUS

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ANALYTICAL LABORATORIES

<p>Issued By: T. A. Lane Manager, Analytical Laboratory</p> <p>Author: S. A. Jones</p>	<p>Title SAMPLE PREPARATION AND ANALYSIS, HIGH ACTIVITY AA-6 ATOMIC ABSORPTION SPECTROPHOTOMETER</p>
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SUMMARY

In atomic absorption, the element of interest in a liquid sample is aspirated into a flame where it is dissociated from its chemical bonds and placed into an unexcited, nonionized ground state. The element is then capable of absorbing radiation at discrete wavelengths called resonance lines. This absorption is due to electron excitation. Narrow emission or resonance lines are generally provided by a hollow cathode lamp which contains a cathode made of the element of interest. A specific resonance line is monitored using a monochromator for tuning and photomultiplier for quantitative detection. The amount of absorbance of the resonance line is proportional to the concentration of the element in the liquid. Quantitative analyses are performed by comparing the absorbances of unknowns with the absorbances of known concentrations of that particular element.

LIMITATIONS

This method is to be used for most routine and nonroutine samples for the atomic absorption spectrophotometer. If there is any question of interference (consistent low or high spike recovery), the sample should be run using Procedure LA-505-124. If there are any major problems with the sample, the scientist in charge should be consulted.

APPLICATIONS

See LA-505-121 for the accuracy and precision statement.

The AA-6 is used for routine analysis of samples which may contain curie levels of radioactivity. Extreme care should be taken during the sample preparation and instrument operation. Specific operating procedures and safety regulations are set forth in detail in LA-505-121 operating procedure. The provisions of "General Regulations and Practices for Radiation Work," RHO-GM-MA-2, Volume 6, Book 1, Standard Requirements and Procedures Section 61-02.5, and Radiation Work Permit SL-8 found in RHO-MA-172 apply to all work performed under this procedure and must be followed at all times.

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SAFETY

Samples can be divided into two categories, according to the type and level of radioactivity. Routine Samples contain less than 0.1 ci of radioactivity and read less than 500 mrad/hr, unshielded at four inches. These can be handled as specified in Radiation Work Permit SL-8. Non-Routine Samples contain greater than 0.1 ci of radioactivity or read greater than 500 mrad/hr, unshielded at four inches. Radiological Protection assistance is required for handling this type of sample. Special provisions of procedure LA-505-121 shall be followed when dealing with non-routine samples.

Frequently monitor the work area and all equipment to detect any contamination. Monitor hands and arms immediately after withdrawal from the hood. If any contamination is found, notify a manager and Radiological Protection immediately and decontaminate according to the procedure agreed upon.

REAGENTS

All reagents are made from reagent grade chemicals unless otherwise specified. All reagents and standards are labeled according to LO-120-001.

Calibration standards for various elements are available on the shelves in Room 1K. Spike stock solutions are available in 1K next to the open-faced hood. These solutions are prepared from commercial solutions. All aspects of the standards preparation and upkeep are discussed in the quality assurance procedure LA-505-123.

EQUIPMENT

This general analytical procedure for routine process samples is designed specifically for use with the high activity AA-6, atomic absorption spectrophotometer located in Room 1K. The radioactive nature of the samples has dictated the use of very specific safety precautions and instrument operating procedures listed in LA-505-121.

PROCEDURE

1. Before proceeding, survey the work area and determine the dose rate of the sample before handling.
2. Obtain an estimate of the concentration of the element of interest. For routine process samples, an estimate can usually be made from previous results. For nonroutine samples, the person submitting the request should also submit an estimate.
3. Using the estimated concentration, prepare two dilutions of the sample in the appropriate matrix such that the sample will read in the middle of the standards range. The matrix and standards range are listed for each element in Appendix A. Never use a dilution factor smaller than 6. Should a smaller dilution factor be necessary or should the sample need to be run undiluted, consult the scientist in charge.
4. Spike a known amount of the element being analyzed into one of the two dilutions. Spike size and concentration are listed in Appendix A.
5. Analyze both dilutions of the sample on the atomic absorption spectrophotometer. See instrument operating procedure LA-505-121.

CALCULATIONS

Currently in use at the 222-S Laboratory, to reduce the AA data, is a computer. To use this computer, the following steps must be performed:

1. Obtain a form entitled "Least Squares Calibration for AAS" (Appendix B) and from the instrument read-out, record the determined absorbances for samples, samples plus spikes, and the calibration standards.
2. Plot the calibration standards on the graph furnished on the calibration form. Visually determine whether the points (a) lie in a straight line; or (b) show a single smooth curve.
3. Using the computer terminal, load and run program CHANT. This program will calculate a first (straight line), second (one smooth curve), and third (smooth double curve) degree equation from the calibration standards. For each equation, it will print a "coefficient of determination" and a "standard error of estimate of Y."

The computer will then automatically select the first equation whose "coefficient of determination" is greater than .9990. Should there be no equation satisfying this criteria, the computer will select the equation of the smallest "standard error of estimate of Y." Upon entry of the sample absorbances, the computer will calculate and print out the concentration (ppm) of each sample, the uncorrected molarity, the spike recovery, the spike corrected molarity, and the dilution factor.

4. In case of computer crash, the standard absorbance curve can be calculated on a pocket calculator such as the HP-67 or 97. See the lab leader or shift manager for program and instructions. The absorbances can be fed into the calculator to get the sample and sample plus spike concentrations. Using the concentrations from the calculator, calculate the spike recovery for the sample on the back of the sample card as follows:

$$\text{a. } \text{ppm (S)} \times \text{Total Volume (s)} = \text{Micrograms (s)*}$$

(in ml's)

$$\text{ppm (S+Sp)} \times \text{Total Volume (S+Sp)} = \text{Micrograms (S+Sp)**}$$

(in ml's)

*S represents sample

**S+Sp represents Sample plus spike

CALCULATIONS (continued)

- b. Micrograms (S+Sp) - Micrograms (S) = Recovered Micrograms of Spike
 - c. Volume of Spike (ml's) x Spike Concentration (ppm) = Micrograms Spiked In
 - d. Recovered Micrograms of Spike (from "B")
-----x 100% = Spike Recov.
Micrograms Spiked In (from "C")
5. Calculate the molarity of the unknown element in the original sample on the back of the sample card as follows:
- $$\text{Molarity} = \frac{\text{ppm}(\text{from sample}) \times \text{DF}(\text{from Procedure Step 3}) \times 10^{-3}}{\text{MW}(\text{molecular weight of the element})}$$
6. The necessity of a rerun, based on spike recovery, should be determined by the criteria set up in the Quality Assurance Procedure. (2)

DISCUSSION

The underlying principle for atomic absorption, like other spectroscopic techniques, is the absorption and emission of energy at specific wavelengths by individual atoms. This absorption or emission of energy takes place as a result of the atom's electrons jumping from one energy level to another. Electron energy levels are well defined for each element, consequently each element has its own characteristic energy emission/absorption spectrum or resonance lines. With atomic absorption, the most common energy jumps or transitions are monitored. The energies associated with these transitions are found in the upper ultra-violet and visible portion of the spectrum (2,000 - 8,000⁰ A) for most elements.

When an atom is exposed to light of the correct wavelength, a valence (outer shell) electron will absorb some of the energy and jump to a higher energy level. The reverse step, the transition of the electron from a higher to a lower energy level, is accompanied by an emission of light at the same wavelength. Atomic absorption, as its name implies, makes use of the absorption phenomena. Light from a hollow cathode lamp, at the resonance energies of a specific element, is passed through the flame. When the sample in the flame passes through the light beam, atoms of the element being analyzed will absorb a fraction of the light. This absorption of energy by the atom population can be detected by the photomultiplier as a decrease in intensity of the original signal (no sample in flame). The

DISCUSSION (continued)

absorbance measured by the photomultiplier is directly proportional to the number of atoms in the flame at a given unit of time. In turn, the number of atoms in the flame is proportional to the concentration of that element in the sample or standard. A plot of absorbance versus concentration will give a linear relationship. If constant conditions are maintained, then a quantitative determination can be made by comparing the absorbance of the sample to the absorbances of known calibration standards.

The key to the accuracy of this method rests on the maintenance of constant conditions. Since the quantitative analysis depends on the comparison of the sample to a set of calibration standards, both must be run under identical conditions. Both must be taken into the flame at the same rate, subjected to the same matrix interferences, and run without a change in instrument parameters. Fortunately, the instrument parameters are inherently fairly stable. However, sample intake, or aspiration, and matrix effects are not as consistent.

Sample aspiration is accomplished by the nebulizer. The nebulizer is simply a Venturi tube: the oxidant gas flowing around a hollow tube at a high velocity creates a suction through the tube which draws up the liquid sample. A fine mist emerges from the rear of the nebulizer which mixes with the fuel gas (acetylene) and is swept up to the burner head and the flame. A change in the aspiration rate can be caused by a change in the oxidant gas flow, a difference in viscosity of the solutions being aspirated, or partial plugging of the nebulizer. Oxidant flow and partial plugging can be checked by routine aspiration of one of the calibration standards. A constant absorbance or peak height for the standard means constant conditions. Viscosity effects can be eliminated by proper dilution of the sample. A dilution factor of 11 should be sufficient for most B Plant samples. In addition, viscosity effects will also be indicated and can be corrected by using the spike recovery. A detailed discussion of quality assurance procedures can be found in Reference 2.

Matrix interferences may result in enhancement or suppression of the sample absorbance. These interferences result in an increase and a decrease in the number of atoms in the flame, respectively. These changes in the atom population correspond to ionization and compound formation, respectively.

Some elements will ionize quite easily in the flame: notably alkali metals (Na, K, Rb, and Cs), alkaline earths (Mg, Ca, Ba, and Sr), aluminum, silicon, and the rare earths (Eu, La, Y). When ionization occurs, a fraction of the atom population will be converted to ions in the flame. If the degree of ionization is the same for both samples and standards, a valid comparison can still be made. However, this situation does not usually exist. More than likely, some other element in the sample will partially

DISCUSSION (continued)

ionize as well and limit the ionization of the analyte. In other words, the degree of ionization of sample and standards will vary depending upon the sample matrix. The easiest method of minimizing ionization interferences is to dilute the sample and prepare the standard in a common matrix which will inhibit ionization. Thus, each element will always be run in a specific matrix (Appendix A). The matrix will minimize ionization and spike recovery will correct for any inequality which might still exist.

If an element forms a compound either in the sample or in the flame which fails to dissociate in the flame, the number of free atoms in the flame is decreased. This problem can be combatted by using a hotter flame (nitrous oxide - acetylene) or by running the sample in a matrix which will complex the interferant (e.g., phosphate will tie up calcium, however, running the analysis in a high lanthanum matrix will free the calcium while a lanthanum-phosphate compound is formed). For routine B Plant analysis, this type of interference can be ignored. Any compound formation which might occur will be reflected by the spike recovery.

The fairly well defined matrices of routine B Plant samples makes it possible to anticipate and minimize enhancement and to totally ignore suppression. However, this general approach should not be immediately applied to nonprocess samples, as the matrices may deviate quite drastically from the process norm. For this reason, nonprocess samples will be handled on day shift where a scientist familiar with the AAS may be consulted. More detailed discussions of all aspects of AA theory and operation can be found in the references.

REFERENCES

Section A - Procedures

1. LA-505-121, "Operating Procedure for the High Activity AA-6 Absorption Spectrophotometer."
2. LA-505-123, "Process Quality Control and the Atomic Absorption Spectrophotometer."
3. LA-505-124, "Application of the Method of Standard Additions to Atomic Absorption."
4. LO-120-001, "Labeling of Standards and Reagents."

Section B - Source Documents

1. J. M. Harnly, ARH-SA-146, "A Facility for the Analysis of Intensely Radioactive Samples by Atomic Absorption," February 27, 1973.
2. J. Ramirez-Minox, "Atomic Absorption Spectroscopy," Elsevier Publishing Company, Amsterdam-London-New York, 1968.

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APPENDIX A
DILUTIONS FOR AAS ANALYSES

<u>ELEMENT</u>	<u>MATRIX</u>	<u>STANDARDS RANGE (PPM)</u>	<u>IDEAL CONCEN- TRATION (PPM)</u>	<u>SPIKE*</u>	
Ag	2% ultrex HNO ₃	0.5 - 15.0	5.0	25 λ of	1000 PPM
Al	1 g/l Cs	5.0 - 120.0	30.0	250 λ of	1000 PPM
Ba	0.5% K + 1% La	1.0 - 40.0	10.0	100 λ of	1000 PPM
Bi	H ₂ O	5.0 - 100.0	25.0	250 λ of	1000 PPM
Ca	0.5% K + 1% La	0.25 - 10.0	2.0	25 λ of	1000 PPM
Cd	2% ultrex HNO ₃	0.5 - 10.0	3.0	50 λ of	1000 PPM
Cr	0.1M ultrex HCL	0.25 - 10.0	3.0	25 λ of	1000 PPM
Cu	H ₂ O	1.0 - 20.0	5.0	50 λ of	1000 PPM
Eu	0.5% K	10.0 - 100.0	25.0	250 λ of	1000 PPM
Fe	0.1 M HCL	0.25 - 20.0	4.0	25 λ of	1000 PPM
Ga	H ₂ O	5.0 - 35.0	10.0	150 λ of	1000 PPM
Hg	2% ultrex HNO ₃	5.0 - 50.0	20.0	250 λ of	1000 PPM
K	1 g/l Cs	0.25 - 10.0	1.0	25 λ of	1000 PPM
La	0.5% K	5.0 - 100.0	20.0	250 λ of	1000 PPM
Mg	0.5% K + 1% La	0.25 - 5.0	1.0	100 λ of	100 PPM
Mn	2% ultrex HNO ₃	1.0 - 20.0	4.0	50 λ of	1000 PPM
Na	1 g/l Cs	0.25 - 7.0	1.0	25 λ of	1000 PPM
Ni	2% ultrex HNO ₃	1.0 - 20.0	4.0	50 λ of	1000 PPM
Pb	2% ultrex HNO ₃	1.0 - 50.0	15.0	100 λ of	1000 PPM
Pd	H ₂ O	1.0 - 10.0	2.0	25 λ of	1000 PPM
Rb	1 g/l Cs	0.5 - 15.0	3.0	25 λ of	1000 PPM
Rh	H ₂ O	1.0 - 10.0	2.0	100 λ of	1000 PPM
Si	1 g/l Cs	10.0 - 250.0	50.0	250 λ of	1000 PPM
Sr	0.5% K + 1% La	0.5 - 5.0	1.0	100 λ of	100 PPM
Y	0.5% K	10.0 - 400.0	50.0	50 λ of	10,000 PPM
Zr	HF, U (K-6)	5.0 - 120.0	25.0	250 λ of	1000 PPM

* THESE SPIKES ARE FOR 10 ml VOLUMES - FOR 5 ml's USE 0.5 OR 0.4 OF THE LISTED VOLUME

APPENDIX B
Page 1
LEAST SQUARES CALIBRATION FOR AAS

ELEMENT K	TECHNOLOGIST & SHIFT	SAGGING —
GATE	MODE Direct mode	AIR ON H2O A.C.
WAVE LENGTH 71.12 Å	LAMP CURRENT .50	RANGE (MV) —
SLIT WIDTH 1.0	GAIN —	BURNER HEIGHT 10

STANDARD CONC.	SA	ABS	% REC.
10		1.37	
7.5		1.03	
5		0.78	
2.5		0.39	
1		0.16	
0.5		0.08	
0.25		0.04	
0.125		0.02	
0.0625		0.01	
0.03125		0.005	
0.015625		0.0025	
0.0078125		0.00125	
0.00390625		0.000625	
0.001953125		0.0003125	
0.0009765625		0.00015625	
0.00048828125		0.000078125	
0.000244140625		0.0000390625	
0.0001220703125		0.00001953125	
0.00006103515625		0.000009765625	
0.000030517578125		0.0000048828125	
0.0000152587890625		0.00000244140625	
0.00000762939453125		0.000001220703125	
0.000003814697265625		0.0000006103515625	
0.0000019073486328125		0.00000030517578125	
0.00000095367431640625		0.000000152587890625	
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APPENDIX B
Page 2

GENERATION

ANALYTICAL LABORATORIES

Issued By:
T. A. Lane

Manager,
Analytical Laboratory

Author: S. A. Jones

Title
APPLICATION OF THE METHOD OF STANDARD
ADDITIONS TO ATOMIC ABSORPTION

SUMMARY

The method of standard additions is the most practical method for dealing with analytical interferences in samples with ill-defined or unknown matrices. Although atomic absorption spectrophotometry (AAS) was initially claimed to be free from interferences, it is now well documented that a wide variety of interferences do exist. These interferences may arise from physical and chemical differences between the sample and standards, or from shifts in the instrumental parameters during the course of an analysis.

There are currently two methods for dealing with the change in sensitivity caused by chemical, physical and instrumental interferences. The first method is to prepare calibration standards with a matrix identical to the sample's matrix. The second method is the method of standard additions. Since the lack of detailed knowledge of the sample matrix or the sheer number of sample eliminates the first method, the method of standard additions has become an important tool for the analysis of samples by atomic absorption at the 222-S Laboratory.

LIMITATIONS

An analysis by the method of standard additions is not valid unless a linear relationship is maintained between the concentration of the element (analyte) being analyzed and the absorbance. Extrapolation of a curved line beyond the determining data points can lead to gross inaccuracies. For this reason, this method is limited to atomic absorption (for application to flame emission, see Reference 1).

The method of standard additions fails to correct for nonspecific background absorption by the sample matrix. The interferences must be eliminated by instrumental methods.² The accuracy and precision are listed in RHO-MA-218.

APPLICATIONS

This procedure can be used to determine samples in any matrix. The procedure is used for samples in which interferences are expected, or extra accuracy is desired. The procedure is also used if the analyte concentration is too low to permit dilution of the sample into the appropriate matrix. When interferences are expected or a new sample matrix is encountered, this procedure can be used to determine how the sample will behave.

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SAFETY

The provisions of "General Regulations and Practices for Radiation Work," RHO-GM-MA-2, Volume 6, Book 1, Standard Requirements and Procedures Section 61-02.5, and Radiation Work Permits SL-3 and SL-9 found in RHO-MA-172 apply to all work performed under this procedure and must be followed at all times. Procedure LA-505-121 shall be followed for special safety requirements concerning the AAS.

REAGENTS

All curve standards shall be made from commercially available Atomic Absorption aqueous standard stock solutions of 1000 ppm concentration. All spikes will be made from the 1000 ppm stock solutions. All dilutions will be made in the appropriate matrices which are available from the Cold Standards Laboratory, and are labeled according to LO-120-001.

EQUIPMENT

Not applicable.

PROCEDURE

1. Prepare four identical dilutions of the sample into the appropriate matrix for the element being analyzed.
2. Prepare an accurate blank sample matrix with the analyte missing.
3. Spike three of the dilutions with different volumes from a stock solution of the element being analyzed, maintaining a spike volume ratio of 1:2:4 (i.e., 25 lambda, 50 lambda, 100 lambda).
4. Set up the Varian AA_6 for the element being analyzed according to procedure LA-505-121.
5. Run the following:
 - a. the appropriate blank
 - b. a complete set of calibration standards
 - c. the sample and the samples-plus-spike
6. Transfer the Calibration Standards data on to an "AAS Least Squares Form."
7. Calculate the results on the computer AAC program.
8. Proceed to the CALCULATIONS Section to determine the Standard Additions values.

CALCULATIONS

1. Calculate the samples' molarity by using the HP-97 program. (See Appendix 1 for example.)
2. Use the following calculations if the program is unavailable:
3. Calculate the final, known spike analyte concentration of each of the three spiked samples based on the final volume of the sample-plus-spike.

$$\text{Spike Concentration} = \frac{C}{V_{s+s}} \times V_s$$

C = concentration of the spike stock in ppm

V_s = volume of the spike in mL

V_{s+s} = volume of the sample-plus-spike in mL

Example:

$$\text{Spike Concentration} = \frac{1000 \text{ ppm} \times 0.025 \text{ mL}}{11.025 \text{ mL}} = 2.27 \text{ ppm}$$

4. Subtract the blank absorbance from the observed absorbances of the sample, the samples-plus-spike and the calibration standards. (See examples in DISCUSSION Section.)
5. Plot the absorbance of the sample and the sample-plus-spike versus concentration on linear graph paper. The spike concentration of the unspiked sample will be zero.
6. Plot the absorbance of the calibration standards versus the standard concentrations on the same graph paper. (See Appendix 2 for an example of the graph.)
7. Examine both plots for linearity. Nonlinearity can indicate inaccurate spiking or unaccounted for interferences.
8. Fit the sample and sample-plus-spike data to a first degree equation using the HP-97 "Curve Fitting Program" or the AAC program on the computer.

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CALCULATIONS (continued)

9. Calculate the sample concentration:

$$\text{SAMPLE CONCENTRATION(ppm)} = B/A$$

B = Y-Axis Intercept
A = Slope

Example:

$$\text{SAMPLE CONCENTRATION(ppm)} = 0.060/0.015 = 4 \text{ ppm}$$

10. Calculate the analyte molarity of the original sample.

$$\text{SAMPLE MOLARITY} = \frac{\text{ppm} \times \text{d.f.} \times 10^{-3}}{\text{M.W.}}$$

ppm = ppm calculated from Step 9
d.f. = dilution factor
M.W. = molecular weight of analyte

Example:

$$\begin{aligned} \text{SAMPLE MOLARITY} &= \frac{4 \text{ ppm} \times 11 \times 10^{-3}}{22.99} \\ &= 1.91 \times 10^{-3} \text{ M} \end{aligned}$$

DISCUSSION

Theory:

The method of standard additions has been applied to many instrumental analytical methods in a wide variety of ways. In general, each application involves the addition of known quantities of the analyte to identical portions of aliquots of the sample. The aliquots of the sample with the additions or spikes are then compared to the unadulterated sample through some measured scale such as absorption, emission, pH, millivolts, etc. Generally, several spiked samples are employed to increase the statistical validity of the analysis. By comparing the sample to the sample-plus-spikes, a ratio can be established. This ratio, or sensitivity, is the measured units per analyte concentration. If the known additions caused the measured differences between the unspiked sample and the spiked samples, then the quantity of analyte necessary to cause the measurement observed for the unspiked sample can easily be calculated. This quantity, provided the zero point is well established, can be arrived at without the use of calibration standards and is equivalent to the analyte concentration in the sample. Thus, the method of standard additions provides concentration values, which have been corrected to account for interferences.

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DISCUSSION (continued)

The method of additions employs three spikes and is used on a nonroutine basis for the analysis of special samples. These can be samples where interferences are expected, extra accuracy is desired or the analyte concentration is too low to permit dilution of the sample into the appropriate matrix. A typical analysis is shown in EXAMPLE 2. Individual spike recoveries are not determined. Instead all four results, absorbances of the unspiked and spiked samples, are given equal weighting by using the least square methods to fit a straight line to the data.

Since the method of additions is based on the ratio of absorbance to analyte concentration, a plot of absorbance versus known spike concentration (based on the final volume after spiking) should yield a straight line. An extrapolation of this straight line to its negative intercept of the X-axis give the absolute value of the analyte's concentration in the sample. The original sample molarity is then calculated using the sample's dilution factor and the analyte's molecular weight.

As mentioned in the LIMITATIONS Section, failure of the sample and the sample-plus-spike to yield a straight line invalidates the analysis. Curvature implies that the ratio of absorbance to analyte concentration is dependent on the analyte concentration. Although a curved line can be fitted quite nicely to the four points, extrapolation to the X-axis intercept is not valid without prior knowledge of the interference mechanisms.

Even though calibration standards are not involved in the calculation of the results for the method of additions, the running of calibration standards is considered important for several reasons. First, the calibration curve is an indication of linearity. Although the total set of standards might not show linearity (Beer's Law fails at higher absorbances due to self-absorption), the lower standards (absorbance 0.3) should show linearity. It is possible that the calibration curve might be totally nonlinear due to an incorrect analytical parameter. This situation would invalidate the analysis as linearity of the sample and sample-plus-spikes would seem unlikely in light of the nonlinearity of the interference-free calibration standards.

Secondly, a comparison of the slope of the linear portion of the calibration standards with the slope of the line fitted to the unspiked and three spiked samples is a quick indicator of the presence of an interference and the nature of the interference. Since interference is any unaccounted for effect, which causes sensitivity to vary between the samples (unspiked and the three spiked samples) and the calibration standards, differences in slope (absorbance per unit of the analyte concentration) will indicate the presence of an interference. If the slope of the calibration standards is greater, then the effect is known as a suppressing interference. The opposite effect, where the slope of the calibration standards is smaller, is known as an enhancing interference.

DISCUSSION (continued)

Finally, a line fitted to the linear portion of the calibration curve should intercept the Y-axis at a value very close to zero. If the Y-axis intercept value is large, or if the Y-axis intercept value is large compared to the absorbance of the unspiked sample, then the validity of the analysis becomes suspect.

It should be noted that the final results for EXAMPLES 1 and 2 were identical. It should also be noted that in both cases perfectly linear calibration curves were assumed which intercepted the Y-axis at zero and a linear 50% interference was hypothesized. In EXAMPLE 3, a case is proposed which could readily be explained by the sample, the sample-plus-spikes, and the calibration standards being prepared in a matrix which contributes a small nonspecific absorbance but where the appropriate blank (an aliquot of the dilution matrix) was not run. Thus, all absorbance values were not corrected by the absorbance of the blank. The result is that the calibration standards Y-axis intercept (0.03) is large with respect to the absorbance of the unspiked sample (0.09).

Consequently, the large Y-axis intercept value must be eliminated or mathematically corrected before a valid result can be obtained.

Although the mathematical correction used in EXAMPLE 3 (Step 5) is easy to apply, in real life situations it may be difficult to justify its use without knowing definitely where the source of the problem lies. In fact, before applying the mathematical correction to EXAMPLE 3 a more logical approach would be to return to the special matrix used for both the sample and standards and examine its absorbance as compared to the absorbance of one of the calibration standards. Once the nonspecific absorbance of the dilution matrix has been confirmed, the analysis could be either completely rerun, using the appropriate blank this time, or the mathematical correction used in Step 5 applied. This type of matrix problem does not effect the spike recovery method since both samples and standards are offset by the same amount.

A special case where the mathematical correction for a nonzero intercept could be applied accurately and effectively would be with respect to automatic background correction. With techniques now available for the background correction of both atomic absorption and flame emission analyses, results might be either over-corrected or under-corrected. Analysis of several of the lower calibration standards would permit the Y-axis intercept to be calculated and allow verification of an under or over correction. Extrapolation of the straight line to this Y-axis intercept value, as shown in EXAMPLE 3 (Step 5), will give the most accurate results.

DISCUSSION (continued)

In EXAMPLE 4, an example is presented which illustrates the need for background correction. Here, the nonspecific absorbance arises not from the special dilution matrix, but from some component of the sample itself. Thus, a small contribution of nonspecific absorbance is being made to the sample absorbance but not to the calibration standards absorbances. Neither the spike recovery method nor the method of standard additions will accurately correct for this interference. Only the use of background correction instrumentation can eliminate the problem.

EXAMPLES

EXAMPLE 1 (Assumption: Sample = 4 ppm; 50% interference)

1. SAMPLE PREPARATION

<u>Sample</u>	<u>Dilution</u>	<u>Spike</u>	<u>Final Volume</u>
s	1 mL - 10 mL	--	11.000 mL
s + s	1 mL - 10 mL	.025 mL	11.025 mL

2. SAMPLE ANALYSIS

<u>Calibration Standards</u>	<u>Abs.</u>	<u>Corrected Abs.</u>	<u>ppm*</u>
blank	.030		
1 ppm	.060	.030	
3 ppm	.120	.090	
5 ppm	.180	.150	
10 ppm	.330	.300	
15 ppm	.480	.450	
20 ppm	.630	.600	
<u>Samples</u>			
s	.090	.060	2.00
s + s	.124	.094	3.13

* Calculated by comparing the sample to the calibration standards.

DISCUSSION (continued)

EXAMPLE 1 (Con't)

3. CALCULATION OF SPIKE RECOVERY

	<u>Abs.</u>	<u>Con'n x Final Volume = Total Micrograms</u>		
s + s	.094	3.13	x 11.025	= 34.5
s	.060	2.00	x 11.000	= 22.0

Since 25 μ L = .025 mL,
then .025 mL x 1000 ppm = 25 Micrograms of original spike.

$$\text{Spike Recovery} = \frac{\text{Micrograms of s+s} - \text{Micrograms of s}}{\text{Micrograms of original spike}} \times 100\%$$

$$= \frac{12.50 \times 100\%}{25.0} = 50\%$$

4. CALCULATION OF ORIGINAL SAMPLE CONCENTRATION (MOLAR)

$$\text{Molarity} = \frac{2.00 \text{ ppm} \times 11 \times 10^{-3}}{22.99} = 9.57 \times 10^{-4}$$

EXAMPLE 2 (ASSUMPTION: Sample = 4 ppm; 50% interference)

1. SAMPLE PREPARATION

<u>Sample</u>	<u>Dilution</u>	<u>Spike</u>	<u>Final Volume</u>	<u>Spike Conc'n</u>
s	1 mL - 10 mL	--	11.000	0.00
s + s ₁	1 mL - 10 mL	25 μ L of 1000 ppm	11.025	2.27
s + s ₂	1 mL - 10 mL	50 μ L of 1000 ppm	11.050	4.52
s + s ₃	1 mL - 10 mL	100 μ L of 1000 ppm	11.100	9.01

2. SAMPLE ANALYSIS

<u>Samples</u>	<u>Abs.</u>	<u>Absolute Abs.</u>	<u>Calibration Stds.</u>	<u>Abs.</u>	<u>Absolute Abs.</u>
s	0.090	0.060	blank	0.030	---
s + s ₁	0.124	0.094	1 ppm	0.060	0.030
s + s ₂	0.158	0.128	3 ppm	0.120	0.090
s + s ₃	0.225	0.195	5 ppm	0.180	0.150
			10 ppm	0.330	0.300
			15 ppm	0.480	0.450
			20 ppm	0.630	0.600

DISCUSSION (continued)

EXAMPLE 2 (Con't)

3. LEAST SQUARES FIT OF CALIBRATION STANDARDS TO A FIRST DEGREE EQUATION

$$Y = AX + B$$

$$\text{Slope} = A = 0.030$$

$$\text{Y-axis Intercept} = B = 0$$

4. LEAST SQUARES FIT OF SAMPLE AND SAMPLES-PLUS-SPIKES TO A FIRST DEGREE EQUATION

$$Y = AX + B$$

$$\text{Slope} = A = 0.015$$

$$\text{Y-axis Intercept} = B = 0.060$$

5. CALCULATION OF SAMPLE CONCENTRATION (PPM)

The X-axis intercept occurs where $Y = 0$

$$Y = AX + B = 0$$

$$-X = \frac{B}{A}$$

$$|X| = \frac{B}{A}$$

$$\text{SAMPLE CONCENTRATION (PPM)} = \frac{.060}{.015} = 4 \text{ ppm}$$

6. CALCULATION OF ORIGINAL SAMPLE CONCENTRATION (MOLAR)

$$\text{Molarity} = \frac{4 \text{ ppm} \times 11 \times 10^{-3}}{22.99} = 1.91 \times 10^{-3} \text{ M (Final Answer)}$$

EXAMPLE 3 (ASSUMPTION: Sample = 4 ppm; 50% interference; blank not analyzed)

1. SAMPLE PREPARATION

<u>Sample</u>	<u>Dilution</u>	<u>Spike</u>	<u>Final Volume</u>	<u>Spike Conc'n</u>
s	1 mL - 10 mL	---	11.000 mL	0.00
s + s ₁	1 mL - 10 mL	25 μ L of 1000 ppm	11.025 mL	2.27
s + s ₂	1 mL - 10 mL	50 μ L of 1000 ppm	11.050 mL	4.52
s + s ₃	1 mL - 10 mL	100 μ L of 1000 ppm	11.100 mL	9.01

DISCUSSION (continued)

EXAMPLE 3 (Con't)

2. SAMPLE ANALYSIS

<u>Calibration Stds.</u>	<u>Abs.</u>	<u>Samples</u>	<u>Abs.</u>	<u>ppm</u>
1 ppm	0.060	s	0.090	2.00
3 ppm	0.120	s + s ₁	0.124	3.13
5 ppm	0.180	s + s ₂	0.158	
10 ppm	0.330	s + s ₃	0.225	
15 ppm	0.480			
20 ppm	0.630			

3. SPIKE RECOVERY METHOD

a. Calculation of Spike Recovery

	<u>Abs.</u>	<u>Conc'n</u>	<u>X</u>	<u>Final Volume</u>	<u>=</u>	<u>Total Micrograms</u>
s + s	0.124	3.13	x	11.025	=	34.5
s	0.090	2.00	x	11.000	=	22.0
						<u>12.5</u>

$$\text{Spike Recovery} = \frac{12.50}{25.0} \times 100\% = 50\%$$

b. Calculation of original sample concentration (Molar)*

$$\text{Molarity} = \frac{2.00 \text{ ppm} \times 11 \times 10^{-3}}{22.99} = 9.56 \times 10^{-4}$$

* Calculated by comparing the samples to the calibration standards.

4. METHOD OF ADDITIONS

a. Least squares fit of calibration standards to a first degree equation (Y = AX + B)

$$\begin{aligned} \text{Slope} &= A = 0.030 \\ \text{Y-axis Intercept} &= B = 0.030 \end{aligned}$$

b. Least squares fit of sample and samples-plus-spike to a first degree equation (Y = AX + B)

$$\begin{aligned} \text{Slope} &= A = 0.015 \\ \text{Y-axis Intercept} &= B = 0.090 \end{aligned}$$

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DISCUSSION (continued)

EXAMPLE 3 (Con't)

c. Calculation of sample concentration (ppm)

The X-axis intercept occurs where $Y = 0$

$$Y = AX + B = 0$$

$$|X| = \frac{B}{A}$$

$$\text{Sample Concentration (ppm)} = \frac{0.090}{0.015} = 6.00 \text{ ppm}$$

d. Calculation of original sample concentration (molar)

$$\text{Molarity} = \frac{6.00 \text{ ppm} \times 11 \times 10^{-3}}{22.99} = 2.87 \times 10^{-3} \text{ M}$$

5. METHOD OF ADDITIONS CORRECTED FOR CALIBRATION STANDARDS Y-AXIS INTERCEPT

a. and b. the same as above.

c. The X-axis intercept occurs where $Y = 0.03$ (Y-axis intercept of calibration standards).

$$Y = AX + B = 0.03$$

$$|X| = \frac{B - 0.03}{A}$$

$$\text{Sample Concentration (ppm)} = \frac{0.090 - 0.030}{0.015} = 4.00 \text{ ppm}$$

d. Calculation of original sample concentration (Molar)

$$\text{Molarity} = \frac{4.00 \text{ ppm} \times 11 \times 10^{-3}}{22.99} = 1.19 \times 10^{-3} \text{ M}$$

EXAMPLE 4 (ASSUMPTION: Sample = 4 ppm; 50% interference; nonspecific absorbance by sample = 0.03)

1. SAMPLE PREPARATION

<u>Sample</u>	<u>Dilution</u>	<u>Spike</u>	<u>Final Volume</u>	<u>Spike Con'n</u>
s	1 mL - 10 mL	---	11.000 mL	0.00
s + s ₁	1 mL - 10 mL	25 μ L of 1000 ppm	11.025 mL	2.27
s + s ₂	1 mL - 10 mL	50 μ L of 1000 ppm	11.050 mL	4.52
s + s ₃	1 mL - 10 mL	100 μ L of 1000 ppm	11.100 mL	9.01

DISCUSSION (continued)

EXAMPLE 4 (Con't)

2. SAMPLE ANALYSIS

<u>Samples</u>	<u>Abs.</u>	<u>Absolute Abs.</u>	<u>Calibration Stds.</u>	<u>Abs.</u>	<u>Absolute Abs.</u>
s	0.120	0.090	blank	0.030	---
s + s ₁	0.154	0.124	1 ppm	0.060	0.030
s + s ₂	0.186	0.158	3 ppm	0.120	0.090
s + s ₃	0.255	0.225	5 ppm	0.180	0.150
			10 ppm	0.330	0.300
			15 ppm	0.480	0.450
			20 ppm	0.630	0.600

3. SPIKE RECOVERY

a. Calculation of Spike Recovery

	<u>Abs.</u>	<u>Conc'n</u>	<u>X</u>	<u>Final Volume</u>	<u>=</u>	<u>Total Micrograms</u>
s + s	0.124	4.13*	x	11.025	=	45.5
s	0.090	3.00*	x	11.000	=	33.0
						<u>12.5</u>

$$\text{Spike Recovery} = \frac{12.5}{25.0} \times 100\% = 50\%$$

b. Calculation of original sample concentration (Molar)

$$\text{Molarity} = \frac{3.00 \text{ ppm} \times 11 \times 10^{-3}}{22.99} = 1.44 \times 10^{-3}$$

* Calculated by comparing the samples to the calibration standards.

4. METHOD OF ADDITIONS CORRECTED FOR CALIBRATION STANDARDS Y-AXIS INTERCEPT

There is no correction as the Y-axis intercept of the calibration standards is zero.

REFERENCES

1. LA-505-122, "Sample Preparation and Analysis, High Activity AA-6 Atomic Absorption Spectrophotometer."
2. LA-505-121, "Operating Procedure for the High Activity AA-6 Atomic Absorption Spectrophotometer."
3. LO-120-001, "Labeling of Standards and Reagents."
4. The Standard Addition Technique in Flame Spectrometry, T. E. Beukelman and S. S. Lord, Jr., Applied Spectroscopy, Vol. 14, No. 1, 12 (1960).
5. Modification of an Atomic Absorption Unit for Dual Beam, Background Correction Measurements, D. L. Dick, S. J. Urtamo, F. E. Lichte, and R. K. Skogerboe, Applied Spectroscopy, Vol. 27, No. 6, 469 (1973).
6. Flame Emission Spectrometry with Repetitive Optical Scanning in the Derivative Mode, W. Snelleman, T. C. Rains, K. W. Yce, H. D. Cook, and O. Menis, Analytical Chemistry, Vol. 42, No. 3, 394 (1970).

APPENDIX 1

Step	Instructions.	Keys
1	Load Side 1	
2	Input Total Volume in milliliters	Enter
3	Enter Spike Volume in milliliters	A
4	Enter Absorbance	B
5	Repeat Steps 2,3 and 4 for all data points	
6	Compute and output coefficient of determination r^2 and a and b	C
7	Input Dilution Factor	Enter
8	Input Molecular Weight and output Sample Molarity	D

**SAMPLE PROGRAM FOR
EXAMPLE 2.**

Total Vol.		
Spike Vol.		
Sample Abs.		
Total Vol.		
Spike Vol.		
Sample Abs.		
Total Vol.		
Spike Vol.		
Sample Abs.		
Total Vol.		
Spike Vol.		
Sample Abs.		

Correlation 0.8841 0.8841
b 0.8841 0.8841
a 0.8841 0.8841

D.F. 200 500
M.W. 200 500
Sample
Molarity-... 500

APPENDIX 2

STANDARD ADDITIONS PLOT

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END