

Instrumentation and Analytical Methods

The Analytical Services Laboratory (ASL) is divided into radiological and nonradiological sections to facilitate analysis of specific parameters in each category. The methods and instrumentation for each category are briefly described below. Only validated and regulatory referenced methods were used during the analysis. All samples were collected and preserved by trained technicians according to appropriate referenced methods. Qualified and trained analysts performed each of the different analyses.

RADIOLOGICAL ANALYTICAL METHODS

The ASL is certified by the New York State Department of Health (NYSDOH) for gross alpha, gross beta, gamma, tritium, and strontium-90 (non-potable water). The following is a description of the radiological analytical methods.

GROSS ALPHA AND GROSS BETA ANALYSIS - WATER MATRIX - EPA 900.0

Water samples are collected in four-liter polyethylene containers by BNL sampling teams and preserved at the time of collection by acidification to pH 2 using nitric acid. Effluent or surface stream samples of 100 ml are extracted for analysis. Groundwater samples are typically analyzed using a 200-mL aliquot. The aliquot is evaporated to near-dryness in a glass beaker. Two drops of concentrated nitric acid are added, after which the solids are polished down the side of the beaker. The sample is transferred to a stainless steel planchet. Four drops of 10 percent Triton-X are added to the sample before it completely evaporates on a hot plate. The planchets are placed in a drying oven at 105°C for a minimum of 2 hours; removed to a desiccator and allowed to cool; and weighed and counted in a gas-flow proportional counter for 50 minutes. Groundwater samples are counted for 200 minutes. Samples are normally processed in batch mode. The first sample of each batch is a background, for which the count rate is subtracted from the raw data before computing net

activity concentration. System performance is checked daily with NIST-traceable standards: americium-241 for alpha, and strontium-90 for beta. Spiked duplicates are performed within each batch of samples to determine precision and accuracy.

GROSS ALPHA AND GROSS BETA ANALYSIS - AIR PARTICULATE MATRIX

Air particulate samples are collected on 50-mm glass fiber filters at a nominal flow rate of 15 liters per minute. At the end of the collection, the filters are returned to the analytical laboratory for assay. After a one-week holding time, filters are counted once in a gas flow proportional counter for 50 minutes. This delay permits the short-lived radon/thoron daughters to decay. The first sample of each batch is a blank filter whose count rate is subtracted from the raw data before calculating net activity concentration. The system's performance is checked daily with National Institute for Standards and Technology (NIST) traceable standards: americium-241 for alpha and strontium-90 for beta.

TRITIUM ANALYSIS - WATER MATRIX - EPA 906.0

Water samples are collected in glass containers. No preservatives are added before collecting the sample. Effluent and surface stream samples, as well as groundwater samples, are analyzed using a 7-mL aliquot. Potable-water samples (as well as other samples requiring a low minimum detection limit) are distilled following the method outlined in EPA Method 906.0 (EPA 1980), and a 7-mL aliquot is analyzed. Liquid scintillation cocktail is added to the aliquot so that the final volume in the liquid-scintillation-counting vial is 7 mL of sample plus 10 ml of cocktail. Samples then are counted in a low-background liquid-scintillation counter for 50 minutes. Samples are normally processed in batch mode. The first sample of each batch is a steam-distilled water background that is subtracted from the raw data before calculating the net activity concentration.

The second sample in each batch is a NIST-traceable tritium standard, which is used to verify the system's performance and efficiency. Each sample is also monitored for quenching. Corrections for background, quenching, and efficiency of the sample matrix are factored into the final net concentrations for each sample. Spiked duplicates are performed within each batch of samples to determine precision and accuracy.

TRITIUM ANALYSIS - AIR MATRIX

Concentration of tritium in ambient and facility air is measured by drawing the air through a desiccant at a rate of approximately 200 cc/min. At the end of each collection period, typically one week, the desiccant is brought to the analytical laboratory for processing. It is heated in a glass manifold system. Dedicated glassware are used for environmental samples. The desiccant, containing moisture from the sampled air, is heated using an electric mantle, and the evaporated moisture is condensed by a water-cooled glass condenser. The total volume of water collected is determined gravimetrically. A 7-mL aliquot of this water is then assayed for tritium content. If the desiccant contains less than 7-mL of condensed liquid, a 1-ml aliquot is used. Liquid scintillation cocktail is then added to the aliquot so that the final volume in the counting vial is 17-mL. Samples are then counted in a low-background liquid-scintillation counter for 50 minutes. If a 1-mL aliquot was used, liquid scintillation cocktail is added to the vial so that the final volume is 11-mL. These samples are counted for 100 minutes. Samples are normally processed in batch mode. The first sample of each batch is a steam-distilled water background whose count rate is subtracted from the raw data before computing net activity concentration. The second sample in each batch is a NIST-traceable tritium standard, which is used to verify the system's performance and efficiency. Each sample is also monitored for quenching. Corrections for background, water recovery, air sample volume, quenching and efficiency for the sample matrix are factored into the final net concentrations for each sample. Spiked duplicates are performed within each batch of samples to determine precision and accuracy, respectively.

STRONTIUM-90 ANALYSIS

Strontium-90 analyses are currently performed on water. Groundwater samples are processed inhouse using either DOE Method RP500, which utilizes a crown ether to selectively separate strontium from the acidified sample matrix or an ion exchange resin method. The strontium is eluted from the resin or filtration disk using dilute nitric acid. The resulting eluent is evaporated on a 5 cm stainless steel planchet and the sample counted in a gas-flow proportional counter. Samples are prepared in batches, including a standard and a method blank in each batch. Chemical recovery is determined for each sample by the recovery of strontium carbonate. NIST-traceable strontium-90 standards are used to calibrate and verify the performance of the counting instrument. Samples are counted once after a two-week radiological in-growth time.

Potable water samples, as well as samples of solids, are shipped to a contractor laboratory, which is certified to perform the EPA (1980), 905.0 method for strontium-90 in drinking water. This method employs time consuming and costly wet-chemistry techniques to isolate strontium from the sample. Samples are counted twice to verify strontium-90 and yttrium-90 in-growth. Samples are typically processed in a batch. Backgrounds and system performance are verified with each batch. Chemical recoveries are determined by either gravimetric or gamma-emitting strontium-85 standard addition techniques.

GAMMA SPECTROSCOPY ANALYSIS - EPA 901.1

Surface, potable, and groundwater surveillance samples are typically of 4 liters and are placed in polyethylene bottles acidified to pH 2 with nitric acid. Samples are then measured into a 4-L Marinelli™ beaker and counted on a calibrated gamma spectroscopy detector for 50,000 seconds. Air-particulate filters and air-charcoal canisters are counted directly on the calibrated gamma spectroscopy detector for 10,000 seconds. Soil, vegetation, and aquatic biota are all processed following collection. Typically, a 100-, 200-, or 300-gram aliquot is taken, placed in a Teflon-lined aluminum can,

Table D-1. ASL Certified Organic Analytes.

EPA 624 Analytes			
Bromoform	1,1-Dichloroethane	Trichloroethene	1,1,2-Trichloroethane
Chloromethane	2-Butanone	1,2-Dichloropropane	Tetrachloroethene
Vinyl Chloride	Chloroform	Bromodichloromethane	2-Hexanone
Bromomethane	1,1,1-Trichloroethane	1,1,2,2-Tetrachloroethane	Dibromochloromethane
Chloroethane	Dibromofluoromethane	4-Methyl-2-pentanone	MTBE
Trichlorofluoromethane	Carbon Tetrachloride	cis-1,3-Dichloropropene	Chlorobenzene
1,1-Dichloroethene	Benzene	p-Bromofluorobenzene	Ethylbenzene
Acetone	1,2-Dichloroethane	Toluene	m/p-xylene
Methylene Chloride	All Dichlorobenzenes	trans-1,3-Dichloropropene	o-Xylene
trans-1,2-Dichloroethene			
EPA 524.2 Analytes			
Dichlorodifluoromethane	Chloroform	1,1,2-Trichloroethane	4-Chlorotoluene
Chloromethane	1,1,1-Trichloroethane	Tetrachloroethene	Tertbutylbenzene
Vinyl Chloride	Carbon Tetrachloride	m,p-xylene	1,2,4-trimethylbenzene
Bromomethane	1,1-Dichloropropene	1,3-dichloropropane	sec-Butylbenzene
Chloroethane	Benzene	Dibromochloromethane	p-Isopropyltoluene
Trichlorofluoromethane	1,2-Dichloroethane	1,2-dibromoethane	n-Butylbenzene
1,1-Dichloroethene	o-Xylene	1,1,1,2-Tetrachloroethane	1,3-Dichlorobenzene
Chlorobenzene	Trichloroethene	Bromoform	1,4-Dichlorobenzene
Methylene Chloride	1,2-Dichloropropane	Isopropylbenzene	1,2-Dichlorobenzene
trans-1,2-Dichloroethene	Dibromomethane	Bromobenzene	1,2-Dibromo-3-Cl-propane
1,1-Dichloroethane	Bromodichloromethane	1,1,2,2-Tetrachloroethane	1,2,4-Trichlorobenzene
2,2-Dichloropropane	cis-1,3-Dichloropropene	n-Propylbenzene	Hexachlorobutadiene
cis-1,2-Dichloroethene	Styrene	1,2,3-Trichloropropane	Naphthalene
Bromochloromethane	Toluene	2-Chlorotoluene	1,2,3-trichlorobenzene
Ethylbenzene	Trans-1,3-Dichloropropene	1,3,5-trimethylbenzene	

and directly counted. For gamma spectroscopy analyses, overnight backgrounds are counted once per week, with calibration and background checked daily. Analytical results reflect net activity that has been corrected for background and efficiency for each counting geometry used.

NONRADIOLOGICAL ANALYTICAL METHODS

The ASL is certified by NYSDOH ELAP for purgeable aromatics, purgeable halocarbons, PCBs, anions, and metal compounds, in both potable and wastewater matrices, using EPA 524, EPA 624, EPA 200.8, EPA 245.2, EPA 236.1, EPA 273.1, and EPA 300.0 methods. Tables D-1 and D-2 list the non-radiological organic and inorganic NYSDOH ELAP certified analytes, respectively.

PURGEABLE AROMATICS AND PURGEABLE HALOCARBONS

Water samples are collected in 40 mL glass vials with removable teflon-lined caps without any headspace, and acidified 1:1 HCl to pH <2.0. Samples are stored at 4°C and analyzed within 14 days. Thirty eight purgeable compounds

Table D-2. ASL Certified Metals and Anions.

Metals	Instrument	Method
Aluminum	ICP/MS	EPA 200.8
Antimony	ICP/MS	EPA 200.8
Arsenic	ICP/MS	EPA 200.8
Barium	ICP/MS	EPA 200.8
Beryllium	ICP/MS	EPA 200.8
Cadmium	ICP/MS	EPA 200.8
Chromium	ICP/MS	EPA 200.8
Cobalt	ICP/MS	EPA 200.8
Copper	ICP/MS	EPA 200.8
Iron	AAS	EPA 236.1
Lead	ICP/MS	EPA 200.8
Manganese	ICP/MS	EPA 200.8
Mercury	AAS	EPA 245.2
Molybdenum	ICP/MS	EPA 200.8
Nickel	ICP/MS	EPA 200.8
Selenium	ICP/MS	EPA 200.8
Silver	ICP/MS	EPA 200.8
Sodium	AAS	EPA 273.1
Thallium	ICP/MS	EPA 200.8
Vanadium	ICP/MS	EPA 200.8
Zinc	ICP/MS	EPA 200.8
Anions	Instrument	Method
Chloride	IC	EPA 300.0
Nitrate	IC	EPA 300.0
Sulfate	IC	EPA 300.0
Notes:		
ICP/MS = Inductively Coupled/Mass Spectrometry		
AAS = Atomic Absorption Spectrometry		
IC = Ion Chromatography		

(including: benzene, toluene, ethyl benzene, total xylenes, chloroform, 1,1-dichloroethane, 1,1-dichloroethylene, tetrachloroethylene, 1,1,1-trichloroethane, trichloroethylene, chlorobenzene, carbon tetrachloride, methyl chloride and acetone) are analyzed under this category following EPA Method 624 protocols using Gas Chromatography/Mass Spectrometry (GC/MS). There are currently two Hewlett-Packard™ GC/MS instruments used to analyze purgeable organic compounds. Since groundwater under BNL is classified as a sole source aquifer under the Safe Drinking Water Act and Class GA groundwater by the New York State Department of Environmental Conservation (NYSDEC), the detection limits reported for the compounds are close to NYS drinking water standards and the ambient water quality standard. EPA drinking water Methods 524.2 and 624 are used to analyze water, based on the project manager's data quality requirements.

The method involves purging a 25-mL aliquot of the sample with ultra pure helium in a specially designed sparger using the Purge and Trap technique. Each sample is spiked with a known concentration of internal standards and surrogates before purging to facilitate identifying, quantifying, and determining the extraction efficiency of analytes from the matrix. The purged analytes are trapped onto a specially designed trap and thermally desorbed onto the capillary chromatographic column by back flushing the trap with helium. Individual compounds are separated with a temperature program of the GC and enter the mass spectrometer where they undergo fragmentation to give characteristic mass spectra. The unknown compounds are identified by comparing their mass spectra and retention times with reference compounds and quantified by internal standard method. The quantitation data are supported by extensive Quality Assurance/Quality Control, such as tuning the mass spectrometer to meet bromofluorobenzene criteria, initial and continuing calibrations verifying daily response factors, method blanks, surrogate recoveries, duplicate analysis, matrix spike and matrix spike duplicate analysis, and reference standard analysis to verify the daily working standard.

PCB ANALYSIS

The ASL is NYSDOH Certified for PCB Aroclors 1016, 1221, 1232, 1242, 1248, 1254 and 1260. Samples are collected in 50-100 mL glass containers with Teflon™-lined lids and stored at 4°C and analyzed within 30 days. Transformer oil, mineral oil, hydraulic fluid, waste oil and spill wipe-samples are analyzed for PCBs using gas chromatography-dual electron capture detector (GC-ECD) method. This method is similar to EPA SW-846 Method 8082 and is targeted to identify and quantify seven different mixtures of PCB congeners in samples.

The method consists of diluting a known weight of the sample with isooctane and removing the interfering compounds with one or more aliquots of concentrated sulfuric acid until the acid layer is almost colorless. The entire oil matrix and other interfering polar compounds are selectively removed from the sample, leaving the PCBs in isooctane solvent.

There is currently a single GC-ECD instrument for analyzing PCB. The PCBs found in the samples are identified and quantified by comparing the retention times and chromatographic patterns with the standards. Methods blanks, duplicates, spikes, calibration, and reference check standards are run as part of Quality Assurance/Quality Control.

ANIONS

Chloride, nitrate-N, and sulfate are analyzed using Dionex™ Ion-chromatography (IC) with ion suppression and conductivity detection technique. Samples from monitoring wells are collected in 100-mL polyethylene bottles, cooled to 4°C, and analyzed within 28 days. For nitrate in drinking water analysis, samples are analyzed within 48 hrs. Holding times were exceeded for nitrate analysis of some nonpotable monitoring well samples, but the depletion of nitrate is expected to be negligible.

The anions are passed through an anion-exchange polymer column and eluted with carbonate/bicarbonate solution. Then the eluent passes through a membrane suppressor, where the background contribution from the eluent is suppressed, improving signal to noise ratio and

detection limits. The target anions are then detected by conductivity meter.

Initially, the system is calibrated with standards to define its working range. The target anions in the samples are identified and quantified by comparing the retention times and areas with the standards. Method blanks, duplicates, replicates, spikes, and reference standards are routinely analyzed as part of Quality Assurance/Quality Control.

METALS

Samples are collected in 500-mL glass bottles and stabilized with ultra-pure nitric acid to a pH of <2. The samples are analyzed within 6 months, except for mercury, which is analyzed within 26 days.

Iron and sodium are analyzed with a Perkin-Elmer atomic absorption spectrometer. Using the flame technique, the sample containing the target element is nebulized and atomized in an oxy-acetylene flame. At the same time, a beam of light from an element-specific hollow cathode lamp corresponding to the absorption frequency of target element is passed through the flame. The atomized element absorbs the energy specific to that element from the cathode lamp and the intensity of absorption is proportional to the concentration of the element in the sample. Calibration curves establish the linearity of the system and samples are quantified by comparing with standards.

Fourteen of the seventeen elements offered for certification in potable water by NYSDOH ELAP are analyzed by Inductively Coupled Plasma/Mass Spectrometry (ICP/MS). Iron and sodium are detailed in the preceding paragraph, and mercury in the following. Including aluminum, cobalt, molybdenum and vanadium, for which only wastewater certification is available, there are eighteen elements analyzed by the ICP/MS technique. Aqueous samples are nebulized, and introduced into a radio frequency argon plasma, at temperatures reaching 8000°K. The de-solvated, atomized analytes are ionized to

predominantly singly-charged cations, which are identified and quantified by the use of a quadrupole mass spectrometer. Isobaric and polyatomic ion interferences are corrected using elemental interference equations based on natural isotopic abundances. Internal standardization eliminates or minimizes instrument drift and matrix-induced signal suppressions and enhancements. Using this technique, sub-part per billion sample detection limits are achievable.

Using a cold-vapor technique for mercury, a 100-mL aliquot of the sample is digested with potassium permanganate/persulfate oxidizing solution at 95°C for two hours to oxidize any organically bound and/or monovalent mercury to mercury (II) oxidation state. Excess oxidizing agent is destroyed with hydroxylamine hydrochloride. The mercuric ion later is reduced to elemental mercury with excess stannous chloride, which is purged with argon into the absorption cell. The absorption is directly proportional to the concentration of mercury in the sample. All the atomic absorption techniques involve initial calibrations to define the calibration range, continuing calibrations, method blanks, duplicates, replicates, matrix spikes, and reference standard analysis as a part of Quality Assurance/Quality Control.

In the fall of 2000, a Leeman PS 200 II automated mercury analyzer was added. This unit enables improved detection limits (<0.1 µg/L), and a more stable baseline than previous instrumentation. This has resulted in improved data quality.

REFERENCES

- DOE. 1995. *Methods for Evaluating Environmental and Waste Management Samples*. DOE/EM 0089T. U.S. Department of Energy. Washington, DC.
- EPA. 1980. *Prescribed Procedures for the Measurement of Radioactivity in Water*. EPA600/480032. U.S. Environmental Protection Agency. Washington, DC. August 1980.
- NYSDEC. 1995. *Analytical Services Protocols*. Bureau of Technical Services and Research, New York State Department of Environmental Conservation. Albany, NY. October 1995.