

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 different analyses.

RADIOLOGICAL ANALYTICAL METHODS

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

Gross Alpha and Gross Beta Analysis - Water Matrix

Water samples are collected in four-liter polyethylene containers and preserved at the time of collection by acidification to pH 2 using nitric acid. If the samples are effluent or surface stream samples from locations DA, EA, HM, HQ, or Building 490 daily process samples, then 100 milliliters (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, which is rinsed to remove the solids. The combined solids and rinsate are transferred to a 5-cm diameter stainless-steel planchet, which is then evaporated to dryness. The planchettes are placed in a drying oven at 221 °F for a minimum of two hours, removed to a desiccator and allowed to cool, and then 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 of which the count rate is subtracted from the raw data before computing net activity concentration. System performance is checked daily with National Institute for Standards and Technology (NIST) traceable standards: americium-241 for alpha and strontium-

90 for beta. Laboratory duplicates and spiked duplicates are performed within each batch of samples to determine precision and accuracy, respectively.

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. Filters are counted twice in a gas flow proportional counter for 50 minutes. The first count occurs immediately upon receipt in the analytical laboratory and is used to screen the samples for unusual levels of air particulate activity. The filters are then recounted approximately one week later. This delay permits the short-lived radon/thoron daughters to decay. The second analysis is used for environmental assessments. The first sample of each batch is a blank filter of which the count rate is subtracted from the raw data before calculating net activity concentration. System performance is checked daily with NIST traceable standards: americium-241 for alpha and strontium-90 for beta.

Tritium Analysis - Water Matrix

Water samples are collected in glass containers. No preservatives are added before collecting the sample. Effluent and surface stream samples from locations DA, EA, HM, HQ, or Building 490 daily process samples as well as groundwater samples are analyzed using a 7-mL aliquot. Potable water samples are distilled following the U.S. Environmental Protection Agency 906.0 method (EPA 1980) and a 7-mL aliquot analyzed. Liquid scintillation cocktail is then 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 are then 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 of which the count rate 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. Laboratory duplicates and spiked duplicates are performed within each batch of samples to determine precision and accuracy, respectively.

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. Effluent samples have dedicated glassware, as do 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. 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 of which the 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. Laboratory duplicates and 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, soil, and aquatic biota

samples. Groundwater samples are processed in-house using U.S. Department of Energy (DOE) method RP500 (DOE 1995), which utilizes a crown ether to selectively separate strontium from the acidified sample matrix. The strontium is then eluted 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, and include 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 twice to verify strontium-90 and yttrium-90 in growth.

Potable water samples as well as samples of solids are shipped to a contractor laboratory, which is certified to perform the EPA 905.0 method (EPA 1980) 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 a combination of gravimetric and strontium-85 standard addition techniques.

Gamma Spectroscopy Analysis

Surface, potable, and groundwater surveillance samples are typically collected in four-liter polyethylene containers and preserved at the time of collection by acidification to pH 2 using nitric acid. Samples are then measured into a 4-liter 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, 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 have been corrected for background and efficiency for each counting geometry used.

NONRADIOLOGICAL ANALYTICAL METHODS

The ASL is certified by the NYSDOH Environmental Laboratory Approval Program (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 (NYSDEC 1995). Tables D-1 and D-2 list the nonradiological NYSDOH ELAP certified analytes.

Purgeable Aromatics and Purgeable Halocarbons

Water samples are collected in 40-mL glass vials with removable Teflon™-lined caps without any headspace, and preserved with 1:1 HCl to pH <2.0. Samples are stored at 39°F and analyzed within 14 days. Thirty-seven purgeable compounds (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 624 method (NYSDEC 1995) protocols using gas chromatograph/mass spectroscopy (GC/MS). There are currently two Hewlett-Packard™ GC/MS instruments used to analyze purgeable organic compounds. Since the groundwater under BNL is classified as a sole source aquifer under the Safe Drinking Water Act and Class GA groundwater by the NYSDEC, the detection limits reported for the compounds are below New York State drinking water standards and the ambient water quality standard. Even though the quality control results generated for the purgeable analysis meets the EPA 524.2 drinking water method requirements as groundwater, which is considered nonpotable until treated, EPA 624 method is used under the nonpotable water category.

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 DB-624 capillary chromatographic column by back flushing the trap with helium. Individual

compounds are separated with a temperature program of the gas chromatograph 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 methods. The quantified data is supported by extensive quality assurance/quality control procedures, 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 a Teflon™-lined lid and stored at 39° F and analyzed within 30 days. Transformer oil, mineral oil, hydraulic fluid, waste oil, and spill wipe-samples are analyzed for PCBs using the gas chromatography-dual electron capture detector (GC-ECD) method. This method is similar to EPA SW-846 method 8082 (NYSDEC 1995) and is targeted to identify and quantify seven different mixtures of PCB congeners in the 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, along with 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 PCBs. 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 the quality assurance/quality control procedures.

Anions

Chloride, nitrate-N, and sulfate are analyzed using Dionex™ ion-chromatography (IC) with the ion suppression and conductivity detection

Table D-1. ASL Certified Organic Analytes

EPA 624 Analytes	EPA 524 Analytes	EPA 524 Analytes
Benzene-d6	Dichlorodifluoromethane	Bromoform
Chloromethane	Chloromethane	Isopropylbenzene
Vinyl Chloride	Vinyl Chloride	p-Bromofluorobenzene
Bromomethane	Bromomethane	Bromobenzene
Chloroethane	Chloroethane	1,1,2,2-Tetrachloroethane
Trichlorofluoromethane	Trichlorofluoromethane	n-Propylbenzene
1,1-Dichloroethene	1,1-Dichloroethene	1,2,3-Trichloropropane
Acetone	Acetone	2-Chlorotoluene
Methylene Chloride	Methylene Chloride	1,3,5-trimethylbenzene
trans-1,2-Dichloroethene	trans-1,2-Dichloroethene	4-Chlorotoluene
1,1-Dichloroethane	1,1-Dichloroethane	Tertbutylbenzene
2-Butanone	2,2-Dichloropropane	1,2,4-trimethylbenzene
Chloroform	cis-1,2-Dichloroethene	sec-Butylbenzene
1,1,1-Trichloroethane	Bromochloromethane	p-Isopropyltoluene
Dibromofluoromethane	2-Butanone	n-Butylbenzene
Carbon Tetrachloride	Chloroform	1,3-Dichlorobenzene
Benzene	1,1,1-Trichloroethane	1,4-Dichlorobenzene
1,2-Dichloroethane	Carbon Tetrachloride	1,2-Dichlorobenzene
Fluorobenzene	1,1-Dichloropropene	1,2-Dibromo-3-chloropropane
Trichloroethene	Benzene	1,2,4-Trichlorobenzene
1,2-Dichloropropane	1,2-Dichloroethane	Hexachlorobutadiene
Bromodichloromethane	Fluorobenzene	Naphthalene
Chloroethylvinyl ether	Trichloroethene	1,2,3-trichlorobenzene
4-Methyl-2-pentanone	1,2-Dichloropropane	
cis-1,3-Dichloropropene	Dibromomethane	
Toluene-d8	Bromodichloromethane	
Toluene	cis-1,3-Dichloropropene	
trans-1,3-Dichloropropene	4-Methyl-2-pentanone	
1,1,2-Trichloroethane	Toluene	
Tetrachloroethene	trans-1,3-Dichloropropene	
2-Hexanone	1,1,2-Trichloroethane	
Dibromochloromethane	Tetrachloroethene	
Chlorobenzene-d5	Tetrachloroethane	
Chlorobenzene	1,3-dichloropropane	
Ethylbenzene	Dibromochloromethane	
m\p-xylene	1,2-dibromoethane	
o-Xylene	Chlorobenzene-d5	
Bromoform	Chlorobenzene	
p-Bromofluorobenzene	Ethylbenzene	
1,1,2,2-Tetrachloroethane	1,1,1,2-Tetrachloroethane	
1,3-Dichlorobenzene	m\p-xylene	
1,4-Dichlorobenzene	o-Xylene	
1,2-Dichlorobenzene	Styrene	

technique. Samples from monitoring wells are collected in 100-mL polyethylene bottles, cooled to 39° F and analyzed within 28 days. For nitrate in drinking water analysis, samples are analyzed within 48 hours. 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 IC 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 the quality assurance/quality control procedures.

Table D-2. ASL Certified Metals and Anions

Metals	Method (ICP/MS)	Metals	Method (AAS)	Anions	Method (IC)
Aluminum	EPA 200.8	Iron	EPA 236.1	Chloride	EPA 300.0
Beryllium	EPA 200.8	Sodium	EPA 273.1	Nitrate	EPA 300.0
Vanadium	EPA 200.8	Mercury	EPA 245.2	Sulfate	EPA 300.0
Chromium	EPA 200.8				
Manganese	EPA 200.8				
Cobalt	EPA 200.8				
Nickel	EPA 200.8				
Copper	EPA 200.8				
Zinc	EPA 200.8				
Arsenic	EPA 200.8				
Selenium	EPA 200.8				
Silver	EPA 200.8				
Cadmium	EPA 200.8				
Barium	EPA 200.8				
Thallium	EPA 200.8				
Lead	EPA 200.8				
Molybdenum	EPA 200.8				
Antimony	EPA 200.8				

Notes:

ICP/MS=Inductively Coupled/Mass Spectrometry

AAS=Atomic Absorption Spectrometry

IC=Ion Chromatography

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 six 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 17 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 18 elements analyzed by the ICP/MS technique. Aqueous samples are nebulized, and introduced into a radio frequency argon

plasma, at temperatures reaching 8,000° K. The desolvated, 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 by the use of 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, subpart 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 203° F for 2 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 the quality assurance/quality control procedures.

APPENDIX D: INSTRUMENTS AND ANALYTICAL METHODS

REFERENCES

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