

Instrumentation and Analytical Methods

The Analytical Services Laboratory (ASL) is divided into radiological and nonradiological sections to facilitate the 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 analysis. All samples were collected and preserved by trained technicians according to appropriate referenced methods. Qualified and trained analysts performed all 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 4-L 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 “policed” down the side of the beaker. The sample is transferred to a stainless steel planchet. Four drops of 10% Triton-X are added to the sample, then it is completely evaporated 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, weighed, and finally 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 the net activity concentration is computed. System performance is checked daily with National Institute for Standards and Technology (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 1.5 cubic feet per minute. At the end of the collection, the filters are returned to the ASL for assay. After a 1-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 the net activity concentration is calculated. The system’s performance is checked daily with 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 the samples are collected. 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 sample that is subtracted from the raw data before the net activity concentration is calculated. 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

The 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 ASL for processing. It is heated in a glass manifold system, using dedicated glassware. 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 added to the aliquot so the final volume in the counting vial is 17 mL, and these samples are 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 the final volume is 11 mL, and 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 the net activity concentration is computed. 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.

Strontium-90 Analysis

Strontium-90 analyses are performed on water. Groundwater samples are processed by the ASL, using either DOE (1995) 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 is 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 2-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 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 (typically 4 liters) are placed in polyethylene bottles acidified to pH 2 with nitric acid. Each sample is then measured into a 4-L Marinelli™ beaker and counted on a calibrated gamma spectroscopy detector for 50,000 seconds (13.8 hours). Air-particulate filters and air-charcoal canisters are counted directly on the calibrated gamma spectroscopy detector for 10,000 seconds (2.8 hours). Soil, vegetation,

and aquatic biota are all processed following collection. Typically, a 100-, 200-, or 300-gram sample 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 has been corrected for background and efficiency for each counting geometry used.

NUCLIDE-SPECIFIC ACTINIDE ANALYSIS; FRISCH GRID METHOD

This method is followed for the determination of ^{241}Am , $^{238,239,240}\text{Pu}$, $^{234,235,238}\text{U}$, and $^{228,232}\text{Th}$ in either solid or liquid matrices. Radium-226 and radon-222 and its progeny can be determined, if necessary. No separation chemistry is required and the pulverized (< 50 mg) or evaporated sample is directly counted in an ApteC Frisch Grid Detector that is capable of resolving alpha peak energies separated by 0.050 MeV (50 keV) in a massless sample. Precision is typically $\pm 2\%$ for a single sample containing 0.6 cps of activity, counted twice for 20 minutes. Alpha-emitting tracers ^{243}Am , ^{236}Pu , ^{232}U , ^{230}Th may be added to the sample prior to counting to determine detection efficiency and/or recovery of added tracer. Typical backgrounds with the detector are <36 cph over a 3- to 9-MeV energy range. Full-Width Half-Maximum (FWHM) resolution ranges from 75 to 100 keV. Alpha efficiencies are matrix-dependent and are typically 0.15 cpm dpm⁻¹ for mg amounts of soil, 0.18 cpm dpm⁻¹ for cellulose-nitrate air filters, and 0.45 cpm dpm⁻¹ for mL amounts of evaporated, untreated water samples. Optimum alpha-peak resolution and detection efficiencies were obtained when absorber thicknesses were maintained below 400 $\mu\text{g cm}^{-2}$ on either 5-cm diameter stainless steel or aluminum planchets or 4.5-cm diameter membrane filters. Minimum detectable levels (MDLs) of 15 pCi/g⁻¹, 0.2 pCi/mL⁻¹, and 0.4 pCi/filter are achievable for 40 mg soil, 1 mL tap water, and 4.5-cm diameter filter samples, respectively, each counted for 60 minutes. The matrices and reported units are soils and sludge (pCi/

kg), liquids (pCi/L), air filters (pCi/cc of air sampled), and other solids (dpm/100 cm²).

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 608, EPA 8082, 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 nonradiological organic and inorganic NYSDOH ELAP-certified analytes, respectively. Not reflected in those tables are the PCB analyses that ASL is certified to conduct, for Aroclors 1016, 1221, 1232, 1242, 1248, 1254, and 1260.

Purgeable Aromatics and Purgeable Halocarbons

Water samples are collected in 40-mL glass vials with removable teflon-lined caps without any headspace, and acidified with 1:1 HCl to a pH <2.0. Samples are stored at 4°C and analyzed within 14 days. Thirty-eight 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 Method 624 protocols using gas chromatography/mass spectrometry (GC/MS). In 2003, two Hewlett-Packard™ GC/MS instruments were used to analyze purgeable organic compounds. Because groundwater at BNL is classified as a sole source aquifer under the Safe Drinking Water Act and as 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 Methods 524.2 and 624 are used to analyze water, based on the project manager's data quality requirements.

The methods involve 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, then quantified by the internal standard method. The quantitation data are supported by extensive Quality Assurance/Quality Control, such as tuning the mass spectrometer to meet bromofluorobenzene criteria, performing initial and continuing calibrations that verify daily response factors, using 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- or 100-mL glass containers with Teflon™-lined lids, 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 the 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. Method blanks, duplicates, spikes, calibration, and reference check standards are run as part of Quality Assurance/Quality Control.

Anions

Chloride, nitrate-N, and sulfate anions are analyzed using Dionex™ Ion-chromatography (IC) with the 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, samples are analyzed within 48 hrs. In 2003 (as in past years), holding times were exceeded for nitrate analysis of some nonpotable monitoring well samples, but the depletion of nitrate is understood 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 a 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 the target element is passed through the flame. The atomized element absorbs the energy specific to that element from the cathode lamp; 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 comparison 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), 18 elements are 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 the mercury (II) oxidation state. Excess oxidizing agent is reduced 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. A Leeman PS 200 II automated mercury analyzer (detection limit = <0.1 µg/L) is used. 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.

REFERENCES AND BIBLIOGRAPHY

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