Consolidated Edison Company of New York, Inc.

Site Characterization Work Plan - Krasdale Foods Inc., Leasehold

Hunts Point Former Manufactured Gas Plant
Bronx, New York

February 2011

ARCADIS

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I Margaret Carrillo-Sheridan, P.E. certify that that I am currently a New York State-registered professional engineer and that this Work Plan was prepared in accordance with all applicable statutes and regulations and in substantial conformance with the DER Technical Guidance for Site Investigation and Remediation (DER-10).

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Acronyms and Abbreviations

AKRF	AKRF, Inc.
bgs	below ground surface
BTEX	benzene, toluene, ethylbenzene, and xylenes
CCTV	closed-circuit television
Con Edison	Consolidated Edison Company of New York, Inc.
cy	cubic yard(s)
DOT	Department of Transportation
ESA	Environmental Site Assessment
FSP	Field Sampling Plan
GPR	ground-penetrating radar
HASP	Health and Safety Plan
Krasdale	Krasdale Foods, Inc.
LMS	Lawler Matusky and Skelley Engineers, LLP
MGP	Manufactured Gas Plant
NAPL	non-aqueous phase liquid
NYCEDC	New York City Economic Development Corporation
NYCRR	New York Codes, Rules, and Regulations
NYSDEC	New York State Department of Environmental Conservation
One Call	New York City/Long Island One-Call Center
ORP	oxidation reduction potential
PAH	polycyclic aromatic hydrocarbon
PCB	polychlorinated biphenyl
PID	photoionization detector
QAPP	Quality Assurance Project Plan

QA/QC	quality assurance/quality control
SOPs	Standard Operating Procedures
SVOC	semivolatile organic compound
TAL	Target Analyte List
TCL	Target Compound List
TPH	total petroleum hydrocarbons
USEPA	United States Environmental Protection Agency
VCA	Voluntary Cleanup Agreement
VOC	volatile organic compound
Work Plan	Site Characterization Work Plan

1. Introduction

This Site Characterization Work Plan (Work Plan) has been developed on behalf of Consolidated Edison Company of New York, Inc. (Con Edison) for the characterization of the Krasdale Foods, Inc. (Krasdale) leasehold in connection with of the Hunts Point former Manufactured Gas Plant (MGP) site (“the site”). This Work Plan has been prepared in accordance with the 6 New York Codes, Rules, and Regulations (NYCRR) Part 375 Environmental Remediation Programs (NYSDEC 2006), DER-10 Technical Guidance for Site Investigation and Remediation (DER-10) (NYSDEC 2010), and the Voluntary Cleanup Agreement (VCA) between the New York State Department of Environmental Conservation (NYSDEC) and Con Edison. The VCA index number for the Hunts Point Former MGP is D2-0003-02-03. Upon NYSDEC approval of this Work Plan, Con Edison will implement this Work Plan as described herein.

1.1 Background

The Hunts Point former MGP was operated by Con Edison from late 1926 to 1962. Demolition of the plant was completed in early 1968. That same year, Con Edison sold the majority of the site to the City of New York for use as a wholesale cooperative food market. On-site portions of the former MGP property have been redeveloped with roads, warehouses, parking areas, a City of New York Department of Sanitation marine transfer station, or remain undeveloped. The approximate extent of the former MGP is shown on Figure 1.

The Krasdale portion of the Hunts Point former MGP is located to the south of Parcel D, as shown on Figure 2. The property is currently used as a warehouse for shipping and receiving of food products.

The New York City Economic Development Corporation (NYCEDC) is currently developing a drainage plan for the Hunts Point Food Distribution Center, including the Krasdale property. As part of the work, AKRF, Inc. (AKRF) completed an evaluation of the storm sewers located on the Krasdale property in 2010. AKRF’s evaluation included video inspection of the storm sewers using closed-circuit television (CCTV), as well as sampling and analysis of water samples collected during a dry weather condition from one catch basin and one outfall (Inlet #120 and OF-1, respectively, on Figure 2). In general, the findings indicated that the northernmost storm sewer just south of Parcel D is in poor physical condition and that the water samples collected during dry weather conditions contained chemical constituents similar to those that have been identified in groundwater at adjacent Parcel D (see Section 2.4.2).

ARCADIS and Savin Engineers, PC (Savin), on behalf of Con Edision, inspected the subject storm sewer on December 14, 2010using CCTV along the entire length of the pipe from the outfall (OF-1) to the last catch basin (Inlet #113). However, certain portions of the storm sewer were inaccessible due to obstructions in the pipe. Significant observations were as follows:

- Evidence of significant erosion to the pipe (note predominately below water line)
- Several blockages due to debris in the pipe
- Evidence of a breach in the pipe structure
- A strong odor related to the presence of hydrogen sulfide
- Blue-green discoloration of concrete at numerous locations
- Groundwater infiltration was noted at several locations throughout the inspection

Based on the information gathered during the sewer inspection, the existing storm sewer is no longer in functional condition, exhibiting major structural defects at multiple locations, including open joints and erosion of the pipe concrete (such that eroded portions of the storm sewer exhibit exposed reinforcing steel).

A Dry Weather Discharge Evaluation Work Plan has been submitted by Con Edison to the NYSDEC to prevent discharge of MGP-impacted water from the storm sewer pipe into the adjacent Bronx River (ARCADIS 2011).

This Work Plan has been developed to investigate the presence of any existing MGP impacts in the vicinity of the northernmost storm sewer and remaining portion of the Krasdale property (excluding Parcel F).

1.2 Work Plan Organization

The remaining portions of this Work Plan are organized into the following sections:

- *Section 2 – Site Description and History*: This section provides an overview of the site setting and history, as well as previous remedial investigations and actions.

- *Section 3 – Site-Characterization Activities*: This section presents the proposed site-characterization activities and the associated procedures.

- *Section 4 –Support Activities:* This section describes the associated permitting, utility clearance, equipment decontamination, waste management, surveying, health and safety, and community air monitoring procedures.

- *Section 5 – Schedule and Reporting*: This section presents the general timeline of site-characterization activities and outlines reporting requirements.

- *Section 6 – References*: This section presents the documents cited in this Work Plan.

The following appendices are provided to support the Work Plan:

- *Appendix A* – Addendum to Field Sampling Plan (FSP; Appendix A to the Off-Site Characterization Work Plan) presents additional Standard Operating Procedures (SOPs) to support executing the field activities.

- *Appendix B* – Addendum to Quality Assurance Project Plan (QAPP; Appendix B to the Off-Site Characterization Work Plan) presents the additional analytical methods and procedures, including laboratory SOPs, that will be used to analyze samples collected during the field activities.

2. Site Description and History

2.1 Site Location

The Hunts Point former MGP is located in the Borough of Bronx, New York City, Bronx County, New York (Figure 1). The former MGP is an approximately 160-acre tract of land on Hunts Point, a peninsula at the confluence of the Bronx and East Rivers.

The Krasdale property is an approximately 11-acre tract of land located on the northeastern portion of the Hunts Point former MGP site. The Krasdale property is bounded by Food Center Drive to the west, Parcel D to the north, Parcel C to the south, and the Bronx River to the east (Figure 2).

2.2 Site History

In 1922, Con Edison began purchasing land for what would become the Hunts Point MGP. Initial construction of the coke ovens and oven gas manufacturing machinery occurred from 1924 through 1927, and the plant went on-line in late 1926. Between 1931 and 1932, the works were enlarged, adding carbureted water gas works. The works were again expanded in 1948. The MGP produced water gas from 1932 to 1962. In 1950, the water gas works were modified to use natural gas in addition to coal or in place of coal.

On-site portions of the former MGP have been divided into parcels (A through F) for purposes of site cleanup, and have or will be investigated and remediated separately by others. The historic use of Parcels C and F included the storage of coal. In addition, two coal bridges were located adjacent to Parcel C and were used to unload the coal via conveyors. Parcel D, located in the northeastern section of the former MGP, did not contain any historic structures. Various investigations and remediation completed to date have documented petroleum and MGP-related residuals—including coal tars, oils, and purifier wastes—as well as constituents associated with these residuals, such as benzene, toluene, ethylbenzene, and xylenes (BTEX) compounds; polycyclic aromatic hydrocarbons (PAHs); and inorganic constituents, such as cyanides, on the former MGP property.

Additional details regarding the history and operations of the Hunts Point former MGP can be found in the Hunts Point Off-Site Manufactured Gas Plant History Report (Parsons 2003), as well as the Off-Site Characterization Work Plan (ARCADIS 2010), which includes historical maps as Appendix A.

Beginning in the early 1950s, portions of the MGP were taken out of service. The liquid petroleum plant was taken off-line in 1952 and the oven/producer gas plant in 1954. The last components of the MGP were taken off-line in 1962, and the remaining buildings and structures were demolished. The large gas holder remained in service until it was demolished in 1968. The majority of the former MGP property was then sold to the City of New York in the late 1960s through early 1970s for use as a wholesale cooperative food market (Parsons 2003). On-site portions of the former MGP property have been redeveloped with roads, warehouses, parking areas, a City of New York Department of Sanitation marine transfer station, or remain undeveloped. Currently, the Krasdale property is used as a warehouse for shipping and receiving of food products.

2.3 Geologic and Hydrogeologic Setting

Based on survey information provided by NYCEDC, topography of the site is relatively flat (less than 1 percent), and slopes east, towards the Bronx River. Except for Parcel F and a grassy area on the western boundary of the site, the Krasdale property is covered by impervious surfaces (generally asphalt and warehouse buildings). Precipitation that falls within the site is generally conveyed via overland flow to catch basins that discharge to the site storm sewers and ultimately to the Bronx River via outfalls OF-1, OF-2, and OF-3 (Figure 2).

Based on observations during previous investigations of nearby Parcels C, D, and F (LMS 2001; LMS 2005; HDR/LMS 2007), the soil stratigraphy varies and is influenced by historic filling activities. Historic fill material—such as coal, slag, ash, and wood intermingled with sand and gravel, and dredged sediment—is present in the surface and shallow overburden to varying depths. Underlying the fill unit is a mixture of clayey silt, sand, and gravel, which has been described as poorly sorted outwash deposits. A silty clay unit, described as a “meadowmat,” underlies the outwash deposits.

The water table generally occurs in the shallow subsurface at depths ranging from approximately 2 to 10 feet below ground surface (bgs). In general, groundwater flow is directed from west to east toward the Bronx River. However, groundwater flow may be influenced by tidal conditions within the adjacent river and the numerous subsurface utilities in the area.

2.4 Previous and Current Investigations

Various investigations and/or remediation of Parcels A through F have been completed and are documented in several reports. The subsections below summarize the investigations, findings, and various remedial efforts completed in connection with Parcels C, D, and F and the Krasdale property, as well as planned activities, based on the following reports:

- Hunts Point Cooperative Market Redevelopment Plan, Response Plan for the Operating Unit Portion of Parcel C, Bronx, New York, Final Revised (LMS 2001)

- Hunts Point Food Distribution Center Redevelopment Plan, Sections of the Redevelopment Plan for the Operable Unit 1 Portion of Parcel C, Bronx, New York, Final Revised (HDR 2009)

- Hunts Point Cooperative Market Redevelopment Plan, Investigative Report for Parcel D, Bronx, New York (LMS 2005)

- Draft Hunts Point Food Distribution Center, Preliminary Alternatives Analysis Report Parcel D, Bronx, New York, Final (HDR 2010a)

- Hunts Point Food Distribution Center Redevelopment Plan, Site Investigative Report for Parcel F, Bronx, New York, Final (HDR/LMS 2007)

- Hunts Point Food Distribution Center, Preliminary Design Investigation Scope of Work, Parcel F, Bronx, New York, Final (HDR 2010b)

- Phase II Environmental Investigation Report of Hunts Point Produce Market Complex Parcel A, B, C, D and E, Bronx, New York (Hygienetics 1997)

Figure 2 shows the approximate locations of the observed impacts on these parcels.

2.4.1 Parcel C

Two subsurface investigations were completed in 1997 and 1999 on Parcel C. The 1997 investigation consisted of the completion of five soil borings to a depth of 6 to 10 feet bgs and the installation of one monitoring well screened across the water table. The 1999 investigation consisted of the completion of four test trenches and five test pits to the water table, one soil boring to 40 feet bgs, as well as the collection and analysis of soil and groundwater samples. A summary of the visual impacts noted during the investigations is presented below.

A coal layer was encountered across most of site from the surface to 2 to 4 feet bgs, with greatest thickness near center of site. Occasional coal tar/tar boils (1 to 4 feet in diameter) were also observed at the surface, and occasionally at 3 to 4 feet bgs. Areas of “soft ground” were also encountered during the 1999 investigation but were not investigated, as the areas could not support the excavator. In addition, petroleum-impacted soils were noted in the southern portion of the parcel.

An occasional sheen on groundwater was noted during completion of the trenches and, during the 1999 investigation, a sheen was also noted on the East River at low tide approximately 20 feet offshore. The sheen was observed adjacent to a former outfall in the bulkhead. Several other unidentified former utilities were noted during the trenching.

Since the investigations described above, Parcel C was sub-divided for redevelopment. The majority of the parcel was redeveloped to a slab on-grade warehouse occupied by Anheuser Busch and an adjacent parking lot to the south of the building. The northern and eastern perimeters are to be occupied by the future Greenway Park as part of the South Bronx Greenway Master Plan. An easement for the Iroquois Pipeline occupies the southern-most portion of Parcel C. As part of the redevelopment project, the bulkhead was rehabilitated. Coal tar-impacted soils encountered on the landward side of the former bulkhead were removed during the rehabilitation project and properly disposed.

The Parcel C remedy, incorporated during redevelopment, included installation of a passive sub-slab depressurization system under the building slab, engineered cap, and 1 foot of imported fill in landscaped areas. In addition, to raise the surface elevation of the parcel 4 to 5 feet out of the Federal Emergency Management Agency flood zone, approximately 14,000 cubic yards (cy) of excavated soils generated during the bulkhead rehabilitation project on Parcel B, as well as an additional 26,000 cy of excavated soils from other areas of the project, were used as fill material on Parcel C.

A Final Engineering Report for Parcel C is currently being prepared by others.

2.4.2 Parcel D

Parcel D is currently undeveloped. A bulkhead was constructed sometime between 1966 and 1974, and a 100-foot-wide area was filled between the shoreline and the bulkhead.

Two subsurface investigations were conducted in 1997 and 2004 on Parcel D. The 1997 investigation consisted of the completion of four soil borings to depths of 6 to 10 feet bgs and the installation of one monitoring well screened across the water table. The 2004 investigation consisted of the completion of 47 soil borings and 7 temporary piezometers, collection and analysis of soil and groundwater samples, as well as the completion of a ground-penetrating radar (GPR) survey.

An area of purifier waste was observed at the ground surface and extended to a maximum depth of 14 feet bgs (upper 4 feet were described as “spongy”) in an approximately 350-foot by 450-foot area to the east of the center of the parcel. Small pockets of coal tar were noted and were generally observed as surface boils (upper 1 to 2 feet). In addition, an area of coal tar from 5 to 10 feet bgs was observed on the western portion of the site. Coal tar was also noted in two wells located adjacent to the western boundary of the parcel (upgradient).

Petroleum-impacted material was noted from 5 to 10 feet bgs across portions of the parcel. Soil and groundwater samples contained constituents associated with petroleum and MGP-related residuals, as well as other constituents, including BTEX compounds, PAHs, phenols, carbon disulfide, styrene, 4-methyl-2-pentanone, polychlorinated biphenyls (PCBs), and inorganic constituents (such as metals, cyanides, sulfur, and ammonia).

During the construction of the Iroquois Pipeline, a gas-transmission line that runs underneath Food Center Drive, coal tar mixed with some purifier waste was noted in a consistent depth layer (4 to 6 feet bgs) throughout the pipeline trench. The material was noted to extend beyond the extent of the trench. Fill material on the western portion was primarily noted as slag, ash, cinders, wood, and brick, whereas the fill in the eastern portion was mainly described as ash, cinders, wood, and brick. Impacts extended beyond the 4-foot-wide pipeline trench in east/west directions.

A Preliminary Alternatives Analysis Report has been prepared and presents four general remedial alternatives that are currently being evaluated (HDR 2010a). Planned development of Parcel D includes an aboveground structure covering a majority of the property, paved or concrete parking areas, and open or green space along the waterfront in accordance with the South Bronx Greenway Master Plan. The four alternatives evaluated include:

- Site leveling and grading, placement of fill material, and construction of an engineered cap
- Excavation and off-site disposal of visually identified MGP material to the groundwater table (approximately 5 to 10 feet bgs) and containment of remaining MGP material with a geotextile fabric at depth and an engineered cap at the surface
- In-situ stabilization of MGP material beneath an engineered cap to a depth of approximately 15 feet bgs with shallow excavation of coal tar
- Excavation and off-site disposal of all visually identified MGP material to a depth of approximately 15 feet bgs

2.4.3 Parcel F

Parcel F is currently undeveloped, vegetated land within the overall Krasdale property. A subsurface investigation was conducted at Parcel F in 2005. The investigation consisted of the completion of 24 soil borings to a maximum depth of 5 feet below the water table, the bottom of the purifier waste or the clay layer; 5 temporary piezometers screened across the water table; and 8 soil gas points, as well as the completion of a GPR survey and collection and analysis of soil, groundwater, and soil gas samples. Soil and groundwater samples contained constituents associated with petroleum and MGP-related residuals, as well as other constituents, including BTEX compounds, PAHs, phenols, carbon disulfide, PCBs, and inorganic constituents (such as metals, cyanides, sulfur, and ammonia).

Purifier waste covers a majority of the parcel, extending to depths up to 16 feet bgs. These wastes were observed up to 10 feet thick, separated with up to 3 feet of fill. The volume of purifier waste on the parcel was estimated to be 17,900 cy—1,800 cy above water table, 16,100 cy below water table. Relatively smaller areas (5 cy) of coal tar impacts were noted and were generally observed as surface boils. In addition, coal tar and purifier waste was observed from 4 to 6 feet bgs in a 100-foot portion of the trench adjacent to Parcel F during construction of the Iroquois Pipeline.

Additional investigation on and around the perimeter of the parcel is planned and detailed in the Preliminary Design Investigation Scope of Work (HDR 2010b). The purpose of this investigation is to asses Parcel F for redevelopment as a parking lot expansion and provide information necessary to recommend a remedial alternative. Planned site- characterization activities include completion of a GPR survey, test pits, soil borings, piezometers, and soil gas sampling locations.

The NYCEDC is currently working on a drainage plan for the food distribution portion of the Hunts Point peninsula. As part of the work, AKRF, on behalf of NYCEDC, completed an evaluation of the three storm sewers and outfalls located on the Krasdale property in September 2010. The inspection included direct observation of the storm sewer structures (e.g., catch basins, outfalls) and CCTV video observation of the storm sewer pipes from the outfall to the first upgradient catch basin. In general, the findings indicated that the northernmost storm sewer (located immediately south of Parcel D), is in poor physical condition. The remaining two storm sewers appeared to be in acceptable physical condition.

During AKRF’s visual inspection, a dry weather discharge was observed at the northernmost storm sewer pipe. As a result, AKRF collected samples of water at the outfall (OF-1) and first upgradient catch basin (Inlet #120). The water samples contained constituents similar to those that have been identified at adjacent Parcel D. Carbon disulfide, cyanide, naphthalenes, and metals, as well as several semivolatile organic compounds (including dibenzofuran, acetophenone, carbazole, fluorene, phenanthrene, and phenols) were detected in the samples. The pH of the dry weather water samples collected from the catch basin and outfall were 2.0 and 2.1, respectively.

ARCADIS, on behalf of Con Edison, inspected the northernmost storm sewer in December 2010 The inspection was performed using CCTV along the entire length of the northernmost storm sewer from the outfall (OF-1) to the last catch basin (Inlet #113). At the time of the inspection, water was observed to be flowing through the storm sewer. The main contributor to water flow in the storm sewer appeared to be infiltrating groundwater, as there had not been a significant precipitation event in the past 24 hours. Based on the storm sewer inspections, the existing storm sewer was found to be in disfunctional condition. On January 14, 2011, Con Edison submitted to the NYSDEC a Dry Weather Discharge Evaluation Work Plan that provides a recommended approach to prevent discharge of MGP-impacted water from the northernmost sewer pipe into the adjacent Bronx River (ARCADIS 2011).

3. Site Characterization Activities

3.1 Site Characterization Objectives and Scope Overview

Characterization of the Krasdale property portion of the Hunts Point former MGP site is proposed in order to achieve the following objective:

- Evaluate the potential presence, if any, and extent of MGP-related impacts adjacent to the northernmost storm sewer pipe and the remaining portion of the Krasdale property

Characterization activities will consist of the following:

- Soil characterization
- Groundwater characterization
- Dry weather storm sewer characterization

The scope associated with these characterization activities is presented in Sections 3.2 through 3.4 below.

Detailed descriptions of the characterization methods and techniques, including SOPs, are provided in the FSP (Appendix A to the Off-Site Characterization Work Plan). Additional SOPs are included in Appendix A of this Work Plan as an addendum to the FSP. Analytical methods and procedures that will be used to analyze samples collected during the field activities and quality assurance/quality control (QA/QC) requirements are provided in the QAPP (Appendix B of the Off-Site Characterization Work Plan). Additional laboratory SOPs and summary of analytical methodologies to be used during implementation of field activates are included in Appendix B of this Work Plan as an addendum to the QAPP. Health and safety considerations for the characterization activities are introduced in Section 4.6 of this Work Plan and further described in the Health and Safety Plan (HASP; Appendix C of the Off-Site Characterization Work Plan). Any deviation from this Work Plan and appended plans will be communicated Con Edison’s Project Manager, and the NYSDEC’s Project Manager for the site, and will be documented in the field book.

3.2 Soil Characterization

3.2.1 Soil Boring Installation

A total of 29 subsurface soil borings (SB-01 through SB-29) will be completed at the proposed locations shown on Figure 3 to evaluate subsurface conditions in the vicinity of the northernmost storm sewer and the conditions on the remainder of the Krasdale property. The rationale for each soil boring is provided in Table 1. Generally, these boring locations were chosen to evaluate the subsurface characteristics immediately adjacent to the storm sewer and Parcel D boundary, or the subsurface characteristics throughout the remaining portion of the Krasdale property. The proposed soil boring locations may be adjusted in the field as necessary based on the locations of aboveground or underground utilities, visual observations, and access. Soil borings will not be relocated more than 10 feet from the proposed location without prior consultation with Con Edison's and the NYSDEC's Project Managers. In addition, proposed soil boring locations are subject to review and approval by the property owner.

Each soil boring will be completed using direct-push technology in accordance with the protocols presented in the FSP (Appendix B to the Off-Site Characterization Work Plan). The direct-push rig is hydraulically powered and uses a probing hammer to advance 2-inch-diameter, 4- or 5-foot-long Macro-Core® samplers into the subsurface. The drilling equipment is typically mounted on a small pickup truck, but can also be mounted on tracks so that difficult terrain can be accessed.

The first 5 feet of each soil boring (i.e., ground surface to 5 feet bgs) will be excavated, to the extent practicable, by non-mechanical means (i.e., hand auger, post-hole digger, air knife, and/or vacuum truck). Below 5 feet, soil samples will be collected continuously from each soil boring with the 4- or 5-foot-long Macro-Cores®. Proposed soil borings will be advanced to the top of the confining layer or refusal, whichever is shallower. Borings not completed in one work day will be covered with a skid-resistant stainless-steel plate and its location marked with safety cones until work is completed.

Air and fugitive dust emissions in the worker breathing zone will be monitored during implementation of the drilling activities using a photoionization detector (PID) and a Real-Time Aerosol Monitor (MIE mini-RAM, or equivalent) as detailed in the HASP (Appendix C to the Off-Site Characterization Work Plan).

Following collection of the subsurface soil samples, each soil boring will be tremie-grouted to the ground surface using a cement-bentonite grout. Soil borings completed in a paved area will be repaired with an asphalt patch or concrete, as appropriate.

Additional details regarding soil boring installation methods, including decontamination procedures, are provided in the FSP (Appendix B to the Off-Site Characterization Work Plan).

3.2.2 Soil Sampling

In general, the Macro-Cores® will be photographed, visually characterized, and screened with a PID for every 1-foot interval. Observations—including the presence of non-aqueous phase liquid (NAPL), purifier waste, or other visual impacts, recovery, lithology, PID readings, and any other pertinent visual observations—will be recorded. Soil samples will be collected, packaged, and shipped to laboratories for analysis as described below. Additional details regarding soil characterization methods and methods for sample collecting, handling, packing, and shipping and the procedures for equipment decontamination are provided in the FSP (Appendix A to the Off-Site Characterization Work Plan).

Soil samples will be selected for laboratory analyses based on the following rationale:

- If purifier wastes, NAPLs, other visual impacts, or elevated PID readings are observed, one sample will be collected from the zone with the highest PID readings, presence of NAPL, purifier waste, or other visual impacts. An additional sample will be collected from the 1-foot interval below the impacted zone, at or near the base of the boring, or above the confining unit to define the vertical extent of impacts.

- If no NAPL, purifier waste, other visual impacts, or elevated PID readings are observed, a sample will be collected from the 1-foot interval directly above the water table.

Soil samples will be analyzed for the following:

- Target Compound List (TCL) volatile organic compounds (VOCs) (USEPA SW-846 Method 8260)

- TCL semivolatile organic compounds (SVOCs) (USEPA SW-846 Method 8270)

- Target Analyte List (TAL) metals (USEPA SW-846 Methods 6010/7470/7471)
- Cyanide, total, amenable and free (USEPA SW-846 Method 9010/9012B/9016)
- pH (USEPA SW-846 Method 9040B)

In addition to the above, select soil samples will be analyzed for the following:

- Total petroleum hydrocarbon (TPH) (USEPA SW-846 Method 8015B)
- Inorganics, including ammonia, nitrate, nitrite, sulfate, sulfide, chloride, phosphate, and carbonate/bicarbonate (Methods E350.1, E300, SM4500S2-E, SM4500P-E, SM-2320B)

TPH analysis will support the evaluation of material (piping and/or grout material) compatibility. Inorganics analysis will establish baseline geochemical characteristics to support the evaluation of remedial options, if appropriate.

QA/QC samples (including trip blank, field duplicate, matrix spike, matrix spike duplicate, and rinse blank samples) will be collected and submitted for laboratory analysis as referenced in the QAPP Addendum (Appendix B). Additional details regarding methods for sample collecting, handling, packing, and shipping and the procedures for equipment decontamination are provided in the FSP (Appendix A of the Off-Site Characterization Work Plan).

3.2.3 Contingency Soil Borings

In the event that NAPL, purifier waste, or other visual impacts are observed in a boring, additional borings may be completed within the Krasdale property, as appropriate, to further delineate the nature and extent of impacts. Contingency boring locations, if any, will be identified in the field and communicated to Con Edison and NYSDEC. If contingency soil borings are completed, soil samples will be collected consistent with methods described in Section 3.2.2.

3.3 Groundwater Characterization

3.3.1 Groundwater Collection

Groundwater monitoring wells will be installed at certain boring locations where NAPL, purifier waste, or other visual impacts are observed. During storm sewer characterization activities, three groundwater monitoring wells will be installed (one upgradient, one midpoint, and one downgradient). During the remaining site-characterization activities, a minimum of 5 and maximum of 10 groundwater monitoring wells will be installed across the site. Monitoring well locations will be selected to spatially represent the groundwater quality within and outside of areas where NAPL, purifier waste, or other potential waste materials are observed.

The monitoring wells will be constructed using 2-inch-diameter Schedule 40 polyvinyl chloride (PVC) pip with 0.020-inch slot screens. The monitoring wells will be screened from approximately 3 feet above the water table to the depth of completion. Each monitoring well will be installed with a 2-foot sump grouted in place if NAPL is encountered and/or suspected. However, if the water table is within 2 feet of the ground surface, an alternate monitoring well installation configuration will be used to confirm that an adequate surface seal is maintained. After installation, the monitoring wells will be developed using the procedures provided in the FSP (Appendix B to the Off-Site Characterization Work Plan).

During groundwater collection field parameters including pH, oxidation reduction potential (ORP), conductivity, and temperature will be measured using a water quality probe. Additional details regarding the collection of water quality parameters are provided in the FSP (Appendix A to the Off-Site Characterization Work Plan).

3.3.2 Groundwater Sampling

The select monitoring wells will be screened across (above and below) the water table, and groundwater samples will be collected from the upper portion of the aquifer and analyzed for the following:

- TCL VOCs (USEPA SW-846 Method 8260)
- TCL SVOCs (USEPA SW-846 Method 8270)
- TAL metals (USEPA SW-846 Methods 6010/7470/7471)

- Cyanide, total, amenable and free (USEPA SW-846 Method 9010/SM4500CN-G/9016)

In addition to the above, select groundwater samples will be analyzed for the following:

- TPH (USEPA SW-846 Method 8015B)

- Inorganics, including ammonia, nitrate, nitrite, sulfate, sulfide, chloride, phosphate, fluoride, and carbonate/bicarbonate (Methods E350.1, E300, SM4500S2-E, SM4500P-E, SM-2320B)

TPH analysis will support the evaluation of material (piping and/or grout material) compatibility. Inorganics analysis will establish baseline geochemical characteristics, to support the evaluation of a remedial strategy, if appropriate.

QA/QC samples (including trip blank, field duplicate, matrix spike, matrix spike duplicate, and rinse blank samples) will be collected and submitted for laboratory analysis as referenced in the QAPP Addendum (Appendix B). Additional details regarding methods for sample collecting, handling, packing, and shipping and the procedures for equipment decontamination are provided in the FSP (Appendix A of the Off-Site Characterization Work Plan).

3.4 Dry Weather Storm Sewer Characterization

3.4.1 Storm Sewer Water Collection

If dry weather discharge is observed in the catch basins along the northernmost storm sewer (Inlets #111, 112, 113, or 120) or at outfall OF-1, up to five water samples will be collected where observed. The collection of water samples from the storm sewer will support the evaluation of material compatibility with site-specific constituents. These samples will be collected in dry weather conditions (i.e., no significant rain event in the past 24 hours). During water sampling from the storm sewer, field parameters including pH, ORP, conductivity, and temperature will be measured using a water quality probe

Water samples from the storm sewer will be collected using a Wildco Kemmerer stainless-steel bottle sampler or directly into laboratory-supplied sample containers. Additional details regarding water collection methods are provided in Appendix A.

3.4.2 Storm Sewer Water Sampling

Water samples from the storm sewer will be analyzed for the following:

- TCL VOCs (USEPA SW-846 Method 8260)
- TCL SVOCs (USEPA SW-846 Method 8270)
- TAL metals (USEPA SW-846 Methods 6010/7470/7471)
- TPH (USEPA SW-846 Method 8015B)
- Cyanide, total, amenable and free (USEPA SW-846 Method 9010/SM4500CN-G/9016)
- Inorganics, including ammonia, nitrate, nitrite, sulfate, sulfide, chloride, phosphate, fluoride, and carbonate/bicarbonate (Methods E350.1, E300, SM4500S2-E, SM4500P-E, SM-2320B)

QA/QC samples (including trip blank, field duplicate, matrix spike, matrix spike duplicate, and rinse blank samples) will be collected and submitted for laboratory analysis as referenced in the QAPP Addendum (Appendix B). Additional details regarding methods for sample collecting, handling, packing, and shipping and the procedures for equipment decontamination are provided in the FSP (Appendix A of the Off-Site Characterization Work Plan*).*

4. Support Activities

4.1 Notification and Access

Prior to implementing characterization activities, Con Edison will obtain access agreements, as appropriate, from government and private entities.

4.2 Utility Clearance

Prior to mobilization, hard copies of available utility plates, drawings, and/or maps from the New York City Department of Environmental Protection, Con Edison, NYCEDC, and other entities will be reviewed to evaluate the approximate size and locations of subsurface utilities in the vicinity of the areas where intrusive work is planned. In addition, the proposed boring locations will be marked and/or staked (with flagging). Once the proposed boring locations are marked, the New York City/Long Island One-Call Center (One Call) will be contacted per 16 NYCRR Part 753 to locate and mark out the subsurface utilities present within the areas where intrusive work is planned. This mark out survey will target areas where soil borings are proposed. Consistent with One Call criteria, a request will be made at least 72 hours prior to initiating fieldwork. Confirmation that mark outs have been completed will be received by facsimile, telephone, or in person from the participating utility companies and will be documented.

A private utility locator service and other parties (as appropriate) will be used to evaluate the presence (using GPR) and location of utilities (both overhead and subsurface) at and adjacent to proposed boring locations.

A site visit will also be conducted with other utility companies, if necessary. If the markings become faint or obscure, they will be refreshed as needed. The sampling locations may be adjusted based on the results of the mark out. In addition, hand excavation, hand auguring, or air knife procedures will be implemented within upper the 5 feet at the locations where soil borings will be located. Field personnel will be notified of the utilities that are present and the dangers associated with working near such utilities. Further safety measures associated with working near utilities and procedures for proper underground utility clearance are included in the HASP (Appendix C of the Off-Site Characterization Work Plan).

4.3 Equipment Decontamination

Equipment decontamination will follow the procedures outlined in the FSP (Appendix A of the Off-Site Characterization Work Plan). In general, non-disposable equipment, including drilling tools and equipment, will be decontaminated prior to first use, between each characterization location, and prior to demobilization (if dedicated equipment is not used).

4.4 Investigative-Derived Waste Management

Investigation-derived waste will be containerized in appropriate waste containers and staged in an on-site area prior to off-site disposal. Soil cuttings and personal protective equipment will be placed in new Department of Transportation- (DOT-) approved steel 55-gallon drums. Water will be stored in polyethylene tanks or new closed-top DOT-approved steel 55-gallon steel drums. Storage containers will be appropriately labeled with the contents, generator, location, and date for appropriate off-site transportation and disposal. One sample of soil cuttings and one sample of the water generated by the field activities will be collected and submitted for waste characterization analysis. Waste classification is expected to consist of toxicity characterization leaching procedure extraction for analysis of VOCs, SVOCs, and metals, and reactivity, ignitability, corrosivity, cyanide, and PCB analysis. Additional details regarding investigation-derived waste management are provided in the SOP: Investigation-Derived Waste Storage and Handling (Appendix A).

4.5 Surveying

Following completion of the characterization, a New York State-licensed Land Surveyor will field survey all soil boring and water sampling locations. Horizontal data will be presented in New York State Plane coordinates (North American Datum of 1983). Vertical data will be presented relative to mean sea level in National Geodetic Vertical Datum of 1929 or North American Vertical Datum of 1988.

4.6 Health and Safety

Potential health and safety issues associated with implementation of this Work Plan have been considered, and a HASP (Appendix C of the Off-Site Characterization Work Plan) was prepared to establish safe working conditions. The safety organizations, procedures, and protective equipment have been established based on an analysis of potential physical, chemical, and environmental hazards. Specific hazard control methodologies have been evaluated and selected to minimize the potential for injury, illness, or other incident.

4.7 Community Air Monitoring

Requirements for additional perimeter monitoring of air emissions at the boundary of the work area during the characterization are detailed in the Community Air Monitoring Plan presented as Appendix E of the Off-Site Characterization Work Plan.

5. Schedule and Reporting

5.1 Site Characterization Report

A Site Characterization Report will be prepared and submitted to the NYSDEC following completion of field activities and receipt of analytical results. The draft report will be prepared in accordance with the requirements of 6 NYCRR Part 375 Environmental Remediation Programs Section 1.6(a) (NYSDEC 2006) and DER-10 (NYSDEC 2010). It is currently anticipated the text of the draft report will contain a discussion of the site and project background, physical characteristics of the characterization area, field activities completed, methodologies used to complete the field activities, findings of the field activities, understanding of the extent of MGP-related impacts, if any, and appropriate recommendations for the site. The text of the draft report will be supported by boring logs, tables, and figures illustrating characterization findings, as appropriate.

5.2 Schedule

Anticipated time periods for performing the main work tasks are as follows:

- Prepare for fieldwork – 30 days
- Mobilize and perform fieldwork – 30 days
- Conduct laboratory analyses and reporting – 30 days
- Perform data validation and reduction – 30 days
- Prepare Site Characterization Report – 90 days

A detailed schedule will be provided to NYSDEC pending approval of the Work Plan and site access. Estimated durations provided above are contingent upon site access, weather-related considerations, permits, and changes in the scope of this Work Plan.

6. References

ARCADIS. 2010. Off-Site Characterization Work Plan, Hunts Point Former Manufactured Gas Plant. November.

ARCADIS. 2011. Dry Weather Discharge Evaluation Work Plan, Krasdale Foods Inc. Leasehold, Hunts Point Former Manufactured Gas Plant. January.

HDR/Lawler Matusky and Skelley Engineers, LLP. 2007. Hunts Point Food Distribution Center Redevelopment Plan, Site Investigative Report for Parcel F, Bronx, New York, Final.

HDR. 2009. Hunts Point Food Distribution Center Redevelopment Plan, Sections of the Redevelopment Plan for the Operable Unit 1 Portion of Parcel C, Bronx, New York, Final Revised.

HDR. 2010a. Draft Hunts Point Food Distribution Center, Preliminary Alternatives Analysis Report Parcel D, Bronx, New York, Final.

HDR. 2010b. Hunts Point Food Distribution Center, Preliminary Design Investigation Scope of Work, Parcel F, Bronx, New York, Final.

Hygienetics Environmental Services, Inc. (Hygienetics). 1997. Phase II Environmental Investigation Report of Hunts Point Produce Market Complex Parcel A, B, C, D and E, Bronx, New York.

Lawler Matusky and Skelley Engineers, LLP. 2001. Hunts Point Cooperative Market Redevelopment Plan, Response Plan for the Operating Unit Portion of Parcel C, Bronx, New York, Final Revised.

Lawler Matusky and Skelley Engineers, LLP. 2005. Hunts Point Cooperative Market Redevelopment Plan, Investigative Report for Parcel D, Bronx, New York.

New York State Department of Environmental Conservation. 2006. 6 New York Codes, Rules, and Regulations Part 375.

New York State Department of Environmental Conservation. 2010. DER-10 Technical Guidance for Site Investigation and Remediation.

Parsons. 2003. Hunts Point Off-Site Manufactured Gas Plant (VCA Index No. D2-003-02-08) History Report.

Tables

Table 1
Soil Boring Locations and Rationale

Site Characterization Work Plan - Krasdale Property
Consolidated Edison Company of New York, Inc.
Hunts Point Former Manufactured Gas Plant - Bronx, New York

Soil Boring Location ID	Coordinates[1]		Chemical Analyses[2]					Rationale
	Northing	Easting	TCL VOCs	TCL SVOCs	TAL Metals	Cyanide (total, amenable, free)	pH	
SB-01	666091.86	720484.51	X	X	X	X	X	Evaluate the presence, if any, of NAPL, purifier waste, or other MGP-related impacts along/near the boundary of Parcel D and the storm sewer pipe.
SB-02	666190.50	720519.69	X	X	X	X	X	
SB-03	666276.23	720563.96	X	X	X	X	X	
SB-04	666363.78	720601.69	X	X	X	X	X	
SB-05	666456.14	720641.49	X	X	X	X	X	
SB-06	666287.79	720537.21	X	X	X	X	X	
SB-07	666377.50	720575.84	X	X	X	X	X	
SB-08	666470.58	720613.97	X	X	X	X	X	
SB-09	665907.84	720381.88	X	X	X	X	X	Evaluate the presence, if any, of NAPL, purifier waste, or other MGP-related impacts along the boundary of Parcel D.
SB-10	666000.69	720424.22	X	X	X	X	X	
SB-11	665964.74	720271.88	X	X	X	X	X	Evaluate the presence, if any, of NAPL, purifier waste, or other MGP-related impacts in the northern parking area, to the south of the storm sewer pipe.
SB-12	666084.59	720322.76	X	X	X	X	X	
SB-13	666210.96	720372.02	X	X	X	X	X	
SB-14	666369.11	720439.15	X	X	X	X	X	
SB-15	666519.51	720507.37	X	X	X	X	X	Evaluate the presence, if any, of NAPL, purifier waste, or other MGP-related impacts along the waterfront.
SB-16	666029.96	720104.51	X	X	X	X	X	Evaluate the presence, if any, of NAPL, purifier waste, or other MGP-related impacts along the western boundary of the site.
SB-17	666105.45	719929.04	X	X	X	X	X	
SB-18	666194.93	719728.52	X	X	X	X	X	
SB-19	666261.57	719581.82	X	X	X	X	X	
SB-20	666515.75	720329.53	X	X	X	X	X	Evaluate the presence, if any, of NAPL, purifier waste, or other MGP-related impacts along the waterfront.
SB-21	666588.28	720180.76	X	X	X	X	X	
SB-22	666637.98	720052.74	X	X	X	X	X	
SB-23	666688.67	719916.02	X	X	X	X	X	
SB-24	666740.56	719793.12	X	X	X	X	X	

Table 1
Soil Boring Locations and Rationale

Site Characterization Work Plan - Krasdale Property
Consolidated Edison Company of New York, Inc.
Hunts Point Former Manufactured Gas Plant - Bronx, New York

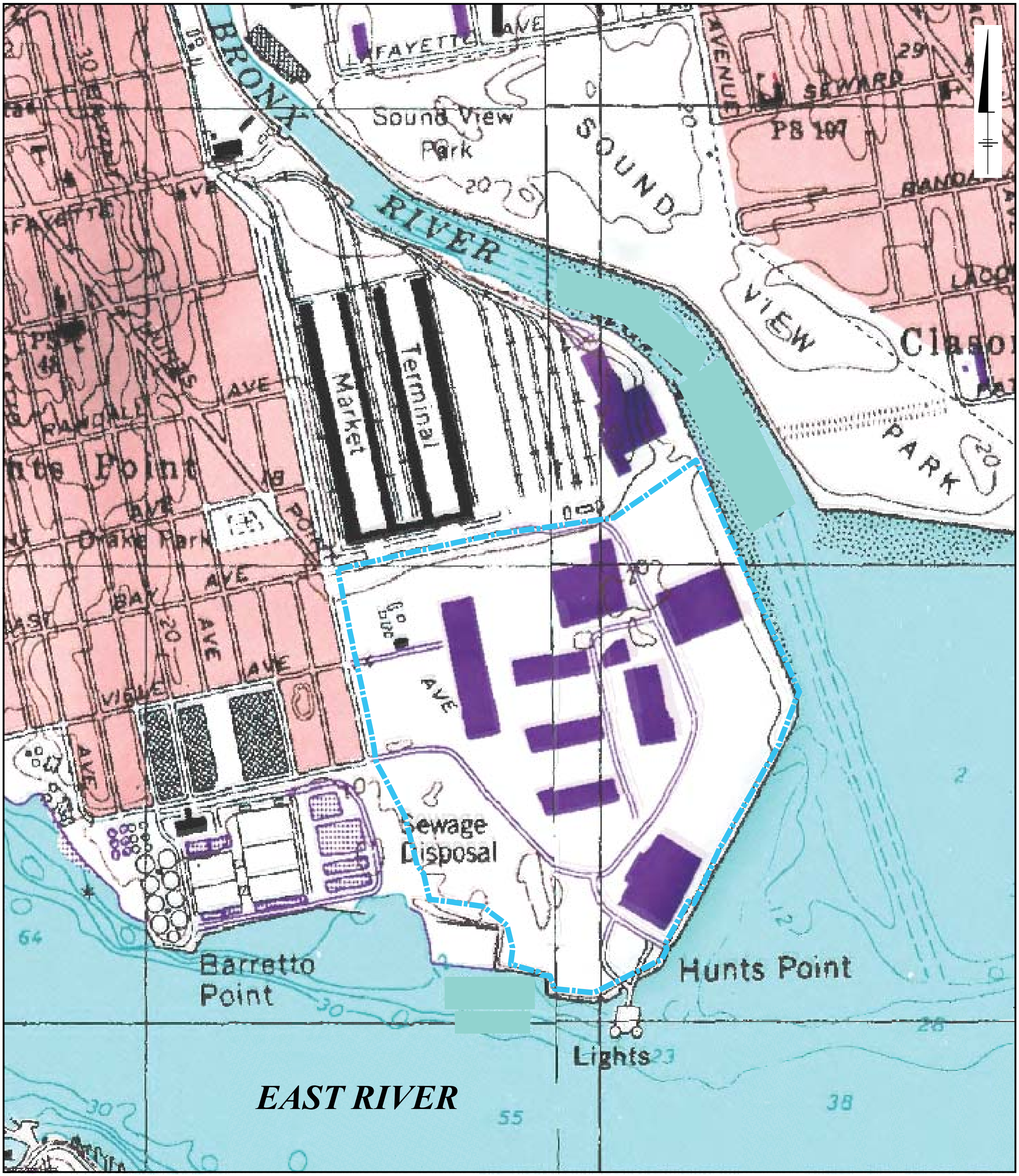
Soil Boring Location ID	Coordinates[1]		Chemical Analyses[2]					Rationale
	Northing	Easting	TCL VOCs	TCL SVOCs	TAL Metals	Cyanide (total, amenable, free)	pH	
SB-25	666340.7	719383.04	X	X	X	X	X	Evaluate the presence, if any, of NAPL, purifier waste, or other MGP-related impacts along the southern boundary of the site.
SB-26	666596.04	719498.71	X	X	X	X	X	
SB-27	666807.3	719591.29	X	X	X	X	X	
SB-28	666648.93	719363.83	X	X	X	X	X	
SB-29	666865.98	719453.05	X	X	X	X	X	

Notes:

1. Coordinates provided in New York State Plane coordinates (North American Datum of 1983).
2. Soil samples will be collected at up to two intervals in borings where NAPL, purifier waste, or MGP-related impacts are observed and at one interval in borings where no NAPL, purifier waste, or other MGP-related imapcts are observed consistent with procedures described in the Work Plan. Contingency borings, if any, will be sampled and analyzed consistent with this sampling and analysis scheme.
3. Select soil samples will also be analyzed for total petroleum hydrocarbons and inorganics (ammonia, nitrate, nitrite, sulfate, sufide, phosphate, chloride, fluoride, carbonate/bicarbonate).
4. Groundwater monitoring wells will be installed at select borings locations where evidence of NAPL, purifier waste, or MGP-related impacts are observed using the procedures described in the Work Plan. At a minimum, groundwater monitoring wells will be installed at three boring locations along the storm sewer pipe (upgradient, midpoint, and downgradient) and at five locations across the remainder of the site. Groundwater samples will be analyzed for the same parameters as soil samples, except for pH which will be collected in-situ with a water quality meter.
5. Borings will be completed to the confining layer or refusal, whichever is encountered first.

MGP = Manufactured gas plant
NAPL = Non-aqueous phase liquid
SVOCs = Semivolatile organic compounds
TAL = Target analyte list
TCL = Target compound list
TPH = Total Petroleum Hydrocarbons
VOCs = Volatile organic compounds

Figures



LEGEND:

▭ SITE BOUNDARY
(APPROXIMATE EXTENT OF FORMER MGP)

0 1,000 2,000 Feet

GRAPHIC SCALE

NOTE:

1. 1979 FLUSHING, N.Y. AND CENTRAL PARK, N.Y. - N.J. USGS QUADRANGLE.

CONSOLIDATED EDISON COMPANY OF NEW YORK, INC.
HUNTS POINT FORMER MANUFACTURED GAS PLANT

SITE INVESTIGATION WORK PLAN

SITE LOCATION MAP

ARCADIS

FIGURE
1

CITY: SYR DIV/GROUP: IM DB: J.RAPP LD: PIC: PM: TM: TR:
Con Ed (B0043026.0000.01000)
Q:\ConEd\HuntsPoint\SiteInvestigationWP\MXD\SiteLocationMap.mxd - 12/21/2010 @ 3:32:28 PM

0 300 600
Feet
GRAPHIC SCALE

NOTES:

1. IMAGERY OBTAINED FROM DIGITAL GLOBE, SEPTEMBER 19, 2009.
2. ALL LOCATIONS ARE APPROXIMATE.
3. PARCEL BOUNDARIES ADOPTED FROM CADD FILE PREPARED BY LAWLER, MATUSKY, AND SKELLY ENGINEERS, LLP.
4. SITE CHARACTERIZATION DETAILS FOR PARCEL D AND ADJACENT PERIMETER PARCEL ADOPTED FROM INVESTIGATIVE REPORT FOR PARCEL D, LAWLER, MATUSKY, AND SKELLY ENGINEERS, LLP, REVISED OCTOBER 2005.
5. SITE CHARACTERIZATION DETAILS FOR PARCEL F ADOPTED FROM SITE INVESTIGATIVE REPORT FOR PARCEL F, HDR/LMS, NOVEMBER 2007.
6. COAL TAR AND PURIFIER WASTE ON PERIMETER PARCEL EXCAVATED DURING THE CONSTRUCTION OF THE IROQUOIS PIPELINE.
7. STORM SEWER LOCATION ON KRASDALE PROPERTY WAS DIGITIZED FROM 2008 MERCATOR TOPOGRAPHIC AND UTILITY SURVEY. STORM SEWER COMPONENTS ASSOCIATED WITH OF-2 AND OF-3 ARE NOT SHOWN.

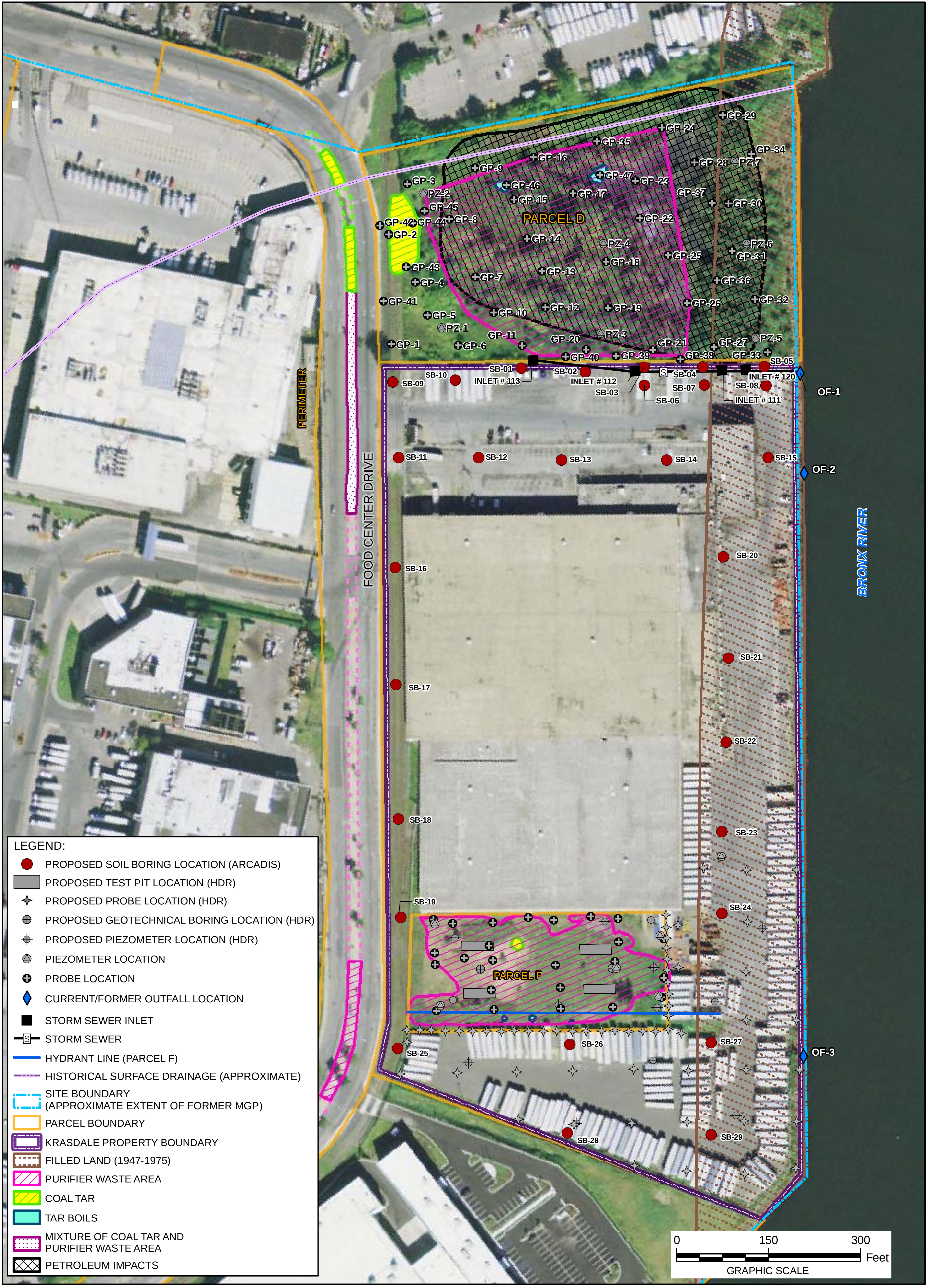
CONSOLIDATED EDISON COMPANY OF NEW YORK, INC.
HUNTS POINT FORMER MANUFACTURED GAS PLANT
SITE CHARACTERIZATION WORK PLAN - KRASDALE PROPERTY

SITE PLAN

ARCADIS

FIGURE
2

CITY:SYR DIV/GROUP: IM DB: J.RAPP LD: PIC: PM: TM: TR:
CON ED HUNTS POINT (43027.0.6000)
Q:\ConEd\HuntsPoint\SiteInvestigationWP\MXD\PropsedSampleLocations.mxd - 2/14/2011 @ 10:27:41 AM



LEGEND:

- ● PROPOSED SOIL BORING LOCATION (ARCADIS)
- ▭ PROPOSED TEST PIT LOCATION (HDR)
- ✧ PROPOSED PROBE LOCATION (HDR)
- ⊕ PROPOSED GEOTECHNICAL BORING LOCATION (HDR)
- ⊕ PROPOSED PIEZOMETER LOCATION (HDR)
- △ PIEZOMETER LOCATION
- ⊕ PROBE LOCATION
- ◆ CURRENT/FORMER OUTFALL LOCATION
- ■ STORM SEWER INLET
- S STORM SEWER
- HYDRANT LINE (PARCEL F)
- HISTORICAL SURFACE DRAINAGE (APPROXIMATE)
- SITE BOUNDARY (APPROXIMATE EXTENT OF FORMER MGP)
- PARCEL BOUNDARY
- KRASDALE PROPERTY BOUNDARY
- FILLED LAND (1947-1975)
- ▨ PURIFIER WASTE AREA
- ▨ COAL TAR
- TAR BOILS
- MIXTURE OF COAL TAR AND PURIFIER WASTE AREA
- ⊠ PETROLEUM IMPACTS

NOTES:

1. IMAGERY OBTAINED FROM DIGITAL GLOBE, SEPTEMBER 19, 2009.
2. ALL LOCATIONS ARE APPROXIMATE.
3. PARCEL BOUNDARIES ADOPTED FROM CADD FILE PREPARED BY LAWLER, MATUSKY, AND SKELLY ENGINEERS, LLP.
4. SITE CHARACTERIZATION DETAILS FOR PARCEL D AND ADJACENT PERIMETER PARCEL ADOPTED FROM INVESTIGATIVE REPORT FOR PARCEL D, LAWLER, MATUSKY, AND SKELLY ENGINEERS, LLP, REVISED OCTOBER 2005.
5. SITE CHARACTERIZATION DETAILS FOR PARCEL F ADOPTED FROM SITE INVESTIGATIVE REPORT FOR PARCEL F, HDR/LMS, NOVEMBER 2007 AND PRE-DESIGN INVESTIGATION SOW, HDR ,OCTOBER 2010.
6. COAL TAR AND PURIFIER WASTE ON PERIMETER PARCEL EXCAVATED DURING THE CONSTRUCTION OF THE IROQUOIS PIPELINE.
7. STORM SEWER LOCATION ON KRASDALE PROPERTY WAS DIGITIZED FROM 2008 MERCATOR TOPOGRAPHIC AND UTILITY SURVEY. STORM SEWER COMPONENTS ASSOCIATED WITH OF-2 AND OF-3 ARE NOT SHOWN.
8. DURING SUBSURFACE INVESTIGATION ACTIVITIES, GROUNDWATER SAMPLES WILL BE COLLECTED AT SOIL BORING LOCATIONS WHERE VISIBLE IMPACTS ARE OBSERVED. A MINIMUM OF EIGHT GROUNDWATER SAMPLES WILL BE COLLECTED.
9. WATER SAMPLES WILL BE COLLECTED FROM STORMWATER INLETS AND OUTFALL OF-1 IF DRY-WEATHER DISHARGE IS OBSERVED.
10. PROPOSED BORING LOCATIONS MAY BE ADJUSTED BASED ON INVESTIGATION LOCATIONS COMPLETED BY HDR.

CONSOLIDATED EDISON COMPANY OF NEW YORK, INC.
HUNTS POINT FORMER MANUFACTURED GAS PLANT

SITE CHARACTERIZATION WORK PLAN - KRASDALE PROPERTY

PROPOSED INVESTIGATION LOCATIONS

ARCADIS

FIGURE
3

Appendices

ARCADIS

Appendix A

Field Sampling Plan Addendum

ARCADIS
Infrastructure · Water · Environment · Buildings

Imagine the result

Water Sampling from Storm Sewer

Rev. #: 0

Rev Date: February 14, 2011

Approval Signatures

Prepared by: ______________________ Date: February 14, 2011

Reviewed by: Matt Biondolillo Date: February 14, 2011

(Technical Expert)

I. Scope and Application

This Standard Operating Procedure (SOP) sets forth the field procedures for collection of water samples under dry weather conditions from a storm sewer (i.e., catch basin and/or outfall).

II. Personnel Qualifications

ARCADIS field sampling personnel will have current health and safety training, including 40-hour Hazardous Waste Operations and Emergency Response training, site supervisor training, site-specific training, first aid, and cardiopulmonary resuscitation (CPR), as needed. In addition, ARCADIS field sampling personnel will be versed in the relevant SOPs and posses the required skills and experience necessary to successfully complete the desired fieldwork.

Personnel responsible for directing, supervising, or leading sample collection activities must have a minimum of 2 years of previous related experience. ARCADIS field sampling personnel must have a minimum of 6 months of related experience or an advanced degree in environmental sciences, engineering, hydrogeology, or geology.

III. Equipment List

The following materials will be available, as required, during sewer discharge sampling:

- Health and safety equipment (as required by the site Health and Safety Plan [HASP])
- Cleaning equipment
- Combination water quality meter
- Duct tape
- Field notebook
- 200-foot measuring tape
- Appropriate transport containers and packing, labeling, and shipping materials, including coolers with ice

- Appropriate water sampler (i.e., Wildco Kemmerer stainless steel bottle sampler [Kemmerer])

- Appropriate sample containers and forms

- Surveyor's rod

IV. Cautions

Sampling must be discontinued during heavy rain if there is a potential that rain water could affect samples.

Indelible ink pens must be used to complete sample labels.

Store and/or stage empty and full sample containers and coolers out of direct sunlight.

To mitigate potential cross-contamination, samples are to be collected in a pre-determined order from least impacted to impacted based on previous analytical data. If no analytical data are available, samples are to be collected in order of upgradient, then furthest downgradient to source area locations.

Samples containers should be packed on ice and stored in a cool, shaded place to maintain a sample temperature of approximately 4°Celsius. Ice must be double-bagged to prevent leakage. Sample containers should be stored inside sealable plastic bags to prevent cross contamination should a container break during transit. Packing tape with volatile adhesives should not be used to seal samples requiring volatile organic analysis to avoid potential contamination.

Be careful not to over-tighten lids with Teflon liners or septa (e.g., 40-milliliter [mL] vials). Overtightening can impair the integrity of the seal.

V. Health and Safety Considerations

All sampling will be performed consistent with the procedures outlined in the site HASP.

If lightning is present, discontinue sampling until at least 30 minutes after the last occurrence of lightning.

Use caution and appropriate cut-resistant gloves when tightening lids to 40-mL vials. These vials can break while tightening and can lacerate the hand. Amber vials (thinner glass) are more prone to breakage.

VI. Procedure

Water samples will be collected using a Kemmerer sampler or by discrete grab collection.

1. Identify sampling location(s) in field notebook along with other appropriate information.

2. Don and/or ensure proper use of health and safety equipment/precautions (as required by the HASP).

3. If non-dedicated sampling containers are used, clean the sampling equipment prior to initial use, between collection of each sample, and at the completion of sampling as follows: alconox rinse, water rinse, isopropanol rinse, and distilled water rinse.

4. Measure the total depth of the water present in the catch basin/sewer (if any) at each inlet or outfall by extending the surveyor's rod or weighted tape measure into the water until it reaches the bottom.

5. If no water is present in the catch basin/sewer, document time of day and location as dry in field notebook.

6. Attach laboratory-supplied container to the surveyor's rod at 0.5 times the total water depth and lower rod to the basin/sewer bottom, or lower the Kemmerer sampler, and release triggers.

7. Raise the surveyor's rod and sample container, or Kemmerer sampler, from the catch basin/sewer with minimal disturbance.

8. If using Kemmerer sampler, remove the covers from the appropriate laboratory-supplied containers and slightly tilt the mouth of the container below the sampling device.

9. Empty the sampler slowly, allowing the sample stream to flow gently down the side of the sample container (with minimal entry turbulence). If the sample was collected directly in the laboratory-supplied container, replace the cover.

10. Repeat Steps 6 through 9 for collection of an additional water sample (if required).

11. At the specified basins/outfalls, collect an additional aliquot of water for in-situ measurements of conductivity, temperature, oxidation reduction- potential, and

pH using the water quality meter. Record results on the appropriate form and/or field notebook.

12. Secure all sample jar caps tightly.

13. Label all sample containers.

14. Place filled sample containers on ice in a cooler.

15. Prepare one rinse-blank sample after sampling activities and sampling equipment cleaning by pouring distilled water through the cleaned Kemmerer sampler and filling the sample containers as described in Steps 8 and 9.

16. Collect field duplicate and matrix spike/matrix spike duplicate (MS/MSD) samples in accordance with the site Quality Assurance Project Plan (QAPP). Field duplicates and MS/MSD samples will be prepared by filling additional sets of sample containers with water collected at the same time and depth. One additional set of sample containers will be filled for field duplicates and two sets of containers will be filled for MS/MSD samples.

17. Follow procedures outlined for preservation of samples and chain-of-custody, handling, packing, and shipping procedures.

18. Record required information on the appropriate forms and/or field notebook.

VII. Waste Management

Materials (e.g., decontamination water) generated during sampling activities, including disposable equipment (PPE), will be placed in appropriate containers. Containerized waste will be disposed of by the client consistent with the procedures identified in the HASP, Work Plan, and/or Field Sampling Plan.

VIII. Data Recording and Management

Initial field logs and chain-of-custody records will be transmitted to the ARCADIS Project Manager or Task Manager at the end of each day unless otherwise directed by the Project Manager or Task Manager.

IX. Quality Assurance

Field-derived quality assurance samples will be collected as specified in the QAPP.

X. References

No references are required to accompany this SOP.

ARCADIS
Infrastructure, environment, buildings

Imagine the result

Investigation-Derived Waste Handling and Storage

Rev. #: 2

Rev Date: March 6, 2009

Approval Signatures

Prepared by: Andrew Kamik Date: 3/6/09

Reviewed by: Liz Marsh Date: 3/6/09
(Technical Expert)

I. Scope and Application

The objective of this Standard Operating Procedure (SOP) is to describe the procedures to manage investigation-derived wastes (IDW), both hazardous and non-hazardous, generated during site activities, which may include, but are not limited to - drilling, trenching/excavation, construction, demolition, monitoring well sampling, soil sampling, decontamination and remediation. Please note that this SOP is intended for materials that have been deemed a solid waste as defined by 40 CFR § 261.2 (which may includes liquids, solids, and sludges). In some cases, field determinations will be made based on field screening or previous data that materials are not considered a solid waste. IDW may include soil, groundwater, drilling fluids, decontamination liquids, personal protective equipment (PPE), sorbent materials, construction and demolition debris, and disposable sampling materials that may have come in contact with potentially impacted materials. IDW will be collected and staged at the point of generation. Quantities small enough to be containerized in 55-gallon drums will be taken to a designated temporary storage area (discussed in further detail under Drum Storage) onsite pending characterization and disposal. Waste materials will be analyzed for constituents of concern to evaluate proper disposal methods. PPE and disposable sampling equipment will be placed in DOT-approved drums prior to disposal and typically does not require laboratory analysis. This SOP describes the necessary equipment, field procedures, materials, regulatory references, and documentation procedures necessary for proper handling and storage of IDW up to the time it is properly disposed. The procedures for handling IDW are based on the United States Environmental Protection Agency's Guide to Management of Investigation Derived Wastes (USEPA, 1992). IDW is assumed to be contaminated with the site constituents of concern (COCs) until analytical evidence indicates otherwise. IDW will be managed to ensure the protection of human health and the environment and will comply with all applicable or relevant and appropriate requirements (ARAR). The following Laws and Regulations on Hazardous Waste Management are potential ARAR for this site.

State Laws and Regulations

- To Be Determined Based on Location of Site and Location of Treatment, Storage, and/or Disposal Facility (TSDF) to be utilized

Federal Laws and Regulations

- Resource Conservation and Recovery Act (RCRA) 42 USC § 6901-6987
- Comprehensive Environmental Response, Compensation and Liability Act (CERCLA) 42 USC § 9601-9675

- Superfund Amendments and Reauthorization Act (SARA)
- Department of Transportation (DOT) Hazardous Materials Transportation

Pending characterization, IDW will be stored appropriately within each area of contamination (AOC). Under RCRA, “storage” is defined as the holding of hazardous waste for a temporary period, at the end of which the hazardous waste is treated, disposed of, or stored elsewhere” (40 CFR § 260.10). The onsite waste staging area will be in a secure and controlled area. Waste characterization can either be based on generator knowledge, such as using materials safety data sheets (MSDS’), or can be based upon analytical results. The laboratory used for waste characterization analysis must have the appropriate state and federal certifications and be approved by ARCADIS and Client. IDW will be classified as RCRA hazardous or non-regulated under RCRA based on the waste characterization.

If IDW is characterized as RCRA hazardous waste, RCRA and DOT requirements must be followed for packaging, labeling, transporting, storing, and record keeping as described in 40 CFR § 262 and 49 CFR § 171-178. Wastes judged to potentially meet the criteria for hazardous wastes shall be stored in DOT approved packaging. Waste material classified as RCRA non-hazardous may be handled and disposed of as an industrial waste.

Liquid wastes judged to potentially meet the criteria for hazardous wastes shall be stored in DOT approved 55 gallon drums or other approved containers that are compatible with the type of material stored therein. Solid materials deemed to potentially meet hazardous criteria will be drummed where practicable. Large quantities of potentially hazardous solid materials must be containerized (such as in a roll-off box) for up to a maximum of 90 or 180 days as described in the Excavated Solids Section. Waste material classified as non-hazardous may be handled and disposed of as an industrial waste and is not subject to the 90-day or 180-day on-site storage limitation.

This is a standard (i.e., typically applicable) operating procedure which may be varied or changed as required, dependent upon site conditions, equipment limitations, or limitations imposed by the procedure. The ultimate procedure employed will be documented in the project work plans or reports. If changes to the sampling procedures are required due to unanticipated field conditions, the changes will be discussed with the Project Manager and Client as soon as practicable and documented in the report.

II. Personnel Qualifications

ARCADIS field sampling personnel will have current health and safety training including 40-hour HAZWOPER training, site supervisor training, site-specific training, first aid, and CPR, as needed. ARCADIS personnel may sign manifests on a case-to-case basis for clients, provided the appropriate agreement is in place between ARCADIS and the client documenting that ARCADIS is not the generator, but is acting as authorized representative for the generator. ARCADIS personnel who sign hazardous waste manifests will have the current DOT hazardous materials transportation training according to 49 CFR § 172.704. ARCADIS field personnel will also comply with client-specific training such as LPS. In addition, ARCADIS field sampling personnel will be versed in the relevant SOPs and posses the required skills and experience necessary to successfully complete the desired field work.

III. Equipment List

The following materials, as required, shall be available for IDW handling and storage:

Appropriate personal protective equipment as specified in the Site Health and Safety Plan

- 55-gallon steel drums, DOT 1A2 or equivalent
- ¾ -inch socket wrench
- Hammer
- Leather gloves
- Drum dolly
- Appropriate drum labels (outdoor waterproof self adhesive)
- Polyethylene storage tank
- Appropriate labeling, packing, chain-of-custody forms, and shipping materials as specified in the *Chain-of-Custody* SOP and *Field Sampling Handling, Packing, and Shipping* SOP.
- Indelible ink and/or permanent marking pens
- Plastic sheeting

- Appropriate sample containers, labels, and forms
- Stainless-steel bucket auger
- Stainless steel spatula or knife
- Stainless steel hand spade
- Stainless steel scoop
- Digital camera
- Field logbook.

IV. Cautions

- Filled drums can be very heavy, always use appropriate moving techniques and equipment.
- Similar media will be stored in the same drums to aid in sample analysis and disposal.
- Drum lids must be secured to prevent rainwater from entering the drums.
- Drums containing solid material may not contain any free liquids.
- Waste containers stored for extended periods of time may be subject to deterioration. Drum over packs may be used as secondary containment.
- All drums must be in good condition to prevent potential leakage and facilitate subsequent disposal. Inspect the drums for dents and rust, and verify the drum has a secure lid prior to use.

V. Health and Safety Considerations

- Appropriate personal protective equipment must be worn by all field personnel within the designated work area.
- Air monitoring may be required during certain field activities as required in the Site Health and Safety Plan.

- If excavating in potentially hazardous areas is possible, contingency plans should be developed to address the potential for encountering gross contamination or non-aqueous phase liquids.

- ARCADIS field personnel will be familiar and compliant with Client-specific health and safety requirements such as Chevron's hand safety policy including the prohibition of fixed and/or folding blade knives.

VI. Procedure

Waste storage and handling procedures to be used depend upon the type of generated waste. For this reason, IDW should be stored in a secure location onsite in separate 55-gallon storage drums, solids can be stockpiled onsite (if non-hazardous), and purge water may be stored in polyethylene tanks. Waste materials such as broken sample bottles or equipment containers and wrappings will be stored in 55-gallon drums unless they were not in contact with sample media.

Management of IDW

Minimization of IDW should be considered by the Project Manager during all phases of the project. Site managers may want to consider techniques such as replacing solvent-based cleaners with aqueous-based cleaners for decontamination of equipment, reuse of equipment (where it can be decontaminated), limitation of traffic between exclusion and support zones, and drilling methods and sampling techniques that generate little waste. Alternative drilling and subsurface sampling methods may include the use of small diameter boreholes, as well as borehole testing methods such as a core penetrometer or direct push technique instead of coring (EPA, 1993).

Drum Storage

Drums containing hazardous waste shall be stored in accordance with the requirements of 40 CFR 265 Subpart I (for containers) and 265 Subpart DD (for containment buildings). All 55-gallon drums will be stored at a secure, centralized on-site location that is readily accessible for vehicular pick-up. Drums confirmed as, or believed to contain hazardous waste will be stored over an impervious surface provided with secondary containment. The storage location will, for drums containing liquid, have a containment system that can contain at least the larger of 10% of the aggregate volume of staged materials or 100% of the volume of the largest container. Drums will be closed during storage and be in good condition in accordance with the Guide to Management of Investigation-Derived Wastes (USEPA, 1992).

Hazardous Waste Determination

Waste material must be characterized to determine if it meets any of the federal definitions of hazardous waste as required by 40 CFR § 262.11. If the waste does not meet any of the federal definitions, it must then be established if any state-specific hazardous waste criteria exist/apply.

Generator Status

Once hazardous waste determination has been made, the generator status will be determined. Large quantity generators (LQG) are generators who generate more than 1,000 kilograms of hazardous waste in a calendar month. Small quantity generators (SQG) of hazardous waste are generators who generate greater than 100 kilograms but less than 1,000 kilograms of hazardous waste in a calendar month. Conditionally exempt small quantity generators (CESQG) are generators who generate less than 100 kilograms of hazardous waste per month. Please note that a generator status may change from month to month and that a notice of this change is usually required by the generator's state agency.

Accumulation Time for Hazardous Waste

A LQG may accumulate hazardous waste on site for 90 days or less without a permit and without having interim status provided that such accumulation is in compliance with specifications in 40 CFR § 262.34. A SQG may accumulate hazardous waste on site for 180 days or less without a permit or without having interim status subject to the requirements of 40 CFR § 262.34(d). CESQG requirements are found in 40 CFR § 261.5. **NOTE**: The CESQG and SQG provisions of 40 CFR § 261.5, 262.20(e), 262.42(b) and 262.44 may not be recognized by some states (e.g. Rhode Island). **State-specific regulations must be reviewed and understood prior to the generation of hazardous waste.**

Satellite Accumulation of Hazardous Waste

Satellite accumulation (SAA) shall mean the accumulation of as much as fifty-five (55) gallons of hazardous waste, or the accumulation of as much as one quart of acutely hazardous waste, in containers at or near any point of generation where the waste initially accumulates, which is under the control of the operator of the process generating the waste, without a permit or interim status and without complying with the requirements of 40 CFR § 262.34(a) and without any storage time limit, provided that the generator complies with 40 CFR § 262.34(c)(1)(i).

Once more than 55 gallons of hazardous waste accumulates in SAA, the generator has three days to move this waste into storage.

Storage recommendations for hazardous waste include:

- Ignitable Hazardous wastes must be >50 feet from the property line per 40 CFR § 265.176 (LQG generators only).
- Hazardous waste must be stored on a concrete slab (asphalt is acceptable if there are no free liquids in the waste) per 40 CFR § 265.176.
- Drainage must be directed away from the accumulation area.
- Area must be properly vented.
- Area must be secure.

Drum/Container Labeling

Drums will be labeled on both the side and lid of the drum using a permanent marking pen. Old drum labels must be removed to the extent possible, descriptions crossed out should any information remain, and new labels affixed on top of the old labels. Other containers used to store various types of waste (polyethylene tanks, roll-off boxes, end-dump trailers, etc.) will be labeled with an appropriate "Waste Container" or “Testing in Progress” label pending characterization. Drums and containers will be labeled as follows:

- Appropriate waste characterization label (Testing In Progress, Hazardous, or Non-Hazardous)
- Waste generator's name (e.g., client name)
- Project name
- Name and telephone number of ARCADIS project manager
- Composition of contents (e.g., used oil, acetone 40%, toluene 60%)
- Media (e.g., solid, liquid)
- Accumulation start date

- Drum number of total drums as reconciled with the Drum Inventory maintained in the field log book.

IDW containers will remain closed except when adding or removing waste. Immediately upon beginning to place waste into the drum/container, a “Waste Container” or “Testing in Progress” label will be filled out to include the information specified above, and affixed to the container. Once the contents of the container are identified as either non-hazardous or hazardous, the following additional labels will be applied. Containers with waste determined to be non-hazardous will be labeled with a green and white "Non-Hazardous Waste" label over the "Waste Container" label. Containers with waste determined to be hazardous will be stored in an onsite storage area and will be labeled with the "Hazardous Waste" label and affixed over the "Waste Container" label. The ACCUMULATION DATE for the hazardous waste is the date the waste is first placed in the container and is the same date as the date on the "Waste Container" label. DOT hazardous class labels must be applied to all hazardous waste containers for shipment offsite to an approved disposal or recycling facility. In addition a DOT proper shipping name shall be included on the hazardous waste label. The transporter should be equipped with the appropriate DOT placards. However, placarding or offering placards to the initial transporter is the responsibility of the generator per 40 CFR § 262.33.

Inspections and Documentation

All IDW will be documented as generated on a Drum Inventory Log maintained in the field log book. The Drum Inventory will record the generation date, type, quantity, matrix and origin (e.g. Boring-1, Test Pit 3, etc) of materials in every drum, as well as a unique identification number for each drum. The drum inventory will be used during drum pickup to assist with labeling of drums. The drum storage area and any other areas of temporarily staged waste, such as soil/debris piles, will be inspected weekly. The weekly inspections will be recorded in the field notebook or on a Weekly Inspection Log. Digital photographs will be taken upon the initial generation and drumming/staging of waste, and final labeling after characterization to document compliance with labeling and storage protocols, and condition of the container. Evidence of damage, tampering or other discrepancy should be documented photographically.

Emergency Response and Notifications

Specific procedures for responding to site emergencies will be detailed in the HASP. If the generator is designated as a LQG, a Contingency Plan will need to be prepared to include emergency response and notification procedures per 40 CFR § 265 Subpart D. In the event of a fire, explosion, or other release which could threaten human health outside of the site or when Client or ARCADIS has knowledge of a spill that has reached surface water, Client or ARCADIS must immediately notify the National Response Center (800-424-8802) in accordance with 40 CFR § 262.34. Other notifications to state agencies may also be necessary.

Drilling Soil Cuttings and Muds

Soil cuttings are solid to semi-solid soils generated during trenching activities, subsurface soil sampling, or installation of monitoring wells. Depending on the drilling method, drilling fluids known as "muds" may be used to remove soil cuttings. Drilling fluids flushed from the borehole must be directed into a settling section of a mud pit. This allows reuse of the decanted fluids after removal of the settled sediments. Soil cuttings will be labeled and stored in 55-gallon drums with bolt-sealed lids.

Excavated Solids

Excavated solids may include, but are not limited to soil, fill and construction and demolition debris. Excavated solids may be temporarily stockpiled onsite as long as the material is a RCRA non-hazardous waste and the solids will be treated onsite pursuant to a certified, authorized, or permitted treatment method, or properly disposed off-site. Stockpiled materials characterized as hazardous must be immediately containerized and removed from the site within 90 days of generation (except for soils using satellite accumulation). Excavated solids should be stockpiled and maintained in a secure area onsite. At a minimum, the floor of the stockpile area will be covered with a 20-mil high density polyethylene liner that is supported by a foundation or at least a 60-mil high density polyethylene liner that is not supported by a foundation. The excavated material will not contain free liquids. The owner/operator will provide controls for windblown dispersion, run-on control, and precipitation runoff. The run-on control system will prevent flow onto the active portion of the pile during peak discharge from at least a 25-year storm and the run-off management system will collect and control at least the water volume resulting from a 24-hour, 25-year storm (EPA, 1992). Additionally, the stockpile area will be inspected on a weekly basis and after storm events. Individual states may require that the stockpile be inspected/certified by a licensed professional engineer. Stockpiled material will be covered with a 6-mil polyvinyl chloride (PVC) liner. The stockpile cover will be secured in place with appropriate material (concrete blocks, weights, etc.) to prevent the movement of the cover. Excavated solids may also be placed in roll off containers and covered with a 6-mil PVC liner pending results for waste characterization.

Decontamination Solutions

Decontamination solutions are generated during the decontamination of personal protective equipment and sampling equipment. Decontamination solutions may range from detergents, organic solvents and acids used to decontaminate small field sampling equipment to steam cleaning rinsate used to wash heavy field equipment. These solutions are to be labeled and stored in 55-gallon drums with bolt-sealed lids.

Disposable Equipment

Disposable equipment includes personal protective equipment (tyvek coveralls, gloves, booties and APR cartridges) and disposable sampling equipment such as trowels or disposable bailers. If the media sampled exhibits hazardous characteristics per results of waste characterization sampling, disposable equipment will also be disposed of as a hazardous waste. These materials will be stored onsite in labeled 55-gallon drums pending analytical results for waste characterization.

Purge Water

Purge water includes groundwater generated during well development, groundwater sampling, or aquifer testing. The volume of groundwater generated will dictate the appropriate storage procedure. Monitoring well development and groundwater sampling may generate three well volumes of groundwater or more. This volume will be stored in labeled 55-gallon drums. Aquifer tests may generate significantly greater volumes of groundwater depending on the well yield and the duration of the test. Therefore, large-volume portable polyethylene tanks will be considered for temporary storage pending groundwater-waste characterization.

Purged Water Storage Tank Decontamination and Removal

The following procedures will be used for inspection, cleaning, and offsite removal of storage tanks used for temporary storage of purge water. These procedures are intended to be used for rented portable tanks such as Baker Tanks or Rain for Rent containers. Storage tanks will be made of inert polyethylene materials.

The major steps for preparing a rented tank for return to a vendor include characterizing the purge water, disposing of the purge water, decontaminating the tank, final tank inspection, and mobilization. Decontamination and inspection procedures are describe in further detail below.

- Tank Cleaning: Most vendors require that tanks be free of any sediment and water before returning, a professional cleaning service may be required. Each specific vendor should be consulted concerning specific requirements for returning tanks.

- Tank Inspection: After emptying the tank, purged water storage tanks should be inspected for debris, chemical staining, and physical damage. The vendors require that tanks be returned in the original condition (i.e., free of sediment, staining and no physical damage).

VII. Waste Characterization Sampling and Shipping

Soil/Solids Characterization

Waste characterization will be conducted in accordance with waste hauler, waste handling facility, and state/federal requirements. In general, RCRA hazardous wastes are those solid wastes determined by a Toxicity Characteristic Leaching Procedure (TCLP) test or to contain levels of certain toxic metals, pesticides, or other organic chemicals above specific federally regulated thresholds. If the one or more of 40 toxic compounds listed in Table I of 40 CFR § 261.24 are detected in the sample at levels above the maximum unregulated concentrations, the waste must be characterized as a toxic hazardous waste. Wastes can also be considered “listed” hazardous waste depending on site-specific processes.

Composite soil samples will be collected at a frequency of one sample per 10 cubic yard basis for stockpiled soil or one per 55-gallon drum for containerized. A four point composite sample will be collected per 10 cubic yards of stockpiled material and for each drum. Sample and composite frequencies may be adjusted in accordance with the waste handling facility’s requirements. Waste characterization samples may be analyzed for the TCLP volatile organic compounds (VOCs), TCLP semi-volatile organic compounds (SVOCs), TCLP RCRA metals, and polychlorinated biphenyls, as well as corrosivity (pH), reactivity and flammability (flashpoint). Additional samples may be collected and analyzed by the laboratory on a contingency basis.

Wastewater Characterization

Waste characterization will be conducted in accordance with the requirements of the waste hauler, waste handling facility, and state/federal governments. In general, purge water should be analyzed by methods appropriate for the known contaminants, if any, that have been historically detected in the monitoring wells. Samples will be collected and analyzed in accordance with the requirements of the waste disposal facility.

Wastewater characterization samples may be analyzed for TCLP volatile organic compounds (VOCs), TCLP semi-volatile organic compounds (SVOCs), TCLP RCRA metals, and polychlorinated biphenyls, as well as corrosivity (pH), reactivity and flammability (flashpoint). Additional samples may be collected and analyzed by the laboratory on a contingency basis.

Sample Handling and Shipping

All samples will be appropriately labeled, packed, and shipped, and the chain-of-custody will be filled out in accordance with the Chain-of-Custody SOP and Field Sampling Handling, Packing, and Shipping SOP and Hazardous Materials Packaging and Shipping SOP.

It should be noted that additional training is required for packaging and shipping of hazardous and/or dangerous materials. Please reference the following ARCADIS intranet team page for more information: http://team/sites/hazmat/default.aspx.

Preparing Waste Shipment Documentation (Hazardous and Non-Hazardous)

Waste profiles will be prepared by the ARCADIS PM and forwarded, along with laboratory analytical data to the Client PM for approval/signature. The Client PM will then return the profile to ARCADIS who will then forward to the waste removal contractor for preparation of a manifest. The manifest will be reviewed by ARCADIS prior to forwarding to the Client PM for approval. Upon approval of the manifest, the Client PM will return the original signed manifest directly to the waste contractor or to the ARCADIS PM for forwarding to the waste contractor.

Final drum labeling and pickup will be supervised by an ARCADIS representative who is experienced with waste labeling procedures. The ARCADIS representative will have a copy of the drum inventory maintained in the field book and will reconcile the drum inventory with the profile numbers on the labels and on the manifest. Different profile numbers will be generated for different matrices or materials in the drums. For example, the profile number for drill cuttings will be different than the profile number for purge water. **When there are multiple profiles it is critical that the proper label, with the profile number appropriate to a specific material be affixed to the proper drums.** A copy of the ARCADIS drum inventory will be provided to the waste transporter during drum pickup and to the facility receiving the waste.

VIII. Data Recording and Management

Waste characterization sample handling, packing, and shipping procedures will be documented in accordance with the *Quality Assurance Project Plan*, if one exists. Copies of the chains-of-custody forms will be maintained in the project file.

Following waste characterization, IDW containers will be re-labeled with the appropriate waste hazardous or non-hazardous waste labels and the client will initiate disposal at the appropriate waste disposal facility.

IX. Quality Assurance

The chain-of-custody and sample labels for waste characterization samples will be filled out in accordance with the *Quality Assurance Project Plan*.

X. References

United States Environmental Protection Agency (USEPA). 1992. Guide to Management of Investigation-Derived Wastes. Office of Remedial and Emergency Response. Hazardous Site Control Division. January 1992.

USEPA. 1991. *Guide to Discharging CERCLA Aqueous Wastes to Publicly Owned Treatment Works (POTWs)*. Office of Remedial and Emergency Response. Hazardous Site Control Division 0S-220W. March 1991.

Appendix B

Quality Assurance Project Plan
Addendum

Table 1
Sample Quantities and Quality Control Frequencies

Quality Assurance Project Plan
Consolidated Edison Company of New York, Inc.
Hunts Point Former Manufactured Gas Plant - Bronx, New York

Parameter	Estimated Number of Samples	Field QC Analyses						Laboratory QC Sample				Total
		Trip Blank		Rinse Blank		Field Duplicate		Matrix Spike		Matrix Spike Duplicate		
		Freq.	No.	Freq.	No.	Freq.	No.	Freq.	No.	Freq.	No.	
Soil												
TCL VOCs (SW-846 8260)	51	1/cooler	1	1/20	2	1/20	2	1/20	2	1/20	2	60
TCL SVOCs (SW-846 8270)	51	NA	--	1/20	2	1/20	2	1/20	2	1/20	2	59
TAL Metals (SW-846/6010/7470/7471)	51	NA	--	1/20	2	1/20	2	1/20	2	1/20	2	59
Cyanide (total, amenable, free) (SW-846 9010/9012B/9016)	51	NA	--	1/20	2	1/20	2	1/20	2	1/20	2	59
TPH (SW-846 8015B)	8	NA	--	1/20	2	1/20	2	1/20	2	1/20	2	16
pH (SW-846 9040B)	29	NA	--	NA	--	NA	--	NA	--	NA	--	29
Other Inorganics [5] (E350.1, 9056, SM4500S2-E, SM4500P-E, SM-2320B)	8	NA	--	1/20	2	1/20	2	1/20	2	1/20	2	16
Forensic PAHs (modified 8270)	4	NA	--	1/20	1	1/20	1	1/20	1	1/20*	1	8
Forensic TPH (modified 8015B)	4	NA	--	1/20	1	1/20	1	1/20	1	1/20	1	8
Water												
TCL VOCs (SW-846 8260)	12	1/cooler	1	1/20	1	1/20	1	1/20	1	1/20	1	17
TCL SVOCs (SW-846 8270)	12	NA	--	1/20	1	1/20	1	1/20	1	1/20	1	16
TAL Metals (SW-846/6010/7470/7471)	12	NA	--	1/20	1	1/20	1	1/20	1	1/20	1	16
Cyanide (total, amenable, free) (SW-846 9010/SM4500CN-G/9016)	12	NA	--	1/20	1	1/20	1	1/20	1	1/20	1	16
TPH (SW-846 8015B)	8	NA	--	1/20	1	1/20	1	1/20	1	1/20	1	12
Other Inorganics [5] (E350.1, E300, SM4500S2-E, SM4500P-E, SM-2320B)	8	NA	--	1/20	1	1/20	1	1/20	1	1/20*	1	12
Sediment												
TCL VOCs (SW 846 8260)	66	1/cooler	3	1/20	4	1/20	4	1/20	4	1/20	4	85
TCL SVOCs (SW-846 8270)	66	NA	--	1/20	4	1/20	4	1/20	4	1/20	4	82
TAL Metals (SW-846/6010/7470/7471)	66	NA	--	1/20	4	1/20	4	1/20	4	1/20	4	82
Cyanide (total, amenable, free) (SW-846 9010/9012B/9016)	66	NA	--	1/20	4	1/20	4	1/20	4	1/20	4	82
TOC (SW-846 9060)	66	NA	--	NA	--	NA	--	NA	--	NA	--	66
Forensic TPH (modified 8015B)	13	NA	--	1/20	1	1/20	1	1/20	1	1/20	1	17
Forensic PAHs (modified 8270)	13	NA	--	1/20	1	1/20	1	1/20	1	1/20	1	17

Notes:

1. Sample counts are an approximation; the final number of samples will be determined in the field pursuant to discussion and agreement with Con Edison and NYSDEC.
2. Rinse blanks are not required with dedicated equipment.
3. 1/20 - one QC sample collected per every 20 environmental samples.
4. 1/cooler - one trip blank per cooler containing TCL VOC groundwater samples.
5. Other Inorganics include: ammonia, nitrite, nitrate, sulfate, sulfide, phosphate, chloride, fluoride, and carbonate/bicarbonate.

* MS/MSD not required for carbonate/bicarbonate.

Freq - Frequency
NA - Not applicable
No. - Number
QC - Quality control
SVOCs - Semivolatile organic compounds
TAL - Target analyte list
TCL - Target compound list
TCLP - Toxicity characteristic leaching procedure
VOCs - Volatile organic compounds

Table 2
Sample Containers, Preservation Methods, and Holding Times

Quality Assurance Project Plan
Consolidated Edison Company of New York, Inc.
Hunts Point Former Manufactured Gas Plant - Bronx, New York

Parameter	Method[1]	Bottle Type[2]	Preservation	Holding Time[3]
Soil/Sediment				
TCL VOCs	8260	1-4 oz wide mouth glass jar with Teflon®-lined lid	Cool to 4°C/minimize head space	10 days to analysis
TCL SVOCs	8270	3-8 oz wide mouth glass jar with Teflon®-lined lid	Cool to 4°C	10 days to extraction; 40 days to analysis
TAL Metals (except mercury)	6010			180 days to analysis
Mercury	7470/7471			26 days to analysis
Cyanide (total, amenable, free)	9010/9012B/901			12 days to analysis
TPH	8015B			10 days to extraction; 40 days to analysis
pH	9040B			As soon as possible
Ammonia	E350.1			26 days to analysis
Sulfide	4500S2-E			5 days from preparation to analysis
Phosphate	4500P-E			26 days to analysis
Carbonate/Bicarbonate	2320B			12 days from preparation to analysis
Nitrite/Nitrate	9056			24 hrs from preparation to analysis
Sulfate, Chloride, Fluoride	9056			26 days to analysis
Forensic PAHs	modified 8270	1-8 oz wide mouth glass jar with Teflon®-lined lid	Cool to -10°C and store in the dark	1year to extraction or analysis
Forensic TPH	modified 8015B			
Water				
TCL VOCs	8260	2-40ml glass vials with Teflon®-lined lid	HCl to pH<2, Cool to 4°C	10 days to analysis
TCL SVOCs	8270	2-1 liter amber glass bottles with Teflon®-lined lid	Cool to 4°C	5 days to extraction; 40 days to analysis
TAL Metals (except mercury)	6010	1-500 mL plastic bottle with Teflon®-lined lid	HNO_3 to pH<2; Cool to 4°C	180 days to analysis
Mercury	7470/7471			26 days to analysis
Cyanide (total, amenable, free)	9010/4500CN-G/9016	2-500 mL plastic bottles with Teflon®-lined lid	NaOH to pH>12, Cool to 4ºC	12 days to analysis
TPH	8015B	2-1 liter amber glass bottle with Teflon®-lined lid	HCl to pH<2, Cool to 4°C	5 days to extraction; 40 days to analysis
Ammonia/Phosphate	E350.1/4500P-E	2-500 mL plastic bottle with Teflon®-lined lid	H_2SO_4 to pH<2, Cool to 4ºC	26 days to analysis
Sulfide	4500S2-E	1-500 mL plastic bottle with Teflon®-lined lid	NaOH and ZnAc to pH>12, Cool to 4°C	5 days to analysis
Carbonate/Bicarbonate	2320B	3-500 mL plastic bottles with Teflon®-lined lid	Cool to 4°C	12 days to analysis
Nitrite/Nitrate	E300			24 hrs from preparation to analysis
Sulfate, Chloride, Fluoride	E300			26 days to analysis

Notes:
1. USEPA. Office of Solid Waste and Emergency Response. Test Methods for Evaluating Solid Waste SW-846 3rd ed. Washington, D.C. 1996.
2. Bottle type may vary depending on the selected analytical laboratory.
3. All holding times are measured from date of laboratory verified time of sample receipt.

°C - degrees Celsius
H_2SO_4 - sulfuric acid
HCl - hydrochloric acid
HNO_3 - nitric acid
mL - milliliter
NaOH - sodium hydroxide
oz - ounce
PAH - polycyclic aromatic hydrocarbon

SVOCs - Semivolatile organic compounds
TAL - Target analyte list
TCL - Target compound list
TPH - Total petroleum hydrocarbons
VOCs - Volatile organic compounds

Table 3
Analytical Quality Control Limits[1]

Quality Assurance Project Plan
Consolidated Edison Company of New York, Inc.
Hunts Point Former Manufactured Gas Plant - Bronx, New York

	Accuracy - % Recovery			**Precision - RPD**		
Parameter	**Surrogate**	**MS/MSD**	**LCS**	**MS/MSD**	**Lab Duplicate**	**Field Duplicate**
Soil/Sediment						
TCL VOCs	34-132	60-140	10-150	25	--	100
TCL SVOCs	10-120	20-140	10-120	40	--	100
TAL Metals	--	75-125	--	--	20	100
Cyanide (total and amenable)	--	--	38-161	--	20	--
Cyanide (free)	--	75-125	30.1-169.9	20	20	--
TPH	50-130	50-150	50-130	30	30	100
pH	--	--	--	--	20	100
Other Inorganics [2]	--	75-125*	Based on Vendors Limits	20*	20	100
Forensic PAHs	50-130	50-150	50-130	30	30	100
Forensic TPH	50-130	50-150	50-130	30	30	100
Water						
TCL VOCs	50-142	60-145	12-150	20		50
TCL SVOCs	20-130	20-130	13-150	40	--	50
TAL Metals	--	75-125	--	--	20	50
Cyanide (total and amenable)	--	75-125	85-115	20	20	50
Cyanide (free)	--	75-125	85-115	20	20	--
TPH	50-130	50-150	50-130	30	30	50
Other Inorganics [2]	--	75-125*	85-115	20*	20	50

Notes:

1. The listed QC limits are based on SW-846 guidance and are advisory. The actual limits are determined based on laboratory performance.
2. Other Inorganics include: ammonia, nitrite, nitrate, sulfate, sulfide, phosphate, chloride, fluoride, and carbonate/bicarbonate.

* No MS/MSD for carbonate/bicarbonate.

LCS - Laboratory control sample
MS/MSD - Matrix spike/matrix spike duplicate
PAHs - Polycyclic aromatic hydrocarbons
RPD - Relative percent difference
SVOCs - Semivolatile organic compounds
TAL - Target analyte list
TCL - Target compound list
TPH - Total petroleum hydrocarbons
VOCs - Volatile organic compounds

Table 4
Parameters, Methods, and Target Reporting Limits

Quality Assurance Project Plan
Consolidated Edison Company of New York, Inc.
Hunts Point Former Manufactured Gas Plant - Bronx, New York

	Water (µg/L)[1]			Soil/(mg/kg)[2]		
Analyte	**NYS GW GV**	**MDL**	**RL**	**State of New York Part 375[4]**	**MDL**	**RL[3]**
TCL VOCs (8260)						
1,1,1-Trichloroethane	5	0.00069	0.005	0.68	0.00053	0.005
1,1,2,2-Tetrechloroethane	5	0.00081	0.005	--	0.00052	0.005
1,1,2-Trichloroethane	1	0.00065	0.005	--	0.00037	0.005
1,1-Dichloroethane	5	0.00103	0.005	0.27	0.0003	0.005
1,1-Dichloroethene	5	0.00083	0.005	0.33	0.00058	0.005
1,2-Dichloroethane	0.6	0.00072	0.005	0.02	0.00058	0.005
1,2-Dichloropropane	1	0.00071	0.005	--	0.00067	0.005
2-Butanone	50	--	0.01	--	0.00159	0.01
2-Hexanone	50	0.00109	0.01	--	0.0012	0.01
4-Methyl-2-pentanone	--	--	0.01	--	0.00055	0.005
Acetone	50	0.00103	0.01	0.05	0.00224	0.02
Benzene	1	0.00074	0.005	0.06	0.00057	0.005
Bromodichloromethane	50	0.00048	0.005	--	0.0003	0.005
Bromoform	50	0.00046	0.005	--	0.00061	0.005
Bromomethane	5	0.00212	0.005	--	0.00208	0.005
Carbon Disulfide	60	0.0009	0.005	--	0.00041	0.005
Carbon Tetrachloride	5	0.00107	0.005	0.76	0.00095	0.005
Chlorobenzene	5	0.00072	0.005	1.1	0.00059	0.005
Chloroethane	5	0.00106	0.005	--	0.00098	0.005
Chloroform	7	0.00067	0.005	0.37	0.00034	0.005
Chloromethane	5	0.00109	0.005	--	0.00078	0.005
cis-1,2-Dichloroethene	5	*	8	0.25	0.00037	0.005
cis-1,3-Dichloropropene	0.4	0.00028	0.005	--	0.00056	0.005
Dibromochloromethane	50	0.00055	0.005	--	0.00035	0.005
Ethylbenzene	5	0.00087	0.005	1.00	0.0007	0.005
Methylene Chloride	5	0.00078	0.005	0.05	0.00109	0.02
Styrene	5	0.00064	0.005	--	0.00015	0.005
Tetrachloroethene	5	0.00081	0.005	1.3	0.00081	0.005
Toluene	5	0.00072	0.005	0.70	0.000074	0.005

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Consolidated Edison Company of New York, Inc.
Hunts Point Former Manufactured Gas Plant - Bronx, New York

Analyte	Water (µg/L)[1]			Soil/(mg/kg)[2]		
	NYS GW GV	MDL	RL	State of New York Part 375[4]	MDL	RL[3]
TCL VOCs (8260) con't						
trans-1,2-Dichloroethene	5	*	*	0.19	0.00039	0.005
trans-1,3-Dichloropropene	0.4	0.00057	0.005	--	0.00027	0.005
Trichloroethene	5	0.00062	0.005	0.47	0.00081	0.005
Vinyl Chloride	2	0.00099	0.005	0.02	0.00023	0.005
Xylenes (total)	5	0.00227	0.005	0.26	0.000486	0.005
TCL SVOCs (8270)						
1,2,4-Trichlorobenzene	5	0.00036	0.004	--	0.0177	0.27
1,2-Dichlorobenzene	3	0.00031	0.004	1.1	0.016	0.27
1,3-Dichlorobenzene	3	0.00025	0.004	2.4	0.0135	0.27
1,4-Dichlorobenzene	3	0.00031	0.004	1.8	0.016	0.27
2,2'-oxybis (1-chloropropane)	5	0.00025	0.004	--	0.014	0.27
2,4,5-Trichlorophenol	--	0.00028	0.01	--	0.0136	1.7
2,4,6-Trichlorophenol	0	0.00037	0.01	--	0.0074	0.27
2,4-Dichlorophenol	5	0.00033	0.004	--	0.0144	0.27
2,4-Dimethylphenol	50	0.00033	0.004	--	0.0131	0.27
2,4-Dinitrophenol	10	0.00043	0.025	--	0.081	1.7
2,4-Dinitrotoluene	5	0.0004	0.004	--	0.116	1.7
2,6-dinitrotoluene	5	0.00026	0.004	--	0.0079	0.27
2-Chloronaphthalene	10	0.00039	0.004	--	0.0115	0.27
2-Chlorophenol	--	0.00023	0.004	--	0.0157	0.27
2-Methylnaphthalene	--	0.00027	0.004	--	0.0077	0.27
2-Methylphenol	--	0.00024	0.004	--	0.0162	0.27
2-Nitroaniline	5	0.00034	0.004	--	0.0164	1.7
2-Nitrophenol	0	0.00027	0.004	--	0.017	0.27
3,3'-Dichlorobenzidine	5	0.00036	0.004	--	0.0555	0.67
3-Nitroanaline	5	0.00023	0.004	--	0.0086	1.7
4,6-Dinitro-2-methylphenol	--	0.00186	0.025	--	0.116	1.7
4-Bromophenyl-phenyl ether	--	0.00044	0.004	--	0.0174	0.27
4-Chloro-3-methylphenol	--	0.00034	0.005	--	0.0111	0.27

Table 4
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Quality Assurance Project Plan
Consolidated Edison Company of New York, Inc.
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	Water (µg/L)[1]			Soil/(mg/kg)[2]		
Analyte	**NYS GW GV**	**MDL**	**RL**	**State of New York Part 375[4]**	**MDL**	**RL[3]**
SVOCs (8270) con't						
4-Chloroaniline	5	0.00029	0.004	--	0.0439	0.27
4-Chlorophenyl-phenyl ether	--	0.00035	0.004	--	0.0199	0.27
3 & 4-Methylphenol	--	0.00029**	0.004**	--	0.0177	0.27
4-Nitroaniline	5	0.0002	0.004	--	0.0207	0.27
4-Nitrophenol	--	0.00145	0.01	--	0.0204	1.7
Acenaphthene	20	0.00031	0.004	20	0.016	0.27
Acenaphthylene	--	0.00034	0.004	100	0.0132	0.27
Anthracene	50	0.00029	0.004	100	0.0105	0.27
Benzyl Alcohol		0.00041	0.004	--	0.0255	0.27
Benzo(a)anthracene	0.002	0.0003	0.004	1	0.0096	0.27
Benzo(a)pyrene	ND	0.00035	0.004	1	0.0073	0.27
Benzo(b)fluoranthene	0.002	0.00036	0.004	1	0.0072	0.27
Benzo(g,h,i)perylene		0.00036	0.004	100	0.0176	0.27
Benzo(k)fluoranthene	0.002	0.0004	0.004	0.8	0.0242	0.27
bis(2-Chloroethoxy) methane	5	0.00031	0.004	--	0.0125	0.27
bis(2-Chloroisopropyl) ether	--	0.00025	0.004	--	0.014	0.27
bis(2-Ethylhexyl)phthalate	5	0.00054	0.004	--	0.0261	0.27
Butylbenzylphthalate	50	0.00035	0.004	--	0.0151	0.27
Carbazole	--	0.00033	0.004	--	0.015	0.27
Chrysene	0.002	0.00025	0.004	1	0.0199	0.27
Dibenz(a,h)anthracene	--	0.00038	0.004	0.33	0.0212	0.27
Dibenzofuran	--	0.00043	0.004	--	0.019	0.27
Diethylphthalate	50	0.00043	0.004	--	0.0272	0.27
Dimethylphthalate	50	0.00038	0.004	--	0.0155	0.27
Di-n-butylphthalate	50	0.00035	0.004	--	0.0392	0.27
Di-n-octylphthalate	50	0.00038	0.004	--	0.0153	0.27
Fluoranthene	50	0.00031	0.004	100	0.0134	0.27
Fluorene	50	0.00026	0.004	30	0.0162	0.27
Hexachlorobenzene	0.04	0.00033	0.004	--	0.0187	0.27

Table 4
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Quality Assurance Project Plan
Consolidated Edison Company of New York, Inc.
Hunts Point Former Manufactured Gas Plant - Bronx, New York

Analyte	Water (µg/L)[1]			Soil/(mg/kg)[2]		
	NYS GW GV	MDL	RL	State of New York Part 375[4]	MDL	RL[3]
SVOCs (8270) con't						
Hexachlorobutadiene	0.5	0.0002	0.004	--	0.0208	0.27
Hexachlorocyclopentadiene	5	0.00035	0.004	--	0.127	0.27
Hexachloroethane	5	0.00037	0.004	--	0.0154	0.27
Indeno(1,2,3-c,d)pyrene	0.002	0.00028	0.004	0.5	0.0175	0.27
Isophorone	50	0.00031	0.004	--	0.0149	0.27
Naphthalene	10	0.0003	0.004	12	0.014	0.27
Nitrobenzene	0.4	0.00028	0.004	--	0.0172	0.27
N-Nitrosodiphenylamine	50	0.00033	0.004	--	0.0152	0.27
N-nitros-di-n-propylamine	50	0.00033	0.004	--	0.0182	0.27
Pentachlorophenol	1	0.00031	0.004	0.8	0.164	1.7
Phenanthrene	50	0.00028	0.004	100	0.0133	0.27
Phenol	1	0.00019	0.004	0.33	0.0179	0.27
Pyrene	50	0.00033	0.004	100	0.0127	0.27
TAL Metals (6010/7470/7471)						
Aluminum	--	0.01	0.25	--	2	50
Antimony	3	0.005	0.015	--	1.02	3.3
Arsenic	25	0.004	0.015	13	1.35	4.2
Barium	1000	0.00025	0.005	350	0.05	1
Beryllium	3	0.00025	0.005	7.2	0.05	1
Cadmium	5	0.001	0.005	2.5	0.2	1
Calcium	--	0.05	0.25	--	10	50
Chromium	50	0.0005	0.005	--	0.1	1
Cobalt	--	0.0005	0.005	--	0.1	1
Copper	200	0.0015	0.01	50	0.38	1.2
Iron	300	0.015	0.125	--	3	25
Lead	25	0.0025	0.015	63	0.62	3
Magnesium	35000	0.005	0.25	--	1.82	50
Manganese	300	0.00025	0.008	1600	0.05	1.5
Mercury	0.7	0.00006	0.0002	0.18	0.004	0.05

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	Water (µg/L)[1]			Soil/(mg/kg)[2]		
Analyte	**NYS GW GV**	**MDL**	**RL**	**State of New York Part 375[4]**	**MDL**	**RL[3]**
TAL Metals (6010/7470/7471) con't						
Nickel	100	0.001	0.005	30	0.2	1
Potassium	--	0.05	0.25	--	10	50
Selenium	10	0.0125	0.038	4	2.5	7.5
Silver	50	0.00025	0.005	2	0.05	1
Sodium	20000	0.05	0.25	--	10	50
Thallium	1	0.0035	0.015	--	0.7	3
Vanadium	--	0.001	0.005	--	0.2	1
Zinc	2000	0.005	0.025	109	1	5
Cyanide (9010/9012B/4500CN-G)						
Cyanide, total	200	0.0029	0.01	27	0.12	0.5
Cyanide, amenable	--	0.0029	0.01	--	0.12	0.5
Cyanide, amenable	--	1.1	5.0	--	0.62	2.3
TPH (8015B)						
Total Petroleum Hydrocarbons (C9-C36)	--	--	--	--	--	--
pH (9040B)						
Total Petroleum Hydrocarbons (C9-C36)	--	--	--	--	--	--
Other Inorganics (E350.1, 9056, E300, SM4500S2-E, SM4500P-E, SM-2320B)						
Ammonia	2000	0.028	0.1	--	2	5
Bicarbonate/Carbonate	--	0.16	2.00	--	20	20
Chloride	250000	0.333	1	--	3.33	10
Fluoride	1500	0.033	0.1	--	0.333	1
Nitrate	10000	0.033	0.1	--	0.333	1
Nitrite	10000	0.033	0.1	--	0.333	1
Phosphate	--	0.0049	0.1	--	0.5411	10
Sulfide	--	0.42	1		4.2	10
Sulfate	--	0.333	1	--	3.33	10

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	Water (µg/L)[1]			Soil/(mg/kg)[2]		
Analyte	**NYS GW GV**	**MDL**	**RL**	**State of New York Part 375[4]**	**MDL**	**RL[3]**
Forensic PAHs (modified 8270)						
cis/trans-Decalin	--	--	--	--	0.119	1
C1-Decalins	--	--	--	--	0.119	1
C2-Decalins	--	--	--	--	0.119	1
C3-Decalins	--	--	--	--	0.119	1
C4-Decalins	--	--	--	--	0.119	1
Benzothiophene	--	--	--	--	0.177	1
C1-Benzo(b)thiophenes	--	--	--	--	0.177	1
C2-Benzo(b)thiophenes	--	--	--	--	0.177	1
C3-Benzo(b)thiophenes	--	--	--	--	0.177	1
C4-Benzo(b)thiophenes	--	--	--	--	0.177	1
Naphthalene	--	--	--	--	0.093	1
C1-Naphthalenes	--	--	--	--	0.093	1
C2-Naphthalenes	--	--	--	--	0.093	1
C3-Naphthalenes	--	--	--	--	0.093	1
C4-Naphthalenes	--	--	--	--	0.093	1
Biphenyl	--	--	--	--	0.208	1
Dibenzofuran	--	--	--	--	0.195	1
Acenaphthylene	--	--	--	--	0.138	1
Acenaphthene	--	--	--	--	0.155	1
Fluorene	--	--	--	--	0.076	1
C1-Fluorenes	--	--	--	--	0.076	1
C2-Fluorenes	--	--	--	--	0.076	1
C3-Fluorenes	--	--	--	--	0.076	1
Anthracene	--	--	--	--	0.117	1
Phenanthrene	--	--	--	--	0.12	1

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Analyte	Water (µg/L)[1]			Soil/(mg/kg)[2]		
	NYS GW GV	MDL	RL	State of New York Part 375[4]	MDL	RL[3]
Forensic PAHs (modified 8270) con't						
C1-Phenanthrenes/Anthracenes	--	--	--	--	0.12	1
C2-Phenanthrenes/Anthracenes	--	--	--	--	0.12	1
C3-Phenanthrenes/Anthracenes	--	--	--	--	0.12	1
C4-Phenanthrenes/Anthracenes	--	--	--	--	0.12	1
Retene	--	--	--	--	0.106	1
Dibenzothiophene	--	--	--	--	0.057	1
C1-Dibenzothiophenes	--	--	--	--	0.057	1
C2-Dibenzothiophenes	--	--	--	--	0.057	1
C3-Dibenzothiophenes	--	--	--	--	0.057	1
C4-Dibenzothiophenes	--	--	--	--	0.057	1
Benzo(b)fluorene	--	--	--	--	0.093	1
Fluoranthene	--	--	--	--	0.125	1
Pyrene	--	--	--	--	0.166	1
C1-Fluoranthenes/Pyrenes	--	--	--	--	0.125	1
C2-Fluoranthenes/Pyrenes	--	--	--	--	0.125	1
C3-Fluoranthenes/Pyrenes	--	--	--	--	0.125	1
C4-Fluoranthenes/Pyrenes	--	--	--	--	0.125	1
Naphthobenzothiophenes	--	--	--	--	0.025	1
C1-Naphthobenzothiophenes	--	--	--	--	0.025	1
C2-Naphthobenzothiophenes	--	--	--	--	0.025	1
C3-Naphthobenzothiophenes	--	--	--	--	0.025	1
C4-Naphthobenzothiophenes	--	--	--	--	0.025	1
Benz[a]anthracene	--	--	--	--	0.166	1
Chrysene/Triphenylene	--	--	--	--	0.157	1
C1-Chrysenes	--	--	--	--	0.157	1
C2-Chrysenes	--	--	--	--	0.157	1
C3-Chrysenes	--	--	--	--	0.157	1
C4-Chrysenes	--	--	--	--	0.157	1
Benzo[b]fluoranthene	--	--	--	--	0.191	1

Analyte	Water (µg/L)[1]			Soil/(mg/kg)[2]		
	NYS GW GV	MDL	RL	State of New York Part 375[4]	MDL	RL[3]
Forensic PAHs (modified 8270) con't						
Benzo[k]fluoranthene	--	--	--	--	0.143	1
Benzo[a]fluoranthene	--	--	--	--	0.191	1
Benzo[e]pyrene	--	--	--	--	0.07	1
Benzo[a]pyrene	--	--	--	--	0.128	1
Perylene	--	--	--	--	0.168	1
Indeno[1,2,3-cd]pyrene	--	--	--	--	0.108	1
Dibenz[a,h]anthracene	--	--	--	--	0.152	1
Benzo[g,h,i]perylene	--	--	--	--	0.161	1
1-Methylnaphthalene	--	--	--	--	0.102	1
2-Methylnaphthalene	--	--	--	--	0.165	1
2,6-Dimethylnaphthalene	--	--	--	--	0.133	1
2,3,5-Trimethylnaphthalene	--	--	--	--	0.106	1
Carbazole	--	--	--	--	0.311	1
4-Methyldibenzothiophene	--	--	--	--	0.057	1
2/3-Methyldibenzothiophene	--	--	--	--	0.057	1
1-Methyldibenzothiophene	--	--	--	--	0.057	1
3-Methylphenanthrene	--	--	--	--	0.12	1
2/4-Methylphenanthrene	--	--	--	--	0.12	1
2-Methylanthracene	--	--	--	--	0.117	1
9-Methylphenanthrene	--	--	--	--	0.12	1
1-Methylphenanthrene	--	--	--	--	0.12	1
Forensic TPH (modified 8015B)						
n-Nonane (C9)	--	--	--	--	0.00644	0.1
n-Decane (C10)	--	--	--	--	0.00707	0.1
n-Undecane (C11)	--	--	--	--	0.00728	0.1
n-Dodecane (C12)	--	--	--	--	0.00939	0.1
n-Tridecane (C13)	--	--	--	--	0.0389	0.1
2,6,10 Trimethyldodecane (1380)	--	--	--	--	0.0389	0.1
n-Tetradecane (C14)	--	--	--	--	0.00696	0.1

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	Water (µg/L)[1]			Soil/(mg/kg)[2]		
Analyte	NYS GW GV	MDL	RL	State of New York Part 375[4]	MDL	RL[3]
Forensic TPH (modified 8015B) con't						
2,6,10 Trimethyltridecane (1470)	--	--	--	--	0.00696	0.1
n-Pentadecane (C15)	--	--	--	--	0.0166	0.1
n-Hexadecane (C16)	--	--	--	--	0.00639	0.1
Norpristane (1650)	--	--	--	--	0.00639	0.1
n-Heptadecane (C17)	--	--	--	--	0.00808	0.1
Pristane	--	--	--	--	0.0108	0.1
n-Octadecane (C18)	--	--	--	--	0.00535	0.1
Phytane	--	--	--	--	0.0056	0.1
n-Nonadecane (C19)	--	--	--	--	0.00541	0.1
n-Eicosane (C20)	--	--	--	--	0.00371	0.1
n-Heneicosane (C21)	--	--	--	--	0.00448	0.1
n-Docosane (C22)	--	--	--	--	0.00288	0.1
n-Tricosane (C23)	--	--	--	--	0.00397	0.1
n-Tetracosane (C24)	--	--	--	--	0.00619	0.1
n-Pentacosane (C25)	--	--	--	--	0.0391	0.1
n-Hexacosane (C26)	--	--	--	--	0.00733	0.1
n-Heptacosane (C27)	--	--	--	--	0.00522	0.1
n-Octacosane (C28)	--	--	--	--	0.0223	0.1
n-Nonacosane (C29)	--	--	--	--	0.00628	0.1
n-Triacontane (C30)	--	--	--	--	0.00665	0.1
n-Hentriacontane (C31)	--	--	--	--	0.00712	0.1
n-Dotriacontane (C32)	--	--	--	--	0.0074	0.1
n-Tritriacontane (C33)	--	--	--	--	0.00735	0.1
n-Tetratriacontane (C34)	--	--	--	--	0.00892	0.1
n-Pentatriacontane (C35)	--	--	--	--	0.00733	0.1
n-Hexatriacontane (C36)	--	--	--	--	0.00692	0.1
n-Heptatriacontane (C37)	--	--	--	--	0.011	0.1
n-Octatriacontane (C38)	--	--	--	--	0.01	0.1
n-Nonatriacontane (C39)	--	--	--	--	NA	0.1

Table 4
Parameters, Methods, and Target Reporting Limits

Quality Assurance Project Plan
Consolidated Edison Company of New York, Inc.
Hunts Point Former Manufactured Gas Plant - Bronx, New York

Analyte	Water (µg/L)[1]			Soil/(mg/kg)[2]		
	NYS GW GV	MDL	RL	State of New York Part 375[4]	MDL	RL[3]
Forensic TPH (modified 8015B) con't						
n-Tetracontane (C40)	--	--	--	--	0.012	0.1
Total Saturated Hydrocarbons	--	--	--	--	0.0113	1.5
Total Petroleum Hydrocarbons (C9-C44)	--	--	--	--	0.0113	3

Notes:

1. Water guidance values (GV) are as presented in the NYSDEC, Division of Water, Technical and Operation Guidance Series (TOGS) document titled, Ambient Water Quality Standards and Guidance Values and Groundwater Effluent Limitations (TOGS 2.2.2), dated June 1998 and revised April 2000.

2. Unrestricted use soil remedial cleanup objectives are provided 375-6.8 in 6 NYCRR Part 375, dated December 14, 2006.

3. The target reporting limits (RL) are based on wet weight. The actual reporting limits will vary based on sample weight and moisture content.

LCS - Laboratory control sample
µg/L - microgram per liter
mg/kg - milligram per kilogram
MDL - method detection limit
MS/MSD - Matrix spike/matrix spike duplicate
PAHs - Polycyclic aromatic hydrocarbons
RPD - Relative percent difference

SVOCs - Semivolatile organic compounds
TAL - Target analyte list
TCL - Target compound list
VOCs - Volatile organic compounds
TPH - Total petroleum hydrocarbons

Title: SOP for Total Alkalinity in Water
[Methods 2320B/4500-CO_2 D]

Approvals (Signature/Date):

Doreen Nemeth 6/8/09
Technical Manager Date

6/8/09
Health & Safety Manager / Coordinator Date

6/8/09
Quality Assurance Manager Date

6-8-09
Laboratory Director Date

This SOP was previously identified as SOP No. CVS00708.CT.

Facility Distribution No. ___________ **Distributed To:**__________________

1.0 APPROVALS

The approval of the Laboratory Director, the Facility QA Manager, Group Leader and Health and Safety Officer signify that the document has been prepared in accordance with the format requirements that have been established in this document. In addition, if the document is a Method SOP the signature signifies that it meets the specified requirements.

2.0 SCOPE AND APPLICATION

2.1 This method is applicable to drinking, surface, and saline waters, domestic and industrial wastes.

2.2 The method has a practical quantitation limit (PQL) of 2.0 mg/L (as $CaCO_3$) and is suitable for all higher concentration ranges of alkalinity. However, aliquots should be used to avoid a titration volume of greater than 50 mL. Automated titrimetric analysis is equivalent.

2.3 The document control number for this SOP is CT-CVS-7, Revision 9.

3.0 TERMS AND DEFINITIONS

3.1 Refer to the SOP for Laboratory Terms and Definitions.

4.0 SUMMARY OF METHOD

4.1 A sample is titrated with a standardized acid to an electrometrically determined end point of pH 4.5. The sample must not be filtered or altered in any way. For samples of low alkalinity (<20 mg $CaCO_3$/L), an extrapolation technique is used. The amount of acid to lower the pH exactly 0.3 pH units is measured after the initial endpoint has been attained. Because this corresponds to an exact doubling of the hydrogen ion concentration, an extrapolation may be made to the equivalence point.

4.2 This method is based upon Standard Methods 2320B and 4500-CO_2 D.

5.0 INTERFERENCES

5.1 Total alkalinity is the measure of primarily the carbonate, bicarbonate, and hydroxide content of a water sample, however, the measured value will also include borates, phosphates, silicates and other bases if they are present.

5.2 Organic material, soaps, oily matter, suspended soils, or precipitates may coat the glass electrode and cause a sluggish response.

5.3 Allow sufficient time between titrant additions to let the electrode response come to equilibrium.

5.4 Do not filter, dilute, concentrate, or alter the sample.

6.0 SAFETY

Employees must abide by the policies and procedures in the Corporate Safety Manual, Radiation Safety Manual and this document. This procedure may involve hazardous material, operations and equipment. This SOP does not purport to address all of the safety problems associated with its use. It is the responsibility of the user of the method to follow appropriate safety, waste disposal and health practices under the assumption that all samples and reagents are potentially hazardous. Safety glasses, gloves, lab coats and closed-toe, nonabsorbent shoes are a minimum.

6.1 SPECIFIC SAFETY CONCERNS OR REQUIREMENTS

There are no specialized safety concerns associated with this method.

6.2 PRIMARY MATERIALS USED

The following is a list of the materials used in this method, which have a serious or significant hazard rating. **NOTE: This list does not include all materials used in the method.** A complete list of materials used in the method can be found in the reagents and materials section. Employees must review the information in the MSDS for each material before using it for the first time or when there are major changes to the MSDS.

Material (1)	Hazards	Exposure Limit (2)	Signs and symptoms of exposure
Sulfuric Acid	Corrosive Oxidizer Dehydra-dator	1 mg/m^3	This material will cause burns if comes into contact with the skin or eyes. Inhalation of vapors will cause irritation of the nasal and respiratory system.
1 – Always add acid to water to prevent violent reactions.			
2 – Exposure limit refers to the OSHA regulatory exposure limit.			

7.0 SAMPLE CONTAINERS AND PRESERVATION

7.1 Samples are to be collected in either a polyethylene or glass bottle and stored unpreserved at 4°C until the time of analysis.

7.2 Samples are to be analyzed within 14 days of sampling or within 12 days of receipt (NYSDEC protocol).

8.0 APPARATUS AND MATERIALS

8.1 A pH meter or electrically operated titrator that uses a glass electrode and can be read to 0.05 pH units. Standardize and calibrate according to the manufacturer's instructions. If automatic temperature compensation is not provided, perform total alkalinity analysis at $25 \pm 2^{o}C$.

8.2 Titration rack and electrode support.

8.3 Magnetic stirrer plate and bar magnets.

8.4 Pipets (Class A).

8.5 Beakers or Erlenmeyer flasks (wide mouth); 250 mL.

8.6 Volumetric flasks (Class A).

8.7 Burets (Class A): 50, 25, and 10 mL.

8.8 Graduated cylinders: 25 and 100 mL.

9.0 REAGENTS AND STANDARD PREPARATION

9.1 All chemicals are to conform to the specifications set by the Reagent Chemical Committee of the American Chemical Society. Laboratory prepared nanopure water is used whenever ASTM II Water (ASTM D11930) reagent grade water is required.

9.2 Sodium carbonate solution (approximately 0.05N): Place 2.5 ± 0.2 grams (to the nearest mg) Na_2CO_3 (dried at 250°C for four hours and cooled in desiccator) into a 1-liter volumetric flask and bring to volume with reagent grade water. Do not keep longer than 1 week.

9.3 Standard sulfuric acid (0.10 N): Dilute 3.0 mL of concentrated H_2SO_4 to 1 liter with reagent grade water. See Section 10.1 for standardization.

9.4 Standard Sulfuric Acid (0.02 N): Dilute 200.0 mL of 0.10 N H_2SO_4 to 1 liter with reagent grade water. See Section 10.2 for standardization.

9.5 Note: Commercially prepared standard sulfuric acid solutions may be used for step 9.3 or

9.4. The normality of the commercially prepared sulfuric acid must be standardized against sodium carbonate solution as in Section 10.0.

10.0 CALIBRATION

10.1 Standard sulfuric acid (0.10 N): Dilute 3.0 mL of concentrated H_2SO_4 to 1 liter with reagent grade water. Standardize versus 40.0 mL of 0.05 N Na_2CO_3 solution (9.2) with 60 mL of reagent grade water by titrating potentiometrically to a pH of approximately 5. Lift the electrode and rinse with reagent grade water into the beaker. Boil the solution gently for three to five minutes under a watch glass. Cool to room temperature. Rinse the watch glass into the beaker and continue the titration to inflection point.

10.2 Standard sulfuric acid (0.02 N): Dilute 200.0 mL of 0.10 N H_2SO_4 to 1 liter with reagent grade water. Standardize by the potentiometric titration of 15.0 mL 0.05 N Na_2CO_3 solution (9.2).

CAUTION: Sulfuric acid solutions are corrosive and cause burns. Avoid contact. Wear gloves and appropriate eye protection at all times.

10.3 Record standard pH calibration readings in the analysis log; include the LIMS standard codes for each pH buffer.

11.0 QUALITY CONTROL

11.1 Method detection limits (MDLs) are calculated based on the 40 CFR chapter 1 definition of method detection limits and are performed annually.

11.2 Practical quantitation limits for this method is 2.0 mg/L as $CaCO_3$.

11.3 All stock solutions, standard preparations, reagents, and LCS's are logged into LIMS.

11.4 All chemicals will conform to minimum specifications set by the Reagent Chemicals Committee of the American Chemical Society. All chemical inventories are used on a first in, first out basis.

11.5 A method blank (MB) must be analyzed for every batch of 20 samples or every day, whichever is more frequent. Method blanks are reagent grade water (nanopure) and processed as a sample.

11.6 A sample duplicate is to be analyzed with each batch of 10 samples. Sample duplicates are prepared by using a second aliquot of sample and processing identically to the original sample. Samples identified as field blanks may not be used for sample duplicate analysis.

11.7 Matrix spikes are not employed for this method.

11.8 One independent standard or laboratory control standard (LCS) is to be analyzed with each batch of 20 samples.

11.9 Standard pH calibration buffers must be analyzed each day that alkalinities are run.

12.0 SAMPLE PREPARATION AND INSTRUMENTAL PROCEDURES

12.1 All samples to be analyzed must be signed out of sample control on the chain-of-custody (COC) for each job. All alkalinity data collected is recorded in the alkalinity log.

12.2 Samples 20 mg/L or above (>2.0 mL of 0.02 N titrant).

12.2.1 Using a graduated cylinder, transfer 100 mL of the well dispersed sample into the titration vessel (beaker or flask). Place a stir bar in the titration vessel.

12.2.2 While stirring gently, but thoroughly, measure the pH of the sample. Record the pH in the analysis log.

12.2.3 Slowly add 0.02 N standard acid allowing the pH meter to equilibrate between additions.

12.2.4 Titrate the sample to pH 4.5. Record the volume of titration in the analysis log.

NOTE: For samples containing >500 mg/L as $CaCO_3$ of alkalinity, use 0.10 N H_2SO_4 as the titrant.

12.3 Samples below 20 mg/L (<2.0 mL of 0.02 N titrant):

12.3.1 Titrate the sample as described in sections 12.2.1 through 12.2.4. Record the volume of titrant used to reach a pH of 4.5 in the analysis log.

12.3.2 Very carefully add titrant to lower the pH 0.3 units to 4.2. Record the additional amount of titrant used to reach 4.2 in the analysis log.

13.0 CALCULATIONS

13.1 All raw data including sample volume, titrant volume, and acid normality are entered into LIMS. LIMS calculates the total alkalinity results for all samples. Bicarbonate, carbonate, and hydroxide alkalinities and free and total carbon dioxide can be calculated by entering raw data into excel. Final results are then entered manually into LIMS.

13.2 The normality of the H_2SO_4 titrant is calculated:

$$N = \frac{A \times B}{53.00 \times C}$$

where: A = grams Na_2CO_3 into 1 liter
B = mL Na_2CO_3 solution
C = mL acid used to inflection point

13.3 Manual alkalinity calculation (titration to pH 4.5).

$$\text{Alkalinity (mg/L as } CaCO_3) = \frac{A \times N \times 50{,}000}{\text{mL of sample}}$$

where: A = mL of acid titrated
N = normality of acid

13.4 Alkalinity calculation for low samples (<2.0 mL 0.02 N titrant).

$$\text{Total Alkalinity (mg/L as } CaCO_3) = \frac{(2B-C) \times N \times 50{,}000}{\text{mL of sample}}$$

where: B = total mL titrant to the first recorded pH
C = total mL titrant to reach 0.3 units lower
N = normality of acid

13.5 The relative percent difference is calculated:

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

where: S = original sample result
D = duplicate sample result

13.6 The LCS Percent Recovery Calculation:

Percent Recovery = (VM / TV) x 100

where: VM = Value measured
TV = True value

13.7 Manual Bicarbonate alkalinity calculation:

$$\text{Bicarbonate Alkalinity (mg/L as CaCO}_3) = \frac{T - 5.0 \times 10^{(pH-10)}}{1 + 0.94 \times 10^{(pH-10)}}$$

where: T = total alkalinity, mg $CaCO_3$

13.8 Manual Carbonate alkalinity calculation:

Carbonate Alkalinity (mg/L as $CaCO_3$) = $0.94 \times B \times 10^{(pH-10)}$

where: B = bicarbonate alkalinity, mg $CaCO_3$

13.9 Manual Hydroxide alkalinity calculation:

Hydroxide Alkalinity (mg/L as $CaCO_3$) = $5.0 \times 10^{(pH-10)}$

13.10 Manual Free Carbon Dioxide calculation:

mg Free Carbon Dioxide = $2.0 \times B \times 10^{(6-pH)}$

where: B = bicarbonate alkalinity, mg $CaCO_3$

13.11 Manual Total Carbon Dioxide calculation:

mg Total Carbon Dioxide = A + 0.44 (2B + C)

where: A = g free carbon dioxide
B = bicarbonate alkalinity, mg $CaCO_3$
C = carbonate alkalinity, mg $CaCO_3$

14.0 ACCEPTANCE OF DATA

14.1 The technical data review includes verifying that samples analyzed were unpreserved and that holding times were met. The raw data is examined for completeness including a secondary signoff. Results entered into LIMS are checked for transcription error against the raw data.

14.2 Method blanks: All method blanks must be less than the practical quantitation limit.

Action on failure: If a method blank's concentration exceeds the reporting limit, all samples that were prepared with the method blank and have a concentration greater than the reporting limit and less than 10 times the method blank concentration, must be rerun.

14.3 Duplicate: The RPD for the duplicate must not exceed 20 percent (see Section 13.5 for PD calculation). If the sample and duplicate concentrations are less than five times the PQL, no criteria is applied.

Action on failure: If the RPD is out of control, rerun the sample and duplicate.

14.4 Laboratory Control Sample (LCS): The recovery of the independent standard must be within 85-115 percent of the known concentration (see Section 13.6 for percent recovery calculation).
Action on failure: If the recovery of the LCS is not in control, the calibration fails. The problem must be identified and corrected prior to any further analysis or acceptance of any data.

14.5 The Initial calibration verification (ICV) must be a second source standard from the initial calibration and must recovery within 90-110 percent of the known concentration. This may be the same standard as the LCS as long as it meets all the criteria for an ICV.

Action on failure: If the recovery of the ICV is not in control, the calibration fails. The problem must be identified and corrected prior to any further analysis or acceptance of any data.

15.0 REPORTING OF RESULTS

15.1 Results are reported by entering the data collected into LIMS. Analytical batches are subjected to primary and secondary reviews.

15.2 NCM’s should be written if there are any holding time or related QC issues or if, during analysis, there was any deviation from the method.

15.3 Case Narratives should include information received on NCM’s and any other problems associated with the analysis of samples.

15.4 The PQL for alkalinity is 2.0 mg/L as $CaCO_3$. Two significant figures are used for results less than 10.0 mg/L, and three significant figures are used for results equal to or greater than 10.0 mg/L.

16.0 POLLUTION PREVENTION

It is TestAmerica’s policy to evaluate each method and look for opportunities to minimize waste generated (i.e., examine recycling options, ordering chemicals based on quantity needed, preparation of reagents based on anticipated usage and reagent stability). Employees must abide by the policies in Section 13 of the Corporate Safety Manual for "Waste Management and Pollution Prevention."

16.1 Pollution prevention is the reduction and/or elimination of wastes or the toxicity of wastes at the point of generation. The laboratory strives to keep all wastes at a minimum through a variety of techniques. These include the following.

16.1.1 Inventory control: Rotate stocks (first in, first out) and only purchase reasonable amounts of chemicals. Do not purchase excessive quantities, which will be discarded as wastes at some future point.

16.1.2 Material Handling and Storage: Keep containers properly labeled. Keep solvents covered. Store and handle all chemicals, reagents, standards, etc. to prevent contamination and degradation.

16.1.3 Personnel: All staff must be trained in the proper handling and disposal of waste.

16.1.4 Waste Reduction: Reduce the volume of waste generated whenever possible.

16.1.5 Chemical/material substitution: Use less toxic chemicals whenever possible. Avoid the use of chromic acid (Chromerge) solutions.

17.0 WASTE MANAGEMENT

Waste management practices are conducted consistent with all applicable rules and regulations. Excess reagents, samples and method process wastes are disposed of in an accepted manner. Waste description rules and land disposal restrictions are followed. Waste disposal procedures are incorporated by reference to the Tracking and Collection of Hazardous Waste SOP. The following waste streams are produced when this method is carried out.

17.1 Waste Streams Produced by the Method:
The following waste streams are produced when this method is carried out.

- Acidic waste generated by the analysis. Dispose of acid waste in the acid waste satellite accumulation drum.

18.0 SUPPLEMENTAL DOCUMENTS

18.1 SOP for Laboratory Terms and Definitions.

19.0 REFERENCES

19.1 Standard Methods for the Examination of Water and Wastewater, 18th Edition, Method 2320B, 1992.

19.2 Standard Methods Online, Methods 2320B and 4500-CO_2 D.

20.0 SUBSTANTIVE REVISIONS

20.1 Original document.

20.2 Section 1.0 removed reference to corporate document. Section 10.6 - Change duplicate criteria to every 10 samples. Replaced IEA with AEN; July 14, 1997.

20.3 Changed name from AEN to STL. Section 12.4; low alkalinity calculation - Feb 2, 1999.

20.4 Added Section 3.0, 09/10/99.
Modified Section 11.3 to refer to Classical Chemistry Sop for Labeling and Coding of Standards.

20.5 Added Section 16.0, 17.0, 10/01/99.

20.6 Revised sections 11.3, 13.1, 14.1, 15.1 to reflect change to Labnet reporting system, 05/29/02.

20.7 Revised section 12.3.2 to reflect change in recording data into logbook, 05/29/02.

20.8 Added reference to method 2320B in section 4.2, 05/29/02.

20.9 Added reference to method 4500-CO_2 D, section 4.2, 06/09/03.

20.8 Added Sections 13.7 through 13.11, 06/09/03.

20.9 Added Health and Safety Officer signature, section 1.0, 10/14/04.

20.10 Revised sections 6.0 and 17.0 to include expanded safety information, 10/14/04.

20.11 No substantive revisions, 05/31/05.

20.12 Section 6.2 added table with sulfuric acid, 05/10/07.

20.13 Sections 11.3, 13.1, 14.1, and 15.1 changed to reference LIMS, 05/10/07.

20.14 Section 15.2 modified to include “NCM’s,” 05/10/07.

20.15 Changed document to TestAmerica format, Removed reference to method 310.1 and added reference to Standard Methods 18th edition in Section 19.1, Added reference to Standard Methods online, Section 19.2, Added Section 5.4, Removed reference to Classical Chemistry SOP for Labeling and Coding of Standards. Updated safety, pollution control and waste management sections. Added ICV criteria, sect 14.5 06/08/09.

Title: SOP for Total Sulfide
[Method SM 4500 S² -E]

Approvals (Signature/Date):

Doreen Nemeth	10/23/09	David W. Helfrich	10/2709
Technical Manager	Date	Health & Safety Manager/Coordinator	Date
Dawn May	10/27/09		11/02/09
Quality Assurance Manager	Date	Laboratory Director	Date

This SOP was previously identified as SOP No. CT-CVS-17_7

Facility Distribution No. Electronic **Distributed To: Facility Intranet**

The controlled copy of this SOP is the PDF copy of the SOP that is posted to the laboratory's SOP Directory. Printed copies of this SOP or electronic copies of this SOP distributed outside the facility are considered uncontrolled.

1.0 APPROVALS

The approval of the Laboratory Director, the Facility QA Manager, Group Leader and Health and Safety Officer signify that the document has been prepared in accordance with the format requirements that have been established in this document. In addition, if the document is a Method SOP the signature signifies that it meets the specified requirements.

2.0 SCOPE AND APPLICATION

2.1 This method is applicable to the measurement of total sulfide in drinking, surface and saline waters.

2.2 Acid insoluble sulfides are not measured by the use of this test (copper sulfide is the only common sulfide in this class).

2.3 The document control number for this SOP is CT-CVS-17 Rev.8.

3.0 TERMS AND DEFINITIONS

3.1 Refer to the SOP for Laboratory Term and Definitions.

4.0 SUMMARY OF METHOD

4.1 Excess iodine is added to a sample which may or may not have been treated with zinc acetate to produce zinc sulfide. The iodine oxidizes the sulfide to sulfur under acidic conditions. The excess iodine is back titrated with sodium thiosulfate.

4.2 This method is based on Standard Methods 4500-S^{2-}E, and is suitable for the measurement of sulfide concentrations above 1.0 mg/L in waters.

5.0 INTERFERENCES

5.1 Reduced sulfur compounds which decompose in acid, such as sulfite and thiosulfate, may yield erratic results. Volatile iodine-consuming substances will give high results.

6.0 SAFETY

Employees must abide by the policies and procedures in the Corporate Safety Manual, Radiation Safety Manual and this document. This procedure may involve hazardous material, operations and equipment. This SOP does not purport to address all of the safety problems associated with its use. It is the responsibility of the user of the method to follow appropriate safety, waste disposal and health practices under the assumption that all samples and reagents are potentially hazardous. Safety glasses, gloves, lab coats and closed-toe, nonabsorbent shoes are a minimum.

6.1 SPECIFIC SAFETY CONCERNS OR REQUIREMENTS

Sodium Sulfide will form Hydrogen Sulfide (HS) gas if combined with water moisture or strong

acids. Inhalation of HS gas may be fatal.

6.2 PRIMARY MATERIALS USED

The following is a list of the materials used in this method, which have a serious or significant hazard rating. **NOTE: This list does not include all materials used in the method. The table contains a summary of the primary hazards listed in the MSDS for each of the materials listed in the table.** A complete list of materials used in the method can be found in the reagents and materials section. Employees must review the information in the MSDS for each material before using it for the first time or when there are major changes to the MSDS.

Material (1)	**Hazards**	**Exposure Limit (2)**	**Signs and symptoms of exposure**
Hydrochloric Acid	Corrosive Poison	5 ppm-Ceiling	Inhalation of vapors can cause coughing, choking, inflammation of the nose, throat, and upper respiratory tract, and in severe cases, pulmonary edema, circulatory failure, and death. Can cause redness, pain, and severe skin burns. Vapors are irritating and may cause damage to the eyes. Contact may cause severe burns and permanent eye damage.
Sodium Hydroxide	Corrosive	2Mg/M3-Ceiling	Severe irritant. Effects from inhalation of dust or mist vary from mild irritation to serious damage of the upper respiratory tract, depending on severity of exposure. Symptoms may include sneezing, sore throat or runny nose. Contact with skin can cause irritation or severe burns and scarring with greater exposures. Causes irritation of eyes, and with greater exposures it can cause burns that may result in permanent impairment of vision, even blindness.
Sodium Sulfide	Corrosive	10 ppm-TWA 15 ppm-STEL	Will **for**m **H**ydrogen Sulfide (HS) gas if combined with strong acids. Inhalation of HS gas may be fatal. Symptoms include painful conjunctivitis, headache, nausea, dizziness, coughing and, in extreme cases, pulmonary edema and possible death. Irritant. Contact with skin can produce serious caustic burns with painful inflammation and possible destruction of tissue. Inflammation, tearing and pain may be expected. Severe contact can cause destruction of tissue.
1 – Always add acid to water to prevent violent reactions.			
2 – Exposure limit refers to the OSHA regulatory exposure limit.			

7.0 <u>SAMPLE CONTAINERS AND PRESERVATION</u>

7.1 Water samples are collected in polyethylene, and preserved with zinc acetate and sodium hydroxide (pH >9). Water should be kept under refrigeration at 4°C until analyzed.

7.2 Samples must be taken with a minimum of aeration. Sulfide may be volatilized by aeration and any oxygen inadvertently added to the sample may convert the sulfide to an immeasurable form.

7.3 All samples should be analyzed within 7 days of the date of collection, and within 5 days of receipt for NYSDEC protocol.

8.0 APPARATUS AND MATERIALS

8.1 Drying oven - capable of maintaining a constant temperature in the range of 103 - 105^{o}C

8.2 Analytical balance - 0.1 mg sensitivity

8.3 Top-loading balance, 0.01 g sensitivity

8.4 Volumetric pipettes, Class A

8.5 Volumetric flasks, Class A, 1L, 500mL, 250mL, 100mL

8.6 Graduated cylinders, 250 mL, 50 mL

8.7 Buret, Class A, 50 mL

8.8 Magnetic stirring plate, stir bar

8.9 GF/A filter paper, 90 mm or equivalent.

8.10 Buchner funnel/suction flask set-up

9.0 REAGENTS AND STANDARD PREPARATION

9.1 All chemicals are to conform to the specifications set by the Reagent Chemical Committee of the American Chemical Society. Laboratory prepared nanopure water is used whenever reagent ASTM Type II Water (ASTM D11930) is required.

9.2 Standard potassium dichromate solution (0.250 N): Dissolve 12.259 g $K_2Cr_2O_7$, primary standard grade, previously dried at 103ºC for two hours, in reagent water and dilute to 1 L.

9.3 Hydrochloric Acid, 1:1 (6 N): Carefully mix equal parts of concentrated HCl (reagent grade) and reagent water. Always add acid to water.

9.4 Standard iodine solution (0.0250 N): Dissolve 25 g of KI (potassium iodide, reagent grade) in a small amount of reagent water in a 1-liter volumetric flask. Add 3.2 g of iodine. Allow to dissolve. Dilute to 1 liter with reagent water and standardize against 0.0250 N sodium thiosulfate.

9.5 Starch indicator: Mix 2.0 g soluble starch with a small amount of reagent water. Dilute to 100 mL with boiling reagent water. Let settle and use the clear supernate.

9.6 Sulfide standard (680 ppm): Weigh about 1.01 g of $Na_2S.9H_2O$, reagent grade and transfer to a 250 mL volumetric flask. Adjust the pH to between 9 and 11, dilute to volume with reagent water and store in a glass amber bottle. Standardize to find true value. This solution is good for one month.

9.7 Standard sodium thiosufate titrant (0.0250 N): Dissolve 6.205 g $Na_2S_2O_3.5H_2O$ in reagent water in a 1L volumetric flask. Add 0.4 g concentrated NaOH pellets and dilute to 1L with reagent water. Standardize daily before use with 0.250 N standard potassium dichromate solution.

10.0 <u>CALIBRATION</u>

10.1 $Na_2S_2O_3$ titrant standardization

10.1.1 Perform standardization in duplicate.

Pipet 3.00 mL of 0.250 N potassium dichromate solution in a 500 mL Erlenmeyer flask containing 50 mL of reagent water. Add 1.00 g of KI and 5 mL of 1:1 HCl. Place both flasks in the dark for approximately 5 minutes, then add 200 mL of reagent water to each flask.

Note: Standardization of $Na_2S_2O_3$ must be performed daily.

10.1.2 Titrate each flask with 0.0250 N $Na_2S_2O_3$ until the amber color fades to yellow. Add the starch indicator and titrate until the blue color disappears.

10.1.3 Record the volume of potassium dichromate solution used and its normality, and the volume of sodium thiosulfate used in the sulfide logbook.

Note: See Section 13.2 for $Na_2S_2O_3$ normality calculation.

10.2 Iodine solution Standardization.

10.2.1 Perform standardization in duplicate.

Pipet 10.0 ml of iodine solution to a 250 ml Erlenmeyer flask containing 100 ml of reagent water. Add 5 ml of 1:1 HCl.

10.2.2 Titrate each flask with 0.0250 N $Na_2S_2O_3$ until the amber color fades to yellow. Add the starch indicator and titrate until the blue color disappears.

10.2.3 Record the volume of potassium dichromate solution used and its normality, and the volume of sodium thiosulfate used in the sulfide logbook.

Note: See Section 13.3 for iodine solution normality calculation.

11.0 QUALITY CONTROL

11.1 Method detection limits (MDLs) are calculated based on the 40 CFR Chapter 1 definition of method detection limits and are performed annually.

11.2 Practical quantitation limits for this method is 1.0 mg/L as S^{-2}.

11.3 All stock solutions and standard preparations are logged into LIMS. All solutions are labeled with the following: analyte, concentration, analyst's initials, date prepared, and expiration date.

11.4 All chemicals will conform to minimum specifications set by the Reagent Chemicals Committee of the American Chemical Society. All chemical inventories are used on a first in, first out basis.

11.5 A method blank or method blank (MB) must be analyzed for every batch of 20 samples or every day, which ever is more frequent. Method blanks are reagent grade water and processed as a sample.

11.6 A sample duplicate is to be analyzed with each batch of 10 samples. Sample duplicates are prepared by processing identically to the original sample. Samples identified as field blanks are not to be used for duplicate analysis.

11.7 A sample spike per matrix is to be analyzed with every batch of 20 or fewer samples unless there is a NYSDEC/SW 846 protocol in which an additional spike duplicate will be analyzed. Samples identified as field blanks are not to be used for spike analysis.

11.8 A blank spike, (MSB), recovery standard is to be analyzed daily.

11.9 An NCM must be written if any problems are associated with the analysis or any deviation of this SOP occurs.

11.10 Record NBS "S" weights where applicable.

12.0 SAMPLE PREPARATION AND PROCEDURE

12.1 All samples to be analyzed must be signed out of sample control on the chain-of-custody (COC) for each job. All sulfide data collected is recorded in the sulfide log.

12.2 Titration procedure:

12.2.1 Pipet 10.0 mL of the 0.0250 N iodine solution and add 15.0 mL of 1:1 HCl into a 500 mL Erlenmeyer flask.

12.2.2 Place 200 mL of the well-dispersed sample into the flask. If the iodine color disappears, add more iodine until the color remains. Record the total mL of standard iodine used.

12.2.3 While agitating, titrate with 0.0250 N $Na_2S_2O_3$ until the amber color fades to yellow. Add the starch indicator and titrate until the blue color disappears. Record the initial and final buret readings, sample volume, and iodine volume used in the logbook.

12.3 To spike a water sample: pipet 2.0 mL of the stock sulfide standard into the flask submerging the tip below the surface of the liquid.

12.4 To prepare a Blank Spike (MSB), add 200 mL of reagent water to a 250 mL Erlenmeyer flask containing 10.0 mL of the iodine solution and 15 mL of 1:1 HCl. Pipet 2.0 mL of the stock sulfide standard into the flask submerging the tip below the surface of the liquid.

12.5 Analysis of water samples with matrix interferences:

12.5.1 Filter 200 mL of well-dispersed water sample through a GF/A filter and Buchner funnel-suction flask set-up collecting the filter residue. Rinse the filter residue with reagent water. Carefully transfer the filter paper and residue into a 500 mL Erlenmeyer flask containing 10.0 mL of the 0.0250 N iodine solution and 5.0 mL of 1:1 HCl. Add 200 mL of reagent water. If the iodine color disappears, add more iodine until the color remains. Titrate as in step 12.2.

13.0 CALCULATIONS

13.1 All raw data including sample volume, titration volumes and normality are entered into LIMS, which will calculate the results.

13.2 $Na_2S_2O_3$ normality calculation:

$$\text{N } Na_2S_2O_3 = \frac{3 \text{ mLs } (K_2Cr_2O_7) \times 0.2500 \text{ N } (K_2Cr_2O_7)}{\text{Avg. mLs of } Na_2S_2O_3 \text{ used}}$$

13.3 Iodine solution normality calculation:

$$N_I = \frac{\text{mLs } Na_2S_2O_3 \text{ used to titrate} \times \text{normality of } Na_2S_2O_3}{\text{mLs iodine solution used}}$$

13.4 Manual sulfide calculation:

$$\text{Sulfide (mg/L)} = \frac{[(A \times B) - (C \times D)] \times 16{,}000}{\text{Sample Volume (mL)}}$$

where:

A = mL iodine solution
B = normality of iodine solution
C = mL $Na_2S_2O_3$ of solution
D = normality of $Na_2S_2O_3$ solution

13.5 Sample Matrix Spike Recovery:

Percent Recovery = (SSR - SR) x 100

SA

where:

SSR = Spiked sample result
SR = Sample result
SA = Spike added (recovery standard result)

13.6 Relative percent difference calculation:

$$RPD = \frac{(S - D)}{(S - D)/2} X 100$$

where:

S = Original sample result
D = Duplicate sample result

14.0 ACCEPTANCE OF DATA

14.1 The technical data review includes verifying that samples analyzed were preserved with sodium hydroxide and zinc acetate and that holding times were met. The raw data is examined for completeness including a secondary review.

14.2 Method Blanks: All method blanks must be less than the practical quantitation limit.

Action of Failure: If a method blank's concentrations exceeds the reporting limit, all samples that were prepared with the method blank and have a concentration greater than the reporting limit and less than 10 times the method blank concentration, must be rerun.

14.3 Duplicate: The RPD for the duplicate must not exceed 20 percent (see Section 13.6 for RPD calculation). If the sample and duplicate concentration are less than five times the PQL, no criteria is applied.

Action on failure: If the RPD is out of control, rerun the sample and duplicate.

14.4 Spike Sample Recovery: The acceptable range for spike recovery is ± 25 percent. If the sample concentration exceeds 4 times the spiking level, no spike criteria is applied.

Action on failure: If the spike fails, the sample must be spiked again and reanalyzed.

15.0 REPORTING OF RESULTS

15.1 Results are reported by entering the data collected into LIMS.

15.2 Case narratives should include information received on NCM's to document any holding time problems or any other problems associated with the analysis of samples.

15.3 The PQL for sulfide is 1.0 mg/L as S^{-2}. Two significant figures are used for results less than 10.0 mg/L, and three significant figures are used for results equal to or greater than 10.0 mg/L.

16.1 POLLUTION PREVENTION

It is TestAmerica's policy to evaluate each method and look for opportunities to minimize waste generated (i.e., examine recycling options, ordering chemicals based on quantity needed, preparation of reagents based on anticipated usage and reagent stability). Employees must abide by the policies in Section 13 of the Corporate Safety Manual for "Waste Management and Pollution Prevention."

16.1 Pollution prevention is the reduction and/or elimination of wastes or the toxicity of wastes at the point of generation. The laboratory strives to keep all wastes at a minimum through a variety of techniques. These include the following:

16.2 Inventory control: Rotate stocks (first in, first out) and only purchase reasonable amounts of chemicals. Do not purchase excessive quantities, which will be discarded as wastes at some future point.

16.3 Material Handling and Storage: Keep containers properly labeled. Keep solvents covered. Store and handle all chemicals, reagents, standards, etc. to prevent contamination and degradation.

16.4 Personnel: All staff must be trained in the proper handling and disposal of waste.

16.5 Waste Reduction: Reduce the volume of waste generated whenever possible.

16.6 Chemical/material substitution: Use less toxic chemicals whenever possible. Avoid the use of chromic acid (Chromerge) solutions.

17.0 WASTE MANAGEMENT AND POLLUTION PREVENTION

Waste management practices are conducted consistent with all applicable rules and regulations. Excess reagents, samples and method process wastes are disposed of in an accepted manner. Waste description rules and land disposal restrictions are followed. Waste disposal procedures are incorporated by reference to the Tracking and Collection of Hazardous Waste SOP. The following waste streams are produced when this method is carried out.

17.1 Waste Streams Produced by the Method

The following waste streams are produced when this method is carried out.

- Acidic waste generated by sample titration. Employees are to collect and dispose of this material in satellite acid waste accumulation drums.

18.0 REFERENCES

18.1 Methods of Chemical Analysis of Water and Wastes, EPA 600, Method 376.1, 1983.

18.2 Standard Methods for the Examination of Water and Wastewater, 18th Edition, Method 4500-S^{2-}E, 1992.

19.0 SUBSTANTIVE REVISIONS

19.1 Original document.

19.2 Inclusion of SW846 Method 9030B, Method 9034, and Standard Methods 4500-S^{2-} Section C as a reference. Incorporated SW846 procedures for soil distillation. Incorporated Standard Methods 4500-S^{2-} Section C for removal of interfering substances in water samples. 02/04/99.

19.3 Added cover page. Changed Section 14.0 to refer to Wet Chem for the program used for reporting Sulfide results. Changed calibration to using 1.0g KI instead of the 10% KI solution. Changed steps with 3.5mL 1:1 HCl addition to 5.0mL 1:1 HCl addition. Added Pollution Prevention Section 15.0 and Waste Management Section 16.0. 06/04/2001.

19.4 Removed soil distillation steps, and added iodine standardization. Section 9.6: revised true value of sulfide standard, amount of $Na_2S.9H_2O$ used, size of the volumetric needed; added standardizing step. Eliminated section 9.8. Revised amount of KI used in section 10.1.1. Revised amount of 1:1 HCl used in section 10.2.2. Revised sections 11.3, 13.1, and 15.1 to reflect change to Labnet reporting system. Revised section 14.3 to refer to correct section for RPD calculation. Eliminated section 18.0 (Supplemental Documents) and renumbered remaining sections. 6/25/02.

19.5 Addition of Health and Safety Officer signature, 06/10/03.

19.6 Revised sections 6.0 and 17.0 to include more detailed safety and waste management information, 10/14/04.

19.7 No substantive revisions, 05/31/05.

19.8 Changed name from “Severn Trent Laboratories” to “TestAmerica Laboratories,”. Revised document to reference Standard Methods 4500-S^{2-}E. (Replaces EPA 600 376.1). Added new TestAmerica SOP header and control number, 08/27/07.

19.9 Removed reference to “soils” from Section 7.1. Safety, pollution control, waste management sections updated. 10/23/09

Sulfide Analysis Logbook Sulfide Method: ________________________

QC#	Sample ID	Sample Vol./wt (ml/g)	Dist Vol. (ml)	Titration Volume (ml)	Buret Reading		Total (ml)	Iodine Used (mls)	Sulfide PPM
					Initial	Final			
STD	$K_2Cr_2O_7$	3ml							
STD	$K_2Cr_2O_7$	3ml							
I_2soln	I_2 Standardization	10ml							
I_2soln	I_2 Standardization	10ml							
Stock									
Stock									
BS									
1									
2									
3									
4									
5									
6									
7									
8									
9									
10									
11									
12									
13									

$Na_2S_2O_3$ Reference: _________________________ Iodine Soln. Reference: _________________________

Analyst: ___________ Date:__________ $Na_2S_2O_3$ Normality = ___________ Iodine Normality = ________

Spike Added: _______ Spike %Rec:________ BS %Rec:_________ Dup %RPD:________

Sulfide Source	Lot #	Wt (g)	Final Vol (ml)	True Value

Reviewed by:_________ Date:____________ Page____ of 60
Form# CVF00101.CT Logbook#CV01.10

TestAmerica
THE LEADER IN ENVIRONMENTAL TESTING

Title: SOP for Amenable Cyanide in Environmental Samples
[Method SM 4500-CN G]

Approvals (Signature/Date):

Doreen Nemeth 2/12/10
Technical Manager Date

2/11/10
Health & Safety Manager / Coordinator Date

Marsha K. Culik-interim 2/11/10
Quality Assurance Manager Date

2/22/10
Laboratory Director Date

This SOP was previously identified as SOP No. CVS02104.CT.

Facility Distribution No. Electronic **Distributed To: Facility Intranet**

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1.0 APPROVALS

The approval of the Laboratory Director, the Facility QA Manager, Group Leader and Health and Safety Officer signify that the document has been prepared in accordance with the format requirements that have been established in this document. In addition, if the document is a Method SOP the signature signifies that it meets the specified requirements

2.0 SCOPE AND APPLICATION

2.1 This method is applicable to the determination of cyanides amenable to chlorination in drinking, ground, surface and saline waters, groundwaters, sediments and other solids, and domestic and industrial wastes.

2.2 This SOP details the cyanide amenable to chlorination preparation procedure prior to determination of cyanide by midi distillation with a semi-automated colorimetric analysis of the distillate.

2.3 The document control number for this SOP is CT-CVS-21, Rev 5.

3.0 TERMS AND DEFINITIONS

3.1 Refer to the SOP for Laboratory Term and Definitions.

4.0 SUMMARY OF METHOD

4.1 An aliquot of a sample is chlorinated at a pH greater than 11 to decompose the cyanide. Cyanide levels in the treated sample and the original sample are then determined by method 335.4. The cyanides amenable to chlorination are then determined by the difference.

4.2 This SOP is based on Standard Methods 4500-CN G.

5.0 INTERFERENCES

5.1 Organic chemicals may oxidize or form breakdown products during chlorination, giving higher results for cyanide after chlorination than before chlorination.

6.0 SAFETY

Employees must abide by the policies and procedures in the Corporate Safety Manual, Radiation Safety Manual, and this document.

6.1 SAFETY CONCERNS OR REQUIREMENTS

Potassium cyanide and sodium cyanide will give off Hydrogen Cyanide (HCN) gas if combined with strong acids. Inhalation of CN gas can cause irritation, dizziness, nausea, unconsciousness and potentially death.

6.2 PRIMARY MATERIALS USED

The following is a list of the materials used in this method, which have a serious or significant hazard rating. **NOTE: This list does not include all materials used in the method. The table contains a summary of the primary hazards listed in the MSDS for each of the materials listed in the table.** A complete list of materials used in the method can be found in the reagents and materials section. Employees must review the information in the MSDS for each material before using it for the first time or when there are major changes to the MSDS.

Material (1)	**Hazards**	**Exposure Limit (2)**	**Signs and symptoms of exposure**
Sulfuric Acid	Corrosive Oxidizer Dehydra-dator	1 mg/m^3	This material will cause burns if comes into contact with the skin or eyes. Inhalation of vapors will cause irritation of the nasal and respiratory system.
Sodium Hydroxide	Corrosive	2 Mg/M3-Ceiling	Severe irritant. Effects from inhalation of dust or mist vary from mild irritation to serious damage of the upper respiratory tract, depending on severity of exposure. Symptoms may include sneezing, sore throat or runny nose. Contact with skin can cause irritation or severe burns and scarring with greater exposures. Causes irritation of eyes, and with greater exposures it can cause burns that may result in permanent impairment of vision, even blindness.
Pyridine	Flammable Irritant	5 ppm-TWA	Inhalation causes severe irritation to the respiratory tract. Symptoms of overexposure include headache, dizziness, nausea, and shortness of breath. Causes severe irritation possibly burns, to the skin. Symptoms include redness and severe pain. Absorption through the skin may occur, resulting in toxic effects similar to inhalation. May act as a photosensitizer. Vapors cause eye irritation. Splashes cause severe irritation, possible corneal burns and eye damage.
Barbituric Acid	Irritant	Not established	Limited information. Inhalation may irritate respiratory tract. Causes skin and eye irritation. Should be treated as potential health hazard; do not ingest.

Material (1)	Hazards	Exposure Limit (2)	Signs and symptoms of exposure
Potassium Hydroxide	Poison Corrosive Reactive	2 mg/m^3 – Ceiling	Inhalation symptoms may include coughing, sneezing, damage to the nasal or respiratory tract. High concentrations can cause lung damage. Swallowing may cause severe burns of mouth, throat and stomach. Other symptoms may include vomiting, diarrhea. Severe scarring of tissue and death may result. Contact with skin can cause irritation or severe burns and scarring. Causes irritation of eyes with tearing, redness, swelling. Greater exposures cause severe burns with possible blindness.
Potassium Cyanide	Poison Corrosive	5 Mg/M3 TWA as CN	**This material will form Hydrogen Cyanide (HCN) gas when combined with strong acids. Breathing HCN gas may result in death.** Corrosive to the respiratory tract. May cause headache, weakness, dizziness, labored breathing nausea and vomiting, which can be followed by weak and irregular heartbeat, unconsciousness, convulsions, coma and death. Solutions are corrosive to the skin and eyes, and may cause deep ulcers, which heal slowly. May be absorbed through the skin, with symptoms similar to those noted for inhalation. Symptoms may include redness, pain, blurred vision, and eye damage.
Silver Nitrate	Poison Corrosive Oxidizer	0.01mg/m^3 (TWA) for silver metal dust and fume as Ag	Inhalation symptoms may include burning sensation, coughing, wheezing, laryngitis, shortness of breath, headache, nausea, and vomiting. May be absorbed into the body following inhalation. Swallowing can cause severe burns of the mouth, throat and stomach. Can cause sore throat, vomiting, and diarrhea. Poison. Symptoms include pain and burning in the mouth, blackening of the skin and mucous membranes, throat, and abdomen, salivation, vomiting of black material, diarrhea, collapse, shock, coma and death. Skin contact can cause redness, pain and severe burns. Eye contact can cause blurred vision, redness, pain, severe tissue burns and eye damage.
Hydrochloric Acid	Corrosive Poison	5 ppm – Ceiling	Inhalation of vapors can cause coughing, choking, inflammation of the nose, throat, and upper respiratory tract, and in severe cases, pulmonary edema, circulatory failure, and death. Can cause redness, pain, and severe skin burns. Vapors are irritating and may cause damage to the eyes. Contact may cause severe burns and permanent eye damage.
1 – Always add acid to water to prevent violent reactions.			
2 – Exposure limit refers to the OSHA regulatory exposure limit.			

7.0 SAMPLE CONTAINERS, COLLECTION AND PRESERVATION

7.1 Samples are collected in plastic bottles, stored at 4°C (±2°C) and transported to the laboratory as soon as possible. Sample bottles are never reused.

7.2 Water samples are preserved with 2 mL of 10N sodium hydroxide per liter of sample (pH > 12) and ascorbic acid at the time of collection.

7.3 Soil samples are not dried prior to analysis; a separate percent solids determination must be made.

7.4 Samples must be analyzed within the 14 days of collection. If samples are delayed in transit or received after the holding time, the client is notified.

8.0 APPARATUS AND MATERIALS

8.1 Magnet stir plate.

8.2 Magnets.

8.3 Beakers, 100 mL.

8.4 Graduated Cylinder.

9.0 REAGENTS AND STANDARD PREPARATION

9.1 All chemicals are to conform to the specifications set by the Reagent Chemical Committee of the American Chemical Society.

9.2 Reagent water (ASTM type II equivalent).

9.3 Sodium hydroxide solution, 0.25N: Dissolve 10g of NaOH in reagent water and dilute to 1 liter.

9.4 Ascorbic acid: crystals.

9.5 Calcium Hypochlorite solution, 5%: Dissolve 5g of $Ca(OCl)_2$ in reagent water and dilute to 1 liter.

10.0 CALIBRATION

10.1 Balance Calibration (only required for soil samples).

The top loading balance used in weighing stock reagents, percent solids, and soil samples is calibrated daily by comparing observed values with known values of 0.50, 5.00, and 50.00g Class S weights.

The calibration is performed in the following manner:

Depress the "Tare" bar on the balance to "zero" the instrument. When the zero (0.00g) signal is stable for 10 seconds or more, place a standard weight onto the pan. Allow the reading to stabilize. When stable for 10 seconds or more, record the reading.

Acceptance criteria is ±0.01g of the true value of the standard weight for the 0.50g and 5.00g Class S weights and ±0.10g for the 50.00 g Class S weight.

11.0 QUALITY CONTROL

11.1 The practical quantitation limit for this method is determined by the distillation and development SOP (CT-CVS-20) utilized following this pretreatment procedure.

11.2 A method blank (MB) consisting of reagent water processed through the pretreatment procedure must be prepared and analyzed with each batch of twenty or fewer samples to be analyzed. The values for the method blank must be recorded in ug/L for aqueous samples and in mg/Kg for solid samples.

11.3 One duplicate sample shall be analyzed from each group of twenty or fewer samples of a similar matrix type (i.e. water, soil). Samples identified as field blanks cannot be used for duplicate analysis.

12.0 SAMPLE PREPARATION AND INSTRUMENTAL PROCEDURES

12.1 Two sample aliquots are required to determine cyanide amenable to chlorination. The first aliquot is analyzed for total cyanide. The second aliquot shall be pretreated by the following procedure prior to distillation.

12.1.1 To one 150 mL beaker, add a 50 mL aliquot of a water sample or 1.0 g of soil with 50 mL of reagent water. Verify pH greater than 11, correct with sodium hydroxide if necessary. Add calcium hypochlorite solution dropwise while agitating and maintaining the pH between 11 and 12 with sodium hydroxide.

CAUTION: The initial reaction product of alkaline chlorination is the very toxic gas cyanogen chloride; therefore, it is required that this reaction be performed in a hood. For convenience, the sample shall be agitated by means of a magnetic stirring device.

12.1.2 Test for residual chlorine with KI-starch paper and maintain this excess for 1 hour while agitating. A distinct blue color on the test paper indicates a sufficient chlorine level. If necessary, add additional hypochlorite solution.

12.1.3 After 1 hour, add small portions of ascorbic acid until KI-starch paper shows no residual chlorine. Add an additional 0.25g of ascorbic acid to ensure the presence of excess reducing agent. Maintain pH between 11 and 12 during entire chlorination/ dechlorination procedure.

12.1.4 Distill and test for total cyanide in both the intact and pretreated aliquots. For distillation procedure, refer to CT-CVS-20. The difference of total cyanide of the intact sample less the cyanide of the pretreated aliquot is reported as "cyanide amenable to chlorination".

13.0 CALCULATIONS

13.1 All distillation (prep) data including sample volume/weight and distillate volume is entered into LIMS. Total cyanide and nonamenable (chlorinated sample) results are exported from the Lachat autoanalyzer instrument into LIMS. Amenable cyanide results are then autocalculated by LIMS.

13.2 Manual Calculation:

Amenable CN = A - B

where:

A = Total CN (ug/L for waters or mg/Kg for soils).
B = Pretreated (chlorinated) aliquot CN (ug/L for waters or mg/Kg for soils). This is the nonamenable cyanide.

NOTE: Soil results are always reported on a dry weight basis.

13.3 Relative Percent Difference

The Relative Percent Difference is calculated as follows:

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

where: S = Sample result
D = Duplicate result

14.0 ACCEPTANCE CRITERIA

14.1 Method blanks: All method blank results must be less than the PQL.

Action on failure: If the cyanide concentration in the blank is above the PQL, the lowest concentration of cyanide in the associated samples must be 10x the blank concentration. Otherwise, all samples associated with the blank with a cyanide concentration less than

10x the blank concentration and above the PQL must be redistilled and reanalyzed.

14.2 Duplicate Sample Analysis: A control limit of 20% for RPD shall be applied for original and duplicate sample results greater than or equal to 5x PQL. A control limit of ± the PQL shall be used if either the sample or the duplicate value is less than 5x PQL.

Action on failure: If the duplicate results are outside the control limits, flag all the data for samples associated with the duplicate sample with an asterisk (*).

15.0 REPORTING OF RESULTS

15.1 All distillation data including sample volume/weight and distillate volume is entered into LIMS in a prep batch. Total cyanide and nonamenable cyanide results are exported from the instrument into LIMS and amenable cyanide results are then autocalculated by LIMS.

15.2 Case narratives should include information received on NCM's to document any holding time problems or any other problems associated with sample analysis.

16.0 POLLUTION PREVENTION

16.1 Pollution prevention is the reduction and/or elimination of wastes or the toxicity of wastes at the point of generation. The laboratory strives to keep all wastes at a minimum through a variety of techniques. These include the following.

16.1.1 Inventory control: Rotate stocks (first in, first out) and only purchase reasonable amounts of chemicals. Do not purchase excessive quantities, which will be discarded as wastes at some future point.

16.1.2 Material Handling and Storage: Keep containers properly labeled. Keep solvents covered. Store and handle all chemicals, reagents, standards, etc. to prevent contamination and degradation.

16.1.3 Personnel: All staff must be trained in the proper handling and disposal of waste.

16.1.4 Waste Reduction: Reduce the volume of waste generated whenever possible.

16.1.5 Chemical/material substitution: Use less toxic chemicals whenever possible. Avoid the use of chromic acid (Chromerge) solutions.

17.0 WASTE MANAGEMENT

17.1 Waste Management and Pollution Prevention

All waste will be disposed of in accordance with Federal, State and Local regulations. Where reasonably feasible, technological changes have been implemented to minimize the potential for pollution of the environment. Employees will abide by this method and the policies in section 13 of the Corporate Safety Manual for "Waste Management and Pollution Prevention."

17.2 Waste Streams Produced by the Method

- Wastewater contaminated with Pyridine. Employees are to collect and dispose of this material in satellite pyridine waste accumulation drums.

18.0 SUPPLEMENTAL DOCUMENTS

18.1 SOP for Cyanide Analysis by Method 335.4 (Doc# CT-CVS-20).

19.0 REFERENCES

19.1 Methods for Chemical Analysis of Water and Wastes, EPA 600, Method 335.1, 1983.

19.2 Standard Methods For the Examination of Water and Wastewater, Method 4500-CN G, 18th Edition, 1992.

20.0 SUBSTANTIVE REVISIONS

20.1 Original document.

20.2 Cover page added; laboratory name changed from "IEA" to "STL"; company name in section 6.2 revised to "STL", 06/25/02.

20.3 Sections 3.0, 16.0, and 17.0 added, remaining sections renumbered, 06/25/02.

20.4 Document reference in section 1.0 revised; document number in sections 11.1 and 18.1 revised; sections 13.1 and 15.1 revised to reflect change to Labnet reporting system; title of section 14.0 revised; reference to Data Reporting SOP in section 18.0 eliminated, 06/25/02.

20.5 Health and Safety Officer signature added, 10/20/04.

20.6 Sections 6.0 and 17.0 revised to reflect more detailed safety and waste management information, 10/20/04.

20.7 No substantive revisions, 06/07/05.

20.7.1 Changed name from "Severn Trent Laboratories" to TestAmerica Laboratories," 08/03/07.

20.8 Revised Section 4.2 and added19.2 to reference Standard Methods 4500-CN G, 08/03/07.

20.9 Eliminated hydrochloric acid and sodium cyanide from Section 6.2, 08/03/07.

20.10 Revised Sections 13.1 and 15.1 to reference LIMS, 08/03/07.

20.11 Added Appendix, 08/03/07.

20.12 Added new TestAmerica SOP header and control number, 08/24/07.

20.13 Revised acceptance criteria for Class S weights in Section 10.1, 12/04/09.

20.14 Added hydrochloric acid to chart in Section 6.2, 12/04/09.

20.15 Changed instructions in Appendix A, 12/04/09.

APPENDIX

Printing the Nonamenable Cyanide Run:

Click on “Tools,” “Custom Report,” then “FIA FORMAT,” then “print.” This provides a hard copy of the analytical run.

To send the run to PDF Creator, chose “PDF Creator” and “print.” The raw data file in PDF Creator can be attached to the LIMS batch.

Exporting the Nonamenable Cyanide Data to LIMS:

To export the nonamenable cyanide data to LIMS, after the analysis is completed, click on the “Run” tab and then click “Export Data To File.” Minimize the screen and doubleclick on the yellow OMNION folder. Find the nonamenable results file and change the name. (For example: C091204.csv) Open the file and click on the FIA Export icon at the top of the screen. (The icon looks like a running man.) This stores the data in FIA LIMS as a text file. Open the results file and change the extension from “Cyanide” to “Cyanide(na).” Click “Save.” Right click and “send to” 4500-CN-G.”

Title: Sop for Ammonia Analysis, Easy-Dist/FIA [Method(s) 350.1, SM 4500NH_3 B and 4500NH_3 H]

Approvals (Signature/Date):

Doreen Nemeth 2/12/10
Technical Manager Date

2/11/10
Health & Safety Manager / Coordinator Date

Marsha K. Culik-Interim 2/11/10
Quality Assurance Manager Date

C.L. 2/22/10
Laboratory Director Date

This SOP was previously identified as SOP No. CVS02605.CT.

Facility Distribution No. Electronic **Distributed To: Facility Intranet**

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1.0 APPROVALS

The approval of the Laboratory Director, the Facility QA Manager, Group Leader and Health and Safety Officer signify that the document has been prepared in accordance with the format requirements that have been established in this document. In addition, if the document is a Method SOP the signature signifies that it meets the specified requirements.

2.0 SCOPE AND APPLICATION

2.1 The distillation procedure is applicable to drinking, surface, saline, and groundwaters, and domestic and industrial wastes, and sediments.

2.2 The working range for ammonia by the automated phenate development procedure is 0.04 to 4.00 mg/L. Working ranges may be extended with sample dilution.

2.3 The document control number for this SOP is CT-CVS-26, Rev 7.

2.4 This method is based upon EPA 600 Method 350.1.This method can also be used for method 4500NH_3 B and 4500NH_3 H (Standard Methods).

3.0 TERMS AND DEFINITIONS

3.1 Refer to the SOP for Laboratory Term and Definitions.

4.0 SUMMARY OF METHOD

4.1 The distillation method is a scaled-down version of Method 350.1 using EASY-DIST: Ammonia Preliminary Distillation Step for Colorimetric Phenate Analysis.

4.1 The sample is buffered at a pH of 9.5 with a borate buffer in order to decrease hydrolysis of cyanates and organic nitrogen compounds, and is then distilled into a solution of 0.04N sulfuric acid.

4.2 The ammonia in the distillate can be determined colorimetrically on the Lachat Quikchem Automated Ion Analyzer. During this procedure, ammonia reacts with alkaline phenol then with sodium hypochlorite producing indophenol blue. Sodium nitroprusside is then added to increase sensitivity. The absorbance of the reaction product is measured at 630nm and is directly proportional to the original ammonia concentration.

4.3 This method is based upon EPA method 350.1.

5.0 INTERFERENCES

5.1 Calcium and magnesium ions may precipitate if present in sufficient concentration; tartrate or EDTA is added to prevent this problem.

5.2 Residual chlorine must be removed by pretreatment of the sample with sodium thiosulfate prior to distillation.

6.0 SAFETY

Employees must abide by the policies and procedures in the Corporate Safety Manual, Radiation Safety Manual and this document.

6.1 SPECIFIC SAFETY CONCERNS OR REQUIREMENTS

Sodium Nitroferricyanide will generate Hyrdogen Cyanide (HCN) gas if combined with strong acids. Inhalation of CN gas can cause irritation, dizziness, nausea, unconsciousness and potentially death.

6.2 PRIMARY MATERIALS USED

The following is a list of the materials used in this method, which have a serious or significant hazard rating. **NOTE: This list does not include all materials used in the method. The table contains a summary of the primary hazards listed in the MSDS for each of the materials listed in the table.** A complete list of materials used in the method can be found in the reagents and materials section. Employees must review the information in the MSDS for each material before using it for the first time or when there are major changes to the MSDS.

Material (1)	Hazards	Exposure Limit (2)	Signs and symptoms of exposure
Phenol	Corrosive	5 ppm-TWA	Breathing vapor, dust or mist results in digestive disturbances. Will irritate, possibly burn respiratory tract. Rapidly absorbed through the skin with systemic poisoning effects to follow. Discoloration and severe burns may occur, but may be disguised by a loss in pain sensation. Eye burns with redness, pain, blurred vision may occur. May cause severe damage and blindness.
Sodium Hydroxide	Corrosive	2 Mg/M3-Ceiling	Severe irritant. Effects from inhalation of dust or mist vary from mild irritation to serious damage of the upper respiratory tract, depending on severity of exposure. Symptoms may include sneezing, sore throat or runny nose. Contact with skin can cause irritation or severe burns and scarring with greater exposures. Causes irritation of eyes, and with greater exposures it can cause burns that may result in permanent impairment of vision, even blindness.
Sodium Nitroferri-cyanide	Poison	5 mg/m^3 as HCN gas	This material may cause irritation if it comes into the contact with the skin. **The materials will give off HCN gas if combined with strong acids. Inhalation of HCN gas can cause irritation, dizziness, nausea, unconsciousness and potentially death.**
Sulfuric Acid	Corrosive Oxidizer Dehydrator Poison Carcinogen	1 Mg/M3-TWA	Inhalation produces damaging effects on the mucous membranes and upper respiratory tract. Symptoms may include irritation of the nose and throat, and labored breathing. Symptoms of redness, pain, and severe burn can occur. Contact can cause blurred vision, redness, pain and severe tissue burns. Can cause blindness.
1 – Always add acid to water to prevent violent reactions.			
2 – Exposure limit refers to the OSHA regulatory exposure limit.			

7.0 SAMPLE CONTAINERS, COLLECTION AND PRESERVATION

7.1 Sample containers may be of plastic or glass, sample containers are not to be reused.

7.2 Soil samples are collected without preservatives. Water samples are preserved with H_2SO_4 at a pH less than 2. Samples are packaged and sent to the laboratory and stored at 4 deg. C until analysis.

7.3 The holding time for ammonia is 28 days from the date and time of sampling for soils and waters. The NYSDEC holding time for ammonia is 26 days from the verified time of sample receipt (VTSR).

8.0 APPARATUS AND MATERIALS

8.1 EASY-Dist distillation apparatus for Ammonia Distillation, shown assembled in Figure 1, consisting of:

Part No.	Description
483-G001-01	Boiling Tube
483-G010-01	Stopper
483-G009-01	Sloped T-joint
483-G012-01	Mini-Allihn Condensers
483-G020-01	Graduated Cylinder, 50-mL
483-1022-01	WestClip7 (size 19/22), 2 each
483-G025-01	Micro-porous boiling stones
483-G016-01	Condenser Stem

8.2 Heater block and Temperature controller

8.3 Volumetric flasks, class A.

8.4 Pipets, class A.

8.5 Lachat QuikChem IC + FIA 8000 equipped with a sampler, proportioning pump, colorimeter with 630nm filter, computer, and printer.

8.6 Lachat ammonia chemistry manifold

8.7 Disposable borosilicate sample tubes

8.8 Analytical balance, 0.1mg sensitivity

8.9 Top-loading balance, 0.1g sensitivity

9.0 REAGENTS AND STANDARD PREPARATION

9.1 Reagent water, ASTM type II equivalent.

9.2 Sodium Hydroxide, 0.1 N: Add 4.00 grams NaOH pellets slowly to 250 mL of nano water in a 1 liter volumetric flask. Dilute to the mark with reagent water.

9.3 Sulfuric Acid Solution, 0.04N: Add 1 mL of concentrated sulfuric acid to 1 L of reagent water and mix thoroughly.

9.4 Sodium Tetraborate Buffer: Dissolve 9.5 g of anhydrous sodium tetraborate in 500 mL of nano water. Add 88 mL of 0.1 N sodium hydroxide and dilute to 1 liter with reagent water and mix thoroughly.

9.5 Phosphate Buffer Solution, pH 7.4 for soils: Dissolve 14.3 g of anhydrous potassium dihydrogen phosphate, KH_2PO_4, and 68.8 g anhydrous dipotassium hydrogen phosphate , KH_2PO_4, and dilute to 1 L with reagent water.

9.6 Ammonium Chloride Stock Solution, 1000 mg/L: Dissolve 3.819 g of ammonium chloride (NH_4Cl) that has been dried for two hours at 110°C in reagent water, and dilute to 1 liter with reagent water.

9.7 Ammonium Chloride Standard Solution, 40.0 mg/L: Dilute 40 mL of ammonium chloride stock solution (9.6) to 1 liter in a volumetric flask with reagent water.

9.8 Ammonium Chloride Standard Solution, 10.0 mg/L: Dilute 10 mL of ammonium chloride stock solution (9.6) to 1 liter in a volumetric flask with reagent water.

9.9 Sodium Hydroxide, 6 N: Add 240 grams NaOH pellets slowly to 750 mL of reagent water in a 1 liter volumetric flask. Dilute to the mark with reagent water.

9.10 Phenolphthalein Indicator: Dissolve 0.080 g of phenolphthalein in 100 mL of methanol.

9.11 Dechlorinating Reagent: Dissolve 3.5 g of sodium thiosulfate (5 hydrate) in reagent water and dilute to 1 liter. One mL of this solution will remove 1 mg/L of residual chlorine in 500 mL of sample.

9.12 Sodium phenolate: In a 1 liter volumetric, dissolve 88mL of 88% liquified phenol (C_6H_5OH) or 83g of crystalline phenol in approximately 600mL of reagent water. While stirring, sowly add 32g of sodium hydroxide (NaOH). Cool, dilute to volume, and invert three times.

9.13 Sodium hypochlorite: Dilute 250mL of household bleach (containing 5.25% NaOCl) to

500mL with reagent water.

9.14 Buffer: In a 1 liter volumetric flask, dissolve 50.0g disodium ethylenediamine tetraacetate (Na_2EDTA) and 5.5g sodium hydroxide (NaOH) in about 900mL of reagent water. Dilute to volume and invert three times.

9.15 Sodium nitroprusside: Dissolve 3.50g of sodium nitroprusside in 1 liter of reagent water.

9.16 Standard Calibration Curve: Prepare the series of standards listed in table 1.

Table 1. Calibration Curve Standards

Initial Standard Concentration (mg/L)	Initial Standard Volume (mL)	Final Volume (mL) Add 50 mls of 0.04 NH_2SO_4	Final Concentration (mg/L)
40.0	25	250	4.00
40.0	10	250	1.60
10.0	25	250	1.00
10.0	10	250	0.40
10.0	2.5	250	0.10
NA	NA	250	0.00 ***

Standards are good for one month.
Bring to volume with reagent water.
***** Use for ICB, CCB's, and diluent.**

10.0 CALIBRATION

10.1 Instrument Calibration

The spectrophotometer must be calibrated each time the instrument is set up. The instrument standardization date and time shall be included in the raw data. Calibration standards must be prepared fresh each month. Prepare a blank and the standards indicated in Section 9.16. NOTE: one calibration standard must be at the Contract

Required Detection Limit (PQL); the PQL for ammonia is 0.10 mg/L. Standards must bracket the concentration of the samples. Results for the calibration standards must fall within 10% of true value. The correlation coefficient for the curve must be greater than or equal to 0.995.

10.2 Refer to Section 12.0 for use of the QuikCalc II/Omnion Software System.

10.3 To set up the standard curve on the sampler: Obtain a vial for each standard. Starting with the 4.00 mg/L standard, fill the vial and place it in the standards rack. Continue with the other standards, in order of decreasing concentration. Refer to section 9.16.

10.4 When the calibration is complete, the analyst will then proceed to review the calibration data. If the correlation coefficient is 0.995 or greater, continue with sample analysis. For calibration failure, determine the cause of failure, correct it, and recalibrate.

10.5 The calibration range for ammonia is 0.10 to 4.00 mg/L.

11.0 QUALITY CONTROL

11.1 Method detection limits are calculated based on the Appendix B 40 CFR Part 136 definition of method detection limit and are performed annually.

11.2 The practical quantitation limit (PQL) for ammonia is 0.10 mg/L.

11.3 Stock solutions and working standards are coded and entered into LIMS.

11.4 All chemicals are to conform to minimum specifications set by the Committee of the American Chemical Society. All chemical inventories are to be used on a first in, first out basis. Reagents are coded and entered into LIMS.

11.5 A preparation blank per matrix using reagent water is to be analyzed with every batch of twenty or fewer samples.

11.6 A sample duplicate per matrix is to be analyzed with every batch of ten or fewer samples. Samples identified as field blanks are not to be used for duplicate analysis.

11.7 A sample spike per matrix is to be analyzed with every batch of twenty or fewer samples unless there is a NYSDEC/SW846 protocol in which an additional spike duplicate will be analyzed. Samples identified as field blanks are not to be used for spike analysis.

Samples are spiked by adding via a pipet 10 mL of 10.0 mg/L to a sample prior to distillation. The theoretical spike added is 2.00 mg/L for waters and 100 mg/Kg for soils.

11.8 One independent standard or laboratory control standard (LCS) for ammonia is to be analyzed with each batch of 20 samples.

11.9 All sample distillates with concentrations above 4.00 mg/L must be diluted and reanalyzed.

11.10 Initial and Continuing Calibration:

Activity	Frequency
Initial Calibration Verification (ICV)	Onset of every analytical run
Initial Calibration Blank (ICB)	Immediately following the ICV
Continuing Calibration Verification (CCV)	After the ICB, every ten samples, and after the last analytical sample.
Continuing Calibration Blank (CCB)	Immediately following each CCV

NOTE: Initial and continuing calibration standards are run at a concentration of 1.00 mg/L.

11.11 Record all NBS "S" weights where applicable.

12.0 SAMPLE PREPARATION AND INSTRUMENTAL PROCEDURES

12.1 Distillation Procedure

12.1.1 Waters: Adjust the pH of a 50 mL sample aliquot to pH 9.5 in a boiling tube using phenolphthalein indicator. Add 6N NaOH dropwise, with mixing, to adjust the sample pH to 9.5; sample will turn pink. Add 5 mL of borate buffer solution (9.4); mix sample. Add 2-3 micro-porous boiling stones.

Soils: Weigh 1.0 g or less of wet sediment into a boiling tube. Add 50 mL of deionized, ammonia-free water.. Add 1.0 mL of phosphate buffer, mix sample. Check pH and re-adjust sample to final pH of 6.6 if necessary using NaOH. Add 2-3 micro-porous boiling stones.

NOTE: Percent solids must be determined for soil sample analysis.

12.1.2 Assemble the distillation apparatus as shown in Figure 1, in the heater block. For each boiling tube, place a 50-mL graduated cylinder containing 10 mL of 0.04N sulfuric acid under the condenser. Turn on condenser water

> Note: Connect the condensers in series as shown in **Figure** 2. Up to ten condensers may be connected in series from a single cold water source. The source may be branched with a "T"-connector to feed two rows of ten condensers. Connect the condensers in series with 12-inch long sections of silicone tubing. The long tubing is required to allow individual movement of the connected condensers.

12.1.3 Place the condenser stem in the graduated cylinder, slide cylinder and stem under condenser, and connect stem to condenser with Westclip. When assembled, the condenser tip of the distillation apparatus will be submerged in the receiving solution contained in the graduated cylinder.

Note: Due to the minimal clearance between the condenser stem and the bottom of the graduated cylinder, it is easiest to place the stem in the cylinder, slide the cylinder under the condenser, and then connect the stem to the condenser.

12.1.4 Heat the distillation apparatus.
Set heater block temperature controls to the following settings:

RATE 1: 15° C/min
TEMP 1: 180° C
TIME 1: 6.0 Hour (max)

RATE 2: 0
TEMP 2: 210° C
TIME 2: 0

Timing Configuration: CONF 1

The rate of distillate collection may vary with laboratory and condenser water temperature. The final volume of distillate may be collected in a shorter or longer period of time, adjust the TIME 1 value accordingly, or manually stop the program.

12.1.5 Set the block temperature to 180° C and distill each sample until 40 to 45 mL of distillate has been collected. As each graduated cylinder collects 40- 45 mL of distillate, carefully remove the stopper from the T-joint ; disconnect the stem from the condenser.

CAUTION: THE STOPPER WILL BE VERY HOT, AND STEAM MAY BE EMITTED; WEAR PROTECTIVE GLOVES AND GLASSES.

12.1.6 Remove the graduated cylinder from the apparatus and dilute the collected distillate to a final volume of 50 mL with reagent water. If the distillate is turbid, filter it through a pre-washed 0.45 pm membrane filter prior to analysis.

12.2 <u>Lachat System Operation</u>:

12.2.1 Inspect modules for proper connections, and turn on the power to all modules.

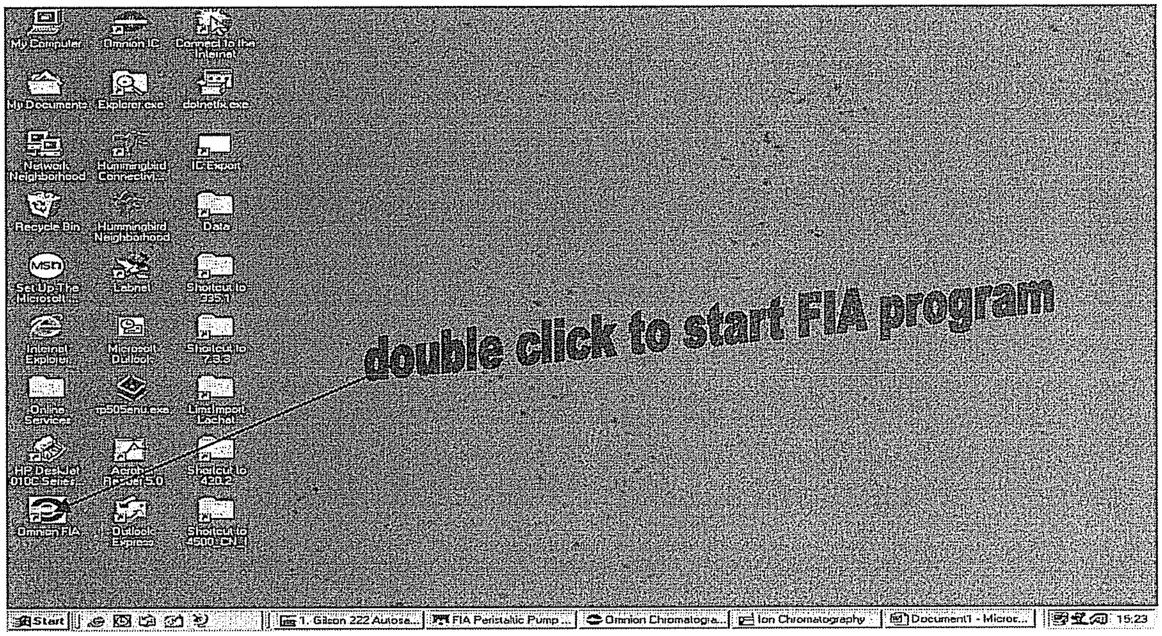
12.2.2 Degas all reagents with Helium prior to use to prevent bubble formation. (The carrier is degassed reagent water.) Use He at $20 lb/in^2$ through a gas dispersion tube. Bubble He vigorously through the solution for one minute. Place reagent feed lines into the proper containers. Raise the tension levers on the pump tube cassettes.

12.2.3 Place the calibration standards in the standard tray in descending order of concentration as detailed in step 10.3. Load the sample tray with calibration verification standards and blank(s) as outlined in step 11.10, laboratory control standard(s), preparation blank(s), sample duplicate(s), and spike(s).

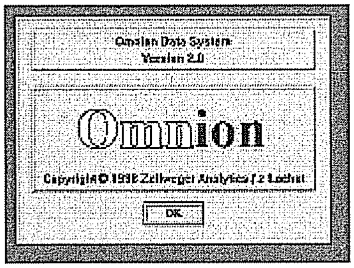
12.2.4 Position the standard and sample trays for proper sampling.

12.2.5 Preparation of Calibration and Sample Trays:

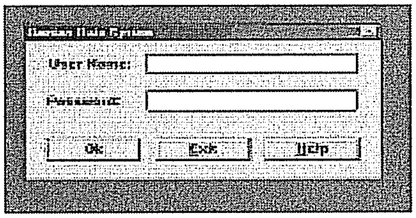
12.2.5.1 Turn on Lachat computer.



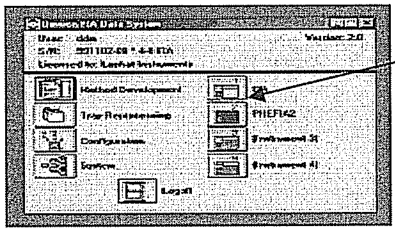
double click to start FIA program



Click OK

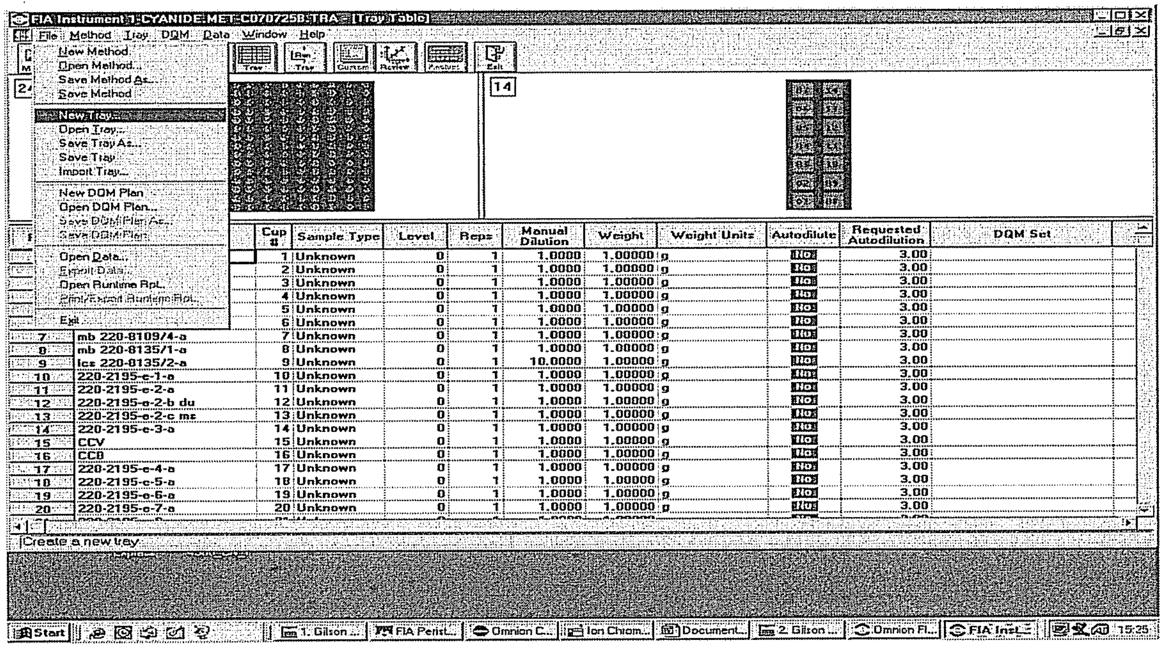


Enter User name and Password then click OK



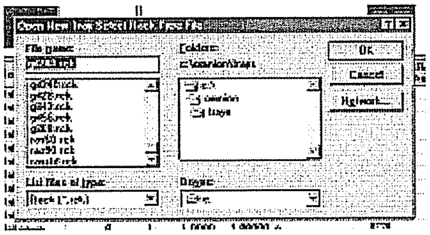
Double click FIA

A screen similar to the one below will appear and click file (the top left menu item) then choose new tray.

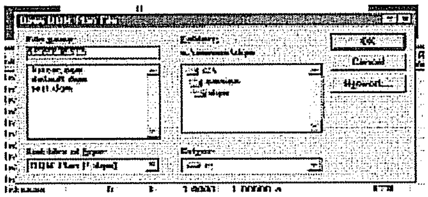


		Cup #	Sample Type	Level	Reps	Manual Dilution	Weight	Weight Units	Autodilute	Requested Autodilution	DQM Set
		1	Unknown	0	1	1.0000	1.00000	g	No	3.00	
		2	Unknown	0	1	1.0000	1.00000	g	No	3.00	
		3	Unknown	0	1	1.0000	1.00000	g	No	3.00	
		4	Unknown	0	1	1.0000	1.00000	g	No	3.00	
		5	Unknown	0	1	1.0000	1.00000	g	No	3.00	
		6	Unknown	0	1	1.0000	1.00000	g	No	3.00	
7	mb 220-8109/4-a	7	Unknown	0	1	1.0000	1.00000	g	No	3.00	
8	mb 220-8135/1-a	8	Unknown	0	1	1.0000	1.00000	g	No	3.00	
9	lcs 220-8135/2-a	9	Unknown	0	1	10.0000	1.00000	g	No	3.00	
10	220-2195-e-1-a	10	Unknown	0	1	1.0000	1.00000	g	No	3.00	
11	220-2195-e-2-a	11	Unknown	0	1	1.0000	1.00000	g	No	3.00	
12	220-2195-e-2-b du	12	Unknown	0	1	1.0000	1.00000	g	No	3.00	
13	220-2195-e-2-c ms	13	Unknown	0	1	1.0000	1.00000	g	No	3.00	
14	220-2195-e-3-a	14	Unknown	0	1	1.0000	1.00000	g	No	3.00	
15	CCV	15	Unknown	0	1	1.0000	1.00000	g	No	3.00	
16	CCB	16	Unknown	0	1	1.0000	1.00000	g	No	3.00	
17	220-2195-e-4-a	17	Unknown	0	1	1.0000	1.00000	g	No	3.00	
18	220-2195-e-5-a	18	Unknown	0	1	1.0000	1.00000	g	No	3.00	
19	220-2195-e-6-a	19	Unknown	0	1	1.0000	1.00000	g	No	3.00	
20	220-2195-e-7-a	20	Unknown	0	1	1.0000	1.00000	g	No	3.00	

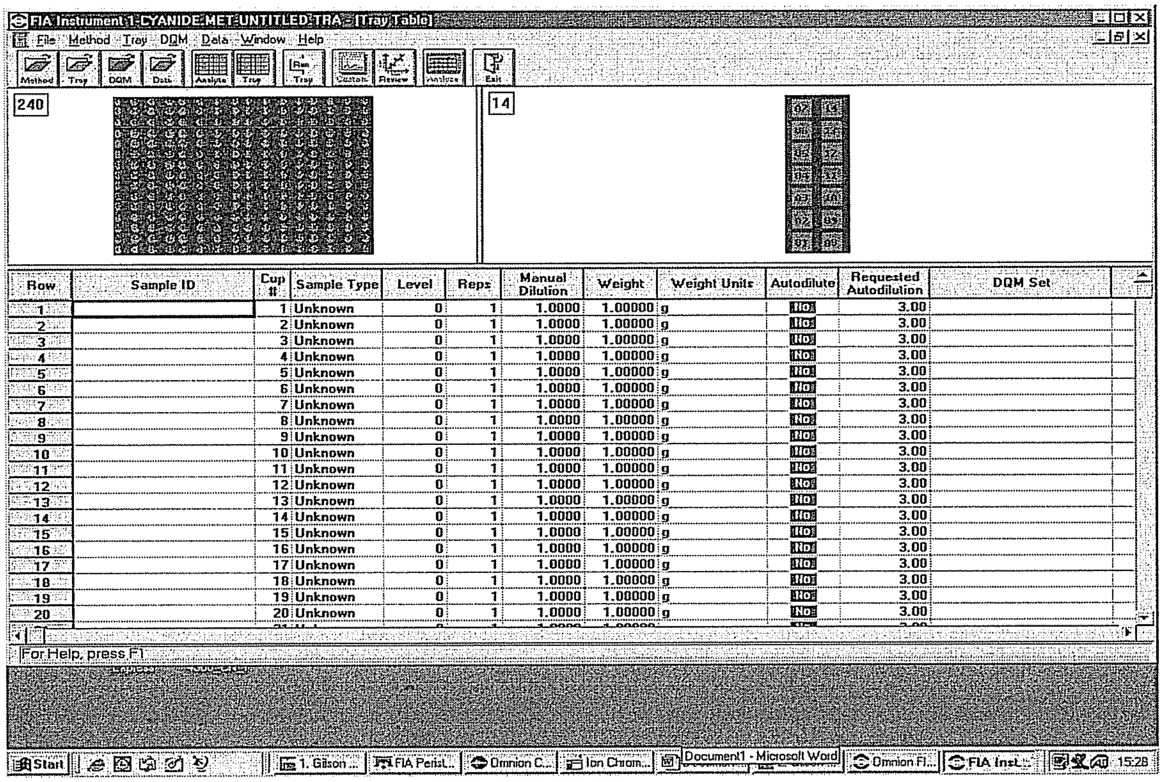
Create a new tray



Click OK

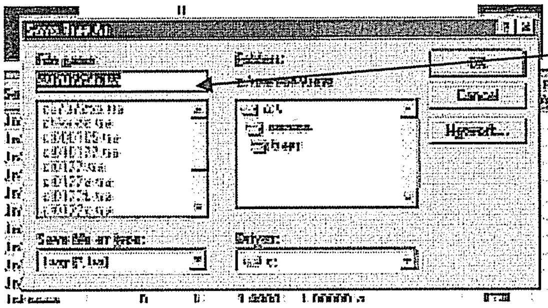


Click OK



Row	Sample ID	Cup #	Sample Type	Level	Reps	Manual Dilution	Weight	Weight Units	Autodilute	Requested Autodilution	DQM Set
1		1	Unknown	0	1	1.0000	1.00000	g	No	3.00	
2		2	Unknown	0	1	1.0000	1.00000	g	No	3.00	
3		3	Unknown	0	1	1.0000	1.00000	g	No	3.00	
4		4	Unknown	0	1	1.0000	1.00000	g	No	3.00	
5		5	Unknown	0	1	1.0000	1.00000	g	No	3.00	
6		6	Unknown	0	1	1.0000	1.00000	g	No	3.00	
7		7	Unknown	0	1	1.0000	1.00000	g	No	3.00	
8		8	Unknown	0	1	1.0000	1.00000	g	No	3.00	
9		9	Unknown	0	1	1.0000	1.00000	g	No	3.00	
10		10	Unknown	0	1	1.0000	1.00000	g	No	3.00	
11		11	Unknown	0	1	1.0000	1.00000	g	No	3.00	
12		12	Unknown	0	1	1.0000	1.00000	g	No	3.00	
13		13	Unknown	0	1	1.0000	1.00000	g	No	3.00	
14		14	Unknown	0	1	1.0000	1.00000	g	No	3.00	
15		15	Unknown	0	1	1.0000	1.00000	g	No	3.00	
16		16	Unknown	0	1	1.0000	1.00000	g	No	3.00	
17		17	Unknown	0	1	1.0000	1.00000	g	No	3.00	
18		18	Unknown	0	1	1.0000	1.00000	g	No	3.00	
19		19	Unknown	0	1	1.0000	1.00000	g	No	3.00	
20		20	Unknown	0	1	1.0000	1.00000	g	No	3.00	

The above Screen appears where you can enter the sample identification and their respective dilutions. Then you can save the file by clicking file at the left top menu and a window like the one below appears.



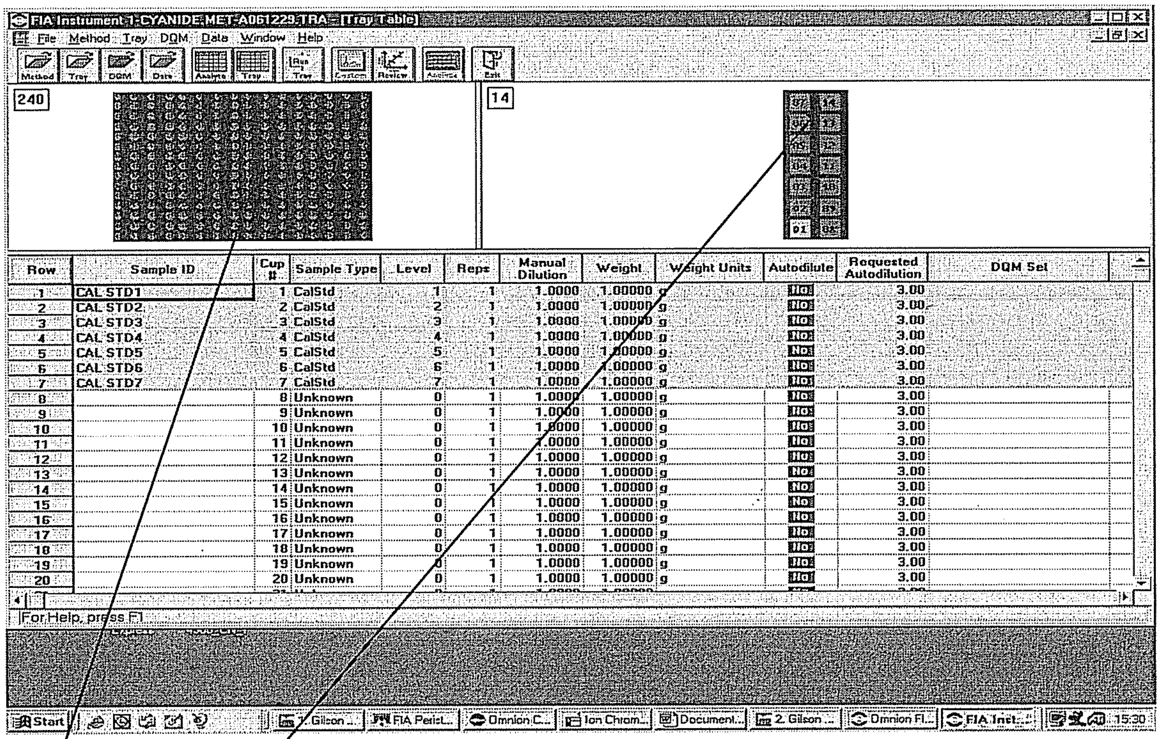
Enter the tray name as AYYMMDDA

Tray letter
Date of month
Month of Year
Year
A for Ammonia

Ie A070728A

For a calibration tray do not add a Tray letter.

Always copy a calibration tray from a previous run tray by opening a previous tray and saving it as a new tray following the above nomenclature without the tray letter. A calibration tray will look like the one below:



Row	Sample ID	Cup #	Sample Type	Level	Reps	Manual Dilution	Weight	Weight Units	Autodilute	Requested Autodilution	DQM Set
1	CAL STD1	1	CalStd	1	1	1.0000	1.00000	g	No	3.00	
2	CAL STD2	2	CalStd	2	1	1.0000	1.00000	g	No	3.00	
3	CAL STD3	3	CalStd	3	1	1.0000	1.00000	g	No	3.00	
4	CAL STD4	4	CalStd	4	1	1.0000	1.00000	g	No	3.00	
5	CAL STD5	5	CalStd	5	1	1.0000	1.00000	g	No	3.00	
6	CAL STD6	6	CalStd	6	1	1.0000	1.00000	g	No	3.00	
7	CAL STD7	7	CalStd	7	1	1.0000	1.00000	g	No	3.00	
8		8	Unknown	0	1	1.0000	1.00000	g	No	3.00	
9		9	Unknown	0	1	1.0000	1.00000	g	No	3.00	
10		10	Unknown	0	1	1.0000	1.00000	g	No	3.00	
11		11	Unknown	0	1	1.0000	1.00000	g	No	3.00	
12		12	Unknown	0	1	1.0000	1.00000	g	No	3.00	
13		13	Unknown	0	1	1.0000	1.00000	g	No	3.00	
14		14	Unknown	0	1	1.0000	1.00000	g	No	3.00	
15		15	Unknown	0	1	1.0000	1.00000	g	No	3.00	
16		16	Unknown	0	1	1.0000	1.00000	g	No	3.00	
17		17	Unknown	0	1	1.0000	1.00000	g	No	3.00	
18		18	Unknown	0	1	1.0000	1.00000	g	No	3.00	
19		19	Unknown	0	1	1.0000	1.00000	g	No	3.00	
20		20	Unknown	0	1	1.0000	1.00000	g	No	3.00	

For Help, press F1

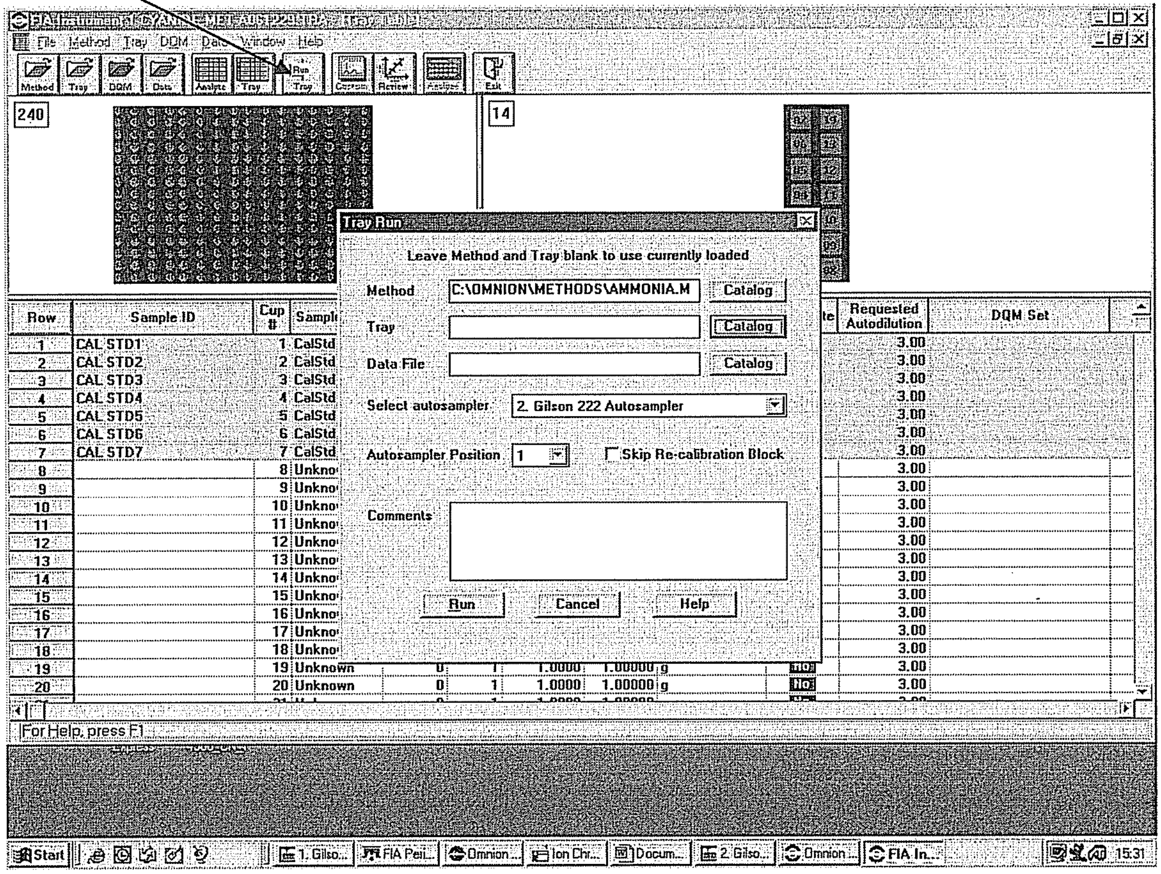
Sample trays

Calibration trays are different from sample trays for they hold only 14 bigger cups while sample trays hold 60 smaller cups.

The Calibration trays are placed to the most right of the tray holder and sample trays are placed to the most left of the tray holder. More than one sample trays can be placed on the tray holder depending on the number of samples. The sample trays are loaded the first tray the first left then followed by the second and so forth, but the last tray holder on the right is the calibration tray.

After placing the calibration tray and /or sample tray, the Instrument is ready to run. Make sure all needed reagents are in place and the ammonia chemistry board is attached with the heater set at 60°C then let the reagents run by turning the reagent pump on. When the heater reaches 60°C the trays are ready to run.

To start a tray run, click the run tray button



Leave Method and Tray blank to use currently loaded

Method: C:\OMNION\METHODS\AMMONIA.M

Tray:

Data File:

Select autosampler: 2. Gilson 222 Autosampler

Autosampler Position: 1 ☐ Skip Re-calibration Block

Comments:

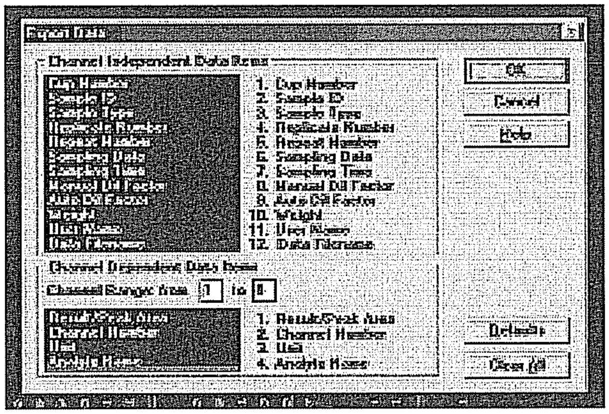
Row	Sample ID	Cup #	Sample	Requested Autodilution	DQM Set
1	CAL STD1	1	CalStd	3.00	
2	CAL STD2	2	CalStd	3.00	
3	CAL STD3	3	CalStd	3.00	
4	CAL STD4	4	CalStd	3.00	
5	CAL STD5	5	CalStd	3.00	
6	CAL STD6	6	CalStd	3.00	
7	CAL STD7	7	CalStd	3.00	
8		8	Unkno	3.00	
9		9	Unkno	3.00	
10		10	Unkno	3.00	
11		11	Unkno	3.00	
12		12	Unkno	3.00	
13		13	Unkno	3.00	
14		14	Unkno	3.00	
15		15	Unkno	3.00	
16		16	Unkno	3.00	
17		17	Unkno	3.00	
18		18	Unkno	3.00	
19		19	Unknown 0 1 1.0000 1.00000 g No	3.00	
20		20	Unknown 0 1 1.0000 1.00000 g No	3.00	

The run tray menu appears as above:
In the method click catalogue on the right pull down menu and choose ammonia.
In the Tray click catalogue on the right pull down menu and choose the tray you want to run Calibration or Sample tray.
In the Data file type the same file name as the tray then click run, and the channel window will appear and you will

see the peaks of the ammonia samples/ calibration as they run.

Exporting data to LIMS

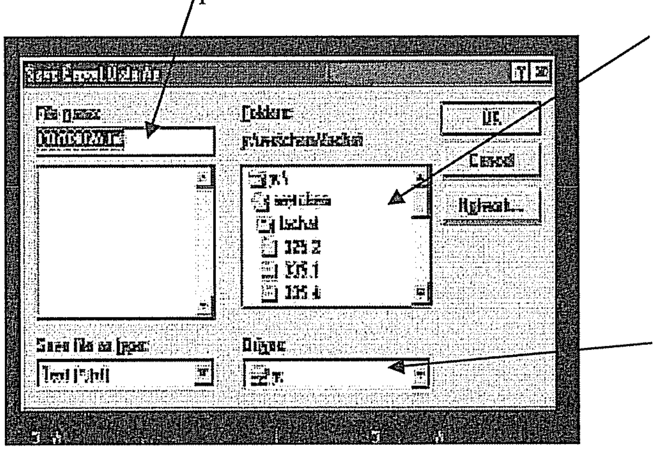
To export data to LIMS, go to file and choose Export data and an export data window as shown below opens



Click OK

The following window appears.

File name to be exported



Choose the method you want to export to

Choose Y drive: \Consvr04\rawdata

The click OK and the data file will be exported to LIMS.

12.2.6 After all the samples have been analyzed, place all the feedlines in reagent water. Flush the system and pump dry. Turn off the pump, and release the tension levers on the pump tube cassettes.

13.0 CALCULATIONS

13.1 The sample results (with dilution factors included) are calculated on the Lachat Quikchem 8000 Autoanalyzer. Results for water samples can be retrieved directly from this data.

13.2 To calculate ammonia content in soils:

$$\text{Ammonia mg/Kg} = \frac{\text{A x DF x V}}{\text{Sample wt.(g) x dec. \% solids}}$$

where: A = sample Lachat result (mg/L)
V = distillation volume (mL)
DF = dilution factor

13.3 Relative Percent Difference Calculation:

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

where: S = Original sample result
D = Duplicate sample result

13.4 Sample Matrix Spike Recovery Calculation:

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

where: SSR = Spiked sample result (mg/L)
SR = Sample result (mg/L)
SA = Spike added (mg/L)

13.5 The LCS, ICV, and CCV recovery are calculated:

$$\text{Percent Recovery} = (VM / TV) \times 100$$

Where: VM = value measured (mg/L).
TV = true value (mg/L).

14.0 ACCEPTANCE OF DATA:

14.1 The technical data review includes verifying that samples analyzed were preserved (if waters) and that the holding times were met (soils and waters). The raw data is examined for completeness. Results are imported into LIMS.

14.2 Initial Calibration Verification (ICV): The control limit for the ICV is ±10 percent of true value.

Action on failure: When measurements exceed the control limit, the analysis must be terminated, the problem corrected, the instrument recalibrated, and the calibration verified.

14.3 Continuing Calibration Verification (CCV): The control limit for the CCV is ±10 percent of true value.

Action on failure: When measurements exceed the control limit, the instrument must be recalibrated, the calibration verified, and the preceding ten samples analyzed since the last compliant calibration verification must be reanalyzed.

14.4 Initial Calibration Blank (ICB) and Continuing Calibration Blank (CCB): The value of the concentration in the blank must be less than or equal to 1/2 the PQL.

Action on failure: If the value of the calibration blank result exceeds 1/2 the PQL, terminate analysis, correct the problem, recalibrate, verify the calibration, and reanalyze the preceding ten analytical samples or all analytical samples analyzed since the last compliant calibration blank.

14.5 All method blank results must be less than the PQL.

Action on failure: If a preparation blank's concentration exceeds the reporting limit, all samples that were prepared with the preparation blank and have a concentration less than ten times the preparation blank's concentration, must be rerun.

14.6 Laboratory Control Standard: The recovery of the independent standard must be within ±10 percent of the known concentration.

Action on failure: If the recovery of the LCS is not within control limits, the calibration fails. The problem must be identified and corrected prior to any further analysis or acceptance of any data.

14.7 Sample Duplicates: The RPD for the sample duplicate must not exceed 20 percent. If the sample and duplicate concentrations are less than five times the PQL, no RPD criteria is applied.

Action on failure: If the RPD is not within control limits, rerun the sample and sample duplicate.

14.8 Spike Sample Recovery: The control limit for spike recovery is ± 10 percent.

Action on failure: If the spike fails, the sample must be spiked again and reanalyzed or if the sample concentration exceeds four times the spiking level, no criteria is applied.

15.0 REPORTING OF RESULTS

15.1 Results are imported into LIMS.

15.2 Aqueous Ammonia results are reported in mg/L; soil results are reported in mg/Kg.

15.3 NCM's must be written if any problems are associated with the analysis.

15.4 Case narratives should include information received on NCM's to document any holding time problems or any other problems associated with sample analysis.

15.5 The practical quantitation limit for water samples is 0.10 mg/L. The practical quantitation limit for soil samples is 5.00 mg/Kg (based an 100 % solids). Report three significant figures for all results.

16.0 POLLUTION PREVENTION

16.1 Pollution prevention is the reduction and/or elimination of wastes or the toxicity of wastes at the point of generation. The laboratory strives to keep all wastes at a minimum through a variety of techniques. These include the following.

16.1.1 Inventory control: Rotate stocks (first in, first out) and only purchase reasonable amounts of chemicals. Do not purchase excessive quantities, which will be discarded as wastes at some future point.

16.1.2 Material Handling and Storage: Keep containers properly labeled. Keep solvents covered. Store and handle all chemicals, reagents, standards, etc. to prevent contamination and degradation.

16.1.3 Personnel: All staff must be trained in the proper handling and disposal of waste.

16.1.4 Waste Reduction: Reduce the volume of waste generated wherever possible.

16.1.5 Chemical/material substitution: Use less toxic chemicals whenever possible. Avoid the use of chromic acid (Chromerge) solutions.

17.0 WASTE MANAGEMENT AND POLLUTION PREVENTION

All waste will be disposed of in accordance with Federal, State and Local regulations. Where reasonably feasible, technological changes have been implemented to minimize the potential for pollution of the environment. Employees will abide by this method and the policies in section 13 of the Corporate Safety Manual for "Waste Management and Pollution Prevention."

17.1 Waste Streams Produced by the Method

The following waste streams are produced when this method is carried out.

- Acidic sample waste generated by sample preparation. Employees are to collect and dispose of this material in satellite acid waste accumulation drums.

- Aqueous waste generated by the Lachat Quickchem 8000. Employees are to collect and dispose of this material in satellite acid waste accumulation drums.

18.0 SUPPLEMENTAL DOCUMENTS

18.1 SOP for Laboratory Term and Definitions.

19.0 REFERENCES

19.1 Methods for Chemical Analysis of Water and Wastes, EPA 600, Method 350.1, Revision 2.0, 1993.

19.2 Standard Methods For the Examination of Water and Wastewater, Methods 4500-NH_3 B and 4500-NH_3 H, 18th edition, 1992.

19.3 Methods Manual for the Quikchem Automated Ion Analyzer, Lachat Instruments, Method 10-107-06-1-C, 1986.

20.0 SUBSTANTIVE REVISIONS

20.1 Original document.
20.2 Modified document to substitute automated phenate method for nessler development, 09/15/99.
Added sections 3.0 and 15.0, 09/15/99.
Revised section 14.0, 09/15/99.

20.3 Added sections 16.0 and 17.0, 10/01/99.

20.4 Revised sections 11.3, 11.4, 14.1, and 15.1 to reflect change to Labnet reporting system, 05/16/02.

20.5 Added Health and Safety Officer Signature, Section 1.0 – 10/14/04.

20.6 Sections 6.0 and 17.0 revised to reflect more detailed safety, waste management information – 10/14/04.

20.7 No substantive revisions – 05/31/05.

20.8 Changed name from "Severn Trent Laboratories" to "TestAmerica Laboratories," 08/01/07.

20.9 Changed Section 12 from Macro distillation to Easy-Dist block distillation, 08/01/07.

20.10 Revised Section 12.2 from QuikChem AE Lachat analysis to QuikChem 8000 Lachat

Analysis, 08/01/07.

20.11 Revised Section 12.2.5 to include illustrations from FIA program on preparation of calibration and sample trays, 08/01/07.

20.12 Added new TestAmerica SOP header and control number, 08/24/07.

20.13 Changed PQL from 0.04 mg/L to 0.10 mg/L, 09/18/07.

20.14 Revised acceptance criteria for LCS and MS to ±10 percent, 12/22/09.

APPENDIX

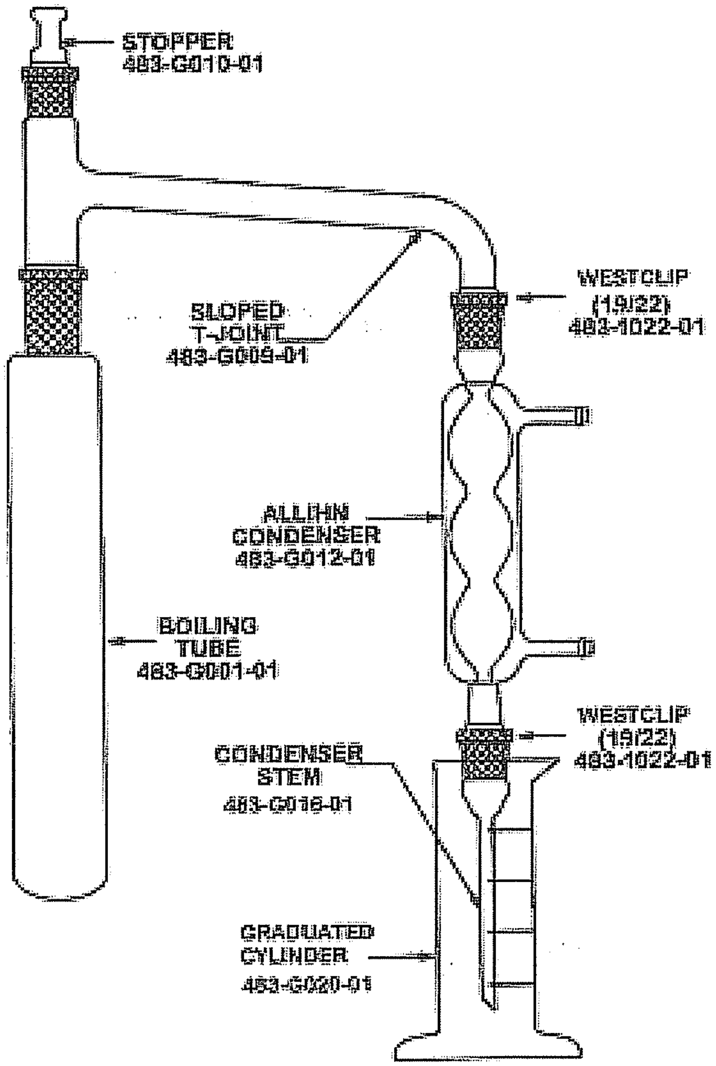


Figure 1: EASY-Dist Ammonia Distillation Apparatus

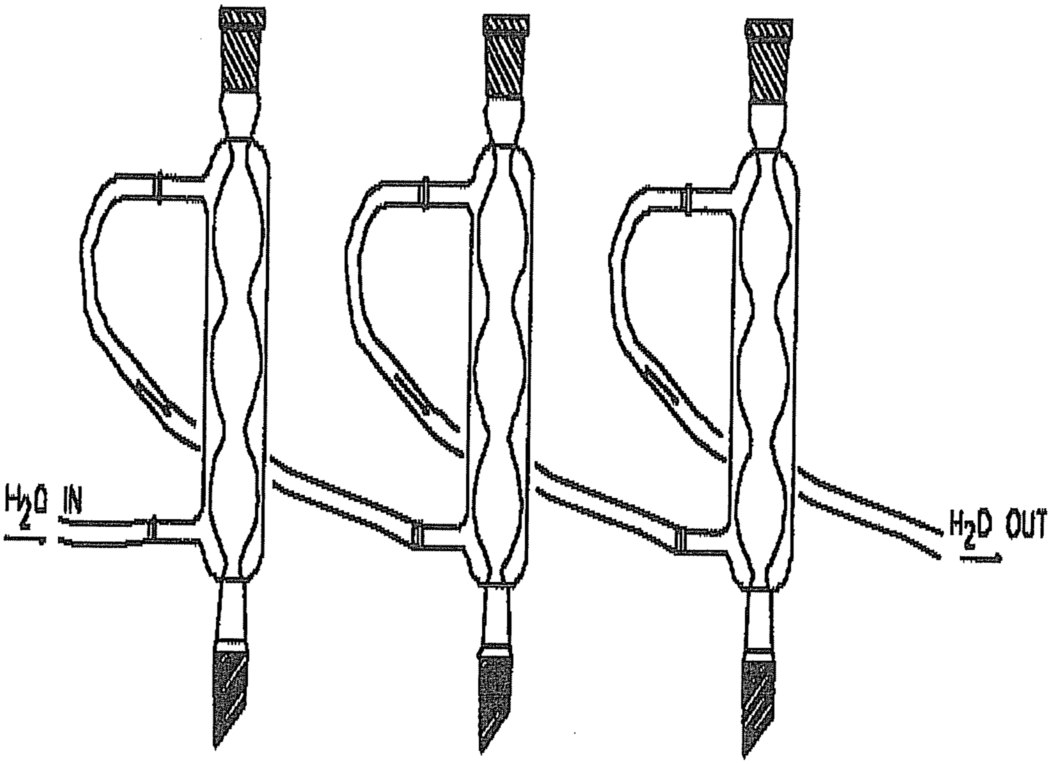


Figure 2: Allihn Condensers Connected in Series

Title: SOP for pH in Soils/Corrosivity
[Method SW846 9045C]

Approvals (Signature/Date):

Dawn Nemeth 8/3/09
Technical Manager Date

David W. Helfrich 8/3/09
Health & Safety Manager/Coordinator Date

Dawn May 8/3/09
Quality Assurance Manager Date

8/3/09
Laboratory Director Date

This SOP was previously identified as SOP No. CVS04605.CT.

Controlled Source: **\\consvr05\users\share\sops\Controlled SOPs**

Distributed to: -

1.0 APPROVALS

The approval of the Laboratory Director, the Facility QA Manager, Group Leader and Health and Safety Officer signify that the document has been prepared in accordance with the format requirements that have been established in this document. In addition, if the document is a Method SOP the signature signifies that it meets the specified requirements.

2.0 SCOPE AND APPLICATION

2.1 This method is applicable to the pH/corrosivity characteristic (per RCRA) of soils and waste samples. Wastes may be solids, sludges, or non-aqueous liquids. If water is present, it must represent less than 20% of the total volume of the sample.

2.2 The document control number for this document is CT-CVS-46, Rev. 6.

3.0 TERMS AND DEFINITIONS

Refer to the SOP for Laboratory Terms and Definitions.

4.0 SUMMARY OF METHOD

4.1 The soil or solid waste is mixed with reagent water and the pH is determined electrometrically using a combination glass electrode after the pH meter has been calibrated using buffers of a known pH. A. The sample exhibits the corrosivity characteristic if it has a pH less than or equal to 2.0 or greater than or equal to 12.5.

4.2 This SOP is based upon EPA SW846 Method 9045C.

5.0 INTERFERENCES

5.1 The combination glass pH electrode, in general, is not subject to solution interferences from color, turbidity, colloidal matter, oxidants, reductants, or high salinity.

5.2 Coatings of oily material or particulate matter can impair electrode response. Electrodes with coatings of oily material or particulate matter can be cleaned with gentle wiping or detergent washing followed by rinsing with reagent water. Electrodes can be additionally treated with 1:10 HCL to remove any remaining film.

5.3 Temperature fluctuations will cause measurement errors. pH meters with an ATC or automated temperature compensation probe will minimize this error.

6.0 SAFETY

Employees must abide by the policies and procedures in the Corporate Safety Manual, Radiation Safety Manual and this document. This procedure may involve hazardous material, operations and equipment. This SOP does not purport to address all of the safety problems associated with its use. It is the responsibility of the user of the method to follow appropriate safety, waste disposal and health practices under the assumption that all samples and reagents are potentially hazardous. Safety glasses, gloves, lab coats and closed-toe, nonabsorbent shoes are a minimum.

6.1 SPECIFIC SAFETY CONCERNS OR REQUIREMENTS

None

6.2 PRIMARY MATERIALS USED

There are no materials used in this method that have a serious or significant hazard rating. **NOTE: This list does not include all materials used in the method.** A complete list of materials used in the method can be found in the reagents and materials section. Employees must review the information in the MSDS for each material before using it for the first time or when there are major changes to the MSDS

6.3 At a minimum, wear PVC gloves, a lab coat and eye protection when handling samples and reagents.

6.4 Always refer to the Corporate Safety Handbook prior to performing laboratory operations.

7.0 SAMPLE CONTAINERS, COLLECTION AND PRESERVATION

7.1 A representative sample must be collected in either a clean 250ml plastic bottle or 4oz glass soil jar.

7.2 Samples should be stored at 4^{o}C. Because pH is considered a field parameter, results are flagged with “HF” signifying that the analysis was not performed within 15 minutes of sampling.

7.3 No preservatives should be added to the samples that will be tested for pH/corrosivity.

8.0 APPARATUS AND MATERIALS

8.1 pH meter with automatic temperature correcting electrode.

8.2 Combination glass electrode, Ross Model 8104 or equivalent

8.3 Beakers, 50ml

8.4 Graduated cylinder, 25ml

8.5 Magnetic Stir Plate, Magnetic Stir Bars, small

8.6 Top-loading balance

8.7 Class S Weights

8.8 Standard pH buffer Solutions, 4.00, 7.00, 10.00.

9.0 REAGENTS AND STANDARD PREPARATION

9.1 Reagent water (ASTM Type II)

9.2 Standard buffers (4.00, 7.00, 10.00) may be prepared from NBS salts or purchased as solutions from commercial vendors. These commercially available solutions have been validated by comparison with NBS standards and are normally used by the laboratory.

10.0 CALIBRATION

10.1 Each pH meter is calibrated following manufacturer's instructions. See Appendix A for specific instrument calibration instructions.

10.2 Each instrument/electrode system must be calibrated at a minimum of two points that bracket the expected pH of the samples and are approximately three pH units or more apart. The VWR meter is calibrated using pH buffers 4.00, 7.00, and 10.00. The pH 7.00 buffer is then used to verify correct instrument operation. Buffers should read within 0.05 pH units of correct value.

10.3 If an automatic temperature correction (ATC) electrode is used, the meter will correct for temperature automatically. If the ATC is not used, the samples must be within 2°C of the buffers used for calibration.

11.0 QUALITY CONTROL

11.1 Method detection limits (MDLs) are not applicable.

11.2 All stock solutions and standard preparations are logged into LIMS and coded. All solutions are labeled with the following: analyte, concentration, analyst's initials, date prepared, and expiration date.

11.3 All chemicals will conform to minimum specifications set by the Reagent Chemicals

Committee of the American Chemical Society. All chemical inventories are used on a first in, first out basis.

11.4 A sample duplicate is to be analyzed with each batch of ten samples. Sample duplicates are analyzed on a separate aliquot of the original sample.

11.5 Matrix spikes are not applicable for this method.

11.6 A Laboratory Control Sample (LCS) is not applicable for this method.

12.0 SAMPLE PREPARATION AND INSTRUMENTAL PROCEDURES

12.1 Standardize the pH meter (see Section 10). Record values in the pH logbook.

12.2 All samples to be analyzed must be signed out of sample control on the chain-of-custody document for each job.

12.3 Sample preparation for soils or wastes: Place 20.0 grams of soil or waste in a clean 50 ml beaker with a magnetic stir bar; add 20 ml reagent water and stir 5 minutes. Record the sample weight and reagent water volume in the pH logbook. Let mixture stand for approximately 15 minutes to allow settling of the suspension. The sample may also be centrifuge or filtered.

Note 1: If the sample is hygroscopic, additional water may be added. If all the water is absorbed by the sample, repeat the test using 20-g sample and 40 mLs water.

Note 2: Verify the balance is operating correctly with a Class S weight. Record the value in the logbook.

12.4 Measurement of pH

12.4.1 Soils: do not stir when taking pH measurements. Immerse the pH electrode(s) in the sample so that the tips of the electrodes are immersed in the clear supernatant or suspension of the sample.

12.4.2 The pH meter READY light will come on when the reading has stabilized. Record the reading in the pH logbook to two decimal places. Also record the temperature to one decimal place.

12.4.3 Thoroughly rinse with reagent water and gently wipe the electrode between measurements.

12.4.4 After the completion of all pH measurements, store the electrode in an electrode storage solution as recommended by the manufacturer. Do not store the electrode in reagent water for an extended period.

13.0 CALCULATIONS

13.1 The pH meter reads directly in pH units. The sample is reported as corrosive, if it has a pH $\leq$2.0 or $\geq$12.5. Enter yes or no under corrosive in the pH logbook.

13.2 The relative percent difference is calculated as:

$$RPD = \frac{(S - D)}{(S + D)(0.5)} \times 100$$

S and D are readouts of sample and the duplicate.

14.0 ACCEPTANCE OF DATA

14.1 The technical data review includes verifying that samples analyzed were unpreserved and that holding times were met. The raw data is examined for completeness including a secondary review. Results directly entered into LIMS are checked for transcription error against the raw data.

14.2 Duplicate: The RPD for the duplicate must not exceed 20 percent (see Section 13.2 for RPD calculation).

Action on failure: If the RPD is out of control, rerun the sample and duplicate.

.

15.0 REPORTING OF RESULTS

15.1 Results are reported by entering the data collected in the pH logbook into LIMS.

15.2 Case narratives should include information received on NCM's. An NCM must be written explaining "HF" flags on sample results or any problems associated with the analysis of samples.

15.3 Report pH to two decimal places. Corrosivity is either a "Yes" or "No". Record the temperature of all pH measurements, including the buffers.

16.0 POLLUTION PREVENTION

It is TestAmerica's policy to evaluate each method and look for opportunities to minimize waste generated (i.e., examine recycling options, ordering chemicals based on quantity needed, preparation of reagents based on anticipated usage and reagent stability). Employees must abide by the policies in Section 13 of the Corporate Safety Manual for "Waste Management and Pollution Prevention."

16.1.1 Pollution prevention is the reduction and/or elimination of wastes or the toxicity of wastes at the point of generation. The laboratory strives to keep all wastes at a minimum through a variety of techniques. These include the following.

16.1.1 Inventory control: Rotate stocks (first in, first out) and only purchase reasonable amounts of chemicals. Do not purchase excessive quantities, which will be discarded as wastes at some future point.

16.1.2 Material Handling and Storage: Keep containers properly labeled. Keep solvents covered. Store and handle all chemicals, reagents, standards, etc. to prevent contamination and degradation.

16.1.3 Personnel: All staff must be trained in the proper handling and disposal of waste.

16.1.4 Waste Reduction: Reduce the volume of waste generated wherever possible.

16.1.5 Chemical/material substitution: Use less toxic chemicals whenever possible. Avoid the use of chromic acid (Chromerge) solutions.

17.0 WASTE MANAGEMENT

Waste management practices are conducted consistent with all applicable rules and regulations. Excess reagents, samples and method process wastes are disposed of in an accepted manner. Waste description rules and land disposal restrictions are followed. Waste disposal procedures are incorporated by reference to the Tracking and Collection of Hazardous Waste SOP. The following waste streams are produced when this method is carried out.

17.1 WASTE MANAGEMENT AND POLLUTION PREVENTION

All waste will be disposed of in accordance with Federal, State and Local regulations. Where reasonably feasible, technological changes have been implemented to minimize the potential for pollution of the environment. Employees will abide by this method and the policies in section 13 of the Corporate Safety Manual for “Waste Management and Pollution Prevention.”

17.2 Waste Streams Produced by the Method

The following waste streams are produced when this method is carried out.

- Acidic sample waste generated by the analysis. (Employees are to collect and dispose of this material in satellite acid waste accumulation drums).

- Alkaline sample waste generated by the analysis. (Employees are to dispose of this material in satellite waste accumulation drums).
- Exhausted soil samples utilized in the analysis. (Employees are to collect and dispose of this material in satellite soil waste accumulation drums).
- Exhausted acidic and/or alkaline buffer solutions utilized in the analysis. (Employees are to collect and dispose of this material in satellite waste accumulation drums).

18.0 SUPPLEMENTAL DOCUMENTS

18.1 SOP for pH in Water – CT-CVS-09.

18.2 SOP for Laboratory Terms and Definition.

19.0 REFERENCES

19.2 Test Methods for the Evaluation of Solid Waste, SW846, 3rd Edition, Method 9045C.

20.0 SUBSTANTIVE REVISIONS

20.1 Original issue - 3/17/97

20.2 Revised to incorporate Method 9040B, June 1999.

20.3 Additions:

(i) Section 3.0: Term and Definition, 10/08/99.
(ii) Section 16.0: Pollution Prevention, 10/08/99.
(iii) Section 17.0: Waste Management, 10/08/99.

20.4 Revised sections 11.3, 14.1, and 15.1 to include new data reporting system (Labnet), 05/29/02.

20.5 Revised title of SOP to include “RCRA”, 05/29/02.

20.6 Section 1: Added Health and Safety Officer signature. Section 6.0: Added new safety information . Section 9.2: Changed buffer solutions to 4.00, and 10.00. Section 8.0: Added pH Buffer Solutions, 4.00,7.00,10.00. Section 10.2: Changed 4,7,10 to 4.00,7.00, and 10.00. Section 11.0: Added section 11.7 stating that an LCS is not applicable for this analysis. Section 14.0: Deleted section 14.4 regarding Laboratory Control Samples. Section 17.0: Added new waste management section. Calibration of pH meter: changed buffers to 4.00,7.00,10.00 (06/08/04).

20.7 No substantive revisions, 05/31/05.

20.8 Changed name from “Severn Trent Laboratories” to “TestAmerica Laboratories,” Removed sections 17.3 and 17.4 from Waste Management. Added Method 9045C to references in Section 19.2, 07/31/07.

20.9 Revised entire document to TestAmerica format. Changed SOP to reference SW846 method 9045C only. Added reference to “HF” flag in sections 7.2 and 15.2. Updated Safety, pollution control and waste management sections. Updated supplemental document section – corrected reference. Corrected sect 5.2, typo from HCI to HCL. Added criteria to Appendix A work instruction. 7/31/09.

Appendix A

CALIBRATION OF VWR/SP MODEL 8025 pH METER

1. Obtain fresh aliquots of pH buffers 4.00, 7.00, & 10.00.

2. Press the “cal” key to initiate the calibration sequence. Select the 3PT, “3P7” calibration option by using the scroll (arrow) keys.

3. Immerse the electrodes in the pH 4.00 buffer. When the ready light comes on, indicating electrode stability, press the yes key to accept the value. Rinse the electrodes and place in reagent water. Buffer should read within 0.05 units of actual reading.

4. Immerse the electrodes in the pH 7.00 buffer. When the ready light comes on, indicating electrode stability, press the yes key to accept the value. Rinse the electrodes and place in reagent water. Buffer should read within 0.05 units of actual reading.

5. Immerse the electrodes in the pH 10.00 buffer. When the ready light comes on, indicating electrode stability, press the yes key to accept the value. Rinse the electrodes and place in reagent water. Buffer should read within 0.05 units of actual reading.

6. The SLP and calculated slope will be displayed for two seconds. The meter will automatically switch to the MEASURE mode.

7. To measure the pH of a sample, immerse the electrodes in the sample with stirring. When the ready light comes on, note the value and repeat the measurement on a fresh aliquot of sample. If the readings agree within 0.1 pH units, record the pH in the logbook.

Title: Sop for Total Phosphorus and Orthophosphate
[Method(s) SM 4500 P B/E]

Approvals (Signature/Date):

Doreen Nemeth 2/12/10
Technical Manager Date

2/11/10
Health & Safety Manager / Coordinator Date

Marsha K. Culik - interim 2/11/10
Quality Assurance Manager Date

2/22/10
Laboratory Director Date

This SOP was previously identified as SOP No. CVS04806.CT.

Facility Distribution No. Electronic **Distributed To: Facility Intranet**

The controlled copy of this SOP is the PDF copy of the SOP that is posted to the laboratory's SOP Directory. Printed copies of this SOP or electronic copies of this SOP distributed outside the facility are considered uncontrolled.

1.0 APPROVALS

The approval of the Laboratory Director, the Facility QA Manager, Group Leader and Health and Safety Officer signify that the document has been prepared in accordance with the format requirements that have been established in this document. In addition, if the document is a Method SOP the signature signifies that it meets the specified requirements.

2.0 SCOPE AND APPLICATION

2.1 This method is applicable to the examination of drinking, surface and saline waters, domestic and industrial wastes.

2.2 This method determines the measurement of total phosphorus and orthophosphate in concentrations above 0.10 mg/L in waters and above 10.0 mg/Kg in soils (based on 100% solids).

2.3 This method is based on the reactions that are specific for the orthophosphate ion. Depending on the pre-treatment, the various forms of phosphorus may be determined.

2.4 The document control number for this SOP is CT-CVS-48, Rev 7.

3.0 TERMS AND DEFINITIONS

3.1 There are many definitions used with in the laboratory, which may be generic to all laboratory analyses, or more specific for certain methods. For the most recent terms and definitions used with in the laboratory, reference the SOP for Terms and Definitions.

4.0 SUMMARY OF METHOD

4.1 Ammonium molybdate and antimony potassium tartrate react in an acid medium with dilute phosphorus solutions to form an antimony-phospho-molybdate complex. This complex is reduced by ascorbic acid to an intensely blue-colored complex, which is proportional to the phosphorus concentration.

4.2 The reporting of results as orthophosphate or total phosphorus is dependent on whether or not the digestion procedure was used.

4.3 This procedure is based on Standard Methods, 4500-P B,5 for persulfate digestion and 4500-P E for ascorbic acid determination of phosphorus.

5.0 INTERFERENCES

5.1 Arsenates react with the molybdate reagent to produce a blue color similar to that formed with phosphate. Concentrations as low as 0.1 mg As/L interfere with the phosphate determination.

5.2 Hexavalent chromium and NO_2^- interfere to give results about 3% low at concentrations of 1 mg/L and 10 to 15% low at 10 mg/L.

5.3 Sulfide (Na_2S) and silicate do not interfere at concentrations of 1.0 and 10 mg/L..

6.0 SAFETY

Employees must abide by the policies and procedures in the Corporate Safety Manual, Radiation Safety Manual and this document.

6.1 SPECIFIC SAFETY CONCERNS OR REQUIREMENTS

None

6.2 PRIMARY MATERIALS USED

The following is a list of the materials used in this method, which have a serious or significant hazard rating. **NOTE: This list does not include all materials used in the method. The table contains a summary of the primary hazards listed in the MSDS for each of the materials listed in the table.** A complete list of materials used in the method can be found in the reagents and materials section. Employees must review the information in the MSDS for each material before using it for the first time or when there are major changes to the MSDS.

Material (1)	Hazards	Exposure Limit (2)	Signs and symptoms of exposure
Potassium dihydrogen phosphate	Irritant Poison	None	May cause mild irritation to the respiratory tract. Potassium poisoning can result in heart effects, change in respiration rate, tingling in the extremities, heaviness in the limbs, nausea and diarrhea. May cause inflammation and pain on prolonged contact, especially with moist skin. Eye contact may cause irritation, redness, and pain. Chronic exposure: may sequester calcium and cause calcium phosphate deposits in the kidneys.
Ammonium Persulfate	Oxidizer	None	Causes irritation to the respiratory tract. Symptoms may include coughing, shortness of breath. Causes irritation to skin and eyes. Symptoms include redness, itching, and pain. May cause dermatitis, burns, and moderate skin necrosis.
Ammonium molybdate	Irritant	5 Mg/M3 TWA (as Mo)	Causes eye, skin, and respiratory tract irritation. Harmful if swallowed; causes gastrointestinal irritation with nausea, vomiting and diarrhea.
Antimony potassium tartrate	Irritant Poison	0.5 Mg (Sb)/M3 TWA	Causes irritation to the respiratory tract; symptoms include sore throat, coughing, and shortness of breath. Toxic! Ingestion may cause salivation, cough, metallic taste, nausea, vomiting, bloody diarrhea, dizziness, irritability, and muscle pains. May cause heart to beat irregularly or stop. Skin or eye contact may cause redness and pain. Chronic skin exposure may cause dermatitis; prolonged or repeated inhalation of dusts may cause blood, liver, and CNS effects, heart muscle damage, laryngitis, headache, weight loss, and anemia.
Ascorbic Acid	Irritant	None	Inhalation, eye or skin contact may cause mild irritation. Large oral doses may cause gastrointestinal disturbances.
Sodium Hydroxide	Corrosive	2 Mg/M3-Ceiling	Severe irritant. Effects from inhalation of dust or mist vary from mild irritation to serious damage of the upper respiratory tract, depending on severity of exposure. Symptoms may include sneezing, sore throat or runny nose. Contact with skin can cause irritation or severe burns and scarring with greater exposures. Causes irritation of eyes, and with greater exposures it can cause burns that may result in permanent impairment of vision, even blindness.
Phenolphthalein	Carcinogen	None	Ingestion can cause vomiting, collapse, and fall of blood pressure or an itching rash that may become ulcerous. Inhalation may cause coughing and sneezing. Eye contact: slight irritant. Skin contact: if absorbed through the skin, may produce symptoms resembling those for ingestion exposure. Chronic exposure: suspect cancer hazard.
Sulfuric Acid	Corrosive Oxidizer Dehydrator Poison Carcinogen	1 Mg/M3-TWA	Inhalation produces damaging effects on the mucous membranes and upper respiratory tract. Symptoms may include irritation of the nose and throat, and labored breathing. Symptoms of redness, pain, and severe burn can occur. Contact can cause blurred vision, redness, pain and severe tissue burns. Can cause blindness.

1 – Always add acid to water to prevent violent reactions.

2 – Exposure limit refers to the OSHA regulatory exposure limit.

7.0 SAMPLE CONTAINERS, COLLECTION AND PRESERVATION

7.1 Total phosphorus water samples are to be collected in plastic or glass, clean, unused bottles preserved with sulfuric acid (to a pH of <2), and stored at 4°C.

7.2 Orthophosphate water samples are to be collected in plastic or glass, unpreserved, and stored at 4°C.

7.3 Soil samples should be collected unpreserved in clean, unused glass bottles and stored at 4°C.

7.4 Samples are to be analyzed within 28 days of collection for total phosphorus. The NYSDEC protocol holding time is 26 days from the verified time of sample receipt (VTSR) at the laboratory for total phosphorus. Samples are to be analyzed within 48 hours of sampling or within 24 hours of receipt (NYSDEC protocol) for orthophosphate.

8.0 APPARATUS AND MATERIALS

8.1 Genesys 10 Series or equivalent visible spectrophotometer capable of measurements at 880 nm with a light path of 1 cm or greater

8.2 Quartz cuvette, 1 cm

8.3 Analytical balance, 0.1 mg sensitivity

8.4 Top-loading balance, 0.01 g sensitivity

8.5 Hot/stir plate

8.6 Beakers, 150 mL

8.7 Class A volumetric flasks, 100 mL, 50 mL

8.8 Class A volumetric pipettes

8.9 Graduated cylinders, 100 mL, 50 mL

Note: Glassware designated solely for phosphorus analysis is to be used. A cleaning procedure utilizing rinsing the designated glassware with 1:1 HCl followed by rinsing of reagent water must be employed. Commercial detergent for cleaning must be avoided.

9.0 REAGENTS AND STANDARD PREPARATION

9.1 All chemicals are to conform to the specifications set by the Reagent Chemical Committee of the American Chemical Society. Laboratory prepared nanopure water is used whenever Reagent ASTM II Water (ASTM D11930) is required.

9.2 Stock phosphorus standard, 50.0 mg/L: Dissolve 0.2195 g of potassium dihydrogen phosphate (KH_2PO_4), anhydrous, reagent grade (which has been previously oven dried at 105°C) in a 1 L volumetric flask containing approximately 800 mL reagent water. Dilute to volume with reagent water. Mix well.

9.3 Standard phosphorus solution, 5.00 mg/L: Dilute 10.0 mL of the stock phosphorus solution (step 9.2) to 100 mL with reagent water. Mix well.

9.4 Spiking Standards: Dilute each standard to 50 mL with regent water and proceed with analysis step 12.2 for total phosphorus and step 12.4 for orthophosphate.

Stock Conc. (mg/L)	Stock Volume (mL)	Final Volume (mL)	Final Conc. (mg/L)
5.00	1.0	50	0.10
5.00	2.0	50	0.20
5.00	3.0	50	0.30
5.00	5.0	50	0.50
5.00	7.5	50	0.75
50.0	1.0	50	1.00

9.5 Sulfuric acid solution, 5 N: Slowly and carefully add 70 mL of concentrated sulfuric acid (reagent grade) to approximately 400 mL reagent water. Cool and dilute to 500 mL with reagent water.

9.6 Ammonium persulfate, $(NH_4)_2S_2O_8$, reagent grade.

9.7 Ammonium molybdate solution: Dissolve 20.0g $(NH_4)_6Mo_7O_{24}.4H_2O$ in 500 mL reagent water.

9.8 Antimony potassium tartrate solution: Dissolve 1.3715g $K(SbO)C_4H_4O_6.1/2H_2O$ in approximately 400 mL of reagent water in a 500 mL volumetric flask. Dilute to volume with reagent water.

9.9 Ascorbic acid, 0.1 M: Dissolve 1.76 g of ascorbic acid, reagent grade in 100 mL of reagent water. This solution is stable for about 1 week at 4°C.

9.10 Sodium hydroxide solution, 6 N: Slowly and carefully add 240 g concentrated sodium hydroxide to approximately 800-mL reagent water. Cool and dilute to 1 L with reagent water.

9.11 Phenolphthalein indicator solution: Dissolve 0.5 g phenolphthalein in a solution of 50 mL ethyl or isopropyl alcohol and 50 mL reagent water.

9.12 Combined reagent: Prepare combined reagent just prior to use as follows.

	200 mL combined reagent	400 mL combined reagent
5 N H2SO4	100 mL	200 mL
Potassium antimony tartrate	10 mL	20 mL
Ammonium molybdate	30 mL	60 mL
Ascorbic acid	60 mL	120 mL

10.0 CALIBRATION

10.1 The spectrophotometer must be calibrated once a year using certified performance standards.

10.2 After 1/2 hour warm-up, set the wavelength to 880 nm, and zero the instrument according to manufacturer's instructions.

10.3 A 3-point curve confirmation will be performed using 0.10 mg/L, 0.50 mg/L, and 1.00 mg/L phosphorus standards prepared in step 9.4 on each day the analysis is run. An acceptable curve confirmation will result when all 3 points fall within 10 % of the annual 6-point curve.

10.4 An annual 6-point curve will be performed using 0.10 mg/L, 0.20 mg/L, 0.30 mg/L, 0.50 mg/L, 0.75 mg/L, and 1.00 mg/L phosphorus standards prepared in step 9.4. An acceptable curve will have a correlation coefficient of 0.995 or greater.

10.5 The working calibration range of this method is 0.10 to 1.00 mg/L.

11.0 QUALITY CONTROL

11.1 Method detection limits (MDLs) are calculated based on the 40 CFR Chapter 1 definition of method detection limit and are performed annually.

11.2 The practical quantitation limit (PQL) for water samples is 0.10 mg/L; for soil samples, the PQL is 10.0 mg/Kg (based on 100 % solids).

11.3 All stock solutions and standard preparations are logged into LIMS. All solutions are labeled with the following: analyte, concentration, analyst's initials, date prepared, and expiration date.

11.4 All chemicals are to conform to minimum specifications set by the Reagent Chemical Committee of the American Chemical Society. All chemical inventories are used on a first in, first out basis.

11.5 The spectrophotometer is zeroed with a calibration blank prior to use.

11.6 A method blank per matrix using reagent water is to be analyzed with every batch of twenty or fewer samples.

11.7 A sample duplicate per matrix is to be analyzed with every batch of ten or fewer samples. Samples identified as field blanks are not to be used for duplicate analysis.

11.8 A sample spike per matrix is to be analyzed with every batch of twenty or fewer samples unless there is a NYSDEC protocol in which an additional spike duplicate will be analyzed. Samples identified as field blanks are not to be used for spike analysis.

To spike: For total phosphorus, pipette 1.0 mL of the 50.0 mg/L stock solution (prepared in step 9.2) into the 150 mL beaker. Add 100 mL of the well-dispersed sample if a water and continue with step 12.2 or add 1.0 g if a soil or sludge and continue with step 12.3. For orthophosphate, pipette 0.5 mL of the 50.0 mg/L stock solution (prepared in step 9.2) into a 150 mL beaker. Add 50 mL of the well-dispersed sample and continue with step 12.4 or add 1.0 g if a soil and continue with step 12.5.

11.9 An independent laboratory control standard (LCS) per matrix is to be analyzed with every batch of twenty or fewer samples.

11.10 Record all NBS "S" weights where applicable.

11.11 Initial and Continuing Calibration Table:

ACTIVITY	FREQUENCY
Initial Calibration Verification	Onset of every analytical run.
Initial Calibration Blank	Immediately after the ICV.
Continuing Calibration Verification	After the ICB, every 10 samples, and at the end of the run.
Continuing Calibration Blank	Immediately after each CCV.

Note: The ICV and CCV are prepared at the concentration of 0.50 mg/L.

12.0 SAMPLE PREPARATION AND INSTRUMENTAL PROCEDURES

12.1 All samples to be analyzed must be signed out of sample control on the chain-of-custody (COC) for each job. All phosphorus data is recorded in the Phosphorus logbook.

12.2 Preparation of water samples for total phosphorus:

12.2.1 Using a graduated cylinder, transfer 100 mL of a well-dispersed sample to a 150-mL beaker.

12.2.2 Use 0.10 mg/L, 0.50 mg/L, and 1.00 mg/L standards prepared in step 9.4 on each day the analysis is run. Additionally prepare an initial calibration verification standard and continuing calibration verification standard at concentrations of 0.50 mg/L.

12.2.3 Transfer 50-mL aliquots of reagent water into beakers to be analyzed as the calibration blank, initial calibration blank, continuing calibration blank, and the preparation blank.

12.2.4 Use an appropriate quantity of a LCS to be analyzed in the working calibration range of the method.

12.2.5 Add 0.05 mL (1 drop) of phenolphthalein indicator solution. If a red color develops, add H_2SO_4 solution dropwise to just discharge the color. Then add 1 mL H_2SO_4 solution.

12.2.6 Add 0.4 g ammonium persulfate.

12.2.7 Boil gently on a preheated hot plate until a volume of approximately 10-20 mL is reached. Do not allow the sample to go to dryness. Cool. Dilute to approximately 30 mL by rinsing the walls of the beaker with reagent water.

Note: If necessary, filter samples before proceeding with neutralization in step 12.2.8.

12.2.8 Add one drop phenolphthalein indicator solution to the sample. Neutralize to a faint pink color with the addition of 6N NaOH.

12.2.9 Transfer 0.10 mg/L, 0.50 mg/L, 1.00 mg/L standards, ICV, ICB, CCV, CCB, LCS, and the preparation blank to 50-mL volumetric flasks and dilute to volume with reagent water.

12.2.10 Transfer the samples to 100-mL volumetric flasks and dilute to volume with reagent water. Using a graduated cylinder, transfer 50-mL of the well dispersed, diluted digestates into clean 150-mL beakers. Proceed with step 12.6.

12.3 **Preparation of soil or sludge samples for total phosphorus:**

12.3.1 Weigh 1.0 g soil or sludge into a 150-mL beaker. Add approximately 100-mL reagent water. Add 0.05 mL (1 drop) of phenolphthalein indicator solution. If a red color develops, add H_2SO_4 solution dropwise to just discharge the color. Then add 1 mL H_2SO_4 solution.

12.3.2 Continue with step 12.2.6 through 12.2.10. If needed, magnetically stir samples during digestion to prevent loss from bumping. Proceed with step 12.6.

Note: Filter samples prior to neutralization in step 12.2.8

12.4 **Preparation of water samples for orthophosphate:**

12.4.1 Using a graduated cylinder, transfer 50 mL of the well-dispersed sample into a 150-mL beaker.

12.4.2 Use 0.10 mg/L, 0.50 mg/L, and 1.00 mg/L standards prepared in step 9.4 on each day the analysis is run. Additionally prepare an initial calibration verification and continuing calibration verification standard at concentrations of 0.50 mg/L.

12.4.3 Transfer 50 mL aliquots of reagent water using a graduated cylinder into 150 mL beakers to be analyzed as the calibration blank, initial calibration blank, continuing calibration blank, and the preparation blank.

12.4.4 Use an appropriate quantity of LCS to be analyzed within the working calibration range of this method. For dilutions using less than 50 mL, dilute to 50 mL with reagent water.

12.4.5 Add one drop of the phenolphthalein indicator solution to each beaker and neutralize to a faint pink color with the addition of 6 N NaOH. Proceed with step 12.6.

12.5 **Preparation of soil or sludge samples for orthophosphate:**

12.5.1 Weigh 1.0 g of the soil or sludge into a 150-mL beaker. Add 100 mL of reagent water.

12.5.2 Using a magnetic stir bar, spin the sample for 30 minutes.

Note: Filter the samples prior to neutralization.

12.5.3 Using a graduated cylinder, transfer 50 mL of the sample filtrate into a 150-mL beaker. Continue with step 12.4.5. Proceed to step 12.6.

12.6 **Colorimetric Determination of phosphorus (all forms):**

12.6.1 Add 8.0 mL of the combined reagent (step 9.12) to each standard, blank, LCS, and prepared sample. Gently mix.

12.6.2 After at least 10 minutes but no more than 30 minutes, read the absorbance at 880 nm on the spectrophotometer. Record in the logbook.

Note: If necessary, dilute any total phosphorus digestates prepared in step 12.2 or orthophosphate samples in step 12.4 to be analyzed within the working calibration range of this method.

13.0 CALCULATIONS

13.1 Manual Phosphorus Calculation:

Phosphorus (mg/L) =

$$\frac{[(A \times S) + Y] \times \text{Digestion vol. (mL)} \times DF}{\text{Sample vol (mL)}}$$

Phosphorus (mg/Kg) =

$$\frac{[(A \times S) + Y] \times \text{Digestion vol. (mL)} \times DF}{\text{Sample wt (g)} \times \text{Dec. \% solids}}$$

where:
A = absorbance @ 880 nm
S = slope
Y = y intercept
DF = dilution factor (50/color volume used)

13.2 Manual Orthophosphate Calculation:

Orthophosphate (mg/L) =

$$\frac{[(A \times S) + Y] \times \text{Extraction vol (mL)} \times DF}{\text{Sample vol (mL)}}$$

$$\text{Orthophosphate (mg/Kg)} = \frac{[(A \times S) + Y] \times DF}{\text{Sample wt (g)} \times \text{Dec. \% solids}}$$

where:
A = absorbance @ 880 nm
S = slope
Y = y intercept
DF = dilution factor (50/color volume used)

13.3 Relative Percent Difference Calculation:

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

where: S = original sample result
D = duplicate sample result

13.4 Sample Matrix Spike Recovery Calculation:

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

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

13.5 LCS, ICV, and CCV Percent Recovery Calculation:

$$\text{Percent Recovery} = (VM/TV) \times 100$$

where: VM = value measured
TV = true value

14.0 ACCEPTANCE OF DATA

14.1 The technical data review includes verifying that samples analyzed were sulfuric preserved for total phosphorus or unpreserved for orthophosphate, and that the holding times were met. The raw data is examined for completeness including a secondary review. Data entered into LIMS is checked for transcription error against the raw data.

14.2 Initial Calibration Verification (ICV): The control limit for the ICV is ± 10 percent of the true value.

Action on failure: When measurements exceed the control limit, the analysis must be terminated, the problem corrected, the instrument recalibrated, and the calibration verified.

14.3 Continuing Calibration Verification (CCV): The control limit for the CCV is ± 10 percent of the true value.

Action on failure: When measurements exceed the control limit, the instrument must be recalibrated, the calibration verified, and the preceding ten samples or all samples analyzed since the last compliant verification must be reanalyzed.

14.4 Initial Calibration Blank (ICB) and Continuing Calibration Blank (CCB): The concentration in the blank must be less than or equal to 1/2 the PQL.

Action on failure: If the value of the calibration blank exceeds 1/2 the PQL, terminate the analysis, correct the problem, recalibrate, verify the calibration, and reanalyze the preceding ten samples, or all samples analyzed since the last compliant calibration blank.

14.5 All method blank results must be less than 1/2 the PQL.

Action on failure: If a method blank's concentration exceeds 1/2 the reporting limit, all samples that were prepared with the method blank and have a concentration less than 10 times the method blank's concentration, must be rerun.

14.6 Laboratory Control Standard: For waters, the recovery of the independent standard must be within ± 15 percent of the known concentration. For soils, the acceptance range is based upon the manufacturer's established guidelines.

Action on failure: If the recovery of the LCS is not within the control limit, the calibration fails. The problem must be identified and corrected prior to any further analysis or acceptance of any data.

14.7 Sample Duplicates: The RPD for the sample duplicate must not exceed 20 percent. If the sample and duplicate concentrations are < five times the PQL, no RPD criteria is applied. For results < five times the PQL, the difference between the two results must be ≤ the PQL. If both results are less than the PQL, no criteria is required.

Action on failure: If the RPD is not within the control limit, rerun the sample and sample duplicate.

14.8 Spike Sample Recovery: The acceptable range for spike recovery is ± 25 percent.

Action on failure: If the spike fails, the sample must be spiked again and reanalyzed or if the sample concentration exceeds four times the spiking level, no spike criteria is applied.

15.0 REPORTING OF RESULTS

15.1 Results are reported by entering the data collected into LIMS.

15.2 The practical quantitation limit for total phosphorus and orthophosphate waters is 0.10 mg/L. The practical quantitation limit for total phosphorus and orthophosphate soils is 10.0 mg/Kg. For waters, if the result is < 1.00, report two significant figures. If the result is ≥ 1.00, report three significant figures. For soils, report three significant figures.

15.4 NCM's must be filed if any problems are associated with the analysis.

15.5 Case narratives should include information received on NCM's to document any holding time problems or any other problems associated with the analysis.

16.0 POLLUTION PREVENTION

16.1 Pollution prevention is the reduction and/or elimination of wastes or the toxicity of wastes at the point of generation. The laboratory strives to keep all wastes at a minimum through a variety of techniques. These include the following.

16.1.1 Inventory control: Rotate stocks (first in, first out) and only purchase reasonable amounts of chemicals. Do not purchase excessive quantities, which will be discarded as wastes at some future point.

16.1.2 Material Handling and Storage: Keep containers properly labeled. Keep solvents covered. Store and handle all chemicals, reagents, standards, etc. to prevent contamination and degradation.

16.1.3 Personnel: All staff must be trained in the proper handling and disposal of waste.

16.1.4 Waste Reduction: Reduce the volume of waste generated wherever possible.

16.1.5 Chemical/material substitution: Use less toxic chemicals whenever possible. Avoid the use of chromic acid (Chromerge) solutions.

17.0 WASTE MANAGEMENT

17.1 WASTE MANAGEMENT AND POLLUTION PREVENTION

All waste will be disposed of in accordance with Federal, State and Local regulations. Where reasonably feasible, technological changes have been implemented to minimize the potential for pollution of the environment. Employees will abide by this method and the policies in section 13 of the Corporate Safety Manual for "Waste Management and Pollution Prevention."

17.2 WASTE STREAMS PRODUCED BY THIS METHOD

The following waste streams are produced when this method is carried out.

- Acidic sample waste generated by the analysis. Employees are to collect and dispose of this material in satellite acid waste accumulation drums.

- Contaminated disposable glass or plastic materials utilized in the analysis. Employees are to collect and dispose of this material in satellite solid waste accumulation drums.

18.0 REFERENCES

18.1 Standard Methods for the Examination of Water and Wastewater, Methods 4500-P B,5 for persulfate digestion and 4500-P E for ascorbic acid determination,18th Edition, 1992.

19.0 SUBSTANTIVE REVISIONS

19.1 Original document.

19.2 Changed name from IEA to STL, corrected typographical errors; June 25, 1999.

19.3 Revised entire document to include a cover page, renumber sections from 3.0, adding Terms and Definitions, and Pollution Prevention and Waste Management; CVS04302.CT, October 26, 1999.

19.4 Removed section 9.5, and renumbered sections 9.6 through 9.13. Removed additions of 11N sulfuric acid from section 12.25, May 29, 2002.

19.5 Revised sections 11.3, 14.1, and 15.1 to reflect change to Labnet reporting system, May 29, 2002.

19.6 Removed section 18.0 and renumbered remaining sections, May 29, 2002.

19.7 Revised section 12.26 to reflect volume of 20 to 30 mLs, May 29, 2002.

19.8 Added Health and Safety Officer signature to section 1.0, Oct 27,2004.

19.9 Revised sections 6.0 and 17.0 to include more detailed safety and waste management information, Oct 27,2004.

19.10 No substantive revisions, 06/07/05.

19.11 Changed name from “Severn Trent Laboratories” to “TestAmerica Laboratories,” 8/30/07.

19.12 Revised SOP to reference Standard Methods 4500-P B,5 for persulfate digestion and 4500-P E for ascorbic acid determination, 08/30/07.

19.13 Changed PQL for total phosphorus and orthophosphate determination of soils to 10.0 mg/Kg, 08/30/07.

19.14 No substantive revisions, 01/11/10.

TestAmerica

THE LEADER IN ENVIRONMENTAL TESTING

Title: SOP for Inoganic Anions By Ion Chromatography
[Method SW846 9056]

Approvals (Signature/Date):

Dawn Nemeth 11/06/09
Technical Manager Date

David W. Helfrich 11/06/09
Health & Safety Manager/Coordinator Date

Dawn May 11/06/09
Quality Assurance Manager Date

11/12/09
Laboratory Director Date

This SOP was previously identified as SOP No. CT-CVS-72_3

Facility Distribution No. Electronic **Distributed To: Facility Intranet**

The controlled copy of this SOP is the PDF copy of the SOP that is posted to the laboratory’s SOP Directory. Printed copies of this SOP or electronic copies of this SOP distributed outside the facility are considered uncontrolled.

1.0 APPROVALS

The approval of the Laboratory Director, the Facility QA Manager, Group Leader and Health and Safety Officer signify that the document has been prepared in accordance with the format requirements that have been established in this document. In addition, if the document is a Method SOP the signature signifies that it meets the specified requirements.

2.0 SCOPE AND APPLICATION

2.1 The method covers the determination of the following inorganic anions:

Bromide	Nitrite-N
Chloride	Ortho-Phosphate-P
Fluoride	Sulfate
Nitrate-N	

2.2 The matrices applicable to this method are as follows:
Drinking water, surface water, mixed domestic and industrial wastewaters, groundwater, reagent waters, solids (using the extraction procedure given in section 8.5), and leachates (when no acetic acid is used).

2.3 The range tested for each anion is as follows:

Analyte	Range, mg/L
O-phosphate-P	0.1 to 5
fluoride, bromide, nitrite-N, nitrate-N	0.1 to 10
chloride	1 to 50
sulfate	1 to 100

Note. The calibrated range for this method is two orders of magnitude. These ranges were based on a 50 uL sample loop.

2.4 When this method is used to analyze unfamiliar samples for any of the above anions, anion identification should be supported by the use of a fortified sample matrix covering the anions of interest.

2.5 Bromide and nitrite react with most oxidants employed as disinfectants for drinking waters. The utility of measuring these anions in treated water should be considered prior to conducting the analysis.

2.6 The document control number for this SOP is CT-CVS-72, Rev 5.

3.0 TERMS AND DEFINITIONS

3.1 Refer to the SOP for Terms and Definitions.

4.0 SUMMARY OF METHOD

4.1 A small volume of sample is introduced into an ion chromatograph. The anions of interest are separated and measured, using a system comprised of a guard column, an analytical column, a suppressor cartridge, and a conductivity detector.

4.2 An extraction procedure must be performed to use this method for solids (See Section 12.8).

4.3 The sample is injected into a stream of carbonate-bicarbonate eluent that carries it through three different ion exchange columns and into a conductivity detector.

4.4 The first two columns, a guard column and a separator column, are packed with low-capacity, strongly basic anion exchanger. Ions are separated into discrete bands based on their affinity for the exchange sites of the resin.

4.5 The last column is a suppressor column that reduces the background conductivity of the eluent to a low or negligible level and converts the anions into their respective acids.

4.6 The separated anions in their respective acid forms are then measured by the conductivity detector and quantified using a calibration curve generated from known standards.

4.7 The anions are identified by their retention times compared to known standards.

4.8 This method is based on SW846 Method 9056.

5.0 INTERFERENCES

5.1 Interferences can be caused by substances with retention times that are similar to and overlapping those of the analyte of interest. Large amounts of an analyte can interfere with the peak resolution of a closely eluting analyte. Sample dilution and/or fortification can be used to solve many interference problems associated with overlapping retention times. However, sample dilution may typically affect the MDL values proportionally.

5.2 Method interferences may be caused by contaminants in the reagent water, reagents, glassware, and other sample processing apparatus that lead to discrete artifacts or elevated baseline in ion chromatograms.

5.3 Any anion that is not retained by the column or only slightly retained will elute in the area of fluoride and interfere. Known coelution is caused by small organic anions. At concentrations of fluoride above 1.5 mg/L, this interference may not be significant. It is, however, the responsibility of the user to generate precision and accuracy information in each sample matrix.

5.4 The acetate anion elutes early during the chromatographic run. The retention times of the anions also seem to differ when large amounts of acetate are present. Therefore, this method is not recommended for leachates of solid samples when acetic acid is used for pH adjustments.

5.5 The quantitation of unretained peaks should be avoided, such as low molecular weight organic acids (formate, acetate, propionate etc.) that are conductive and coelute with or near fluoride and would bias the fluoride quantitation in some drinking waters and most wastewaters.

6.0 SAFETY

Employees must abide by the policies and procedures in the Corporate Safety Manual, Radiation Safety Manual and this document. This procedure may involve hazardous material, operations and equipment. This SOP does not purport to address all of the safety problems associated with its use. It is the responsibility of the user of the method to follow appropriate safety, waste disposal and health practices under the assumption that all samples and reagents are potentially hazardous. Safety glasses, gloves, lab coats and closed-toe, nonabsorbent shoes are a minimum.

6.1 SPECIFIC SAFETY CONCERNS OR REQUIREMENTS

Sodium Fluoride is Highly Toxic.

Exercise caution when using syringes with attached filter assemblies. Application of excessive force has, upon occasion, caused a filter disc to burst during the process.

6.2 PRIMARY MATERIALS USED

The following is a list of the materials used in this method, which have a serious or significant hazard rating. **NOTE: This list does not include all materials used in the method. The table contains a summary of the primary hazards listed in the MSDS for each of the materials listed in the table.** A complete list of materials used in the method can be found in the reagents and materials section. Employees must review the information in the MSDS for each material before using it for the first time or when there are major changes to the MSDS.

Material (1)	Hazards	Exposure Limit (2)	Signs and symptoms of exposure
Methanol	Poison Flammable	200 ppm TWA: 260 mg/m^3 TWA	Moderate eye and skin irritant. May be fatal or cause blindness if swallowed. Inhalation can cause CNS depression with nausea, headache, vomiting, dizziness and incoordination. Severe nervous system and visual effects including blindness may be incurred by inhalation.
Potassium Phosphate	Irritant	None	May cause mild irritation to the respiratory tract. Eye and skin irritant. Chronic exposure: may sequester calcium and cause calcium phosphate deposits in the kidneys.
Potassium Sulfate	Irritant	None	Dust may induce sneezing and coughing. Eye contact may cause mechanical irritation. Large oral doses may produce gastrointestinal disturbances and irritation.
Sodium Nitrate	Oxidizer Irritant Poison	None	Causes irritation to the respiratory tract, skin and eyes. Symptoms may include coughing, shortness of breath. Symptoms include redness, itching, and pain. Ingestion may cause irritation of the digestive tract- may cause cyanosis, convulsions, and death.
Sodium Nitrite	Oxidizer Irritant Poison	None	Eye and skin contact can cause irritation, redness, and pain. Inhalation causes irritation to the respiratory tract and systemic poisoning with symptoms paralleling ingestion. Symptoms of ingestion include cyanosis, nausea, dizziness, vomiting, collapse, spasms of abdominal pain, rapid heart- beat, irregular breathing, coma, convulsions, and death. Estimated lethal dose 1 to 2 grams.
Sodium Bicarbonate	Mild irritant	None	High concentrations of dust may cause coughing and sneezing. Ingestion of large doses may cause gastrointestinal disturbances. Contact with eyes may cause mild irritation, redness, and pain.
Sodium Bromide	Irritant	None	Eye and skin irritant. May cause respiratory tract irritation with effects similar to ingestion. Ingestion may cause central nervous system depression, characterized by excitement, followed by headache, dizziness, drowsiness, and nausea. Advanced stages may cause collapse, unconsciousness, coma, and possible death due to respiratory failure.

Material (1)	Hazards	Exposure Limit (2)	Signs and symptoms of exposure
Sodium Chloride	Irritant	None	May cause skin irritation. Contact with eyes can cause irritation or redness due to abrasion. Ingestion of large amounts can cause vomiting and diarrhea.
Sodium Carbonate	Irritant	None	Inhalation of dust may cause irritation to the respiratory tract. Symptoms include coughing and difficulty breathing. Ingestion of large doses may be corrosive to the gastrointestinal tract where symptoms may include severe abdominal pain, vomiting, diarrhea, collapse and death. Eye and skin irritant.
Sodium Fluoride	Poison	2.5 mg/m^3 - TWA as F	**Highly Toxic.** Causes severe irritation to the respiratory tract, symptoms may include coughing, sore throat, and labored breathing. Causes irritation, with redness and pain. Solutions are corrosive. Eye irritant! May cause irritation and serious eye damage. Effects may not appear immediately.
Sulfuric Acid	Corrosive Oxidizer Dehydrator Poison Carcinogen	1 mg/m^3 - TWA	Inhalation produces damaging effects on the mucous membranes and upper respiratory tract. Symptoms may include irritation of the nose and throat, and labored breathing. Symptoms of redness, pain, and severe burn can occur. Contact can cause blurred vision, redness, pain and severe tissue burns. Can cause blindness.
1 – Always add acid to water to prevent violent reactions.			
2 – Exposure limit refers to the OSHA regulatory exposure limit.			

6.3 The toxicity or carcinogenicity of each reagent used in this method has not been fully established. Each chemical should be regarded as a potential health hazard and exposure should be as low as reasonably achievable.

6.4 At a minimum, wear PVC gloves, a lab coat, and eye protection when handling samples and reagent. Use a suitable fume hood for the analysis.

6.5 Always refer to your Corporate Safety Handbook prior to performing laboratory operations.

7.0 SAMPLE COLLECTION, PRESERVATION, AND STORAGE

7.1 Samples are collected in plastic or glass bottles. All bottles must be used only once. Volume collected should be sufficient to ensure a representative sample, allow for replicate analysis (if required), and minimize waste disposal.

7.2 Sample preservation and holding times for the anions that can be determined by this method are as follows:

Analvte	Preservation	Holding time
Bromide	cool to 4^0C	28 days
Chloride	cool to 4^0C	28 days
Fluoride	cool to 4^0C	28 days
Nitrate-N	cool to 4^0C	48 hours
Nitrite -N	cool to 4^0C	48 hours
Nitrate/Nitrite (Combined)	conc. H_2S0_4 to pH <2	28 days
Ortho phosphate-P	cool to 4^0C	48 hours
Sulfate	cool to 4^0C	28 days

8.0 EQUIPMENT AND SUPPLIES

8.1 Analytical Balance -capable of accurately weighing to the nearest 0.0001 g.

8.2 Glassware--Class A volumetric flasks and pipettes as required.

8.3 Ion Chromatograph -- Analytical system complete with ion chromatograph and all required accessories including analytical columns and detectors.

8.3.1 Anion guard column: QS-AlG (Lachat part no.28085) A protector of the separator column. If omitted from the system, the retention times will be shorter.

8.3.2 Anion profiling column: QS-A1 (Lachat part no.28084).

8.3.3 Anion suppressor cartridge: QE-Al (Lachat part no.28097). The replacement suppressor cartridge has Lachat part no 28098.

8.3.4 Detector -- Temperature controlled conductivity detector: CM- 100. Approximately 0.25 µL internal volume.

8.4 Lachat's Omnion IC Software.

9.0 REAGENTS AND STANDARDS

9.1 Sample bottles: glass or polypropylene of sufficient volume to allow replicate analyses of anions of interest.

9.2 Reagent water: Use ASTM Type II water (nanopure water) for all solutions.

9.2 **Eluent solution: Prepare Weekly.** Dissolve 0.5376 g sodium bicarbonate ($NaHCO_3$) and 0.8816 g of sodium carbonate (Na_2CO_3) in reagent water (9.2) and dilute to **4 L**. Degas the eluent by helium sparging (one minute for each liter) or by vacuum sonication. Filter through a 0.22 µm nylon filter.

It has been observed that phosphate and sulfate peaks are not resolved when the eluent is prepared using oven-dried and desiccated chemicals. Therefore, to prepare the eluent, use chemicals directly from the vendor's bottle.

9.3 **Regenerant**: Sulfuric acid (CAS RN 7664-93-9) 0.25 M

Regenerant Stock Solution, 1.0 M sulfuric acid

To a 1L volumetric flask containing 800 ml of reagent water add 56 ml of concentrated sulfuric acid (H_2S0_4). Caution the flask will become warm. Cool to room temperature and dilute to the mark. May be stored at least 4 weeks.

Working Regenerant, 0.25 M sulfuric acid

In a 1 L container, add 250 mL of Regenerant Stock Solution and 750 mL reagent water. Stir to mix. May be stored at least 4 weeks.

Alternative: To 2L volumetric containing 1600 ml of reagent water, add 28 ml of concentrated sulfuric acid and dilute to volume with reagent water. Mix by inverting three times.

9.5 20 % Methanol (self-flush reagent for eluent pump)

To a 200 ml container, add 40 ml methanol (CH_3OH). Fill with reagent water and invert to mix.

9.6 **Stock Standard Solutions, 1000 mg/L (1 mg/ml):** Stock standards may be purchased as certified solutions or prepared from ACS reagent grade materials (dried at 105^0C for 30 min) as listed below. To a 1.0 L volumetric flask, add the exact weight of reagent listed below and fill the flask to the mark with DI water. Stir to dissolve.

REAGENT	Weight (g)	Concentration
Sodium Fluoride NaF	2.2100	1000 mg F/L
Sodium Chloride NaCI	1.6485	1000 mg Cl/L
Sodium Nitrite $NaNO_2$	4.9257	1000 mg NO_2-N/L
Sodium Bromide NaBr	1.2876	1000 mg Br/L
Sodium Nitrate $NaNO_3$	6.0679	1000 mg NO_3-N/L
Potassium Phosphate KH_2P04	4.3937	1000 mg HPO_4-P/L
Potassium Sulfate K_2SO_4	1.8141	1000 mg SO_4/L

NOTE: Stability of standards: Stock Standard Solutions (9.6) are stable for at least one year when stored at 4^0C. Diluted Stock Standard Solutions (9.7-Table 1) are prepared weekly and stored at 4^0C. Diluted Stock Standard Solutions for Nitrite and Phosphate (9.7- Table 2) are made daily and added to the solution in Table 1.

9.7 **Working Mixed Standard A**

To a 500 mL volumetric flask or container, transfer the volumes of the Stock Standard Solutions. Fill to the mark with DI water. Invert to mix. Store at 4^0C.

Table 1

Stock Standard	Number of ml	Concentration mg/L
Fluoride 1000 mg/L	5	10
Chloride 1000 mg/L	25	50
Bromide 1000 mg/L	5	10
Nitrate-N 1000 mg/L	5	10
Sulfate 1000mg /L	50	100

Table 2

Stock Standard	Number of ml	Concentration mg/L
Nitrite-N 1000 mg/L	5	10
Phosphate-P 1000 mg/L	2.5	5

9.8 **Working Mixed Standards B through F**

Working Mixed Standards B through F are prepared by diluting Working Mixed Standard A (9.7) as listed below. Standard A is repeated for reference.

Std	Standard A ml	Final sol'n ml	Concentration (mg/L)						
			F^-	Cl-	NO_2^--N	Br-	NO_3^--N	HPO_4^{2-}	SO_4^{2-}
A	----	----	10.0	50.0	10.0	10.0	10.0	5.0	100.0
B	120	200	6.0	30.0	6.0	6.0	6.0	3.0	60.0
C	20.0	200	1.0	5.0	1.0	1.0	1.0	0.5	10.0
D	10.0	250	0.4	2.0	0.4	0.4	0.4	0.2	4.0
E	2.0	200	0.10	0.5	0.10	0.10	0.10	0.05	1.0
F	1.0	200	0.05	0.25	0.05	0.05	0.05	0.025	0.5

Example: To prepare standard B, add 120 ml of standard A to a 200-mL volumetric flask or bottle. Fill to the mark.

10.0 CALIBRATION AND STANDARDIZATION

10.1 Prepare reagents as described in Section 9. Calibration standards are prepared at six concentration levels, excluding the blank. The recipe for the calibration standards is in Section 9. The calibration standards employed must bracket the concentration of the analytes of interest in the unknown samples.

10.2 Set up the IC manifold according to the flow diagram as shown in the appendix section. Inspect carefully for proper connections.

10.3 Input the data system parameters as shown in the appendix section.

10.4 Calibrate the instrument, following the start-up procedures given in Section 11. First run an injection of DI water or a standard to completion. Then run the calibration standards in succession. After calibration, a blank should be run for validation. The calibration criterion is a correlation coefficient of ≥ 0.995.

10.5 The data system will associate the known concentrations with the peak heights or peak areas recorded for each standard. These responses are then used to prepare a calibration curve for each analyte. The instruments software does not include the blank standard in the curve if there is no response for that analyte; standards are analyzed at a concentration lower than the reporting limit to cover the calibration working range.

10.6 The calibration must be verified on each working day with an ICV, or whenever the eluent is changed, and after every 10 samples with a CCV. If the instrument response for any analyte varies from the expected values by more than 5%, recalibrate.

10.7 Nonlinear response can result when the analytical column capacity is exceeded (overloading). The responses for the sample when diluted 1:1, and when not diluted, should be compared. If the determined results are the same, accounting for dilution, then the samples having this total ionic concentration need not be diluted.

11.0 QUALITY CONTROL

11.1 Initial Calibration Verification (ICV)

Immediately after the Lachat Ion Chromatograph Analyzer has been calibrated, the accuracy of the initial calibration shall be verified and documented by the analysis of the Initial Calibration Verification Standard. The instrument response should be within 10%.

11.2 Continuing Calibration Verification (CCV) {Instrument Performance Check Solution}

To ensure calibration accuracy during each run, a mid-range standard must be used for continuing calibration verification and must be analyzed at a frequency of 10% of samples. The standard must be analyzed at the beginning of the run, after ten samples, and after the last analytical sample. If the instrument response has changed by more than 5%, recalibrate.

11.3 Laboratory Control Samples (LCS) { Quality Control Samples}

To ensure calibration accuracy during each run, an LCS must be run with every batch of twenty samples. The LCS is obtained from an outside vendor. The criterion for the LCS is ± 10 % of the true value.

11.4 Initial Calibration Blank (ICB), Continuing Calibration Blank (CCB), and Method Blank (MB) Analyses

A calibration blank must be analyzed at the beginning of the run, after every initial and continuing calibration verification, at a frequency of 10 percent of samples and after the last analytical sample. The concentration of the calibration blank must be less than ½ the PQL

At least one method blank consisting of reagent water must be analyzed with each batch of twenty or fewer samples run. The concentration of the MB should be less than the PQL.

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

11.5 Spike Sample and Spike Blank Analysis

One blank spike must be performed with each batch of samples. The blank spike data will be used to assess the laboratory performance against the required control limits of ± 20% of the true value. The spike sample analysis is designed to provide information about the effect of the sample matrix on the measurement methodology. At least one spike must be performed on each group of twenty or fewer samples of a similar matrix (i.e. water, soil). Samples identified as field blanks cannot be used for spike sample analysis. Control limit for the matrix spike recovery is ± 20 %.

11.6 Duplicate Sample Analysis

One duplicate sample shall be analyzed from each group of ten or fewer samples of a similar matrix type (i.e. water, soil). Samples identified as field blanks cannot be used for duplicate analysis. The criterion for duplicate analyses is an RPD ≤ 20 %.

11.7 Method Detection Limit (MDL) Determination

Every 6 months, the method detection limit (in mg/L) shall be determined by multiplying by 3.14, the standard deviation obtained from the analysis of seven digested standard solution replicates at a concentration up to five times the estimated Instrument Detection Level.

11.8 Instrument Maintenance

An instrument maintenance log is kept for the Lachat Autoanalyzer.

12.0 PROCEDURE

12.1 Follow the sample collection, pretreatment and preservation procedures given in Section 7.

12.2 Turn on the power to all modules.

12.3 Add eluent to the eluent reservoir, and prime the eluent delivery pump. Be sure that all air bubbles are eliminated from the eluent inlet filter and the eluent inlet tubing. Tap the inlet filter on the bottom of the eluent container to dislodge bubbles. To rewet a brand-new or dried-out inlet filter, unscrew the filter from the inlet line, push methanol backward through the filter using a wash bottle or syringe. Rinse thoroughly with DI water, and reconnect the filter to the inlet line.

12.4 With the columns disconnected, pump eluent until the connecting tubing is flushed and all air is removed. Stop the pump and then connect the columns. Briefly turn on the eluent delivery pump to check for leaks and excessive back pressure.

12.5. Add DI water and regenerant to the respective reservoirs, as appropriate to the method.

12.6. Initialize the instrument.

12.6.1. For QC 8000: With the regenerant and DI wash lines in DI water, turn on the peristaltic pump and check for leaks around the suppressor. Then place these lines into the respective containers.

12.7. Place samples (which have been filtered through a 0.45 µm nylon filter) in the autosampler. Input the sample identification, run order, vial number, and number of replicates as required by the data system and the QC procedure.

12.8 Solid Material Extraction Procedure:

Add an amount of reagent water ten times the weight of solid material taken as sample. Mix the slurry for ten minutes using a magnetic stirring device. Filter the slurry through a 0.45 µm nylon filter. Care should be taken to make sure that identification of peaks and resolution of the peaks is good. A solid spike should be run with the soil samples. Spiking should be done prior to sample extraction.

12.9 Start the eluent pump and the peristaltic pump. Submit the Batch for analysis.

NOTE : ***An initial injection of DI water or a standard should be run as the first sample.***

In order to perform USEPA compliance monitoring, the suppressor cartridge must be in-Line during sample processing. Any data generated without the in-Line, fully activated suppressor cartridge, cannot be reported for compliance monitoring.

12.10. If one or more analyte responses exceed the calibration range, dilute the sample with reagent water or an appropriate diluent and reanalyze.

12.11. Should more complete resolution be needed between peaks, the eluent can be diluted 10% to 30%. This will increase separation but will also cause the later eluting analytes to be retained longer. This dilution should not be considered a deviation from the method. Alternately, slowing the eluent flow rate by 20% to 40% can increase separation slightly.

12.12. System shut-down. At the end of each day's work, flush all columns with DI water. If the system will be idle for longer than three days, disconnect the columns and suppressor and install end caps. Refer to the information sheet provided with the analytical column for specific information relating to column care, including long-term storage and column cleaning procedures. To flush the regenerant, place the regenerant inlet line in DI water. Pump reagent water through the system. For long-term storage of the eluent pump, prime with isopropanol.

12.13. SYSTEM NOTES

12.13.1. For information on system maintenance and troubleshooting refer to the System Operation Manual and Trouble Shooting Guide.

12.13.2. Do not suddenly release the pressure from the columns or they may be damaged.

12.13.3. The retention times for each of the analytes are affected by eluent concentration, flow rate, extreme range of analyte concentration, and column performance. The user may need to make minor adjustments in the Integration Events Table and the Peak Table to ensure each peak is identified correctly and integrated properly.

12.13.4 As preventative maintenance, the guard column should be replaced periodically.

13.0 DATA ANALYSIS AND CALCULATIONS

13.1 Calibration is done by injecting standards. Analyte concentrations for unknown samples are calculated from the respective regression equations. The calibration criterion is a correlation coefficient of ≥ 0.995.

13.2 Analyte identification and retention time determination are performed by injecting standards of known concentrations into the IC column. Analytes are identified based upon the order of elution.The retention time (peak maximum) for each analyte is measured and entered into the Peak Table. The retention time window used to identify calibrated peaks can be established by entering a value for the window in the Define Peak command under Method, Graphical Events Programming. The window is then calculated by multiplying the peak's expected retention time by the Peak Window %. The resulting window is centered around the peaks' expected retention time. If a peak's retention time, adjusted for reference peak shift, falls outside this window, it is not considered to be the calibrated peak. (It may be necessary to measure and revise retention times as retention times.may shift because of eluent strength, column performance, etc,.)

13.3 Report only those values that fall between the lowest and the highest calibration standards. Samples exceeding the highest calibration standard should be diluted and reanalyzed. Sample concentrations less than the lowest calibration standard should not be reported unless the MDL standard is included in the calibration model.

13.4 Report results in mg/L.

13.5 Report $NO_{2\sim}$as N
$N0_3$- as N
HPO_4^{2-} as P

13.6 Concentration in Samples:

13.6.1 Calculate the aqueous samples in mg/L of original sample, as follows:

mg /L = A x D If dilution factor is not entered in the Lachat IC tray.

where: A = mg /L sample from Lachat print-out.

D = any other dilution factor necessary for sample to be below the high standard.

The minimum value that can be substituted for A is the practical quantitation limit.

13.6.2 Calculation of solid samples in mg/Kg of original sample, as follows: (A separate determination of percent solids must be performed: Appendix II.)

The concentration of sample is determined as follows:

$$\text{mg/Kg} = \frac{A \times D \times F}{B \times E}$$

where:
A = mg /L of sample from Lachat print-out
B = wet weight of original sample **(in g)**.
D = any other dilution factor necessary for sample to be below the high standard.
E = % solids (See Appendix II)/100
F = final sample volume **(in ml)** after extraction.

The minimum value that can be substituted for A is the practical quantitation limit.

13.7 Percent Recovery

13.7.1 Spike recoveries are calculated as follows:

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

where:
SSR = Spiked Sample Result
SR = Sample Result
SA = Spike Added

When sample concentration is less than the practical quantitation limit, use SR = 0 for calculating percent recovery.

13.7.2 Percent Recovery of Initial, Continuing Calibration Verification and LCS

For Initial Calibration Verification (ICV):

$$\%\text{ Recovery} = \frac{\text{Found (ICV) value} \times 100}{\text{True (ICV) value}}$$

For Continuing Calibration Verification (CCV):

$$\%\text{ Recovery} = \frac{\text{Found (CCV) value} \times 100}{\text{True (CCV) value}}$$

For Laboratory Control Sample (LCS):

$$\%\text{ Recovery} = \frac{\text{Found LCS value} \times 100}{\text{True LCS value}}$$

13.8 Relative Percent Difference

The Relative Percent Difference is calculated as follows:

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

where: S = Sample result and D = Duplicate result

14.0 ACCEPTANCE OF DATA

14.1 Initial Calibration Verification (ICV): The control limit for the ICV is ±10 % of the true value.

Action on failure: When measurements exceed the control limit, the analysis must be terminated, the problem corrected, the instrument recalibrated, and the calibration verified.

14.2 Continuing Calibration Verification (CCV: The instrument response should not change by more than 5%.

Action on failure: If the instrument response has changed by more than 5%, recalibrate. If recalibration is necessary, an ICV must be run to verify the calibration.

14.3 Matrix Spike Blank (MSB): The control limit for the MSB is ±10 % of true value.

Action on failure: If the deviation of the MSB is greater than the control limit, the MSB must be reanalyzed. If recalibration is necessary, an ICV must be run to verify the calibration.

14.4 Initial Calibration Blank (ICB), and Continuing Calibrations Blank (CCB): The absolute value of the concentration in the blank must be less than ½ the PQL.

Action on failure: If the absolute value of the calibration blank result exceeds ½ the PQL, reanalyze the preceding ten analytical samples or all analytical samples analyzed since the last compliant calibration blank. If recalibration is necessary, an ICV must be run to verify the calibration.

14.5 Method Blank (MB): All method blank results must be less than the PQL.

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

Action on failure: If the concentration in the blank is greater than the PQL, the lowest concentration of sample in the associated samples must be ≥ 10X the blank concentration. Otherwise, all samples associated with the blank with a concentration less than 10X the blank concentration and greater than the PQL must be reanalyzed with a new blank that meets criteria.

14.6 Spike Sample Recovery: The acceptable range for spike recovery is ± 20 % percent of the spike amount added; no spike criteria is applied if the sample concentration exceeds the spike level by a factor of four or more.

Action on failure: When the spike recovery falls outside the control limits and the sample result does not exceed 4x the spike added, the spike must be rerun. If it still fails criteria and all other QC and blank spike pass, then the cause of the failure is matrix related.

14.7 Duplicate Analysis RPD: The acceptable RPD is less than or equal to 20%.

Action on Failure: Another duplicate has to be analyzed.

15.0 REPORTING OF RESULTS

15.1 Results are reported by importing the data onto LIMS; the analyst checks the data and first level reviews the batch.

15.2 The LIMS batch is subjected to a secondary review.

15.3 NCM's are written to address any problems such as holding time violations, QC failures, etc.

15.4 Case narratives should include any information received on NCM's

16.0 POLLUTION PREVENTION

It is TestAmerica's policy to evaluate each method and look for opportunities to minimize waste generated (i.e., examine recycling options, ordering chemicals based on quantity needed, preparation of reagents based on anticipated usage and reagent stability). Employees must abide by the policies in Section 13 of the Corporate Safety Manual for "Waste Management and Pollution Prevention."

16.1 Pollution prevention is the reduction and/or elimination of wastes or the toxicity of wastes at the point of generation. The laboratory strives to keep all wastes at a minimum through a variety of techniques. These include the following.

16.1.1 Inventory control: Rotate stocks (first in, first out) and only purchase reasonable amounts of chemicals. Do not purchase excessive quantities, which will be discarded as wastes at some future point.

16.1.2 Material Handling and Storage: Keep containers properly labeled. Keep solvents covered. Store and handle all chemicals, reagents, standards, etc. to prevent contamination and degradation.

16.1.3 Personnel: All staff must be trained in the proper handling and disposal of waste.

16.1.4 Waste Reduction: Reduce the volume of waste generated wherever possible.

16.1.5 Chemical/material substitution: Use less toxic chemicals whenever possible. Avoid the use of chromic acid (Chromerge) solutions.

17.0 WASTE MANAGEMENT

Waste management practices are conducted consistent with all applicable rules and regulations. Excess reagents, samples and method process wastes are disposed of in an accepted manner. Waste description rules and land disposal restrictions are followed. Waste disposal procedures are incorporated by reference to the Tracking and Collection of Hazardous Waste SOP. The following waste streams are produced when this method is carried out.

17.1 Waste Streams Produced by the Method

The following waste streams are produced when this method is carried out.

- Alkaline and/or acidic waste generated by the analysis. Employees are to dispose of acid waste in the satellite acid waste drum in the laboratory**.** Alkaline waste is decanted into the sink while flushing with tap water.
- Contaminated plastic materials such as IC syringes, filters, caps and vials utilized for sample preparation. Employees are to collect and dispose of this material in satellite waste accumulation drums.

18.0 SUPPLEMENTAL DOCUMENTS

18.1 SOP for Terms and Definitions.

19.0 REFERENCES

19.1. Pfaff, S.D., USEPA Method 300.0, "Determination of Inorganic Anions by Ion Chromatography". EMSL, Office of Research and Development, USEPA, Cincinnati, OH 45268, USA, rev. 2.1, 1993.

19.2 SW846 method 9056, "Determination of Inorganic Anions by Ion Chromatography". Revision 0, September 1994.

19.3 Lachat IC Operating Manuals, Lachat Instruments Inc., Milwaukee, WI, USA.

19.4 Desk Audit Report, U.S. Army Corps of Engineers, HTRW Center of Expertise,Omaha, Nebraska, December, 2003.

20.0 REVISIONS

20.0 Original Document, 05/19/05.

20.1 Added method number to title, 06/21/05.

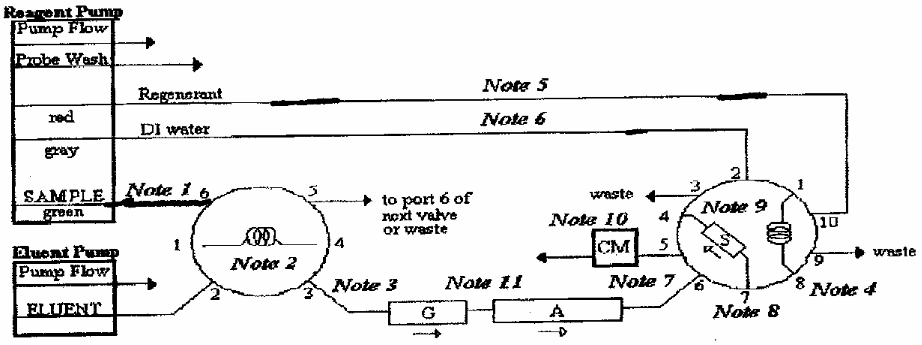
20.2 Changed name from “Severn Trent Laboratories” to “TestAmerica Laboratories,”. Revised Section 10.5 to state that standards are analyzed at a level less than the PQL. Added chemicals to Section 6.2, 09/14/07.

20.3 Removed all ACOE references. Updated Sect 11.3, 11.5 and 14.6 to 10% recovery limits.
20.4 Updated 11.7 to 6 month MDL requirement. Revised Section 9.6 to establish holding times for Nitrite and Phosphate as “make daily” and changed Section 9.7 tables for making standards based on the holding times. Revised Section 9.2 for making Eluent, 10/22/09.

20.5 Updated 11.5 to 20% MS criteria. Revised Section 9.6 to indicate weekly standard prep, 11/06/2009.

APPENDIX A

MANIFOLD DIAGRAM FOR QC 8000(12-16 Channel Peristaltic Pump)



C	guard column QS-A1G (Lachat part no 28085)
A	analytical column QS-A1 (Lachat part no.28084)
S	suppressor cartridge QE-Al Lachat part no.28097) *The suppressor cartridge* is *replaceable (replacement cartridge part no. 28098)*
CM	conductivity module

Note#	Tubing Type	Connected to:
*Note 1	Green/Green sample line	six-port valve port 6
Note 2	PEEK sample Loop – 200 µL	six-port valve port1 to port 4
Note 3	Yellow PEEK Tubing - 25 cm	six-port valve port 3 to guard column
Note 4	0.8 mm id Teflon Tubing - 225cm	ten-port valve port 1 to on 8
** Note 5	Red/Red sulfuric acid line	Peristaltic pump to ten-port valve port 10
***Note 6	Gray/Gray DI water line	Peristaltic pump to ten-port valve port 2
Note 7	Yellow PEEK Tubing - 34 cm	analytical column to ten-port valve port 6
Note 8	Tan PEEK Tubing - 12 cm	ten-port valve port 7 to Suppressor
Note 9	Tan PEEK Tubing - 12 cm	suppressor to ten-port valve port 4
Note 10	Yellow PEEK Tubing - 20 cm	CM inlet to ten-port valve port 5
Note 11	Yellow PEEK Tubing - 6 cm	guard to analytical column

***   Green/Green sample tube can be replaced with RedlRed to reduce sample consumption if running IC alone without dilutor. Use Green/Green tubing if running IC with FIA or IC with dilutor.***

**** *   Connect Red/Red pump tubing to port 10 (ten-port valve) using 100 cm of 0.8mm i.d. Teflon tubing.***
**** * * Conned Gray/Gray pump tubing to port 2 (ten-port valve) using 100 cm of 0.8 mm id Teflon tubing.***

<u>PARAMETERS AND VALIDATION DATA</u>

Parameters

Separation Conditions

Eluent: 2.0 mM $NaHCO_3$ + 2.6 mM Na_2CO_3
Regenerant: 0.25 M sulfuric acid
Sample loop: 100 µL
Expected pressure: 1250 ± 250 psi

Pump Settings

Eluent flow rate: 2.0 ml/min
High pressure limit: 1500 psi
Low pressure limit:500 psi

Acquisition Setup

Sample Frequency: 1Hz
Run Time*: 12 ± 1 min
Channel Status: On
Analyze After Acq.: On
Trigger Type: Contact open
Acquisition Delay: 1.4 mm
Probe in Sample: 65 s
(Set under Method Menu)

* ***Run Time*** *is the time required to return to baseline after the last peak is eluted. The test sheet included with the analytical column shows the actual Run Time for that column.*

Integration Events Table A*

Event	Start Time	Stop Time	Value
Integration Off	0	*1.7*	0
Threshold	1.5	1.9	750
Width	2.2	2.5	0.3
Valley to Valley	2.3	5.5	0
Shoulder Sensitivity	2.3	3.1	100
Threshold	3.5	4.5	400
Width	4.5	5.1	0.6
Valley to Valley	8.0	9.0	0
Width	7.0	8.0	1.1

**Sample table only. The experienced user may program these events graphically.*

Peak Table

Name	Retention Time*	Window*	Units

Fluoride	2.3	0.3	mg/L
Chloride	3.25	0.5	mg/L
Nitrite-N	3.9	0.5	mg/L
Bromide	5.25	0.7	mg/L
Nitrate-N	6.2	0.9	mg/L
Phosphate-P	8.25	1.1	mg/L
Sulfate	10.0	2.0	mg/L

**These parameters may have to be adjusted for the software to label each analyte peak correctly.*

Calibration Setup

Time Unit	min
*Peak Attribute/Quantitate	**
*Calibration Fit/Fit Type	linear
*Weighting Method	1/x
*Force Through Zero	no
*Peak Area/Calib. Flag	replace
*Scaling	None
*RT Update After Calib.	No
*RT Update After Run	No
ISTD Amount	0
Sample Amount	1
Multiplication Factor/Manual Dilution	1

** In Omnion IC version 2.0 these parameters are selected in the Peak table. Version 2.0 also allows differing parameters for each analyte.*

** Use either Peak heights or Area for the anions.

External Events Table

B. External Events Table for QC8000 IC+ Automated Ion Analyzer

Event Name	Time	1	2	3
LOAD	0.05	0	0	1
INJECT	1.4	0	0	0

This example assumes that the IC SPM cable is connected to VALVE 3 on the valve distribution panel. The LOAD event actuates VALVE 3 as per column 3 of the table.

Display **Options - Channel A**

X-axis min	0 min
X-axis max.	12 mm
Y-axis min	-25 µS/cm

Y-axis max.	350 µS/cm
Attenuation:	1024

Detector Configuration*

Type:	Analog
Name:	Conductivity
Connected to Analog Input #:	**
Y-Axis Label:	µS/cm
Y-Axis Multiplier:	0.0001
Maximum # of Peaks:	50
Maximum # of Named Peaks:	25

*** For QC 8000 select the letter that indicates the channel used by IC on the detector distribution board.*

Detector Settings

Zero/Background:	Background
Gain:	1
Fast Response:	off
Temperature Setting:	33°C
Inverse Polarity :	off

PERCENT SOLIDS DETERMINATION PROCEDURE

1. Weigh out 5-10 g of sample to a tared weighing dish. Weigh and record the weight to the nearest 0.01 g.

2. Place weighing dish plus sample in a drying oven maintained at 103-105^{0}C. Sample handling and drying should be conducted in a well-ventilated area.

3. Dry the sample overnight (12-24 hours) but no longer than 24 hours. If dried less than 12 hours, it must be documented that constant weight was attained. Remove the sample from the oven and cool in a dessicator with the weighing dish cover in place before weighing. Weigh and record weight to nearest 0.01 g. Do not analyze the dried sample.

NOTE: Drying time is defined as the elapsed time in the oven; thus raw data must record time in and out of the oven to document the 12 hour drying time minimum. In the event it is necessary to demonstrate the attainment of constant weight, data must be recorded for a minimum of two repetitive weigh/dry/dessicate/weigh cycles with a minimum of 1 hour drying time in each cycle. Constant weight would be defined as a loss in weight of no greater than 0.01 g between the start weight and final reweigh of the dried sample.

4. Duplicate percent solids determinations are required at a frequency of one in every twenty samples or less.

5. For the duplicate percent solids determination, designate one sample aliquot as the "original" sample and the other aliquot as the "duplicate" sample. Calculate dry weight using the results of the "original" sample aliquot.

6. Calculate percent solids by the formula below. This value will be used for calculating analytical concentration on a dry weight basis.

$$\%\ \text{Solids} = \frac{\text{Sample Drv Weight}}{\text{Sample Wet Weight}} \times 100$$

7. Calculate the RPD of the % solids as follows:

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

where: S = Sample result
and D = Duplicate result

The acceptable RPD is $\leq$20 %.
Action on Failure: Another percent solid has to be determined.

Title: SOP for Free Cyanide In Water, Soils and Solid Wastes By Microdiffusion [Method 9016]

Approvals (Signature/Date):

Technical Manager	Date	Health & Safety Manager / Coordinator	Date
Quality Assurance Manager	Date	Laboratory Director	Date

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1.0 Scope and Application

1.1 This test method covers the determination of free cyanide in wastewaters, ground waters, surface waters, drinking waters, soils and solid wastes. This test method reports the cyanide that dissociates from simple cyanides or weakly-bound metal cyanide complexes at room temperature, from a solution of pH 6-6.5.

1.2 This method does not determine strongly-bound metal cyanide complexes that resist dissociation, such as the hexacyanoferrates and gold cyanide, nor does it determine thiocyanate and cyanohydrin.

1.3 This method is restricted to use by, or under supervision of, properly experienced and trained personnel. Each analyst must demonstrate the ability to generate acceptable results with this method. Prior to performing sample analysis, analysts must document the ability to provide accurate results through IDOC (Initial Demonstration Of Capability) analysis and yearly, by CDOC (Continuing Demonstration Of Capability) analysis.

1.4 The document control # for this standard operating procedure is CT-CVS-88, Rev.0.

2.0 Summary of Method

2.1 The sample preparation is carried out using a microdiffusion cell. The water, wastewater, or extract sample is introduced in the outer chamber of the microdiffusion cell and is buffered at pH 6 and placed in the dark for 6 hours of diffusion. The free cyanide diffuses as HCN gas and is absorbed as CN^- into the sodium hydroxide solution located in the center chamber of the microdiffusion cell.

2.2 An aliquot of the sodium hydroxide absorber solution is removed and treated with acidified phosphate buffer and chloramine-T to convert the CN^- to cyanogen chloride. The cyanogen chloride is reacted with pyridine-barbituric acid to form a color complex that absorbs at 578 to 587 nm. The free cyanide is determined spectrophotometrically by measuring the absorbance of the sample and determining the concentration through comparison with a standard calibration curve.

2.3 Solids are first extracted prior to analysis using pH 12.3-12.5 NaOH solution. The filtered extracts are then diffused and analyzed spectrophotometrically. The extraction conditions described in this method have been found to be effective at extracting free cyanide from a variety of solid wastes.

2.4 The extraction conditions in this method may be modified as needed to improve free cyanide extraction efficiency from other matrices. For example, certain relatively complicated wastes or waste mixtures may not yield acceptable matrix spike recoveries. In such cases, additional refinement of the extraction step and/or the use of chemical pretreatments may be necessary to improve free cyanide recovery. Such flexibility is allowed as long as the data meets the quality objectives of the specific project.

3.0 Definitions

3.1 There are many definitions used with in the laboratory, which may be generic to all laboratory analyses, or more specific for certain methods. For the most recent terms and definitions used with in the laboratory, reference the SOP for Laboratory Terms and Definitions.

4.0 Interferences

4.1 Interferences, such as chlorine and sulfides, can degrade samples by reacting with the free cyanide present. All aqueous samples should be checked at the time of collection to determine the presence of oxidizing agents and/or sulfides. If present, the samples should be immediately treated prior to their storage for future analysis.

4.1.1 Oxidizing agents such as chlorine decompose free cyanide. Chlorine interferences can be removed by adding excess amounts of sodium arsenite or sodium thiosulfate to the sample prior to storage. Both sodium arsenite and sodium thiosulfate reduce the chlorine to chloride which does not react with free cyanide or otherwise interfere in its analysis.

4.1.2 Sulfide oxidation products can rapidly convert free cyanide to thiocyanate especially at high pH. Sulfide interferences (hydrogen sulfide, metal sulfides, or other compounds that may produce sulfide) can be removed by adding an excess of either lead carbonate or lead acetate to the sample. The addition of either reagent forms insoluble lead sulfide so that it may be removed via filtration prior to storage or analysis.

4.2 Volatility losses of free cyanide (as HCN) can occur in samples having pH values less than 12. If samples cannot be analyzed immediately after field collection and treatment for oxidizing agents and sulfides, they must be preserved by adjusting the pH to 12 or greater prior to storage.

4.3 Free cyanide can react with other chemicals such as aldehydes. Because of the reactivity of free cyanide, it is important that analysis is completed as soon as possible after sample collection.

4.4 Hexacyanoferrate complexes in water samples can decompose when exposed to UV light and produce free cyanide. This decomposition is virtually eliminated during the test procedure by allowing samples to diffuse in the dark.

4.5 Solvents, reagents, glassware, and other sample processing hardware may yield artifacts and/or interferences to sample analysis. All of these materials must be demonstrated to be free from interferences under the conditions of the analysis by analyzing method blanks.

5.0 Safety

Employees must abide by the policies and procedures in the Corporate Safety Manual, Radiation Safety Manual and this document. This procedure may involve hazardous material, operations and equipment. This SOP does not purport to address all of the safety problems associated with its use. It is the responsibility of the user of the method to follow appropriate safety, waste disposal and health practices under the assumption that all samples and reagents are potentially hazardous. Safety glasses, gloves, lab coats and closed-toe, nonabsorbent shoes are a minimum.

5.1 Specific Safety Concerns or Requirements

5.1.1 Because of the toxicity of cyanide, exercise great care in its handling. Acidification of cyanide solutions produces lethal, toxic hydrogen cyanide gas (HCN). Prepare all cyanide containing solutions within a ventilation hood. Wear hand and eye protection and a lab coat at all times when working with cyanide.

5.2 Primary Materials Used

The following is a list of the materials used in this method, which have a serious or significant hazard rating. **NOTE: This list does not include all materials used in the method. The table contains a summary of the primary hazards listed in the MSDS for each of the materials listed in the table.** A complete list of materials used in the method can be found in the reagents and materials section. Employees must review the information in the MSDS for each material before using it for the first time or when there are major changes to the MSDS.

Material (1)	**Hazards**	**Exposure Limit (2)**	**Signs and symptoms of exposure**
Sodium Hydroxide	Corrosive Poison	2 ppm, 5 mg/m^3	This material will cause burns if comes into contact with the skin or eyes. Inhalation of Sodium Hydroxide dust will cause irritation of the nasal and respiratory system.
Chloramine-T Hydrate	Poison		May be harmful by inhalation, ingestion, or skin absorption. This material is irritating to mucous membranes and upper respiratory tract. Avoid contact and inhalation.
Barbituric Acid	Irritant	None	Causes irritation to the eyes and skin. May cause respiratory tract irritation.

Material (1)	Hazards	Exposure Limit (2)	Signs and symptoms of exposure
Pyridine	Flammable Irritant	5 ppm-TWA	Inhalation causes severe irritation to the respiratory tract. Symptoms of overexposure include headache, dizziness, nausea, and shortness of breath. Causes severe irritation possibly burns, to the skin. Symptoms include redness and severe pain. Absorption through the skin may occur, resulting in toxic effects similar to inhalation. May act as a photosensitizer. Vapors cause eye irritation. Splashes cause severe irritation, possible corneal burns and eye damage.
Potassium Phosphate Monobasic	Irritant	None	May cause mild irritation to the respiratory tract. Eye and skin irritant. Chronic exposure: may sequester calcium and cause calcium phosphate deposits in the kidneys.
Hydrochloric Acid	Corrosive Poison	5 ppm-	Inhalation of vapors can cause coughing, choking, inflammation of the nose, throat, and upper respiratory tract, and in severe cases, pulmonary edema, circulatory failure, and death. Can cause redness, pain, and severe skin burns. Vapors are irritating and may cause damage to the eyes. Contact may cause severe burns and permanent eye damage.
Sodium Arsenite	Poison Irritant	10 ug/m^3 (TWA)	May be fatal if swallowed or inhaled. Cancer hazard. Contains inorganic arsenic which can cause cancer. Risk of cancer depends on duration and level of exposure. Causes irritation to skin, eyes, and respiratory tract. May cause liver and kidney damage. Use only with adequate ventilation and respiratory equipment.
Lead Carbonate	Poison Irritant	0.05 mg/m^3 (TWA)	Poison. May be fatal if swallowed or inhaled. Causes irritation to skin, eyes, and respiratory tract. Neurotoxin. Affects the gum tissue, central nervous system, kidneys, blood and reproductive system.
Lead Acetate, Trihydrate	Poison Irritant	0.15 mg/m^3 (TWA)	Causes irritation. May be fatal if swallowed. Harmful if inhaled or absorbed through skin. This substance is listed as an NTP anticipated human carcinogen.
Potassium Cyanide	Poison Corrosive	5 Mg/M3 TWA as CN	**This material will form Hydrogen Cyanide (HCN) gas when combined with strong acids. Breathing HCN gas may result in death.** Corrosive to the respiratory tract. May cause headache, weakness, dizziness, labored breathing nausea and vomiting, which can be followed by weak and irregular heart beat, unconsciousness, convulsions, coma and death. Solutions are corrosive to the skin and eyes, and may cause deep ulcers, which heal slowly. May be absorbed through the skin, with symptoms similar to those noted for inhalation. Symptoms may include redness, pain, blurred vision, and eye damage.
1 – Always add acid to water to prevent violent reactions.			
2 – Exposure limit refers to the OSHA regulatory exposure limit.			

6.0 Equipment and Supplies

6.1 Supplies/equipment for sample collection, preservation, and handling

6.1.1 Potassium iodide-starch test paper

6.1.2 Lead-acetate test paper

6.1.3 pH test paper

6.2 Supplies/equipment for extraction of solid samples

6.2.1 Extractor (TCLP) Spinners

6.2.2 Extraction bottles, HDPE, 1000-mL capacity or larger

6.2.3 Balance, capable of weighing 0.001g

6.3 Supplies/equipment for microdiffusion processing

6.3.1 Plastic Conway-type microdiffusion cell, 68-mm or 83-mm OD-Equipped with a fitted lid for use in maintaining an airtight seal when in place

6.3.2 Micropipets, 0.20-mL, 0.50-mL, 1.00-mL, 1.50-mL, 2.50-mL, 5.00-mL, 10.0-mL, 15.0-mL, and 30.0-mL

6.3.3 Adjustable pipet or calibrated syringe-capable of being adjusted to deliver exactly 3.00 mL of solution

6.3.4 Adjustable pipet or calibrated syringe-capable of being adjusted to deliver exactly 1.30 mL of solution

6.3.5 Thermo Electron Genesys10 Series Spectrophotometer, 1 cm pathlength @ 578 nm.

6.3.6 Disposable cuvets, 10mm lightpath, 4.5 mL capacity.

7.0 Reagents and Standards

7.1 Reagent-grade chemicals must be used in all tests. Unless otherwise indicated, it is intended that all reagents conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society. Reagents should be stored in glass to prevent the leaching of contaminants from plastic containers. Note, however, that sodium hydroxide solutions of relatively moderate strength (4g/L and greater), should be stored in HDPE plastic containers whenever possible.

7.2 The expiration dates for chemicals used in this analysis are five years from time of receipt for raw, solid materials and two years from time of receipt for raw, liquid materials except where noted. Reagents made from raw materials are good for one year except where noted.

7.3 Reagent water - (ASTM Type II) deionized water.

7.4 Reagents for sample collection, preservation, and handling

7.4.1 Sodium arsenite, $NaAsO_2$

7.4.2 Sodium thiosulfate, $Na_2S_2O_3$

7.4.3 Lead acetate trihydrate, $Pb(CH_3COO)_2 \cdot 3H_2O$

7.4.4 Lead Carbonate, $PbCO_3$

7.4.5 Sodium hydroxide (50% w/v), NaOH: dissolve 500g of sodium hydroxide pellets in approximately 500 mL of reagent water. Let cool and dilute to 1 L with reagent water.

7.5 Reagents for extraction of solid samples

7.5.1 Sodium hydroxide (50% w/v), NaOH: dissolve 500g of sodium hydroxide pellets in approximately 500 mL of reagent water. Let cool and dilute to 1 L with reagent water.

7.5.2 Sodium hydroxide extraction solution (pH 12.3-12.5)-Weigh 2.53g of 50% sodium hydroxide solution and transfer to a 1-L volumetric flask containing approximately 800 mL of reagent water. Stir until dissolved. Adjust the final volume to 1-L using reagent water. Using pH test paper, check to ensure that the extraction solution is in the proper pH range. Add additional 50% NaOH, if necessary, to adjust to the pH to the proper range.

7.6 Reagents needed for microdiffusion processing and spectrophotometric analysis

7.6.1 Sodium hydroxide solution (2.05 g/L), NaOH – Weigh 4.10g of 50% sodium hydroxide solution and transfer to a 1-L volumetric flask containing approximately 800 mL of reagent water. Stir until dissolved. Cool the solution to room temperature and adjust the final volume to 1 L using reagent water. This solution is used only for the preparation of initial demonstration of capability samples, method blanks, matrix spikes, and laboratory control standards.

7.6.2 Sodium hydroxide solution (4.1 g/L) – Weigh 8.20g of 50% sodium hydroxide solution and transfer to a 1-L volumetric flask containing approximately 800 mL of reagent water. Stir until dissolved. Adjust the final volume to 1-L using reagent water.

7.6.3 Stock cyanide standard (1000 mg/L) – purchased commercially with Certificate of Analysis.

7.6.4 Standard cyanide solution (2mg/L) – pipet 2.00mL of 1000mg/L stock cyanide solution into a 1-L volumetric flask and dilute to volume using 4.1-g/L sodium hydroxide solution. This solution is used in the preparation of calibration standards.

7.6.5 Potassium phosphate monobasic, KH_2PO_4

7.6.6 Sodium hydroxide solution (100g/L), NaOH – Weigh 200g of 50% sodium hydroxide solution and transfer to a 1-L volumetric flask containing approximately 800mL of reagent water. Stir until dissolved. Cool the solution to room temperature and adjust the final volume to 1 L using reagent water.

7.6.7 Concentrated phosphoric acid (sp gr 1.69), H_3PO_4

7.6.8 Potassium phosphate solution (190g/L) – add 400mL of reagent water to a 2-L beaker. Next, weigh 29g 50% sodium hydroxide solution, transfer to the beaker, and dissolve. Add 190g of potassium phosphate monobasic and stir to dissolve. Bring the volume to approximately 950-mL to aid in dissolution. Adjust the pH of the solution so that it is within the range of 5.9-6.1, using 100-g/L sodium hydroxide or concentrated phosphoric acid. Transfer the solution to a 1-L volumetric flask, and dilute to volume with reagent water.

7.6.9 Potassium phosphate buffer solution (acidified) – Add 8.0mL of concentrated phosphoric acid to 100mL of 190-g/L potassium phosphate solution.

7.6.10 Chloramine-T reagent (10g/L) – Dissolve 1.0g of chloramine –T in 50mL of reagent water contained in a 100-mL volumetric flask. Dilute to volume with reagent water. Prepare fresh daily.

7.6.11 Barbituric acid, $NHCONHCOCH_2CO$

7.6.12 Pyridine, C_5H_5N

7.6.13 Concentrated hydrochloric acid (sp gr 1.19), HCL

7.6.14 Pyridine-barbituric acid reagent – Add 15.0g of barbituric acid to a 250-mL volumetric flask. Wash down the sides of the flask with just enough reagent water to moisten the barbituric acid. Add 75mL of pyridine and swirl to mix. Using reagent water, bring volume to approximately 230mL. Stir to dissolve and cool the solution to room temperature. Dilute to final volume with reagent water and mix. It is recommended that the reagent be prepared fresh weekly and stored in a dark place. Discard and prepare a new batch if a precipitate develops.

Warning: Pyridine is toxic; avoid contact or inhalation. Prepare this reagent in an exhaust hood.

8.0 Sample Collection, Preservation, Shipment and Storage

8.1 Samples should be collected in plastic or glass (preferably plastic) containers that are either amber or covered in aluminum foil so as to filter UV light at 400 nm and below in order to prevent photodecomposition of metal cyanide complexes. Sample bottles are never reused.

8.2 A single, satisfactory preservation technique is not available for samples containing free cyanide. Reactions between free cyanide and oxidizing agents, sulfides and aldehydes will occur. The following procedural steps are strongly recommended in order to inhibit analyte degradation reactions that may take place.

8.3 Testing and treatment for oxidizing agents

8.3.1 All samples whose origin or composition is not well known should be tested for the presence or absence of oxidizing agents, such as chlorine, ideally at the time of sample collection.

8.3.2 Place a drop of sample on a strip of potassium iodide-starch test paper. A bluish discoloration indicates the presence of oxidizing agents. If this occurs, add sodium arsenite (approximately, 0.1g $NaAsO_2$/L sample).

8.3.3 Continue testing the sample for the presence of oxidizing agents, making repeat additions of sodium arsenite, as needed, until all oxidizing agents have been treated as evidenced by a lack of color change on the test paper.

Note: Sodium thiosulfate may be used instead of sodium arsenite, but it should not be added in excess of 0.1g/L sample.

8.4 Testing and treatment for sulfides

8.4.1 All samples whose origin or composition is not well known should be tested for the presence or absence of sulfides, ideally just following sample collection and testing/pretreatment for oxidizing agents.

8.4.2 Place a drop of sample on a strip of lead-acetate test paper. Darkening of the test paper indicated the presence of sulfides. If this occurs, add sodium arsenite (approximately, 0.1g $NaAsO_2$/L sample).

8.4.3 Continue testing the sample for sulfides, making repeat additions of sodium arsenite, as needed, until all sulfides have been treated as verified when the test paper no longer darkens.

Note: if the sulfide concentration appears too high, powdered lead carbonate should be substituted for sodium arsenite in order to avoid significantly lowering the sample pH.

8.4.4 Filter the sample to remove any precipitated lead sulfate.

8.5 Analyze samples immediately; otherwise preserve them at the time of collection, following any treatment for oxidizing agents or sulfides by adding 50% sodium hydroxide, until the pH is equal to or slightly greater than 12. This minimizes cyanide losses due to volatilization of HCN.

8.6 Store properly preserved samples in the dark at 4 ± 2ºC.

8.7 Sample container, preservation techniques and holding times may vary and are dependent on sample matrix, method of choice, regulatory compliance, and/or specific contract or client requests. Listed below are the holding times and the references that include preservation requirements.

Matrix	Sample Container	Min. Sample Size	Preservation	Holding Time	Reference
Waters	Plastic or glass	25 mL	NaOH, pH ≥12; Cool 4 ± 2ºC	14 Days*	SW846 Method 9016
Soils	Plastic or glass	25 g	Cool 4 ± 2ºC	14 Days**	SW846 Method 9016

*When properly preserved, cyanide samples can be stored for up to 14 days from collection prior to analysis.

** Extract solids within 14 days of sample collection. Analyze extracts of solid samples within 24 hrs following extraction.

8.8 If results for soil samples are to be reported on a dry weight basis, a separate percent solids determination must be made. Percent solids for soils are performed by the Metals or Sample Control Departments. Refer to Section 11.3 for calculation options.

9.0 Quality Control

9.1 Initial Demonstration Of Capability (IDOC)

Each analyst must demonstrate initial proficiency with each sample preparation and determinative method combination utilized by generating data of acceptable accuracy and precision for the target analyte in a clean matrix. The analyst must also repeat the demonstration of proficiency yearly (CDOC) or whenever a significant change in instrumentation is made. The IDOC, consisting of four Laboratory Control Samples (LCS's) or four Matrix Spike Blanks (MSB's), must be performed prior to sample analysis. The acceptable recovery range is 85-115%.

NOTE: The free cyanide IDOC samples should be prepared in 2.05 g/L sodium hydroxide.

9.2 Method Blank

Method blanks are analyzed every twenty samples or less per matrix.

Before processing any samples, the analyst should demonstrate that all parts of the equipment in contact with the sample and reagents are interference-free. This is accomplished through the analysis of a method blank. As a continuing check, each time samples are extracted, cleaned up, and analyzed, and when there is a change in reagents, a method blank should be prepared and analyzed for the compounds of interest as a safeguard against chronic laboratory contamination. If a measurable absorbance is observed at or in close proximity to the measurement wavelength of the target analyte that would prevent the accurate determination of that analyte, determine the source and eliminate it, if possible, before processing the samples. The blanks should be carried through all stages of sample preparation and analysis. When new reagents or chemicals are received, the laboratory should monitor the preparation and/or analysis blanks associated with samples for any signs of contamination. It is not necessary to test every new batch of reagents or chemicals prior to sample preparation if the source shows no prior problems. However, if reagents are changed during a preparation batch, separate blanks need to be prepared for each set of reagents.

The results of the method blank should not be subtracted from those of any associated samples. Such "blank subtraction" may lead to negative sample results. If the method blank results do not meet the project-specific acceptance criteria and reanalysis is not practical, then the data user should be provided with the sample results, the method blank results, and a discussion of the corrective actions undertaken by the laboratory.

9.3 Sample quality control for preparation and analysis

Procedures for documenting the effect of the matrix on method performance (precision, accuracy, method sensitivity) include the analysis of QC samples including a method blank, a matrix spike, a duplicate, and a laboratory control sample in each analytical batch (20 samples or less). Any method blanks, matrix spike samples, and replicate samples must be subjected to the same analytical procedures as those used on actual samples.

The following should be included within each analytical batch.

9.3.1 Method Blank

A method blank (MB) is prepared from a 2.05 g/L sodium hydroxide solution and treated exactly as a field sample, including exposure to all glassware, equipment, solvents, filtration, and reagents that are used with field samples. Analysis of an MB is used to assess contamination from the laboratory environment, equipment, and/or reagents. Any free cyanide measured in the MB that exceeds the lower limit of quantitation (LLOQ) indicates that contamination is present. The source of the contamination should be determined and corrected prior to performing any sample analysis. Any sample included in an analysis batch that has an unacceptable MB concentration should be reanalyzed in a subsequent batch after the contamination problem is resolved.

9.3.2 Duplicate, Matrix Spike, Matrix Spike Duplicate

Documenting the effect of the matrix should include the analysis of at least one matrix spike (MS) and one duplicate unspiked sample or one matrix spike/matrix spike duplicate (MS/MSD) pair. Both aqueous samples and solid sample extracts should be represented by a minimum of one DU/MS or MS/MSD pair for each respective matrix per twenty samples or less. The decision on whether to prepare and analyze duplicate samples or an MS/MSD must be based on knowledge of the samples in the sample batch. If samples are expected to contain the target analyte, laboratories may use a matrix spike (MS) and a duplicate analysis of an unspiked field sample. If samples are not expected to contain the target analyte, the laboratories should use an MS/MSD pair. Acceptable recovery for spikes is ± 25 % of spike added. A control limit of $\leq$20% for RPD shall be used for original and duplicate samples greater than or equal to 5x's the Reporting Limit. If both samples are less than 5x's the RL, the difference between the two results must be less than the RL. If both sample values are less than the reporting limit, the RPD is not calculated. Project-specific QC requirements may be requested by the client.

NOTE: **Spiking immediately prior to microdiffusion processing is of critical importance when preparing Matrix Spikes of extracts from solid samples.** This is because soils and related solid wastes typically contain relatively large levels of free transition metals, which can potentially form complexes with the spiked free cyanide, resulting in low spike recovery values.

9.3.3 Laboratory Control Sample

A laboratory control sample (LCS) should be included with each analytical batch of twenty samples or less. The LCS consists of an aliquot of a clean (control) matrix similar to the sample matrix and of the same weight or volume. The LCS is spiked with the same analytes at the same concentrations as the matrix spike, when appropriate. When the results of the matrix spike analysis indicate a potential problem due to the sample matrix itself, the LCS results are used to verify that the laboratory can perform the analysis in a clean matrix. The control limits for an aqueous LCS are 85-115%; the acceptance criteria for the soil LCS is based upon the vendor's established limits.

NOTE: The free cyanide LCS sample should be prepared in 2.05 g/L sodium hydroxide.

9.4 Initial calibration verification (ICV)

Immediately after the calibration standards have been analyzed, the accuracy of the calibration must be verified by the analysis of an ICV standard. The ICV is prepared in the same manner as a calibration standard (i.e., the sample is **NOT** processed through the microdiffusion procedure) at a concentration level within the calibration range of the method and using a **second source** standard (prepared using standards different from the calibration standards) spiked into 4.1g/L sodium hydroxide. The control limit for the ICV is ±15% of the true value. When the ICV exceeds the control limits, the analysis should be terminated, the problem corrected, the instrument recalibrated, and the calibration re-verified.

9.5 Continuing calibration verification (CCV)

Once the calibration curve has been established, the continuing accuracy must be verified by analysis of a CCV after every tenth field sample, and at the end of the analysis sequence. The CCV is equivalent to or prepared in the same manner as a calibration standard (i.e., the sample is **NOT** processed through the microdiffusion procedure) at a concentration level within the calibration range of the method and using the same source standard (prepared using the same source standards as those used to prepare the calibration standards) spiked into 4.1 g/L sodium hydroxide. CCV concentrations alternating between the low- and mid-range calibration standard concentrations are recommended. The control limit for the low-range CCV is ± 50% and for the mid-range CCV is ± 15% of the true value. When the CCV exceeds the control limits, the analysis should be terminated, the problem corrected, the instrument recalibrated, and the calibration re-verified using an ICV analysis. Samples that are not bracketed by acceptable CCV runs must be reanalyzed.

9.6 Lower Limit of Quantitation (LLOQ) check standard

The laboratory should establish the LLOQ as the lowest point of quantitation which, in most cases, is the lowest concentration in the calibration curve. The LLOQ verification is recommended for each project application to validate quantitation capability at low analyte concentration levels. This verification may be accomplished either with clean control material (e.g., reagent water, method blank, Ottawa sand, diatomaceous earth, etc.) or a representative sample matrix (free of target compounds). Optimally, the LLOQ should be less than or equal to the desired regulatory action levels based on the stated project-specific requirements.

9.6.1 The determination of LLOQs using spiked clean control material represents a best-case scenario, and does not evaluate the potential matrix effects of real-world samples. For the application of LLOQs on a project-specific basis, with established DQOs, a representative matrix-specific LLOQ verification may provide a more reliable estimate of the lower quantitation limit capabilities.

9.6.1.1 A matrix-free LLOQ check standard is prepared by spiking a clean control material with the analyte(s) of interest at the predicted LLOQ concentration level(s). This LLOQ check is carried through the same preparation procedures as the environmental samples and other QC. Recovery should be ±50% (or other such project-required acceptance limits for accuracy and precision) of the true value to verify the data reporting limit. The low-range CCV standard, if prepared at the appropriate concentration, may also serve as the LLOQ verification for confirming method sensitivity.

9.6.1.2 Alternatively, a representative sample matrix may be spiked with the analytes of interest at the predicted LLOQ concentration levels. This LLOQ check is carried through the same preparation procedures as the environmental samples and other QC. Individual LLOQs are verified when each respective analyte is recovered at ±50% of the predicted LLOQ concentration or established DQO criteria. This check may also be applied towards establishing the individual analyte reporting limit(s).

9.6.2 In-house limits may be calculated when sufficient data points exist.

9.7 The analysis of proficiency samples for free cyanide by method 9016 is not currently required but is recommended.

9.8 Summary of Sample QC

Quality Controls	Frequency	Control Limit
Initial Demonstration Of Capability (IDOC)	Initially; prior to sample analysis	85-115%
Continuing Demonstration Of Capability (CDOC)	Yearly or when changes to instrumentation are made	85-115%
Method Blank (MB)	1 in 20 or fewer samples/matrix	<LLOQ
Laboratory Control Sample (LCS)	1 in 20 or fewer samples/matrix	85-115% for waters; established vendor limits for soils
Sample Duplicate (DU)*	1 in 20 or fewer samples/matrix	≤20 RPD for samples > 5x's the LLOQ; ± the LLOQ for samples < 5x's the LLOQ; no RPD criteria for both results <LLOQ
Matrix Spike (MS)	1 in 20 or fewer samples/matrix	75-125%
Matrix Spike Duplicate(MSD)*	1 in 20 or fewer samples/matrix	75-125% for spike; for RPD criteria, see DU

*Either a Sample Duplicate or a Matrix Spike Duplicate may be analyzed based upon the criteria in Section 9.3.2.

Note: alternately, laboratory generated statistical limits may be used and updated annually.

9.9 Summary of Instrument QC

Step	Standards	Type	Control Limit	Frequency
Method # 9016				
Initial Cal	Conc and # of stds- refer to Section 10.3.1	Type of Cal: first order linear regression	Correlation Coefficient ≥0.995	Daily
ICV	Second source; within calibration range of curve	Not processed through micro-diffusion procedure	85-115%	Immediately after calibration curve
ICB	1mL of 4.1 g/L NaOH developed same as curve/ samples	Not processed through micro-diffusion procedure	<LLOQ	Immediately following the ICV
CCV	Same source as calibration curve stock; concentration within range of calibration curve- (concentrations alternating between low- and mid-range recommended)	Not processed through micro-diffusion procedure	±50% for low-range CCV ±15% for mid-range CCV	Following ICB, after every tenth sample, and at end of run
CCB	1mL of 4.1 g/L NaOH developed same as curve/ samples	Not processed through micro-diffusion procedure	<LLOQ	Following each CCV
LLOQ Check Standard*	Same source as calibration curve; concentration at data reporting limit	Not processed through micro-diffusion procedure	50-150%	Daily

*Can use a low-range CCV as the LLOQ check standard.

10.0 <u>Procedure</u>

<u>CAUTION:</u> This method requires manual dexterity, practice, and meticulous attention to operational consistency. Best practices are noted throughout this section to assist analysts in achieving optimum results. Adherence to these practices is highly recommended for attaining precise and accurate data.

NOTE: Observe the specified time periods in the procedural steps where noted. Establish provisions so as to guarantee that all spectrophotometric measurements are able to be completed in the 3-6-min time interval recommended in the procedure.

NOTE: Store all samples in the dark whenever possible during processing. Light of 400 nm and under can dissociate metal cyanide complexes, thus yielding artificially high free cyanide values.

10.1 Extraction of free cyanide from solid samples

Extract solid samples prior to microdiffusion and analysis, otherwise proceed to Section 10.2.

10.1.1 Weigh 250 mg PbCO3 and transfer to an extraction bottle.

NOTE: Since, sulfides are often present in soils and solid wastes, lead carbonate is added to all extract samples in order to fix sulfides as PbS.

10.1.2 Weigh a 1g sample of the solid to be analyzed, recording the sample mass to 0.001 g. Transfer the weighed sample to the extraction bottle containing the lead carbonate.

10.1.3 Add 500 mL of pH 12.3-12.5–NaOH solution to the extraction bottle and gently rotate the bottle so as to mix the contents.

10.1.4 Cap the extraction bottle, place on agitation apparatus and agitate for 5 min. After 5 min, use a strip of pH test paper check the sample mixture pH to verify that it is within the range of 12.3-12.5. If it is not, add 50% NaOH drop-wise, to bring the pH to within the proper range. Recap the bottle and restart agitation. Extract the free cyanide in this manner for a period of 60 min.

10.1.5 At the end of the extraction period, use a strip of pH test paper to verify that the sample mixture pH is 11 or greater. If the pH is in the correct range, the extraction may be deemed to be acceptable – proceed to Sec. 10.2. If it is not, extract a new sample by repeating Sections. 10.1.1-10.1.5, except using an initially higher-pH extraction solution (e.g., pH 13)

10.1.6 Following a successful extraction, decant the sample supernatant into a clean container. Filter the supernatant through a 0.45µm membrane filter to remove particulate material and any PbS that may have formed.

10.1.7 If necessary, centrifuge the extraction mixture at 5,000 rpm for 20 min, or other such velocity and time, as needed to remove fine particles and afford an adequate separation, as evidenced by a relatively clear final extract solution.

10.2 Microdiffusion of free cyanide in aqueous samples and extracts (see Attachment 2 for process overview)

NOTE: At a minimum, perform microdiffusion of all samples in duplicate. More diffusion replicates can be performed, if desired, for greater statistical confidence in the final result.

10.2.1 Using a pipet or calibrated syringe, dispense 3.00 mL of sample into the outer chamber of a clean, dry microdiffusion cell (see Attachment 1).

10.2.2 Using an adjustable pipet or calibrated syringe, dispense exactly 1.30 mL of 4.1-g/L sodium hydroxide solution into the center chamber of the microdiffusion cell.

10.2.3 Using a calibrated syringe (or pipet), immediately inject 1.0 mL of 190-g/L potassium phosphate solution into the sample located in the outer chamber of the microdiffusion cell. Inject at an angle in order to force the solution around the chamber.

NOTE: The force of ejection of aids in the proper mixing of the solutions.

10.2.4 Perform this step as quickly and carefully as possible in order to avoid loss of free cyanide: Carefully tilt and rotate the cell once to mix the constituents and immediately, use pH test paper to check the sample and ensure that it has attained a pH of 6. If the sample pH is greater than 6, add additional 190-g/L potassium phosphate solution, using 1.0-1.5 mL, increments, as necessary, to adjust the sample pH to 6.

NOTE: When analyzing an unknown sample, it is strongly recommended that the sample be pre-tested prior to microdiffusion analysis in order to determine the exact amount of potassium phosphate solution needed to adjust the sample pH to 6. This may be accomplished by pipetting 3.0 mL of sample into a small container (e.g., volume capacity of 10 mL) followed by addition of 1.0 mL of 190-g/L potassium phosphate solution. After mixing the solutions well, determine the amount of potassium phosphate solution required to attain a pH of 6.

NOTE: The pH measurement step in Sec. 10.2.4 may be eliminated based upon historical knowledge of the sample.

10.2.5 Quickly, seal the cell by fitting it with a lid.

10.2.6 Carefully tilt and rotate the cell for 5 seconds to ensure proper mixing.

NOTE: Exercise great care during mixing of solutions by tilting and rotating the microdiffusion cell carefully so as to avoid spilling or splashing the contents from one chamber of the cell to the other.

10.2.7 Place the covered cell in the dark at room temperature for a period of 6 hr.

NOTE: It is essential that the microdiffusion cell be protected from light at all times during the 6-hr diffusion period in order to avoid photolysis of hexacyanoferrate complexes.

10.2.8 Proceed to analyze the diffused samples and standards as described in Sec. 10.4.

10.3 Calibration

10.3.1 Preparation of calibration standards - Pipet 0, 0.20, 0.50, 1.00, 2.50, 5.00, 10.0, 15.0, and 30 mL of the 2.0-mg/L cyanide standard solution into nine separate 200-mL volumetric flasks. Dilute each of the flasks to volume with 4.1-g/L sodium hydroxide solution. These dilutions yield calibration standards that contain approximately 0, 2.0, 5.0, 10, 25, 50, 100, 150, and 300µg/L cyanide, respectively. Additional calibration standards may be added if desired.

NOTE: The 0 µg/L cyanide standard sample is used as the calibration blank.

10.3.2 To establish the calibration curve, analyze the calibration standards in accordance with the procedure in Section 10.4. This is accomplished by carrying out color development and spectrophotometric analysis on a 1.00 mL aliquot of standard as described in Secs. 10.4.1-10.4.9. Prepare a duplicate set of spectrophotometric samples for each respective calibration standard to provide for duplicate spectrophotometric analyses of each standard. In order to avoid a method bias, the calibration standards must be analyzed directly and not processed through the microdiffusion procedure.

10.3.3 Calculate the average absorbance reading for each duplicate set of calibration standards analyzed.

10.3.4 Establish the calibration curve by plotting average absorbance versus cyanide concentration. A new calibration curve should be established daily with each analysis. Perform a first-order linear regression of the calibration curve (i.e., $y = ax + b$ function). The acceptance criterion for the calibration curve should be a correlation coefficient of 0.995 or higher.

10.3.5 Verify the accuracy of the initial calibration curve as described in Sec. 9.0.

10.4 Sample Analysis - Color development and spectrophotometric analysis of diffused samples and standards

NOTE: Ensure that the spectrophotometer cells used for analysis are optically-matched prior to use.

10.4.1 Prepare the spectrophotometer for analysis according to the manufacturer's instructions.

10.4.2 Set the spectrophotometer wavelength to 578 nm or other optimum wavelength, as determined by this method.

10.4.3 When the instrument has stabilized, zero the detector against the 4.1-g/L sodium hydroxide solution.

10.4.4 At the end of the diffusion period, pipet a 1.00-mL aliquot of the sodium hydroxide solution from the center chamber of the microdiffusion cell and dispense into a clean, dry, spectrophotometer cell.

CAUTION: Complete mixing as indicated in each of the following steps is critical for accurate analysis.

10.4.5 Using a micropipet, dispense 0.1 mL of acidified potassium phosphate buffer into the spectrophotometer cell. A small piece of Parafilm M® is used to provide a seal and prevent leakage. The parafilm should form a watertight seal. While holding the parafilm tightly against the cell, invert the cell 4-5 times to mix.

10.4.6 Dispense 0.50 mL of chloramine-T reagent into the spectrophotometer cell using a micropipet. Seal the cell tightly again with the parafilm and invert 4-5 times to mix.

10.4.7 Pipet 1.00 mL of pyridine-barbituric acid reagent into the spectrophotometer cell and replace the parafilm. Note the time and invert the cell 8-10 times to mix.

10.4.8 Within 3-6 min from the start of mixing, the development of the color complex, as well as its stability, will be optimum for performing spectrophotometric readings. Read the absorbance of the spectrophotometric sample at 578 nm during this time interval. The time interval at which readings are taken must be consistent to the extent possible for all samples and standards.

NOTE: The wavelength maximum of the color-complex can vary slightly with each bottle or lot of barbituric acid reagent due solvatochromic effects. For optimum results, the absorbance maximum for the color complex can be determined by performing a spectral scan of a prepared 150-µg/L calibration standard prior to analysis each day. The sample and calibration standard absorbance readings may then be measured at the determined wavelength maximum, instead of at 578 nm.

10.4.9 Measure the absorbance for each sample replicate. Average the replicate results to yield a single absorbance value for each sample.

NOTE: Disposable spectrophotometer cells are used for sample/standard development and are not reused.

NOTE: The total volume of liquid in the spectrophotometer cell is 2.6 mL. This is normally sufficient for measuring the absorbance in most spectrophotometers. However, if a larger cell is used and/or a greater sample volume is needed, the volume of acidified potassium phosphate buffer added to the sample may be increased, as long as it is performed consistently for other samples and calibration standards.

11.0 Calculations / Data Reduction

11.1 For each spectrophotometric sample, obtain the µg/L free cyanide concentration from the calibration curve established in Section 10.3.4.

11.2 Determine the actual free cyanide concentration in an aqueous (or solid extract) sample by mathematically adjusting the free cyanide concentration determined in Sec. 11.1 to account for the concentration effect of the microdiffusion process as follows:

$$\frac{\mu g}{L}\text{ free CN}^{-}\text{ in aqueous sample} =$$

$$\frac{1.3\text{ mL (center chamber solution volume)}}{3.0\text{ mL (outer chamber solution volume)}} \times \frac{\mu g}{L}\text{ free CN}^{-}\text{ in spectrophotometric sample}$$

NOTE: Samples having a free cyanide concentration that exceeds that of the highest calibration standard, as determined in Sec. 11.1, must be diluted appropriately and reanalyzed spectrophotometrically (Sec. 10.4). Dilute the sample as needed using 4.1 g/L sodium hydroxide so that the concentration is within the calibration range. Analyze the diluted sample using a 3.00 mL aliquot as described in Section 10.4. Correct the final concentration result by multiplying by the appropriate dilution factor.

11.3 In the case of an extract, calculate the actual free cyanide concentration in the original solid that was extracted as follows:

$$\frac{\mu g}{g}\text{ free CN}^{-}\text{ in solid sample} = \frac{\mu g}{L}\text{ free CN}^{-}\text{ in extract sample} \times \frac{\text{Final extract solution volume (L)}}{\text{Sample mass (g)}}$$

Per SW846 MICE, there is no official RCRA policy determining whether soil results should be reported on a wet or dry basis. The decision is made by the final user (client) and may be based on project-specific or risk assessment guidelines. The determination, therefore, depends on the intended use of the data. For dry weight reporting, percent solids must be taken into account; the final result is divided by the decimal percent solids.

11.4 Accuracy

$$\text{ICV, CCV, LCS \% Recovery} = \frac{\text{observed concentration}}{\text{known concentration}} \times 100$$

$$\text{MS, MSD \% Recovery} = \frac{\text{(spiked sample)} - \text{(unspiked sample)}}{\text{spiked concentration}} \times 100$$

11.5 Precision (RPD)

Matrix Duplicate (DU) =

$$\frac{\text{Original sample value} - \text{dup. Sample value}}{\text{(Original sample value} + \text{dup. Sample value)/2}} \times 100$$

Matrix Spike Duplicate (MSD) =

$$\frac{\text{Matrix Spike sample value} - \text{Matrix Spike Dup. Sample value}}{\text{(Matrix Spike sample value} + \text{Matrix Spike Dup. Sample value)/2}} \times 100$$

11.6 Data Review

Analytical batches are subjected to a first level review by the analyst performing the test; the first level review process checks for accuracy and completeness. During the first level review process, NCM’s are generated noting any method deviations or noncompliance issues.

A secondary review is conducted by a qualified laboratory staff member; the secondary review ensures that the batch has been check for accuracy and completeness and that NCM’s have been written where applicable.

12.0 Method Performance

12.1 Method Detection Limit Study (MDL)

The method detection limit (MDL) is the lowest concentration that can be detected for a given analytical method and sample matrix with a 99% confidence that the analyte is present. The MDL is determined according to the laboratory’s MDL procedure. This guidance is provided in the SOP for Conducting MDL Studies, CT-QAS-17. MDLs reflect a calculated (statistical) value determined under ideal laboratory conditions in a clean matrix, and may not be achievable in all environmental matrices. The laboratory maintains MDL studies for analyses performed; these are verified at least annually through the analysis of Method Detection Limit Verifications (MDLVs).

12.2 Demonstration of Capabilities

Further guidance for Demonstration of Capabilities is provided in the SOP for Demonstration of Capability, CT-QAS-27.

12.3 Training Requirements

Additional information regarding training requirements is available in the SOP for Employee Training, CT-QAS-16.

13.0 Pollution Control

It is TestAmerica's policy to evaluate each method and look for opportunities to minimize waste generated (i.e., examine recycling options, ordering chemicals based on quantity needed, preparation of reagents based on anticipated usage and reagent stability). Employees must abide by the policies in Section 13 of the Corporate Environmental Health and Safety Manual (CW-E-M-001) for "Waste Management and Pollution Prevention."

14.0 Waste Management

Waste management practices are conducted consistent with all applicable rules and regulations. Excess reagents, samples and method process wastes are disposed of in an accepted manner. Waste description rules and land disposal restrictions are followed. Waste disposal procedures are incorporated by reference to the SOP for Tracking and Collection of Hazardous Waste, CT-SFS-1. The following waste streams are produced when this method is carried out.

Waste Streams Produced by the Method

The following waste streams are produced when this method is carried out.

- Soil extracts containing soil, sodium hydroxide and lead carbonate - employees are to collect and dispose of the waste in the satellite caustic waste accumulation drum.
- Caustic cyanide waste from calibration standards and microdiffusion cells - employees are to collect and dispose of the waste in the satellite caustic waste accumulation drum.
- Pyridine waste – employees are to collect and dispose of the waste in the satellite pyridine waste accumulation drum; observe proper safety procedures regarding ventilation and respiratory protection – pyridine is toxic; avoid inhalation.
- Disposable spectrophotometer cells – rinse interior three times with tap water and dispose of rinsings in the satellite pyridine waste accumulation drum; observe proper safety procedures regarding ventilation and respiratory protection – pyridine is toxic; avoid inhalation; dispose of the cuvets in the solid waste accumulation drum.

15.0 References / Cross-References

15.1 Method 9016, SW846, Revision 0, June, 2010.

15.2 SOP for Laboratory Terms and Definitions, CT-QAS-19.

15.3 SOP for Demonstration of Capability (DOC's), CT-QAS-27.

15.4 SOP for Employee Training, CT-QAS-16.

15.5 SOP for Conducting MDL Studies, CT-QAS-17.

15.6 Corporate Environmental Health and Safety Manual, CW-E-M-001.

15.7 Reference to use of percent solids for soil samples: Ray Anderson from MICE SW846 office, 9/24/10.

16.0 Method Modifications

N/A

17.0 Attachments

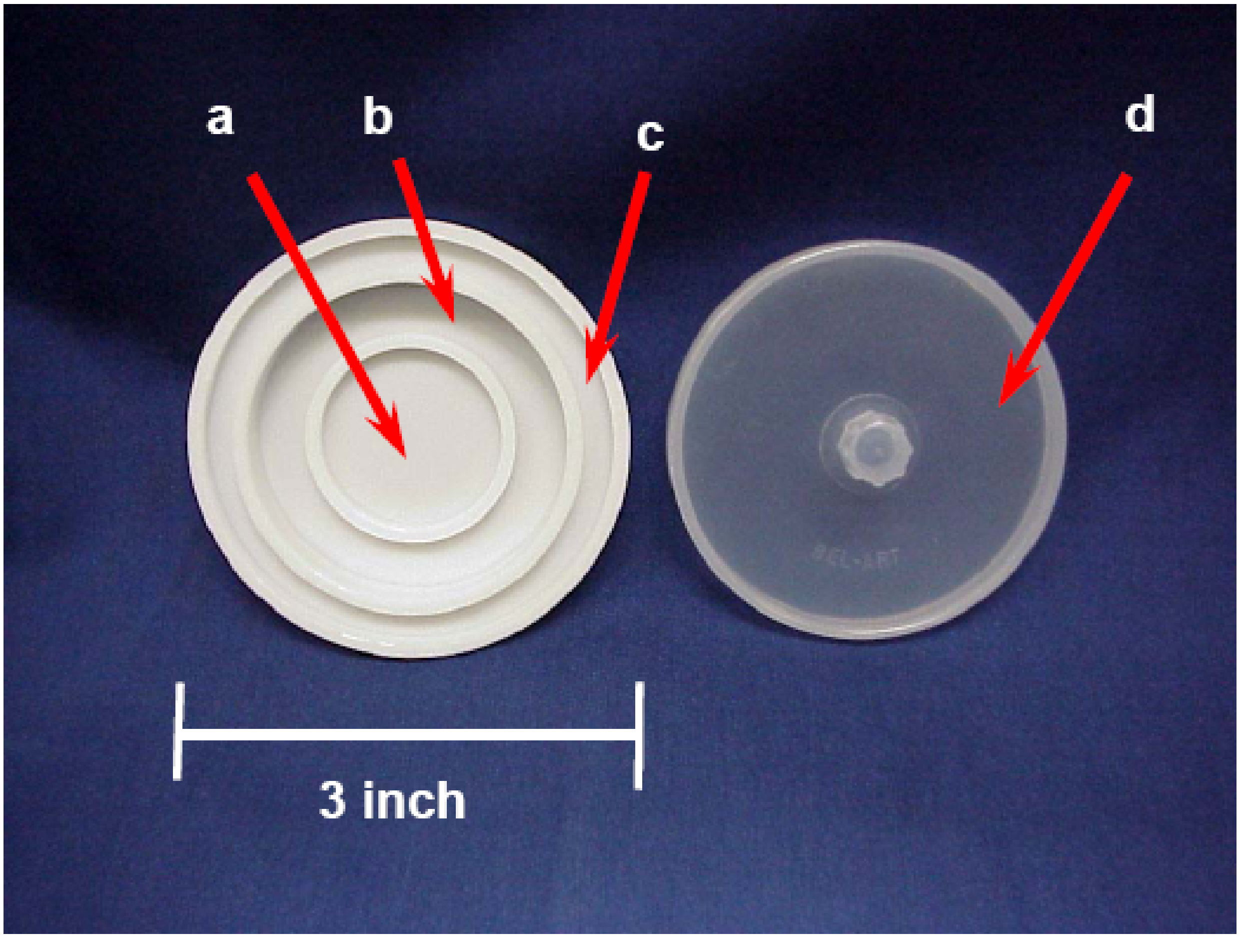
Attachment 1: Microdiffusion Cell
Attachment 2: Microdiffusion Process Overview

18.0 Revision History

- Revision 0, dated September 28, 2010

Attachment 1

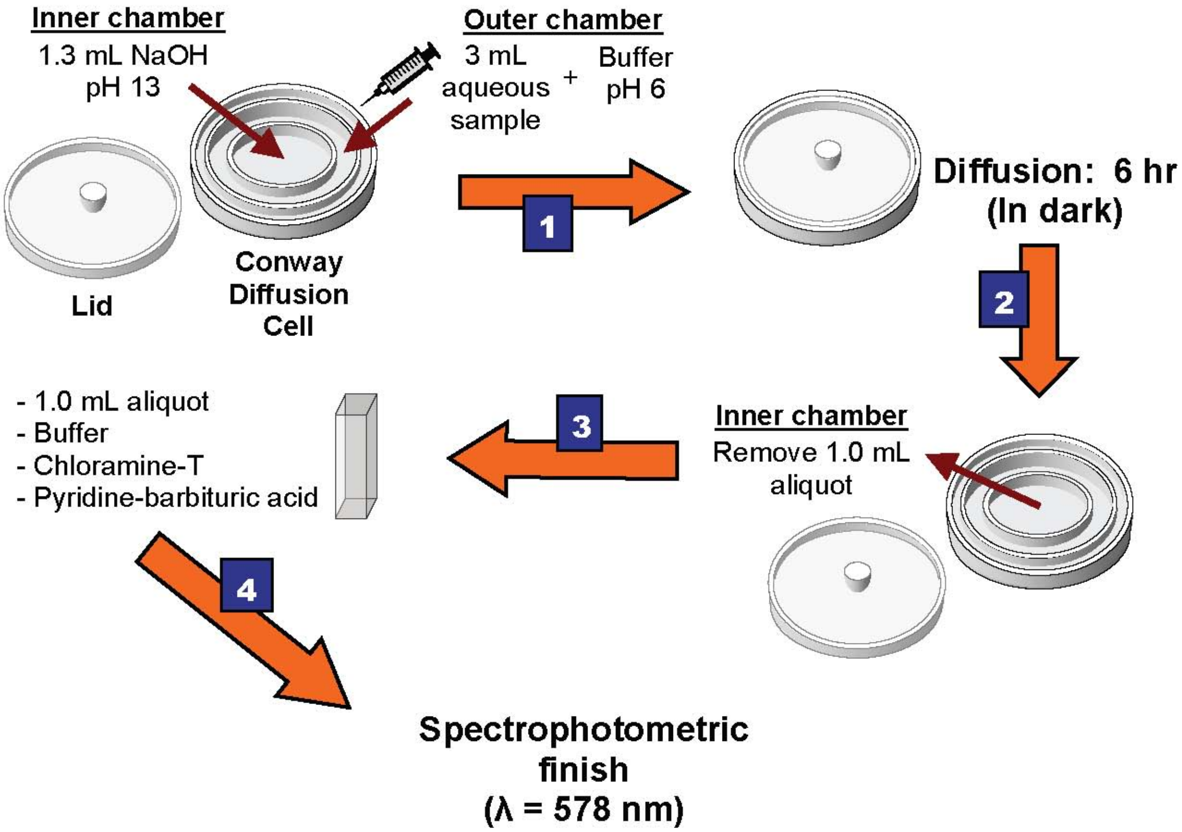
MICRODIFFUSION CELL



a) Center cell chamber for containment of sodium hydroxide absorber solution;
b) Outer cell chamber for introduction of sample;
c) Groove for holding and sealing cell cover; and
d) Cell cover

Attachment 2

Microdiffusion Process Overview



Title: SOP for Diesel Range Organics Analysis
[Method SW846 8015B]

Approvals (Signature/Date):

10/23/09
Technical Manager Date

Daniel W. Helfrich 10/26 /09
Health & Safety Manager/Coordinator Date

Dawn May 10/23 /09
Quality Assurance Manager Date

10/24/09
Laboratory Director Date

This SOP was previously identified as CT-GCS-18_6.

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1.0 APPROVALS

The approval of the Laboratory Director, the Facility QA Manager, Group Leader and Health and Safety Officer signify that the document has been prepared in accordance with the format requirements that have been established in this document. In addition, if the document is a Method SOP the signature signifies that it meets the specified requirements.

2.0 SCOPE AND APPLICATION

2.1 The objective of this document is to outline the techniques for determining the presence and concentration of total hydrocarbons in multi-media, multi-concentration samples. The target compounds for this method are listed in Table 1.0. The method used in this procedure is a solvent extraction and gas chromatography/ flame ionization detector (FID) analysis.

2.2 The target compounds are those hydrocarbons found within the C10–C28 range.

2.3 The document control number for this SOP is CT-GCS-18, Rev 7.

3.0 TERMS AND DEFINITIONS

3.1 There are many definitions used with in the laboratory, which may be generic to all laboratory analyses, or more specific for certain methods. For the most recent terms and definitions used with in the laboratory, reference the SOP for Terms and Definitions.

4.0 SUMMARY OF METHOD

4.1 This method employs the technique of solvent extraction using methylene chloride, coupled with a gas chromatography/FID analysis. An aliquot of sample extract is injected onto a gas chromatograph. A fused silica capillary column is then temperature programmed to separate the components prior to detection by FID.

4.2 This method is based on SW846 Method 8015B.

4.3 Samples are prepared for analysis in accordance with methods SW846 3510C for aqueous samples and 3550B for solids.

5.0 INTERFERENCES

5.1 Interferences include all compounds, which are methylene chloride extractable and FID responsive. All materials used are demonstrated to be free from interferences by running laboratory method blanks.

5.2 Samples that contain high molecular weight compounds have a tendency to leave residues throughout the GC system, which may interfere with subsequent injection. Any samples, which have chromatography indicating the possibility of carryover, will have solvent blanks analyzed after the sample injection, until the system has returned to normal.

6.0 HEALTH AND SAFETY

Employees must abide by the policies and procedures in the Corporate Safety Manual, Radiation Safety Manual and this document. This procedure may involve hazardous material, operations and equipment. This SOP does not purport to address all of the safety problems associated with its use. It is the responsibility of the user of the method to follow appropriate safety, waste disposal and health practices under the assumption that all samples and reagents are potentially hazardous. Safety glasses, gloves, lab coats and closed-toe, nonabsorbent shoes are a minimum.

6.1 SPECIFIC SAFETY CONCERNS OR REQUIREMENTS

The gas chromatograph contains zones that have elevated temperatures. The analyst needs to be aware of the locations of those zones, and must cool them to room temperature prior to working on them.

There are areas of high voltage in both the gas chromatograph. Depending on the type of work involved, either turn the power to the instrument off, or disconnect it from its source of power.

6.2 PRIMARY MATERIALS USED

The following is a list of the materials used in this method, which have a serious or significant hazard rating. **NOTE: This list does not include all materials used in the method. The table contains a summary of the primary hazards listed in the MSDS for each of the materials listed in the table.** A complete list of materials used in the method can be found in the reagents and materials section. Employees must review the information in the MSDS for each material before using it for the first time or when there are major changes to the MSDS.

Material	**Hazards**	**Exposure Limit (1)**	**Signs and symptoms of exposure**
Methylene Chloride	Carcinogen Irritant	25 ppm-TWA 125 ppm-STEL	Causes irritation to respiratory tract. Has a strong narcotic effect with symptoms of mental confusion, light-headedness, fatigue, nausea, vomiting and headache. Causes irritation, redness and pain to the skin and eyes. Prolonged contact can cause burns. Liquid degreases the skin. May be absorbed through skin.
Methanol	Flammable Poison Irritant	200 ppm-TWA	A slight irritant to the mucous membranes. Toxic effects exerted upon nervous system, particularly the optic nerve. Symptoms of overexposure may include headache, drowsiness and dizziness. Methyl alcohol is a defatting agent and may cause skin to become dry and cracked. Skin absorption can occur; symptoms may parallel inhalation exposure. Irritant to the eyes.
Acetone	Flammable	1000 ppm-TWA	Inhalation of vapors irritates the respiratory tract. May cause coughing, dizziness, dullness, and headache.
1 – Exposure limit refers to the OSHA regulatory exposure limit.			
TWA = Time weighted average STEL = Short term exposure limits			

7.0 SAMPLE CONTAINERS, COLLECTION AND PRESERVATION

7.1 Sample Containers

- Water samples are collected in 2x1 liter amber glass containers with Teflon-coated liner.
- Soil samples are collected in 250 or 500 mL glass containers with Teflon coated caps.
- Sample bottles are never reused.

7.2 Sample Collection

- Samples are secured against breakage in the shipping containers and kept at 4°C for transport to the laboratory. Samples should arrive at the laboratory the next day following collection.

7.3 Sample Preservation

- Samples are preserved by cooling to 4°C.

7.4 Holding Times

- Water samples must be extracted within 7 days from collection.

  Soil samples must be extracted within 14 days from collection.
- All extracts must be analyzed within 40 days from date of extraction.

8.0 APPARATUS AND MATERIALS

8.1 GC/FID/DS System

8.1.1 HP Model 5890 GC with FID Detector or HP 7890 GC with FID Detector

8.1.2 Split/Splitless Injection Port

8.1.3 GC Column – ZB-1, 30meter,.53 mm ID Column or the equivalent

8.1.4 Perkin Elmer TurboChrom Data Aquistion System or Chemstation

8.1.5 Target Software

8.2 Syringes - Various size 10 uL to 1 mL Hamilton or equivalent

9.0 REAGENT AND STANDARD PREPARATION

9.1 Solvent: Methylene Chloride, should be pesticide grade or equivalent

9.2 Alkane standard, which contains a homologous series of n-alkanes for establishing retention times (C10 thru C28). Any alkane mix which contains at least C10 and C28 hydrocarbons may be used to determine the appropriate carbon range. This standard is prepared in Hexane and at a concentration of 400ug/mL. See table 4.0

9.3 Standards such as #2 Fuel oil (Diesel) are purchased from a commercial source. #2 Fuel oil will be used for the calibration curve. See Table 5.0 for preparation of levels. Other oils may be used on a project specific basis (i.e. #4 fuel oil #6 fuel oil, kerosene, etc).

Compound	Final Conc. (ug/ml)
#2 Fuel Oil	500
	1,000
	2,000
	4,000
	5,000

9.4 Standard Storage and Preparation

9.4.1 All received stock standards shall be stored according to manufacturer recommendations. Manufacturer expiration date applies to unopened standards. Once a stock standard is opened and transferred to another vial, a 6 month expiration date shall be applied.

9.4.2 All prepared working standards shall be stored in either 2ml vials or screw top bottles at 4°C and replaced after six months or earlier if necessary.

10.0 CALIBRATION

10.1 A five-point calibration curve is prepared as described in Section 9. Analysis of the curve shall meet the criteria of ≤ 20% relative standard deviation (RSD). If the %RSD cannot be met using the average calibration factor, an alternate curve type can be used. The criteria is 0.990 or higher for the coefficient. A Quadratic curve fit may be used as long as a 6 point calibration curve is prepared and the correlation coefficient is 0.990 or higher.

10.2 Continuing calibration check standards are analyzed each 12 hour shift, at a minimum, and shall be within ± 15 percent difference for both the beginning and end bracketing standards. If the end bracketing standard fails to meet criteria, all samples that are bracketed either before or after the failing standard must be re-analyzed.

10.3 If the beginning continuing calibration criteria of ± 15% is not met, then a new calibration curve shall be analyzed.

10.4 A second source ICV of #2 Fuel Oil should be analyzed immediately following the initial calibration curve. The source material shall be from a different lot/source (and preferably different vendor), than the material from which the initial calibration is prepared. The concentration is at 2000ug/mL. The % difference between the ICV and the initial calibration curve must be ±25%. If ICV fails to meet criteria, re-prep and re-analyze standard before continuing analysis.

11.0 QUALITY CONTROL

11.1 Ortho-terphenyl shall be used as the surrogate(s) added to each sample, blank and QC.

11.2 #2 Fuel oil shall be used for the LCS, Matrix spike and Matrix spike duplicates. The LCS shall be extracted once per batch or every 20 samples and shall be from an alternate source than the calibration standards. The MS/MSD shall be extracted every 20 samples per matrix.

11.3 Calibration checks shall be analyzed each 12 hour shift with a ± 15 percent difference.

11.4 A Method blank is extracted each batch, per 20 samples.

11.5 Analytical Documentation Procedures

11.5.1 Instrument Batches

An instrument batch is created for each analytical sequence to organize all the associated data. Batch designations are of the format:

XXnnn

where: XX = instrument identifier
nn = number of batch

(i.e. D3001)

Instrument batches are numbered sequentially so a unique batch identifier identifies each analytical sequence. The batch consists of a file folder with all the associated QC information for the analytical sequence. The raw data is then bound together with the file folder to complete the batch.

11.5.2 Data Archiving

All data files are archived on a daily basis using a 12.0gb data storage cartridge. The associated method files are also archived daily to provide an accurate historical record. Care shall be exercised when purging data off the hard drives to ensure that all data being purged has been archived.

11.5.4 Instrument Run Logs

It is the company’s policy that all measurement data be recorded in logbooks or on preprinted log sheets in permanent ink. Run logs are created from the Target data system by generating a file which contains a sequential list of all files analyzed. The record shall reflect the measurement performed and all appropriate details for conclusions related to the measurement. The record shall be signed and dated by the individual performing the measurement on the day the measurement is performed. Corrections shall be made by drawing a single line through the error, and initialing and dating the correction. A secondary authorization of the logbook is required and shall be performed by the department's manager or designee.

Each instrument has its own set of bound run logs which are sequentially numbered and paginated.

Run logs are filed in the laboratory once they have been filled, for future reference. Each analytical sequence shall be started on a new page of the log and continued on the next page, if necessary. The header information designating the standard codes used shall be completed for each sequence. All standards used are recorded in this field for future traceability. The data file, sample number, dilution factor, analyst's signature, and date are recorded.

11.6 Corrective Action Reports

A corrective action report (CAR) is initiated when a problem is encountered during analysis, data reduction or deliverables preparation, data validation, or when any deviations from this SOP occur. The CAR is initiated by the analyst or dept. manager first identifying the problem through the NCM module in the LIMS system. It is then electronically forwarded to all appropriate departments, QA officer, and Lab Manager. Reference SOP for correction action reports.

11.7 Chain of Custody Record

When samples are removed from storage for preparation or analysis they must be signed out utilizing the chain of custody record (COC). The samples shall then be signed back in on the COC upon their return to storage or designated "used" if the sample volume is consumed during the preparation or analysis.

11.8 Sample Tracking Record

Notification of sample arrival is done by the Sample Control department by issuing an email for Rush samples. Samples are tracked for analysis by using the laboratory’s LIMS system.

11.9 MDLs are performed annually as per 40 CFR chapter 1.

12.0 SAMPLE PREPARATION AND INSTRUMENTAL PROCEDURES

12.1 Instrumental preparation:

Install appropriate column ZB-1 manufactured by Phenomenex or equivalent 30 m or a 15m column.

Establish column flow rate at approximately 15 mL/min and column head pressure at 10 psi. Make sure the make up gas is fully open. Set hydrogen at 40 psi and air at 30 psi. Light the FID detector. Wait about 10 minutes for signal to stabilize. The flows can be adjusted to maximize sensitivity.

Set temperature parameters as follows (HP5890):

Initial temperature:	40°C	Initial time: 0.50 min.
Rate:	30°C/min.	Final time: 10 min.
Final temperature:	310°C	Detector temperature: 330°C
Injector temperature:	300°C	

Set temperature parameters as follows (HP7890):

Septum Purge Flow = 3ml/min

Purge Flow to split vent – 50ml/min @ 0.5min

	Initial temperature: 40°C	Initial time: 0.50 min.
Rate: 75°C/min.	Temp: 70°	Hold time: 0.0 min.
Rate: 45°C/min.	Temp: 115°	Hold time: 0.0 min.
Rate: 35°C/min.	Temp: 175°	Hold time: 0.0 min.
Rate: 25°C/min.	Temp: 225°	Hold time: 0.0 min.
Rate: 20°C/min.	Final Temp: 350°	Hold time: 1.2 min.

Detector temperature: 300°C
Injector temperature: 250°C
Column Flow (Helium) : 10ml/min Hold time: 5min
Rate: 20ml/min Final rate: 40ml/min

H2 Flow = 30ml
Air Flow = 400ml

12.2 Sample preparation:

Extracts are taken from the refrigerator and chain of custody is signed.

Then the extracts are loaded, under a hood, into 2 mL HP autosampler vials with 250ul inserts. Currently National Scientific HP5890 AS vials with screw caps are used but any equivalent is acceptable. Extracts are loaded using new pasteur pipet for each individual sample to avoid any cross contamination. The autosampler vials are placed in the tray on the instrument.

The run sequences are programmed in the Perkin Elmer TurboChrom data system or Chemstation and the run is started.

12.3 If Qualitative analysis is requested, the chromatograms of the samples are compared with the chromatograms of each standard and if the pattern of the sample chromatogram matches the pattern of any of the standard, the compound is qualitatively identified. Very often, however, the match is incomplete and therefore only an approximate identification is possible due to a weathering of the sample. In that case, the closest resemblance is reported and any weathering is documented in the case narrative.

12.4 Establishing the baseline

Column bleed is defined as the reproducible baseline shift that occurs during temperature programming of the GC column oven. To determine this area, a methylene chloride blank injection should be analyzed at the beginning of the day and after every 12 hours to determine the baseline response. This run is then used to perform baseline subtraction, using the TurboChrom Data System, in subsequent runs until the next methylene chloride blank is run.

For newer instrumentation(HP7890), column bleed does not interfere with the baseline. Samples and standards can be analyzed without the need for baseline subtraction. If the baseline is horizontal over the retention range for which it is being analyzed, baseline subtraction will not be necessary.

12.4.1 The baseline for the sample is determined by beginning the integration at the desired start time

(C10) and extending the baseline horizontally to the desired stop time (C28). A sum total area is used for calculations.

12.4.2 The integration is performed to incorporate the total area response between the C10 and C28 carbon range, established by running an alkane standard. This area should include all resolved and unresolved peaks. This total area must be adjusted to remove the area response contributed from column bleed (by using baseline subtraction) and from surrogates and peaks outside of the set retention time range.

12.5 Quantitation is performed by a summation of peak areas within a determined peak range based on the alkane standard.

12.5.1 An alkane standard should be analyzed to establish the C10-C28 alkane range, each time a new column is installed, or a major change is made to the instrument or operating conditions. This information is kept on file at the laboratory.

13.0 CALCULATION

Water sample:

$$\frac{\text{(area sample) (final volume [uL])(dilution factor)}}{\text{(avg. Cf of Standard) (sample volume [mLs])(ul inj.)}} = \text{ug/L}$$

area/ng

Water sample by Linear regression:

$$b + (\text{Area})/m1 = \text{on column concentration (ng)}$$

$$\frac{\text{(cn column concentration-ng) (final volume [uL])(dilution factor)}}{\text{(sample volume [mLs])(ul inj.)}} = \text{ug/L}$$

Water sample by Quadratic:

$$b + m1(\text{Area}) + (m2)*(\text{Area})^2 = \text{on column concentration (ng)}$$

$$\frac{\text{(cn column concentration-ng) (final volume [uL])(dilution factor)}}{\text{(sample volume [mLs])(ul inj.)}} = \text{ug/L}$$

Soil sample:

$$\frac{\text{(area sample) (final volume [uL])(dilution factor)}}{\text{(average Cf of Standard) (wt [g])(dec. \% solids)(ul inj.)}} = \text{ug/Kg}$$

area/ng

Oil sample:

$$\frac{\text{(area sample) (final volume [uL])(dilution factor)}}{\text{(average Cf of Standard) (wt [g]) (ul inj.)}} = \text{ug/Kg}$$

area/ng

All areas are a summation of peaks for a determined time period which is consistent between the sample and standard.

14.0 ACCEPTANCE OF DATA

14.1 Method blanks should be free of any target compounds greater than the RL.

14.2 The recovery of the LCS shall be within laboratory established control limits as listed in Table 1.0. If the recovery is out of criteria, reanalysis of the LCS must be performed. If the LCS is still out of criteria reextraction of the batch may be necessary.

14.3 The recovery limits for MS/MSDs extracted every 20 samples are listed in table 2.0. Reextraction is not required if recoveries are outside the QC limits unless the LCS failed control limits.

14.4 Daily calibration check standard verification of the calibration curve is required every 12 hours with the criteria of +/- 15 % difference.

15.0 REPORTING OF RESULTS

15.1 All results are reported to two significant figures. Water samples are reported in ug/L, soil samples are reported in ug/Kg dry weight and waste samples are reported in ug/Kg.

Check reporting deliverables required from the lims system in the job deliverable section.

16.0 SUPPLEMENTAL DOCUMENTS

16.1 SOP for Extraction of Diesel Range Organics by Method 3510C.

16.2 SOP for Extraction of Diesel Range Organics by Method 3550B.

17.0 POLLUTION PREVENTION

It is TestAmerica’s policy to evaluate each method and look for opportunities to minimize waste generated (i.e., examine recycling options, ordering chemicals based on quantity needed, preparation of reagents based on anticipated usage and reagent stability). Employees must abide by the policies in Section 13 of the Corporate Safety Manual for “Waste Management and Pollution Prevention.”

17.1 Pollution prevention is the reduction and/or elimination of wastes or the toxicity of wastes at the point of generation. The laboratory strives to keep all wastes at a minimum through a variety of techniques. These include the following.

17.1.1 Inventory control: Rotate stocks (first in, first out) and only purchase reasonable amounts of chemicals. Do not purchase excessive quantities, which will be discarded as wastes at some future point.

17.1.2 Material Handling and Storage: Keep containers properly labeled. Keep solvents covered. Store and handle all chemicals, reagents, standards, etc. to prevent contamination and degradation.

17.1.3 Personnel: All staff must be trained in the proper handling and disposal of waste.

17.1.4 Waste Reduction: Reduce the volume of waste generated wherever possible.

17.1.5 Chemical/material substitution: Use less toxic chemicals whenever possible. Avoid the use of chromic acid (Chromerge) solutions.

18.0 WASTE MANAGEMENT

Waste management practices are conducted consistent with all applicable rules and regulations. Excess reagents, samples and method process wastes are disposed of in an accepted manner. Waste description rules and land disposal restrictions are followed. Waste disposal procedures are incorporated by reference to the Tracking and Collection of Hazardous Waste SOP. The following waste streams are produced when this method is carried out.

18.1.1 Personnel who handle or generate waste must be trained within six months of employment in proper waste handling and requirements.

18.2 All autosampler vials containing methylene chloride as the main solvent should be disposed of in the 5 gallon bucket labeled for Hexane vial waste.

19.0 REFERENCES

19.1 Method 8015B, SW846, Test methods for Evaluating Solid Wastes, Third Edition including updates.

19.2 Method 3510C, SW846, Test methods for Evaluating Solid Wastes, Third Edition including updates.

19.3 Method 3550B, SW846, Test methods for Evaluating Solid Wastes, Third Edition including updates.

20.0 SUBSTANTIVE REVISIONS

20.1 Revision of GCS01800.CT in response to comments form ACOE. Revisions are in italics; June 1, 1998.

20.2 March 10, 2000 – Added to Supplemental Document section. Made name changes from IEA to STL. Modified Reporting of Results section. Updated References section. Added to Sample Prep and Instrumental Procedures section criteria for frequency of alkane standard analysis. Updated Table 1.0 LCS Control Limits. Added sections clarifying integration and baseline subtraction. Added example chromatograms.

20.3 Added to safety section and waste management section.

20.4 Revised Safety and Waste Management Sections to more Corporate standarized-1/2004.

20.5 Updated Tables with most current Control limits-1/2004.

20.6 Revised CAR process section, and annual Review done-11/2005.

20.7 Removed footnote 1 in sect. 6.2. Replaced STL or Severn Trent with TestAmerica. Section 9.2 added alkane standard concentrations. Sect. 10.1 added Quadratic curve requirements. Sect. 7.2 – added caps. Added Tables 4.0 and 5.0. Added TWA and STEL definitions. Section 10.4 added 2nd source ICV. Sect. 11.5.4-updated for target generated run logs. Sect. 11.6 updated for the CAR process. Change tables 1-3 to reference LIMS system. Added new TestAmerica SOP header and control number; 9/8/07

20.8 Section 10.2 updated to clarify end standard calibration criteria. Updated with newer instrumentation. Updated Reporting section. Updated Safety, Pollution control and waste management sections. Sect 9.4 clarified std storage and expiration dates. Sect 12.1 added 7890 program. Sect 14.1 changed MB criteria. Sect 19.4 removed QAM reference. 10/23/09.

TABLE 1.0

LCS CONTROL LIMITS

Compound	Soil	Water
#2 Fuel Oil	See LIMS system for most recent limits.	See LIMS system for most recent limits.

TABLE 2.0

MS/MSD CONTROL LIMITS

Compound	Soil	Water	RPD
#2 Fuel Oil	See LIMS system for most recent limits.	See LIMS system for most recent limits.	See LIMS system for most recent limits.

TABLE 3.0

SURROGATE CONTROL LIMITS

Compound	Soil	Water
o terphenyl	See LIMS system for most recent limits.	See LIMS system for most recent limits.

TABLE 4.0

DRO44 - Level 4	Initial conc.	Mls used	Final volume	Final conc- each alkane (ug/ml)	**G_C44_LV4_**	Total Conc.	Range
TPH Mix 3 (861394-U)	1000	1	10	100	GdroC44STK_	1200	C9-36
o-terphenyl (NSI 1341H-02-08)	10000	0.2	10	200	Goterphstk_	1500	C8-44

DRO44- Level 4 is to be prepared in Hexane

TABLE 5.0

Diesel Range Organics

Prepare in Methylene chloride

	Initial Conc ug/ml	Amount Used ml	Final Volume mls	Final Conc. ug/ml	Lims codes
#2 Fuel Oil Level 1					**G_#2F1_WRK_**
#2 Fuel Oil (NSI UST-145-09)	50000	0.1	10	500	G_#2F_STK_
o-terphenyl (NSI 1341H-02-08)	10000	0.1	10	100	GOTERPHSTK_
#2 Fuel Oil Level 2					**G_#2F2_WRK_**
#2 Fuel Oil (NSI UST-145-09)	50000	0.2	10	1000	G_#2F_STK_
o-terphenyl (NSI 1341H-02-08)	10000	0.2	10	200	GOTERPHSTK_
#2 Fuel Oil Level 3					**G_#2F3_WRK_**
#2 Fuel Oil (NSI UST-145-09)	50000	0.4	10	2000	G_#2F_STK_
o-terphenyl (NSI 1341H-02-08)	10000	0.3	10	300	GOTERPHSTK_
#2 Fuel Oil Level 4					**G_#2F4_WRK_**
#2 Fuel Oil (NSI UST-145-09)	50000	0.8	10	4000	G_#2F_STK_
o-terphenyl (NSI 1341H-02-08)	10000	0.4	10	400	GOTERPHSTK_
#2 Fuel Oil Level 5					**G_#2F5_WRK_**
#2 Fuel Oil (NSI UST-145-09)	50000	1	10	5000	G_#2F_STK_
o-terphenyl (NSI 1341H-02-08)	10000	0.5	10	500	GOTERPHSTK_
#2 Fuel Oil Level 3 - ICV					**G_#2F3_ICV_**
#2 Fuel Oil (Supelco 47515-U)	20000	1	10	2000	G#2FSS_STK_
o-terphenyl (NSI 1341H-02-08)	10000	0.3	10	300	GOTERPHSTK_