Sampling and Analysis at the Vortec Vitrification Facility in Paducah, Kentucky

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SAMPLING AND ANALYSIS AT THE VORTEC VITRIFICATION FACILITY IN PADUCAH, KENTUCKY

1.0 INTRODUCTION

The Vortec Cyclone Melting System (CMS®) facility, to be located at the U.S. Department of Energy (DOE) Paducah Gaseous Diffusion Plant, is designed to treat soil contaminated with low levels of heavy metals and radioactive elements, as well as organic waste. The primary components of Vortec's CMS® are a counter-rotating vortex (CRV) reactor and cyclone melter. In the CMS® process, granular glass-forming ingredients and other feedstocks are introduced into the CRV reactor where the intense CRV mixing allows the mixture to achieve a stable reaction and rapid heating of the feedstock materials. Organic contaminants in the feedstock are effectively oxidized, and the inert inorganic solids are melted.

The University of North Dakota Energy & Environmental Research Center (EERC) has been contacted to help in the development of sampling plans and to conduct the sampling at the facility. This document is written in a format that assumes that the EERC will perform the sampling activities and be in charge of sample chain of custody, but that another laboratory will perform required sample analyses.

During the initial phases of start-up and during the first months of stable operation, sampling of the gas, water, and solid materials is necessary for three primary reasons:

- Provide shakedown data for use in development of standard operating procedures.
- Meet permitting requirements.
- Provide mass balance data for compounds of interest.

To assure that costs of sampling and analysis are contained, Vortec and the DOE Federal Energy Technology Center (FETC) have decided that initially the primary focus of the sampling activities will be on meeting permitting requirements of the state of Kentucky. Therefore, sampling will be limited to the feedstock entering the system, and the glass, flue gas, and water leaving the system. To limit the numbers of samples that must be collected, it is assumed that the feed stream composition will be constant over periods of at least 1 week. Data analysis should provide limited information to refine operating procedures and give rudimentary mass balances, but no additional sampling is planned to support these activities. However, in this report we provide suggestions for optional sampling points and procedures in case there is later interest in operations or mass balance data.

The permits do not require speciation of the materials in the effluents, only opacity, total radioactivity, total particulate, and total HCl emissions for the gaseous emissions and total radioactivity in the water and solid products. In case future testing to support operations or mass balances is required, we include in this document additional information on the analyses of some species of interest. They include heavy metals (RCRA [Resource Conservation and Recovery Act] and Cu and Ni), radionuclides (Th^{230} , U^{235} , Tc^{99} , Cs^{137} , and Pu^{239}), and dioxins/furans.

The sampling team will follow health and safety protocols established by Vortec and will have successfully completed the 40-hour training for Hazardous Waste Operations and Emergency Response (29 CFR 1910.120). Additionally, each member of the EERC sampling team will fulfill the requirements of EERC Standard Practices: No. 303 – Personal Protective Equipment, No. 327 – Respiratory Protection, and No. 355 – Medical Surveillance Program.

2.0 GAS STREAM SAMPLING

The following methods will be used to sample for flue gas contaminants. Each method is described in Appendix A.

Basic Sampling for Permitting

- Particulate matter – U.S. Environmental Protection Agency (EPA) Method 5 (traverse flue gas measurements will be made using EPA Methods 1 through 4)
- HCl – EPA Method 26A

Optional Sampling for Operations and Mass Balances

- Dioxins/furans – EPA Method 23
- Heavy metals – EPA Method 29
- Radionuclides – filters and solutions from EPA Methods 5 and 26A

2.1 Basic Gas Stream Sampling Plan For Permitting Requirements

The demonstration of the CMS[®] will be conducted in two stages. The first stage involves the shakedown of the system. During this period, each part of the system will be tested and brought on-line until the entire system is operational. This is expected to take approximately 3 months. During the final 3 weeks of the shakedown, the CVR will be brought on-line, and clean feedstock will be processed. The EERC will begin sample operations during this last stage of the shakedown.

Once shakedown has been completed, the facility is then expected to be operated at steady-state conditions for a total of 30 days. During this period, low-level radioactive soils, RCRA wastes, and PCB (polychlorinated biophenyl)-contaminated materials will be processed. To contain sampling costs, initial sampling will be performed in such a way as to ensure that emissions permit requirements are met, and no additional sampling will be performed in support of system operations or for performing mass balances. In the future, additional sampling may be required to aid in refining operations and determining mass balances for individual species, so sampling to support this work is described in this document as optional.

The EERC will collect samples, including feedstocks, vitrified product, and liquid waste streams. In addition, flue gas sampling will also be conducted at three locations for permitting

purposes, with a fourth optional location. The emission gas sampling locations are designated using the notation from Figure 7.1-1 of the Phase 3 Test Plan "Innovative Fossil Fuel Fired Vitrification Technology for Soil Remediation" prepared by the Vortec Corporation on October 23, 1996. Sampling Point S6 is an additional point for operations and mass balance purposes.

Basic Permitting

- Feed preparation and blending facilities (Sampling Point E1)
- Soda ash and limestone silos (Sampling Points E3 and E4)
- Outlet stack (Sampling Point E7)

Optional

- CVR exit gas stream prior to the wet ESP (S6)
- Additional Sampling at E7

Sampling Point E5 is the glass cullet silo and E2 is the exhaust gas of the air heater for the dryer. These locations will not be sampled. The glass cullet material is not hazardous and does not present a particulate problem. The air heater is propane-fired; therefore, the uncontaminated exhaust gas is particulate-free and contains CO₂ and water.

2.1.1 Feed Preparation and Blending Facilities (Sampling Point E1)

The purpose of the feed preparation system is to transform drummed waste soils into dry bulk powder that meets the size and moisture specifications required by the vitrification system. The entire preparation facility is to be kept under negative pressure to prevent dust-laden gases from leaving the facility. The shredders, dryer, crusher, sizing screens, mill, and belt conveyors are completely enclosed. The final exhaust gas passes through a bank of high-efficiency particle (HEPA) filters to remove virtually all of the particulate matter.

The feedstock mixing tank consists of a dust collector, a blend hopper, and material transport systems. In this tank, the feedstock is mixed with glass, limestone, and soda ash. The dust collector located above the blender is designed to recirculate the collected material back into the mixing tank. It is used when filling the silo and during blending. The final exhaust gas then passes through the HEPA filter system.

HEPA filters are extremely efficient; therefore, the outlet dust loading should be very low. The permit requirement at this location is for particulate emissions and radionuclides. It is expected that the HEPA filters will have a collection efficiency of >99.99%; therefore, the maximum allowable particulate emission limit of 7.86 lb/hr should easily be met. The opacity limit of 20% should also not be a problem. We assume that Vortec will have in place an opacity monitor that will automatically keep track of that parameter. To verify that the requirements are being met for particulate and radioactivity emissions, each day an EPA Method 5 sample will be taken at the stack of the preparation facility. Because it is expected that the particulate level at this point will be very low, necessitating a long sampling period, only one 6-7-hour EPA Method 5 sample per day will be taken. The sample filter from EPA Method 5 should be analyzed for total radioactivity. Also, the two water impingers specified in EPA Method 5 will be replaced by an acid impinger

followed by a caustic impinger to capture any volatile radionuclides. These solutions should also be analyzed for total radioactivity.

2.1.2 Limestone and Soda Ash Silos (Sampling Points E3 and E4)

These materials pose primarily a fugitive dust emission issue. During filling and emptying of these silos, a dust collector is used to prevent dust from entering the air. We assume that Vortec will install an opacity monitor to assure that the 20% opacity limit is not surpassed. The exit gas from the dust collectors will be sampled using EPA Method 5 to ensure that the particulate emissions are less than the permit requirement of 6.05 lb/hr. One EPA Method 5 will be completed each day, which will be alternated between the two sample locations. If, during shakedown, it is found that the dust levels are above the permit requirement, additional EPA Method 5 samples will be completed after the dust collectors are adjusted to reduce the dust level to below 6.05 lb/hr. The sample filters and impingers from the EPA Method 5 trains for Points E3 and E4 should be analyzed for radioactivity.

2.1.3 Final Outlet Exhaust Stack (Sampling Point E7)

Prior to the flue gas exiting the plant, there is an extensive pollution control system in place. The gas first passes through a venturi scrubber, which is designed to removed most of the acid gases and some of the particulate matter. The gas then passes through a wet electrostatic precipitator (ESP), which removes a high percentage of the particulate matter. This is then followed by a bank of HEPA filters for final cleanup. It is therefore expected that the particulate level will be much lower than the permit requirement of 7.86 lb/hr and opacity should be much less than 20%. At this location, there is also a permit requirement for HCl. The maximum allowable emission is 8.24 lb/hr. To verify the opacity requirements are met, we assume that Vortec will have installed an opacity monitor. For particulate requirements, an EPA Method 5 sample will be taken at the stack each day. Because it is expected that the particulate level at this point will be very low, necessitating a long sampling period, only one 6-7-hour EPA Method 5 sample per day will be taken. The sample filter from EPA Method 5 should be analyzed for total radioactivity. Also, one sample will be similarly collected each day with an EPA Method 26A train modified to capture HCl and any volatile radionuclides.

2.2 Optional Gas Stream Sampling and QA/QC Protocol for Mass Balance Determinations

In order to ensure defensible data from flue gas sampling for purposes of determining species mass balances, four critical QA/QC (quality assurance/quality control) categories must pass successfully: 1) sample concentration greater (preferably 10 times greater) than the detection limit of the analytical method, 2) presence of low reagent and field blanks, 3) acceptable matrix spike samples, and 4) a statistically valid number of sample points. The application of these QA/QC criteria to the development of a flue gas-sampling plan at the Vortec facility are discussed below.

2.2.1 Detection Limit

Before sampling commences, the minimum detection limit (DL) and lower limit of quantitation (defined as 10 times the detection limit) for both the sampling and analytical methods must be determined. Based on this value and the "expected" flue gas concentration, the length of sampling period required is calculated. Data from the shakedown sampling will be used to determine the optimum sampling periods required for the 30-day sampling period. If the data from a sampling train are below the detection limit, it will be reported as "not detected - less than the established detection limit" or $ND < DL$.

2.2.2 Reagent and Field Blanks

It is critical to data quality that the reagents used in the sample train, breakdown, and analysis have only a very low level of contamination of the element/compound in question. All reagents used must be analyzed and any background contaminations subtracted from the sample value as instructed by the method.

Field or method blanks are also critical to data quality. Field blanks are sample trains assembled, transported, recovered, and analyzed in the same manner and locations as the sample trains. Their purpose is to pinpoint a false high sample value resulting from laboratory or field contamination. If the method blank value exceeds 25% of the mean, the sample is invalid. All sampling data reported by the EERC will be accompanied by a pass/fail designation for both reagent and field blanks.

2.2.3 Matrix Spike Recovery

Successful matrix spike recoveries are critical to gas stream sample data evaluation. Samples can be spiked in the field or lab. Both spiked and unspiked samples must be available to make an accurate comparison. It is suggested that spiking for each critical element be done at least once per week.

Acceptable spike recoveries as defined by the methods can range from 20% to 150%. The EERC recommends that only data having spike recoveries of 70%-125% be used for mass balance calculations. The magnitude of the upper bound is lower than the magnitude of the lower bound because it is easier to justify analytically recovering less than the total than to justify recovering more than the total. As with the method blanks, the reported sampling data will be accompanied by a pass/fail designation for spike recovery. Table 1 gives the suggested pass/fail criteria for the sampling.

2.2.4 Statistically Valid Number of Data Points

The number of replicate data points used to calculate the mean value for a sample location determines the amount of confidence that can be associated with that value. Although current regulatory practice requires only one sample at each flue gas sample point to determine emission levels, a more comprehensive approach involving quadrain sampling is recommended for mass balance determination. Quadtrains provide four simultaneous identical samples as opposed to four single samples taken over the period of a day or week. Variation between the single samples

TABLE 1

QA/QC Criteria for Gas-Sampling Data

Blanks	
P = Pass	Blanks with less than 25% of the given analyte
F = Fail	Blanks with greater than 25% of the given analyte
Matrix Spike Recoveries	
P = Pass	Inorganic sample recoveries of $125\% \geq x \geq 70\%$
F = Fail	Inorganic sample recoveries of $> 125\%$ or $< 70\%$
P = Pass	Organic recoveries of $150\% \geq x \geq 20\%$
F = Fail	Organic recoveries of $> 150\%$ or $< 20\%$
Detection Limit	
P = Pass	Values above DL
F = Fail	Values below DL
Lower Limit of Quantitation (LLQ)	
P = Pass	Values above $LLQ = 10 \times DL$
F = Fail	Values below $LLQ = 10 \times DL$

comes from many sources, which are difficult, if not impossible, to assess: variability in feedstock, in operating conditions, in sampling methods, and in contamination levels. Variations between quadrain samples can be attributed only to the sampling technique itself. If one of four samples appears anomalous, Dixon's Criteria of Outliers can be used to eliminate that value with a known level of confidence; i.e., a marginal outlier value may be eliminated with some certainty, or an extreme outlier can be eliminated with high certainty, for example, 70% and 99%, respectively. The remaining three values can be used to determine a mean and standard deviation while retaining a reasonable confidence in the data that can only be achieved with a minimum of three data points. If all four values are good, the mean and standard deviation can be calculated with an even higher degree of confidence. If only three values are taken and one is anomalous, it cannot be eliminated, leading to a low confidence interval for the mean.

Statistically, assuming a 95% confidence interval, there is not much difference between three and four replicate samples. However, if only two data points are available, there is almost an order of magnitude increase in the calculated confidence interval. Therefore, for the trace metals, dioxins/furans, and radionuclides, it is necessary to use quadrains to ensure valid data. High confidence in the data results from a confidence interval that is very close in range to the data. A low confidence interval is much larger than the range of the data. A value of 5 with a confidence interval of 6 has a high confidence interval (where the difference between the value and the

confidence interval is a low percentage of the value). A value of 5 with a confidence interval of 15 has a low confidence interval (where the difference between the value and the confidence interval is a high percentage of the value.)

The following is an example from a previous sampling effort for trace elements across an ESP. The inlet data (high concentration and easy to measure) had three good data points with a tight (high) confidence interval. The outlet data had three data points (very low concentrations that were difficult to measure), of which two were good data points and one was impossibly high, throwing the average of the three outlet values higher than the inlet. Dixon's Criteria of Outliers could not be applied to only three data points. However, the confidence interval for the two reasonable remaining data points became so wide that there was no statistical difference between the inlet and outlet data. Therefore, none of the six inlet and outlet data points proved useful. Use of quadtrains provides the minimum number of points to work with and still retain the statistical value of the data.

Particulate loadings are measured from the particulate captured on the filter placed before the impinger trains, which contain solutions to capture the desired compounds. Therefore, not only the data from EPA Method 5 (particulate measurement) but also the particulate data from EPA Method 29 (multimetals train) filters and EPA Method 26A (acid gases and halogens) filters can be used. Since the particulate loadings following control devices are expected to be very low, the data from all the methods can be pooled, thereby obtaining much better information. See Appendix A for a description of the various sampling methods.

2.2.5 Optional Exhaust Stack Sampling

Although dioxins/furans are not a permit issue, they may be an issue of concern. The temperatures encountered in the CMS® are high enough ($> 2200^{\circ}\text{C}$) to ensure that all of the organic constituents will be completely destroyed, but there may be some concern that dioxins/furans can reform at the cooler temperatures downstream. Therefore, a sampling option is to perform EPA Method 23 sampling to show that the levels of dioxins/furans are below any level of concern.

To provide speciation data for refining system operations or performing mass balances, additional sampling is required. The optional daily sampling plan at E7 is to first do an EPA Method 29 quadtrain for volatile metals such as mercury and a dual train of EPA Method 26A modified to also capture HCl and radionuclides. These samples would all be done simultaneously. This would then be followed by an EPA Method 23 quadtrain for dioxins/furans while also doing another modified EPA Method 26A. This would give four measurements each for all of the heavy metals, radionuclides, HCl, and dioxins/furans. In addition, the filter samples from each of these methods would be weighed to give 12 particulate emission data points.

Quadtrains are recommended for volatile metals such as mercury because it is more difficult to show that an element/compound does not exist with a high degree of certainty than to show that a high concentration exists with similar certainty. It is a catch-22, but once the attempt is made to sample (find) an element/compound, it is impossible to show that it does not exist at the null level. It can simply be shown to exist as $\text{ND} < \text{DL}$. So, it is even more important to have extra data points available to use Dixon's criteria for outliers.

2.2.6 Optional CVR Exit Gas Stream Prior to the Wet ESP (S6)

The only purpose of sampling at this location is to provide data to determine the mass balance and partitioning of the heavy metals and radionuclides. This sampling location is located after the venturi scrubber and prior to the wet ESP. Although the venturi scrubber will remove some particulate matter, it is expected that the particulate loading will still be relatively high. Nearly all of the trace elements (with the exception of vapor-phase mercury) are expected to be captured before the stack, so plant mass balances cannot be accomplished using stack data. EPA Method 29 quadtrains and Modified EPA Method 5 trains (modified to collect radionuclides) will be performed each day, or as needed, for level mass balance information desired by Vortec.

Scrubber effluents and ESP hopper catches do not suffice for mass balance information for many reasons. The scrubber slurry itself is not homogeneous at the trace element level and contains additives, recycled materials, etc. Previous mass balance information attempted from scrubber solution sampling performed by DOE at coal-fired utilities has not yielded definite data. Also, it is difficult to obtain ESP hopper samples (usually residing in several different hopper fields) that are representative of the flue gas particulate, since the particulate settles in different fields by size. Different size fractions tend toward different mineral compositions.

The complete optional flue gas-sampling plan for each day is shown in Table 2.

TABLE 2

Optional Flue Gas-Sampling Plan for Operations and Mass Balancing					
Sample Point	No. of Particulate Samples per Day	No. of Radionuclide Samples per Day	No. of HCl Samples per Day	No. of Heavy Metals Samples per Day	No. of Dioxins/Furans Samples per Day
E1	1	1	- ^a	-	-
E3	1	-	-	-	-
E4	-	-	-	-	-
S6	8	4	-	4	-
E7	12	4	4	4	4

^a No sample to be taken.

3.0 SOLID AND WATER SAMPLING

This sampling and analysis plan includes the following information:

- Sampling point descriptions
- Sample collection method
- Sampling schedule
- Constituents to be analyzed
- Total composition and toxicity characteristic leaching procedure (TCLP) extracts
- Sample containerization and preservation
- Design and operating data collection

Any samples obtained during the sampling period will be collected in a manner that ensures they are representative of the process and free of contaminants from sources other than the immediate environments being sampled. The equipment and the techniques that will be employed to obtain representative, unbiased samples will be in accordance with U.S. EPA-recommended procedures.

3.1 Feedstock and Vitrified Product Sampling

The demonstration plant will provide access for sampling feedstock materials and vitrified products. Vortec will supply prelabeled sample containers containing the necessary preservatives. All sample containers will be cleaned prior to use, following EPA protocols specified in SW-846 (Test Methods for Evaluating Solid Waste, SW-846, 1986). The sample containers may be cleaned in the laboratory or may be purchased precleaned. EERC personnel will conduct the sampling events. The sample point designations are taken from the Phase 3 test plan, Section 6.3, dated October 23, 1996.

3.1.1 Feedstock Batch Materials (Sampling Point S1)

Feedstock will be taken from Sampling Point S1. The feedstock sample will consist of a composite of no less than three and as many grab samples as is deemed necessary to ensure representative characteristics of the feedstock. The sample collection point, a diverter valve on the final pneumatic feed line, must be equipped to obtain as representative a sample as possible considering the heterogeneities of the feedstock. Clean utensils will be used for collection of each sample to avoid contamination. If this is not possible, the sampling equipment will be thoroughly cleaned after each use. The sample aliquots for each analytical test will be obtained from the composited sample. Duplicate samples will be collected as a backup in the event of breakage of the primary sample or uncertainty of a given analytical result. Duplicate samples will be marked "Hold for Analysis." The collected samples will be stored in laboratory-prepared sample containers supplied by Vortec.

3.1.2 Vitrified Product (Sampling Point S2)

Vitrified product will be sampled at 30-minute intervals from the drag conveyor (Sampling Point S2) during melter operation. The samples will be collected as a granular solid using clean stainless steel utensils and stored in laboratory-prepared sample containers provided by Vortec. Only selected samples will be analyzed for characterization of the vitrified product. Sample selection will be coordinated with steady-state operation based on operating data. With the greater number of vitrified product samples collected, it may not be necessary to collect the samples in duplicate.

3.2 Wastewater Treatment System Sampling

The primary wastewater treatment system consists of wastewater holding tanks, reaction tanks, clarifiers, filters, and ion-exchange units. The system is designed to handle a wide variety of ions and relatively high suspended solids loadings (1%-3% range). Performance criteria for the wastewater treatment system are based on drinking water standards for the state with Kentucky under Wastewater Permit No. KY000409. Sampling of the wastewater treatment system can be

conducted not only to verify compliance with Kentucky Drinking Water Standards, but also to characterize the performance of the various unit operations that make up the treatment system. Limited wastewater treatment system sampling and analysis will be conducted during shakedown, operation with cullet feed, and operation with clean soil feed. More detailed sampling and analysis events will be conducted during the processing of low-level radioactive soils and the processing of soils blended with RCRA and Toxic Substances Control Act (TSCA) wastes.

The wastewater treatment system description and process and instrumentation diagram drawings are provided in Vortec Phase 3 Test Plan (October 23, 1996). Sampling of the system for permitting purposes will be at only the system outlet into the main gaseous diffusion plant water system. As an option, additional points, including the system influent and after each stage of the system could be included in order to refine system operations. The optional sampling point descriptions are provided in Table 3. Sampling after each stage or unit operation of the wastewater treatment system during the demonstration tests can provide a comprehensive evaluation of treatment performance and identify any problems or deficiencies with the individual unit operations. Thus any wastewater treatment system problems can be identified, addressed, and remedied during the demonstration.

Each sample will be collected in duplicate with a frequency of one sampling event every 8 hours during steady-state operation during shakedown and cullet processing. To provide a more detailed analysis and characterization of system performance, the sampling frequency will be increased to two samples every 8 hours of steady-state operation during the processing of clean soils and low-level radioactive soils. Analysis of selected samples will be determined in conjunction with a review of system operational data.

Wastewater treatment system characterization samples will be collected from areas of completely mixed zones following individual unit operations through a sample valve to allow a slipstream of the sample to be diverted to a closed and vented sample container. Cleaned sample containers with preservatives for specified analytical parameters will be provided by Vortec.

3.3 Blanks

Blank samples, i.e., equipment blanks, trip blanks, and field blanks, will be collected during characterization sampling visits and treatment tests according to the discussion provided below. Analysis of blanks collected during the characterization sampling visits is not a requirement, although analysis would be warranted in cases where contamination is suspected.

Trip Blanks. One trip blank that is not opened in the field will be collected. This blank will be used to determine whether any contamination resulted from sample transport, shipping, or site conditions. The trip blank will be prepared using laboratory-pure water, preserved as required. (Laboratory-pure water, as defined in SW-846, is distilled or deionized water or Type II reagent water that is free of contaminants that may interfere with the analytical test.) The blank will be packed and shipped with the sample containers throughout the entire process.

TABLE 3

Optional Sampling Points for the Evaluation of the Wastewater Treatment System	
Sample Location	Sample Type
Influent to Wastewater Holding Tank Just Before T-601 (flocculation tank) ^a	Liquid
Effluent from Wastewater Holding Tank (T-600)	Liquid
Wastewater Holding Tank (T-100) Underflow	Sludge
Reaction Tank A (T-610) Effluent	Liquid
Reaction Tank B (T-611) Effluent	Liquid
Clarifier Tank (ME-600) Overflow (polishing filter feed tank, T-602)	Liquid
Clarifier Tank (ME-600) Underflow ^a	Sludge
Polishing Filter (ME-602A, B, C) Effluent	Liquid
Ion Exchange (ME-603A, B, C) Effluent	Liquid
Treated Effluent Tank (T-605) (final system effluent) ^b	Liquid
Sludge Holding Tank (T-603)	Sludge
Filter Press (ME-601) Filtrate	Liquid
Filter Press (ME-601) Cake	Semisolid

^a Required for mass balance.

^b Permit requirement.

Field Blanks. A field blank for metals should be taken if metal dust and potential atmospheric deposition of the dust are problems at the location and may be a potential source of contamination, especially in the treated residuals. Each field blank will consist of laboratory-pure water taken to the field, poured into a 150-mL Teflon bottle in the area where the treatment system is located, and preserved accordingly.

If constituents of interest are measured in the blank, documentation will be presented in the on-site engineering report (OER) that explains the impact of the contamination on the samples collected.

4.0 OPTIONAL ANALYSES FOR SPECIATION OF THE EFFLUENTS

For permitting purposes alone it is not necessary to quantify individual species in the effluents. However, for future refinement of system operations and performing mass balances, analyses of particular species will be required. When these optional speciation analyses are

performed, appropriate analytical techniques must be used and adherence to a strict QA plan is necessary to provide Vortec and DOE with meaningful data of defensible quality. Compatibility with sampling methods must be considered when the appropriate analytical techniques are selected. Close communication between the sampling team and the analytical personnel is essential to help ensure quality data by preserving sample integrity for all sampling and analytical activities. This communication will be facilitated by following a detailed chain-of-custody protocol.

The sampling activities will generate three types of samples for chemical analysis: solid, liquid, and flue gas samples. Appropriate analytical methods will be selected for the analysis of these sample types.

4.1 Analytical QA/QC

The analytical QA/QC for this project will focus on ensuring that the data generated meet the specified method performance criteria. Standard methods (EPA and ASTM [American Society for Testing and Materials]) will be used whenever possible to help determine the quality of the data. Any modifications to existing methods or development of new methods should be well documented, reviewed, and approved by the QA officer before implementation. The QA/QC protocols for analysis are taken from the EPA certification manual. Additional QA/QC protocols, which are expansions of the EPA protocols, have been added for digestion, preparation, and sampling; Table 4 lists the anticipated analytical methods to be used for this project. According to the methods shown in Regulation 40 CFR 61, Subpart H, both alpha and gamma spectrophotometry will be needed to detect all five of the radionuclides of interest.

Careful consideration should be given to method detection limits, minimum sample size, and compatibility with sampling methods when the appropriate analytical method is selected.

4.2. Pretesting of Qualified Analytical Laboratories

In past sampling projects, potentially valuable field data were questioned because of large variations or spurious results from QA/QC samples. To maximize the potential for the best-quality data, it is recommended that a presampling laboratory exercise be carried out. Some of the benefits of the exercise are that it will 1) allow the lab to become familiar with the preparation procedures for the sample types, thus improving data quality; 2) pretest the laboratory and the proposed procedures prior to expensive sampling; and 3) identify potential procedural problems that may be resolved prior to sampling. The exercise should include the preparation and analysis of blanks, spikes, fortified samples and/or simulated impinger samples, and certified reference materials where applicable. The inclusion of an auditor in the presampling exercise would provide an evaluation of the externally spiked samples, as well as a reference for analytical techniques. The presampling exercises would demonstrate the ability of a laboratory to yield qualifying blanks from clean analytical equipment and to recover matrix-spiked samples as well as standard reference materials.

4.3 Sample Preparation for Solid Samples

To determine total metal concentrations in the solid materials, they must be dissolved in a mixed acid solution. Microwave digestion methods using sealed digestion vessels are recommended

TABLE 4

Summary of Analytical Methods

Category	Parameter	Analytical Method
RCRA Metals	Arsenic	GFAAS ^a
	Barium	ICPAES
	Cadmium	GFAAS
	Chromium	ICPAES
	Lead	GFAAS
	Mercury	CVAAS ^b
	Selenium	HGAAS ^c
	Silver	GFAAS
Halogens	Chlorine	IC ^d
	Fluorine	IC or ISE ^e
Metal Oxides	Aluminum	ICPAES ^f
	Calcium	ICPAES
	Iron	ICPAES
	Magnesium	ICPAES
	Potassium	ICPAES
	Silicon	ICPAES
	Sodium	ICPAES
	Titanium	ICPAES
Other Metals	Copper	ICPAES
	Nickel	ICPAES
Radionuclides	Cesium ¹³⁷	Spectrophotometry
	Plutonium ²³⁹	Spectrophotometry
	Technitium ⁹⁹	Spectrophotometry
	Thorium ²³⁰	Spectrophotometry
	Uranium ²³⁵	Spectrophotometry
Solid Material	Leachability	TCLP ^g
	Chemical durability	PCT ^h
	Total digestion	Microwave ⁱ

^a Graphite furnace atomic absorption spectroscopy.

^b Cold-vapor atomic absorption spectroscopy.

^c Hydride generation atomic absorption spectroscopy.

^d Ion chromatography.

^e Ion-specific electrode.

^f Inductively coupled plasma atomic emission spectroscopy.

^g Toxicity characteristic leaching procedure (EPA Method 1311).

^h Product consistency test (ASTM Method C1285-94).

ⁱ Modified EPA 3051 as described below in sample preparation for solid materials.

to help ensure total dissolution and eliminate loss of volatile species during heating. To determine method precision, duplicate digestions for each type of solid material are required at a minimum frequency of 10%. A method blank is also included to determine the possibility of contamination from the digestion procedure. The blank contains all of the reagents used in preparing the solid samples and is carried through the complete digestion procedure. A certified standard reference material of a matrix similar to that for the solid samples is included with each batch to verify the accuracy of the digestion procedure.

If the analytical laboratory selected for this project is not familiar with this type of digestion procedure, several standard reference materials should be digested and analyzed to verify the precision and accuracy of the method. Some suggested reference materials are NIST 2709 (soil), NIST 2711 (soil), NIST 1633b (fly ash), and NIST 612 (glass).

4.4 Instrumental Analysis

The quality of the analytical data will be monitored by analysis of instrumental duplicates, matrix spikes, blanks, and calibration verification standards. A summary of the QA/QC requirements for the optional instrumental analysis is listed in Table 5.

4.5 Chain of Custody

Chain-of-custody procedures require accurate documentation of sample possession throughout the entire project. Executing proper chain of custody requires a written record of collecting, handling, storing, transporting, and analyzing various types of field samples. This requires rigorous documentation and safeguarding to maintain data and sample integrity and to ensure against loss of valuable test results.

All field personnel who handle field samples are responsible for proper data and sample logging and custody. Chain-of-custody forms and sample labels will be completed by each of the respective field-sampling team members responsible for equipment operation, sample recovery, and data logging.

The sampling team members responsible for sample acquisition will maintain a detailed log of testing activities including the details of sample acquisition. Sample data sheets will be completed in ink, dated, and signed by the operator. At a minimum, the log will itemize the following for each sample.

- Client – job name (Vortec, FETC at Morgantown)
- Sample identification number
- Sample identification or description
- Sample location
- Date and time of sampling
- Sampling method
- Method of processing or preserving field samples
- Sampler's name

TABLE 5

Summary of QA/QC Requirements for Optional Instrumental Analysis

Method/Analyte	Quality Control Check	Frequency	Acceptance Criteria	Corrective Action	Comments
Microwave Digestion (Method SW 3051) As, Cd, Cr, Pb, Hg, Ni, Se and Ag	Duplicate samples	10% or minimum of one per batch	None	None	Used to determine overall variability of sample preparation
	Method blank	10% or minimum of one per batch	$\leq 10 \times$ Method detection limit (MDL)	Repeat digest and evaluate source of contamination	Used to determine analytical contamination
	NIST-certified standard reference material (control sample)	Weekly or minimum of one per five sets digested	85%–115% recovery for most metals. May vary depending on levels	Redigest batch and repeat analysis	Used to determine method accuracy
ICPAES (Method SW 6010, Cr and Ni and ASTM D3682, Al, Ca, Fe, Mg, K, Si, Na, Ti)	Three-point mixed standard calibration plus blank	Daily	$r > 0.995$	Repeat calibration	
	Initial calibration verification (ICV)	Immediately after calibration	Measured value within 95%–105% of true value for element of interest	Repeat calibration	Used to verify calibration accuracy
	Continuing calibration verification (CCV)	10% or minimum of one per batch	Measured value within 90%–110% of true value for element of interest	Repeat calibration and reanalyze previous ten samples	Used to determine instrument drift
	Matrix spike analysis	10% or minimum of one per batch	Recovery within 85%–115%	Flag data and notify lab supervisor to determine appropriate corrective action	
	Duplicate analyses	10% or minimum of one per batch	$< 10\%$ difference	Flag data	Used to determine instrument precision

Continued . . .

Table 5 (continued)

Method/Analyte	Quality Control Check	Frequency	Acceptance Criteria	Corrective Action	Comments
GFAAS and HGAAS SW 7060 Arsenic, SW 7180 Cadmium, SW 7421 Lead, SW 7741 Selenium	Three-point calibration plus blank	Daily or before each different analyte determination	$r > 0.995$	Repeat calibration	
	ICV ^a	Immediately after instrument calibration	Measured value within 95%–105% of true value for element of interest	Repeat calibration	Used to verify calibration accuracy
	CCV ^b	10% or minimum of one per batch	Measured value within 90%–110% of true value for element of interest	Repeat calibration and reanalyze previous ten samples	Used to determine instrument drift
	Matrix spike analysis	10% or minimum of one per batch	Recovery within 85%–115%	Flag data and notify lab supervisor to determine appropriate corrective action	
	Duplicate analyses	10% or minimum of one per batch	< 10% difference	Flag data	Used to determine instrument precision
CVAAS, SW 7470, Mercury	Three-point calibration plus blank	Daily	$r > 0.995$	Repeat calibration	
	ICV	Immediately after instrument calibration	Measured value within 95%–105% of true value for element of interest	Repeat calibration	Used to verify calibration accuracy
	CCV	10% or minimum of one per batch	Measured value within 90%–110% of true value	Repeat calibration and reanalyze previous ten samples	Used to determine instrument drift
	Matrix spike analysis	10% or minimum of one per batch	Recovery within 85%–115%	Flag data and notify lab supervisor to determine appropriate corrective action	

Continued . . .

Table 5 (continued)

Method/Analyte	Quality Control Check	Frequency	Acceptance Criteria	Corrective Action	Comments
Anions by IC (Cl and F)	Duplicate samples	10% or minimum of one per batch	< 10% difference	Flag data	Used to determine overall variability of sample preparation
	Three-point calibration plus blank	Daily	$r > 0.995$	Repeat calibration	Used to determine instrument precision
	ICV	Immediately after instrument calibration	Measured value within 95%–105% of true value for element of interest	Repeat calibration	Used to verify calibration accuracy
	Matrix spike analysis	10% or minimum of one per batch	Recovery within 85%–115%	Flag data and notify lab supervisor to determine appropriate corrective action	
	Duplicate analyses	10% or minimum of one per batch	< 10% difference	Flag data	Used to determine instrument precision
	CCV	10% or minimum of one per batch	Measured value within 90%–110% of true value for element of interest	Repeat calibration and reanalyze previous ten samples	Used to determine instrument drift

^a Initial calibration verification.^b Continuing calibration verification.

Laboratory sample custody begins with the receipt of samples in the laboratory and ends with sample disposal. Receipt of samples in the analytical laboratory will be documented in a bound laboratory record notebook. Sample transfers, retrievals, and storage will be documented in a bound laboratory record book associated with individual laboratory analyses throughout analytical activities, so that the location of a sample can be determined at any time. Documentation will include date and time of activity, name of person retrieving, transferring, or storing the sample, and location and conditions of storage.

At the completion of the laboratory analyses, samples will be archived for a sufficient period of time to allow for a complete review of the analytical data and chain-of-custody forms. The personnel responsible for sample disposal will be determined at a later date. Final disposition of all samples will conclude sample custody requirements.

4.6 External QA Audit

An external audit of all sampling and analytical activities is an important part of the overall QA plan for the optional speciation analyses. It provides an objective, independent assessment of the sampling and analytical efforts. Typically, the audit consists of two parts—systems and performance evaluation. The systems audit comprises observation and documentation of all aspects of the measurement effort, including the following:

- Calibration procedures
- Completeness of data forms notebooks and other reporting requirements
- Data review and validation procedures
- Data storage filing and record-keeping procedures
- Chain-of-custody procedures
- Quality control procedures
- Operating conditions of facilities and equipment
- Documentation of equipment maintenance
- Systems and operations overview

The performance evaluation audit (quantitatively) assesses the quality of the measurement data. The performance evaluation audit usually consists of the analysis of blind spikes and QC samples by the laboratories responsible for the analytical data. The results of a performance evaluation audit will help answer questions regarding accuracy and precision of the analytical equipment, QC data compared to the actual data collected, and significant variation in data quality over time.

APPENDIX A

EPA METHOD SUMMARIES

EPA METHOD SUMMARIES

EPA Method 26A

This method is used to collect hydrogen chloride (HCl), chlorine (Cl₂), and particulate in stack gas emission samples from hazardous waste incinerators, municipal waste combustors, boilers, and industrial furnaces.

Gaseous and particulate pollutants are withdrawn using a probe from an emission source and are collected in an optional cyclone (required for high particulate loadings or collection of water droplets), a fine particulate filter, and absorbing solutions. The Teflon mat or quartz-fiber filter collects other particulate matter, including chloride salts. Acidic and alkaline solutions collect gaseous HCl and Cl₂, respectively (for application to the Vortec facility, the acidic and alkaline solutions will be used to capture vapor-phase radionuclides as well).

EPA Methods 1-5

These are five methods for measuring the particulate matter in flue gas ducts. Method 1 is for developing a proper traversing grid for determining the flow patterns within the duct. Methods 2 and 3 are for properly measuring the flow patterns within the duct. Method 4 is to determine the moisture content in the gas stream, and finally EPA Method 5 is for measuring the particulate matter in the duct.

EPA Method 23

EPA Method 23 is used to determine polychlorinated dibenzo-*p*-dioxins (PCDDs) and polychlorinated dibenzofurans (PCDFs) from stationary sources. A sample is withdrawn isokinetically from the stack through a probe, a filter, and a trap packed with a solid adsorbent. The PCDDs and PCDFs are collected in all three components: probe, filter, and trap.

EPA Method 29

EPA Method 29 is used to determine metals from combustion processes. The source sample is withdrawn isokinetically from the stack through a heated probe. The majority of the particulate emissions are collected on a filter in a heated filter holder that is located after the probe outside of the stack. The gaseous emissions are collected in a series of chilled impingers located after the filter. Impingers containing a dilute nitric acid in hydrogen peroxide solution collect the metals (Al, Ag, Sb, As, Ba, Be, Cd, total Cr, Co, Cu, Fe, Pb, Mn, oxidized Hg, Mo, Ni, P, Se, Ti, V, and Zn). Impingers containing a solution of potassium permanganate dissolved in dilute sulfuric acid collect the elemental mercury.

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