ELECTRIC POWER
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Responding to the EPA Information Collection Request for Electric Utility Steam Generating Units

Fuels

Background

On December 24, 2009, the U.S. Environmental Protection Agency (EPA) issued an Information Collection Request (ICR) requiring owners of coal- and oil-fired power plants to test stack emissions from selected electricity generating units (EGUs) for a range of hazardous air pollutants (HAPs) and potential surrogate species. The ICR also requires facilities to sample and analyze the fuels burned during the test period. The Electric Power Research Institute (EPRI) has prepared a series of technical papers to help power plant owners improve the quality of the test results by raising awareness of technical issues related to the sampling and analytical methods. As EPA's plan is to use the ICR results to establish emission standards for the power industry, it is important to collect and report measurements that are accurate, unbiased, and representative of the stationary sources tested.

The objective of these papers is to provide technical information that will assist power plant owners and stack testing contractors in identifying appropriate technical resources, developing test plans, streamlining testing, selecting appropriate sampling and analytical methods, and avoiding common errors. The information provided includes "lessons learned" and recommendations from several stack testing firms that provided testing services on recent EPA ICRs. These recommendations are not intended as universal guidance; each power plant owner should evaluate their applicability for a specific situation.

Changes and clarifications to the ICR requirements are posted on the Electric Utilities MACT ICR web page: http://utilitymacticr.rti.org/FAQ.aspx. Power plant owners should consult that resource for any guidance that may impact the recommendations in this paper.

About Fuel Sampling and Analysis for the ICR

The ICR requires fuel sampling and analysis for fuels burned during the testing period. The EPA intends to use the fuel data to attempt to establish correlations between fuel composition and stack emissions. Because these correlations may have an impact on any MACT limits established for the power industry, it is very important to provide EPA with fuel measurements that are accurate and representative of the fuel burned during the stack tests.

The specific fuels to be tested are listed in the Section 114 letters received by each selected facility — they may include coal, oil, biomass, petroleum (pet) coke, or other solid fuels. The table below summarizes the fuel parameters to be measured in association with each stack test group

Stack Test Group	Fuel Parameters
Acid gas HAP	Chlorine, fluorine, and sulfur content; HHV, and proximate/ultimate analyses of the coal being utilized during the test
Dioxin/furan organic HAP	Chlorine and sulfur content, HHV, and proximate/ultimate analyses of the coal being utilized during the test
Non-dioxin/furan organic HAP	HHV and proximate/ultimate analyses of the coal being utilized during the test
Mercury and non-mercury metallic HAP	Antimony, arsenic, beryllium, cadmium, chromium, cobalt, lead, manganese, mercury, nickel, selenium, chlorine, and provide the HHV and proximate/ultimate analyses of the coal being utilized during the test
"Bottom 88" list (coal-fired units)	Antimony, arsenic, beryllium, cadmium, chromium, cobalt, lead, manganese, mercury, nickel, selenium, chlorine, fluorine, and sulfur content, HHV, and proximate/ultimate analyses of the coal being utilized during the test
IGCC units	Antimony, arsenic, beryllium, cadmium, chromium, cobalt, lead, manganese, mercury, nickel, selenium, chlorine, fluorine, and sulfur content, HHV, and proximate/ultimate analyses of the coal being utilized during the test
Oil-fired units	Antimony, arsenic, beryllium, cadmium, chromium, cobalt, lead, manganese, mercury, nickel, selenium, chlorine, fluorine, sulfur, and provide HHV and proximate/ultimate analyses of the oil being utilized during the test
Pet coke units	Antimony, arsenic, beryllium, cadmium, chromium, cobalt, lead, manganese, mercury, nickel, selenium, chlorine, fluorine, and sulfur content, HHV, and proximate/ultimate analyses of the petroleum coke being utilized during the test

Sources of Methods

The methods discussed below can be obtained from one of the following sources:

- ASTM standards can be purchased from http://www.astm.org/Standard/index.shtml
- EPA SW-846 methods are available online at: http://www.epa.gov/waste/hazard/testmethods/sw846/online/index.htm
- EPA Office of Water methods (e.g., EPA Method 1631E) are available from: http://www.epa.gov/water-science/methods/method/

Sample Collection, Compositing, and Preparation

The ICR lists multiple methods that can be used for sampling, compositing, and preparation of fuels for analysis. Alternative methods are acceptable if they meet EPA's definition of "equivalent" methods. If they do not meet the definition, approval must be obtained from EPA.

EPA defines "equivalent" for fuel sampling, compositing and preparation methods as follows:

- *An equivalent sample collection procedure means a published voluntary consensus standard or practice (VCS) or EPA method that includes collection of a minimum of three composite fuel samples, with each composite consisting of a minimum of three increments collected at approximately equal intervals over the test period.*
- *An equivalent sample compositing procedure means a published VCS or EPA method to systematically mix and obtain a representative subsample (part) of the composite sample.*

- *An equivalent sample preparation procedure means a published VCS or EPA method that: Clearly states that the standard, practice or method is appropriate for the pollutant and the fuel matrix; or is cited as an appropriate sample preparation standard, practice or method for the pollutant in the chosen VCS or EPA determinative or analytical method.*

Solid Fuels (Coal, Pet Coke and Biomass)

Coal Sample Collection – The ICR requires one composite coal sample to be prepared and analyzed for each stack test run. Procedures for sampling solid fuel from belt or screw feeders and fuel piles or trucks are provided in the ICR Part B, Section 2.1.

The EPA procedure for the feeders requires collection of three two-pound increments for compositing. The procedure for piles/trucks requires five increments of unspecified size ("a shovel-full"). This is fewer increments and a much smaller volume of sample than required by the alternative method suggested by EPA, ASTM D2234/D2234M-09a, *"Standard Practice for Collection of a Gross Sample of Coal"*. The ASTM method requires 15 increments of 2 to 15 lb. (1 to 7 kg) each; the weight depends on the top size of the coal. In order to obtain a representative sample of coal for the ICR with a known precision and bias, EPRI recommends use of the ASTM method for manual sampling (to the extent possible) rather than the procedures in the ICR.

Automatic sampling equipment, as described in ASTM Method D7430, *"Practice for the Mechanical Sampling of Coal"*, can also be used to provide representative samples, for those power plants that already have the equipment in place.

ASTM D2234 describes collection procedures for two increment types:

1. Type I (No Human Discretion)
2. Type II (Human Discretion)

Under each increment type, the spacing of sampling increments is divided into Systematic and Random categories and the categories further divided into four conditions:

1. Condition A, stopped belt cut
2. Condition B, full stream cut
3. Condition C, part-stream cut
4. Condition D, stationary sampling

Coal delivery systems differ from one power plant to the next; the appropriate sampling protocol depends on the delivery system. For most plants, the following approach is recommended:

- Type I (No Human Discretion), in which specific pieces or portions are not subject to selection on a discretionary basis and which the increment is collected in precise accord with previously assigned rules on timing or location that are free of any bias. Type I selection increments generally yield more accurate coal data results.
- Condition A (Stopped-Belt Cut), for coal conveyer belt systems, in which a loaded conveyer belt is stopped and a full cross-section cut with parallel sides is removed from the coal stream. The distance between the parallel faces shall not be less than three times the normal top size of the coal. Safety considerations also support using this approach.
- Condition D (Stationary Coal Sampling), for situations in which there is no coal conveyer or other access and a portion of coal is collected from a pile, a rail car, a barge, or a shiphold.

- Systematic Spacing, in which the movements of individual increment collection are spaced evenly in time or position over the lot.

Since belt sampling is typically conducted on a conveyer belt leading to a coal storage bunker that holds a several-hour supply of coal, the coal collected from a belt may not be representative of the coal fired during the test. The representativeness of the sample can be improved by sampling the fuel as close to the point of combustion as practical, typically at the mill feeders, using the ASTM D2234 I–C–I increment collection classification. Samples can be collected from each operating mill feeder, at predetermined intervals, to obtain a minimum of 15 increments, divided by the number of operating mills. A facility will need to obtain EPA approval for this approach.

A "coal cutter" device can be used to collect the samples directly from the belt. The coal cutter provides solid sides to define the 6-inch wide section of the belt for the required sample. If plant personnel do not collect the coal sample it may take two people to collect all the material (fines and coarse) in the full cross-section of the belt. Deposit the sample in a clean plastic bag for further processing.

Before sampling, make sure the conveyor belt is stopped and locked out, and plant personnel are aware that coal sampling is commencing. After each sample is collected, notify plant personnel that coal sampling has ended. **Do not smoke during the collection and processing of the samples and always wear personal protective equipment.**

It is advisable to collect a duplicate sample during one of the three test runs to assess relative percent differences in the sampling and analysis procedures.

Coal Compositing and Size Reduction – The ICR, Part B, Enclosure 1, Section 2.2 requires a 7-step compositing procedure involving iterative quartering and size reduction. The size reduction procedure that is cited in this procedure is a withdrawn ASTM standard for milling refuse derived fuel (RDF), ASTM E829-94. The ICR, Part B, Enclosure 1, Table 2.2 also indicates that ASTM D2013 should be used to prepare composite coal samples for analysis. These requirements conflict, because ASTM D2013-07 includes a complete procedure for size reduction and compositing of coal samples.

EPRI recommends following the more rigorous procedures in ASTM D2013-07 to ensure that the coal sample is appropriately sized and homogenized for use in laboratory analysis. Reduction and division procedures in Group A (manual riffle) are most suitable, as they allow preparation of smaller weight samples for laboratory analysis. However, the specific procedure should be selected based on the equipment available at the facility or laboratory.

The ICR states that coal samples for analysis of selenium should be milled using procedures in SW-846, Method 7740, to avoid loss of volatile selenium. However, Method 7740 (an older analytical method no longer included in SW-846) does not discuss sample reduction. EPRI suggests using the procedures in ASTM D2013-07; these are unlikely to lead to loss of selenium. The more likely route of loss is during acid digestion, if this is conducted in an open vessel.

Pet Coke Sample Collection and Compositing – The ICR recommends that the coal methods discussed above also be used for pet coke. EPRI suggests instead the use of procedures in ASTM D346-04e1, which are specifically designed for pet coke. This method meets all of the ICR criteria to be considered an "equivalent" method.

- ASTM D 346-04, *Standard Practice for Collection and Preparation of Coke Samples for Laboratory Analysis*

Biomass Sample Collection, Compositing and Size Reduction – The ICR suggests that biomass samples be collected and processed using the same procedures as for coal. In the limited U.S. utility sector testing to date, that has been the most common approach. It is not clear what standard or method would be most appropriate for sampling and preparation of biomass samples, particularly non-wood biomass.

Liquid Fuels (Oil)

Oil Sampling – The ICR requires oil samples to be collected using one of the following two methods:

- ASTM D4057-06, *Standard Practice for Manual Sampling of Petroleum and Petroleum Products*
- ASTM D4177-95(2005) *Standard Practice for Automatic Sampling of Petroleum and Petroleum Products*

Typically, most plants have a fuel oil tap that is to be used to collect the sample. Ask plant personnel if unsure of the location. During each test run, collect two fuel samples in 1-liter amber, glass bottles. For two of the three runs, designate one sample as the primary sample and the other as a backup. For the remaining run, designate a sample as primary and the other as a duplicate for assessment of sampling and analytical variability. After sample collection, label the samples, document the samples in a logbook and complete chain of custody forms for the laboratory requesting the required analyses. **Do not smoke during the collection and processing of the samples and always wear personal protective equipment.**

Fuel Analysis

The ICR lists multiple methods that can be used for analysis of fuels. Alternative methods are acceptable if they meet EPA's definition of "equivalent" methods. If they do not meet the definition, approval must be obtained from EPA. EPA defines "equivalent" for fuel analysis methods as follows:

- *An equivalent procedure for determining heat content means a published voluntary consensus standard or practice (VCS) or EPA method to obtain gross calorific (or higher heating) value.*
- *An equivalent procedure for determining fuel moisture content means a published VCS or EPA method to obtain moisture content. If the sample analysis plan calls for determining metals (especially the mercury, selenium, or arsenic) using an aliquot of the dried sample, then the drying temperature must be modified to prevent vaporizing these metals. On the other hand, if metals analysis is done on an "as received" basis, a separate aliquot can be dried to determine moisture content and the metals concentration mathematically adjusted to a dry basis.*
- *An equivalent pollutant (mercury, TSM, or total chlorine) determinative or analytical procedure means a published VCS or EPA method that clearly states that the standard, practice, or method is appropriate for the pollutant and the fuel matrix and has a published detection limit equal to or lower than the methods listed in this test plan.*

The ICR recommendations for analysis of coal, "Other Solids", biomass and liquid fuel (oil) are shown below. Other Solids includes pet coke and other non-biomass solid fuels such as refuse derived fuel (RDF). The right-most column lists EPRI recommendations for one or more methods that EPRI has found to be appropriate for the matrix of interest. **These recommendations are not intended be prescriptive;** other methods listed in the ICR may also be appropriate. If the EPRI recommended method is not one of the methods listed in the ICR (or a more recent version of a listed method), the reason for recommending it is shown in a footnote. Likewise, if EPRI has information that a particular method is not appropriate for the ICR, that is noted below the table. Note that laboratories may not run the same version of a method that EPA is requiring; generally, newer versions are acceptable but older versions than required by EPA may not be.

Higher Heating Value (HHV)

Fuel	ICR Listed Methods	EPRI Recommended Method
Coal	ASTM D5865-07, ASTM D240, ASTM E711-87 (1996)	ASTM D5865-07
Other Solids	ASTM-5865-03a, ASTM D240, ASTM E711-87 (1997)	ASTM D5865-07
Biomass	ASTM E711-87 (1996) or equivalent, ASTM D240, or ASTM D5865-04	ASTM D5865-07 or ASTM E870-82 (2006)[1]
Liquid	ASTM-5865-03a, ASTM D240, ASTM E711-87 (1996)	ASTM D5865-07 or ASTM D240-09

[1] Specifically for wood fuels.

Proximate Analysis (Ash, Moisture, Volatiles)

Fuel	ICR Listed Methods	EPRI Recommended Method
Coal	ASTM-D3173-03, ASTM E871-82 (1998) or equivalent, EPA 160.3 Mod., or ASTM D2691-95	ASTM D5142-09[1] or ASTM D3173-07a
Other Solids	ASTM-D3173-03, ASTM E871-82 (1998) or equivalent, EPA 160.3 Mod.	ASTM D5142-09[1] or ASTM D3173-07a
Biomass	ASTM-D3173-03, ASTM E871-82 (1998) or equivalent, EPA 160.3 Mod.	ASTM E870-82(2006)[2]
Liquid	Not listed	D482-07 D1796-04(2009)

[1] Automated method for proximate analysis of coal/coke. The automated method is preferable as it is less subject to error due to absorption of moisture. This method should meet EPA's definition of equivalence.

[2] Standard ASTM method for proximate/ultimate analysis of wood fuels.

Technical standards for biomass analysis developed by the European Committee for Standardization (CEN) appear to meet EPA's definition of equivalent methods for proximate/ultimate analysis. A recent paper by CONSOL Energy evaluating the comparability of ASTM and CEN methods can be obtained from:

http://www.consolresearch.com/_images/BIOMASS%20CONFERENCE%202009%20Presentation%20Final.pdf

Ultimate Analysis (Carbon, Nitrogen, Ash, Oxygen, Sulfur)

Fuel	ICR Listed Methods	EPRI Recommended Method
Coal	None listed	ASTM D5373-08 and D4239-08 or ASTM D3176-89(2002)
Other Solids	None listed	ASTM D5373-08 and D4239-08 or ASTM D3176-89(2002)
Biomass	None listed	ASTM E870-82(2006) or ASTM D5373-08 and D5373-08
Liquid	None listed	ASTM D5291-02(2007) and D4294-08ae1 or D2622-08 (for No. 2 oil)

Mercury

Fuel	ICR Listed Methods	EPRI Recommended Method
Coal	ASTM D6722-01, EPA Method 1631E, SW-846-1631, EPA 821-R-01-013, or equivalent	ASTM D6722-01(2006) or ASTM D6414-01(2006)[1]
Other Solids	SW-846-7471A, EPA Method 1631E, SW-846-1631, ASTM D6722-01, EPA 821-R-01-013, or equivalent	ASTM D6722-01(2006)
Biomass	SW-846-7471A, EPA Method 1631E, SW-846-1631, ASTM D6722-01, EPA 821-R-01-013, or equivalent	ASTM D6722-01(2006)
Liquid	SW-846-7470A, EPA Method 1631E, SW-846-1631, EPA 821-R-01-013, or equivalent	ASTM D6722-01(2006) or CVAFS[2]

[1] A comparison of the performance of mercury methods for coal can be found in the following EPRI report. ASTM D6414 (acid extraction/ cold vapor atomic absorption) was shown to give performance equivalent to ASTM D6722. *Evaluation of Methods for Analysis of Mercury and Chlorine in Coal*, EPRI, Palo Alto, CA: 2000.1000287.

[2] None of the methods listed in the ICR are validated for oil – EPA Method 7470A is for **aqueous** liquid waste and may require stronger acid and longer digestion time for complete digestion of oil; EPA Method 1631E is for low-level analysis of mercury in water; EPA 821-R-01-013 is intended for preparation of tissue, sludge, sediment or soil samples for analysis by Method 1631 but is not validated for petroleum products. EPRI suggests the use of ASTM D6722 (Direct Combustion/AAS) or SW-846-3051A, Microwave Assisted Acid Digestion followed by cold vapor atomic fluorescence spectrometry (SW-846 Methods 7470 or 7471) modified to use CVAFS rather than CVAAS.

As noted above, selecting an appropriate sample preparation method is critical for good data quality. EPRI recommends ASTM Method D6722 (Direct Combustion/AAS) for all fuels, because it has no digestion step and consequently reduces the potential for mercury loss and cross-contamination. The ICR does not list this method for liquid fuels, so approval would need to be obtained from EPA. An equivalent method to D6722 that will be more familiar to oil laboratories is UOP 938; however, this vendor-developed method may not be considered a “consensus organization” method as defined by EPA.

SW-846 Methods 7470 and 7471 are CVAAS methods for liquid and solid samples, respectively. These methods produced a high percentage of nondetected measurements for oil and biomass samples in the Industrial Boiler MACT ICR. Modifying the methods to use a CVAFS detector would give better sensitivity.

EPA Method 1631 is a highly sensitive method that was developed for trace mercury analysis in water. This cold vapor atomic fluorescence spectroscopy (CVAFS) method has been applied to analysis of mercury in activated carbon sorbent, but is not routinely used or validated for coal or other fuels. Although it may be usable for fuel analysis, its highly rigorous quality control requirements make it expensive and the extremely low detection limits are not required for most fuels.

Note that "SW-846-1631" is apparently a mistake; there is no method with this number in SW-846.

To verify the performance of the sample preparation and analysis, it is advisable to submit a Standard Reference Material (SRM) to the laboratory if one is available. SRMs for coal are available from the U.S. Institute of Standards and Technology (NIST) and other sources; the SRM selected should be similar in rank and ash content to the samples and should be submitted blind along with the test samples.

Antimony, Arsenic, Beryllium, Cadmium, Chromium, Cobalt, Lead, Manganese, Selenium and Nickel

Analysis of fuels for trace metals is complex; no single method will provide good results for all fuels and elements. Best results will be obtained finding a laboratory that is highly experienced with the fuel and can document past performance by providing SRM results and detection limits for similar fuels.

Fuel samples generally must be ashed and/or digested to dissolve the matrix prior to analysis for trace metals. Samples for analysis of arsenic and selenium should not be ashed prior to digestion. It is important to select a sample preparation technique that is appropriate for the analytical method. The ICR recommendations for sample preparation methods are listed in Table 2.2 of the ICR, Part B, Enclosure 1:

- **Coal:** ASTM D2013-04
- **Other Solids:** SW-846-3050B or EPA 3050
- **Biomass:** ASTM D5198-92 (2003) or equivalent, EPA 3050, or TAPPI T266 for total selected metal preparation
- **Liquid:** SW-846-3020A or any SW-846 sample digestion procedures giving measures of total metal

The method listed in the ICR for coal (D2013) is a compositing technique, not an analytical preparation method. One common digestion method is SW-846, Method 3050B; however, this method may not give complete recovery of trace metals from some coals. EPRI recommends the use of the digestion procedure in ASTM Method D6357, which includes hydrofluoric acid.

Pet coke is a difficult matrix to digest with acids. Oil is also a difficult matrix to digest. SW-846 Method 3051A (Microwave Assisted Digestion) is a stronger digestion than Method 3050B and may give better results for these matrices.

For biomass, ASTM D5198 and TAPPI T266 are both hydrochloric acid (HCl) digestions. ASTM D5198 is a digestion for **total recoverable metals** from solid waste, not total metals. TAPPI 266 is for pulp and paper and has not been validated for all the target elements. SW-846 Method 3050B is the standard digestion technique used by most laboratories. Depending on the type of biomass, Method 3050B or 3051A may give better recoveries.

In selecting a sample preparation technique, the laboratory must ensure that it is suitable for the analytical method that will be used. For example, digestions containing HCl will cause difficulties for ICP-MS analysis because the chlorine interferes with accurate measurement of arsenic and selenium.

Fuel	ICR Listed Methods	EPRI Recommended Method
Coal	SW-846-6010B, ASTM D3683-94 (2000), SW-846-6020, -6020A or ASTM D6357-04 (all metals except Se and As) ASTM D4606-03 or SW-846-7740 (Se) SW-846-7060 or 7060A (As)	ASTM D6357-04 ASTM D4606-03 (As/Se)[1]
Other Solids	SW-846-6010B, EPA 200.8	ASTM D6357-04 ASTM D4606-03 (As/ Se)[1]
Biomass	SW-846-6010B, ASTM D6357-04, SW-846-6020, -6020A, EPA 200.8, or ASTM E885-88 (1996) or equivalent	ASTM D6357-04 ASTM D4606-03 (As/Se)[2]
Liquid	SW-846-6020, -6020A, SW-846-6010B SW-846-7740 for Se SW-846-7060 or -7060A for As	SW-846 6020A or 6010C[3]

[1] ICP-MS can be used for both As and Se if the digestion technique for Se is appropriate and the instrument is capable of minimizing interferences – see below.

[2] ASTM D4606-03 is validated for both As and Se.

[3] In the Industrial Boiler MACT ICR, these methods were used for both arsenic and selenium and gave adequate detection limits for petroleum-based fuel oils. ICP-MS can be used for both As and Se if the instrument is capable of minimizing interferences – see below.

The most common techniques used for non-mercury trace metal analysis are Inductively Coupled Plasma Atomic Emission Spectrometry (ICP-AES), Inductively Coupled Plasma Mass Spectrometry (ICP-MS), and Graphite Furnace Atomic Absorption Spectrometry (GFAAS). Methods using these three techniques are available from ASTM, the EPA Office of Solid Waste and Emergency Response (OSWER) and the EPA Office of Water. For example, the following are all ICP-MS methods: SW-846 6020, EPA Method 200.8, and ASTM D6357. Which method is offered by a laboratory is less important than how the analytical technique is carried out. However, these methods do not all have the same sample digestion procedure and quality control specifications and other details may differ, so the equivalence of methods should be verified with EPA if there is a question.

Each of the three techniques has advantages and disadvantages for fuel analysis.

- ICP-AES is typically less sensitive than ICP-MS; lower-concentration elements in coal (e.g., antimony, beryllium, and cadmium) are likely to be below detection limits.
- Conventional ICP-MS is prone to interferences on some elements (particularly arsenic and selenium from ions formed from chlorine and the argon used as the instrument plasma gas) so it may not be a good choice for high-chlorine coals. Labs that utilize Dynamic Reaction Cell (DRC) or collision/reaction cell ICP-MS instruments can provide more accurate results because these instruments can better overcome interferences.
- GFAA results are very matrix-dependent; certain trace elements can be lost as volatile species (i.e., metal chlorides) during sample analysis before the analyte is measured. The magnitude of this dependence varies from coal to coal.

ASTM Method D6357 is appropriate for all trace metals except arsenic and selenium. The method can use any of the above measurement techniques. ASTM D3683 is a GFAAS method. SW-846 Method 6010C is an ICP-AES method. SW-846 Method 6020A and EPA Method 200.8 are ICP-MS methods. These methods must be used with an appropriate digestion technique, as discussed above.

For fuel oil, an alternative approach used by some laboratories is to treat the petroleum like a used oil sample. The sample is diluted with a solvent and analyzed by ICP-AES in an organic matrix, calibrating the instrument with organometallic standards. This approach minimizes the risk of losing volatile elements. ICP-AES provides adequate sensitivity, particularly if used in the axial configuration. This approach is not equivalent to any of the methods listed in the ICR and would require EPA approval.

Selenium and arsenic must be prepared and analyzed separately from the other metals. Selenium can be accurately measured by several methods including DRC or collision/reaction cell ICP-MS, hydride generation AAS and GFAAS. ASTM Method D4606 (Hydride generation AAS) is an appropriate method for these two elements. Laboratories often substitute ICP-AES or ICP-MS for AAS in this method for better sensitivity. EPA Method 7740 and 7060A are older GFAAS methods that are not listed in the current version of SW-846. In the Boiler MACT ICR, oil and biomass samples analyzed for selenium with SW-846 Method 7740 had elevated detection limits.

As noted previously, to verify the performance of the sample preparation and analysis, it is advisable to submit duplicate samples and Standard Reference Materials (SRM) to the laboratory in a way that is blind to the lab, where possible.

Chlorine

Chlorine is generally not present in fuels in elemental form, but rather as halides or other compounds. Thus, the methods for this element generally do not measure chlorine but chloride.

Fuel	ICR Listed Methods	EPRI Recommended Method
Coal	SW-846-9250 or ASTM D6721-01 or equivalent, SW-846-5050, -9056, -9076, or -9250, ASTM E776-87 (1996)	ASTM D6721-01(2006)
Other Solids	ASTM E776-87 (1996), SW-846-9250, SW-846-5050, -9056, -9076, or -9250	ASTM D6721-01(2006)[1]
Biomass	ASTM E776-87 (1996), SW-846-9250, SW-846-5050, -9056, -9076, or -9250	ASTM E776-87(2009) or SW-846 5050/9056
Liquid	ASTM E776-87 (1996), SW-846-5050, -9056, -9076, or -9250	ASTM D7359-08[2]

[1] Expected to be more sensitive and accurate than listed methods for pet coke.

[2] Expected to be more sensitive and accurate than listed methods for fuel oil.

EPRI recommends using ASTM D6721 for any coal (and pet coke) in which the chlorine concentration is expected to be less than 200 ppm. Most other chlorine methods have poor accuracy and precision at those concentrations and detection limits may not be adequate. This problem was observed in the 1999 Clean Air Mercury Rule ICR, where a large fraction of the chlorine analyses for Powder River Basin (PRB) coal were below detection limits. D6721 measures all halogens including fluoride, bromide and iodide as chloride; however, levels of those halogens are typically much lower than chlorine and so will not produce a significant positive bias. D6721 should not be used if bromine is being added for mercury control. A comparison of coal chlorine methods can be found in the following EPRI reports.

- Evaluation of Methods for Analysis of Mercury and Chlorine in Coal, EPRI, Palo Alto, CA: 2000. 1000287.
- Technical Evaluation: Analysis of Chlorine in Coal by Oxidative Hydrolysis Microcoulometry, EPRI, Palo Alto, CA: 2000. 1000846.

Bomb combustion methods (e.g., ASTM D4208 and D808, SW-846 Method 5050, ASTM E776-87) should generally be avoided for chlorine analysis, as they have been demonstrated to give poorer accuracy and precision for many coals and can suffer from cross-contamination problems. However, in the Boiler MACT ICR, SW-846 Method 5050 used with a Method 9056 (ion chromatography) analysis was the predominant technique used for biomass samples and provided adequate detection limits. For fuel oil, ASTM D4208 and SW-846 Method 9056 gave a significant number of results below detection limits. EPRI recommends using ASTM D7359, which can measure chloride and fluoride in a single run.

Fluorine

Fluorine is generally not present in fuels in elemental form, but rather as halides or other compounds. Thus, the methods for this element generally do not measure fluorine but fluoride.

Fuel	ICR Listed Methods	EPRI Recommended Method
Coal	ASTM D3761-96(2002), D5987-96 (2002)	ASTM D5987-96(2007)
Other Solids	None listed	ASTM D5987-96(2007)
Biomass	None listed	ASTM D5987-96(2007)
Liquid	None listed	ASTM D7359-08

EPRI recommends ASTM Method 5987 as the sole technique for fluorine in coal and pet coke. The bomb combustion method, ASTM D3671, has been shown to give incomplete recovery of fluorine from coal. ASTM Method D5185, an ICP-AES method for used oils, gave better sensitivity for low-level metals in fuel oil in the Boiler MACT ICR than did ASTM D3761. However, a new method specific to fluorine in oil, ASTM D7359-08 is more sensitive and can also be used for chlorine.

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