

Appendix A. Pertinent flue gas monitoring reference methods

Table 10 lists reference methods used, their associated title, what is measured, and its units.

Table 10. Reference methods

Reference method	Title	Sampling/Analysis result	Units
EPA method 1	Sample and velocity traverses for stationary sources		
EPA method 2	Determination of stack gas velocity and volumetric flow rate (Type S pitot tube)	Stack velocity profile and aggregate volumetric flow rate	volume flow rate
EPA method 3A	Determination of oxygen and carbon dioxide concentrations in emission from stationary sources (instrumental analyzer procedure)	O ₂ , CO ₂	% vol, dry
EPA method 5	Determination of particulate matter emissions from stationary sources	Total particulate matter	Mass per unit volume flue gas
EPA method 6C	Determination of sulfur dioxide emissions from stationary sources (instrumental analyzer procedure)	SO ₂	ppmv, dry
EPA method 7E	Determination of nitrogen oxides emissions from stationary sources (instrumental analyzer procedure)	NO _x	ppmv, dry as NO ₂
EPA method 25A	Determination of total gaseous organic concentration using a flame ionization analyzer	Total gaseous organic concentration	ppmv propane equivalent
EPA CTM-027	Procedure for collection and analysis of ammonia in stationary sources	NH ₃	ppmv, dry
EPA method 29	Determination of metals emissions from stationary sources	Sb, As, Ba, Be, Cd, Cr, Co, Cu, Pb, Mn, Mg, Ni, P, Se, Ag, Hg	Mass per unit volume flue gas
NACSI method 8A	Determination of sulfuric acid vapor or mist and sulfur dioxide emissions from Kraft recovery furnaces	H ₂ SO ₄ and SO ₃	ppmv, dry

Appendix B. Flue gas amine / amine degradation product sampling

Background

TCM DA is planning to operate the PCC test unit at the facility with MEA solvent and no additives or amine blending. The solvent will be continuously cycling through the system for 1440 hours (60 days). Testing will be performed for a variety of operational parameters, including chemical characterization of the air and liquid waste streams. In particular, air emissions testing of the solvent and potential degradation products (amines, nitrosamines, and aldehydes) will be performed. This will be done during selected operational periods, including base-case testing.

Recommendations

Although other PCC tests have been performed with longer solvent cycling times, published studies suggest the presence of complex mixes of solvent degradation products that are emitted into the flue gas streams, even after shorter operational times. At least several days' worth of 'later' samples should be taken near the end of the 2-month period, during normal operations, in addition to the samples planned during the parametric and base-case testing.

Any testing undertaken for these solvent and degradation products should be performed isokinetically. A variety of sample collection processes can be of use, including impingers that are empty or charged with acidic solution.

NH₃ should be measured regularly as a frequently-observed high emission rate product. This is often done with FTIR, especially in situations where operations are expected to change quite substantially over time. Thus it can be a

proxy for operational tracking as well as for the purposes of emission rate quantification. During stable operations, other methods which can have lower detection limits (such as an EPA Method 5 / Method 17 approach, collection with impinger, and analysis by ion chromatography) can be used on samples collected from various impinger approaches.

Due to its relevance and high abundance in the mist observed in several PCC test facilities, SO₃ should also be measured at the absorber outlet. Submicron mist and aerosols may form in the absorber as a result of heterogeneous condensation followed by dissolution and enrichment with the highly soluble amines in the mist. Several studies have shown that high quantities of mist composed partly of SO₃ can be observed. The mist may be a large sink of nitrogenous compounds of interest (primarily the amines as opposed to degradation products) due to their alkalinity.

A recent EPRI report contains details, features, and difficulties with multiple options for sampling and analysis of each compound class [6]. It should be noted that it is likely that only a subset of chemicals with a given compound class can be analyzed with any particular technique. Knowledge of the specific target compounds of interest, or a desire to measure as much of the total mass of the compounds class, is needed to recommend any particular suite of methods. Specific issues of importance include the need for very stable elevated temperatures of the entire sampling train (no unheated tubing gaps) and appropriate elimination or addressing of sampling and analytical interferences from water.

Amine sampling could be attempted with FTIR but it is possible to likely that any emissions would fall below detection limits due to chemical interferences. Thus manual sampling is recommended, with approaches similar to EPA Method 5 [6].

Nitrosamine sampling must be done manually; sufficient testing and use of continuous methods is not available to justify its use for this purpose. The most reasonable approaches at this time center on cartridges loaded with Thernosorb/N, with later extraction and analysis by HP liquid chromatography or gas chromatography following, or slightly modified from, the OSHA 27 method. It is likely that multi-stage sampling trains will be required to obtain the suite of desired nitrosamines. Both aqueous and vapor phases should be collected. If water removal methods are used, condensed phase must also be collected and analyzed.

Whatever methods are chosen to be applied must include multiple field blanks collected under conditions as close to those used for sampling full operations as possible. Serious consideration should be given to the feasibility of undertaking method validation tests at the stack (such as spike tests at the sample train inlets in order to estimate potential sample losses through the sampling train, as they can be quite high for the types of compounds of interest).

Appendix C. Relative accuracy test audits

The CHP flue gas supply and product CO₂ flow meters installed do not conform to ASME PTC 19.5, Standard for Flow Measurement [7]. It is recommended here that these flow meters be subjected to a RATA prior to or during base-case testing. Three options for conducting such an audit are described below.

Note that use of one of these RATA calibration methods for CHP flue gas flow could provide calibrations for the flow meters described in Table 11.

Table 11. RATA methods for CHP flow meters

Meter location	RATA method	Meter type
CHP after DCC	8610-FT-0150	Ultrasonic
CHP after DCC	8610-FT-0124	TORBAR pitot tube
Absorber inlet	8610-FT-2039	TORBAR pitot tube
Absorber outlet	8610-FT-2431	TORBAR pitot tube

Use of these RATA/calibration methods for product CO₂ flow could provide simultaneous calibrations for the product CO₂ flow meters given in Table 12.

Table 12. RATA methods for product CO₂ flow meters

Meter location	RATA method	Meter type
Product CO ₂	8615-FT-0010	Vortex
Product CO ₂	8615-FT-2203	TORBAR pitot tube

Pitot tube traverse method

The unobstructed CHP flue gas duct lengths allow pitot tube traverses to be used to calibrate the CHP flow meters. ASME PTC19.5 describes how such a pitot tube traverse for flow is to be conducted. The practice in the US is to conduct a minimum of nine (9) separate flow traverses during which the challenged flow meter data is also collected. A maximum of three (3) of the flow traverse data sets may be discarded as outliers. The calibration flow and uncertainty are then calculated from remaining flow traverse data sets. The procedure is summarized in Section 2 of EPRI publication TR-104527 [8]. Duct nozzles allowing the use of traversing pitot tubes would need to be installed in the CHP flow duct to accomplish the flow traverses.

Dilution method

The flow meters may be calibrated by a dilution procedure. This is not a reference method, but it can be acceptable if the injection flow and concentrations are measured with sufficient accuracy. The general approach is to inject a tag gas far upstream of the flow meter (to allow for good mixing) and measure the concentration of the tag gas at the flow meter. The calibrated flow is then calculated by:

$$q_{meter} = q_{tag} \frac{C_{tag}}{C_{tag, meter}}$$

where:

- q_{meter} = mass flow rate at the metering location
- q_{tag} = measured mass flow rate of the tag gas injected
- C_{tag} = measured concentration of tag gas injected
- $C_{tag, meter}$ = measured concentration of tag gas at the flow meter.

A suitable tag commonly used is helium in air. The tag gas is supplied in high pressure gas bottles. A certified concentration of helium is required from the supplier. The tag gas is metered through a critical orifice (upstream pressure greater than ~2.5 bar). The flow through the orifice is directly proportional to the upstream (absolute) pressure. The concentration of helium can be measured at the flow meter using a thermal conductivity detector. A second cylinder of helium in air at the anticipated span concentration is required to calibrate the detector as is a helium-free air zero gas. Thermal conductivity detectors for helium are available from a number of manufacturers (and rental companies). These are normally used to detect helium leaks in lab equipment but are suitable also for sampling. Typical detection limit is 25 ppmv. In order to achieve ~1% uncertainty in the measured concentration, a measured concentration at the flow meter would be 2500 ppmv (0.25%).

Using this procedure to calibrate the flow meter at the absorber outlet would require a separate C_{tag} concentration measurement at the absorber outlet flow meter location.

Radioactive tracer method

The flow meters may also be calibrated by a procedure to measure transit time of a radioactive tracer. The method is described in a British Standard [9]. By this method, a radioactive tracer is pulse-injected upstream and radiation detectors are located a measured distance apart downstream. The method reports average velocity by measuring the transit time of the radiation pulse between the injection and detector locations. Mass flow is then calculated by multiplying the measured velocity, the pipe cross section and the gas density:

$$q_{meter} = \frac{d\rho\pi D^2}{4t}$$

where:

q_{meter}	= mass flow rate
d	= distance between radiation detectors
ρ	= gas density
D	= duct diameter
t	= time of radiation pulse transit.

Particular care must be taken in locating the injection point, and the radiation detectors. All three locations should be located on a long straight pipe run with minimal obstructions and no side taps. Conduct of this calibration procedure requires careful attention to a number of design and operating factors and should be undertaken only by personnel experienced in conduct of the procedure.

References

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