Establishing Measurement Traceability for Gaseous Mercury Emissions Monitoring

On March 15, 2005 the U.S. Environmental Protection Agency (EPA) issued the Clean Air Mercury Rule (CAMR) that defined a cap on the amount of mercury that could be emitted from coal-fired power plants, and also provided for an emissions trading program for flexibility in attainment. The EPA requested NIST to support this ruling by providing traceability for measurements of the emitted gas-phase mercury (Hg). Mercury is a neurotoxin that accumulates in the food chain and is therefore a health concern. Concentrations of mercury in the air are of little direct health concern. However, when the mercury in the air re-deposits, it enters the food chain and bioaccumulates. Fish can have mercury levels several orders of magnitude greater than the level found in air.

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EPA requested NIST to provide traceability for measurements of mercury emitted from coal-fired power plants. Initial efforts were focused on developing gas standards for elemental mercury. Two sources for providing standard gas mixtures containing elemental mercury were considered: gas cylinders containing mercury in air and devices that generate elemental mercury gas mixtures. In both cases, the mercury sources have to be calibrated to quantify their mercury output. At NIST, isotope dilution - cold vapor - inductively coupled plasma mass spectrometry (ID-CV-ICP-MS) is used for the analysis of mercury in the gas phase. ID-CV-ICP-MS has been used at NIST for many years for certifying mercury in Standard Reference Materials of both solid and liquid matrices. This technique is a high-accuracy analytical technique, and was modified and evaluated as a method to be used for measuring mercury in the gas phase. Another analytical technique used by NIST for mercury quantification is the gold amalgam trap-and-purge with subsequent detection using a cold vapor atomic absorption spectrometry (CVAAS) system. This instrument must be calibrated with a traceable mercury solution, such as an SRM.

NIST worked with a commercial specialty gas vendor to procure three sets of gas mixtures of elemental mercury (Hg^0) in nitrogen. The nominal concentrations of the Hg^0 in the cylinders are 2 µg/m^3, 5 µg/m^3, and 20 µg/m^3. NIST analyzed and delivered one of the sets of three cylinders to the EPA, with concentrations certified and traceable to the SI (International System of Units) by CVAAS using a gold amalgam trap and ID-CV-ICP-MS. (The cylinders are re-analyzed on a periodic basis to determine whether or not there is any degradation of the Hg^0 concentration.) While seeking traceable standards in the 2% relative uncertainty range, NIST has moved from CVAAS (uncertainties in the 6 % relative range) to ID-CV-ICP-MS (uncertainty about 1 % relative) as the primary reference method for mercury analysis.

The outputs of a single mercury generator from each of five different manufacturers were also quantified by both the ID-CV-ICP-MS and the CVAAS. The better reproducibility of the results of these experiments led to a decision to use generators rather than cylinders as the primary traceability mechanism.

The proposed protocol is for NIST to certify one generator from each of the manufacturers, and then have each manufacturer calibrate generators that they sell by using a continuous mercury analyzer that is calibrated with the NIST-certified generator. Experiments performed at NIST have demonstrated that these calibrations can be accomplished to within 1% precision.

Impact: EPA is using the certified cylinder mixtures in their program to audit mercury-monitoring sites to determine compliance with regulations. These cylinders have been characterized by NIST using ID-CV-ICP-MS and CVAAS to determine concentration and stability of the gas mixture. This project has also provided data on the performance of mercury generation devices, and the data have shown that they are suitable for providing traceability. A protocol is being written by EPA and NIST to establish a traceable linkage to NIST using mercury gas generators and cylinder gas mixtures.

Future Plans: The Traceability Protocol using mercury generators will be finalized in 2007. Work has begun on development of a method for studying oxidized mercury (Hg^{++}) to provide traceability for measurements being made in support of EPA's proposed regulations. Gas standards for Hg^{++} are produced from a generation system that differs from the Hg^0 system. Experiments are ongoing to establish a procedure to employ the ICP-MS to characterize Hg^{++} generation systems. Cylinders containing mercury in air are also being developed to meet the program requirements.