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Project Summary

Validation of an Emission Measurement Method for Inorganic Arsenic from Stationary Sources: Proposed Method 108—Laboratory and Field Test Evaluations

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The U.S. Environmental Protection Agency's Proposed Method 108 for measurement of inorganic arsenic emissions from stationary sources has been evaluated both in the laboratory and field. Details of the evaluations are given through analysis of laboratory samples, preparation of filter and impinger audit samples for field use and stability studies, and two field tests of the method using dual and quad sampling trains at a copper smelter plant and a glass manufacturing plant. Several conclusions and recommendations have been made regarding the method.

This Project Summary was developed by EPA's Environmental Monitoring Systems Laboratory, Research Triangle Park, NC, to announce key findings of the research project that is fully documented in a separate report of the same title (see Project Report ordering information at back).

Introduction

The Environmental Monitoring Systems Laboratory (EMSL) of the U.S. Environmental Protection Agency has determined the industries and processes of stationary sources which emit significant inorganic arsenic emissions. Included among these are the five most significant sources chosen by EPA's Office of Air Quality Planning and Standards (OAQPS) for original consideration for regulation of inorganic arsenic emissions: glass plants, secondary load smelters; primary copper smelters; cotton ginning activities; and zinc oxide manufacturing. Presently OAQPS is recommending only primary copper smelters and glass plants for these regulations.

A primary concern of EMSL has been validation of the procedure used for sampling and analysis of the arsenic-containing emissions. EMSL determined that the proposed EPA Method 108, which involves collection in impinger solutions and on filters and measurement using atomic absorption spectrophotometry, was the best available method for measuring these arsenic emissions. Therefore a program to validate this method was designed by EMSL. The validation approach included a multicomponent project which involved both laboratory and field studies. Research Triangle Institute reviewed reports describing sampling and analysis of arsenic, evaluated EPA Method 108 through analysis of laboratory samples, prepared audit samples for field use and studied the stability of audit samples. PEDCo Environmentalists, Inc., collected samples at a copper smelter and a glass manufacturing plant and analyzed the collected samples.

Results and Discussion

Laboratory studies conducted to evaluate the performance of EPA Method 108 included: recovery and measurement of audit materials; stability of audit materials, precision of the method from sample preparation to measurement, and recommendations regarding analytical aspects of the method. Standard samples containing arsenic with loadings approximating emissions expected at field test sites were prepared in the laboratory. A total of 36 impinger samples and 36 filter samples at six different concentrations were prepared. Concentrations ranged from 0.013 mg to 5.0 mg arsenic for the impinger samples and from 1.4 mg to 52 mg arsenic for the filter samples. Ampules were used to contain the impinger samples. Selected filter and impinger samples from each concentration set were analyzed by atomic absorption spectrophotometry. The precision of the measurement phase of Method 108 was determined from triplicate analyses of standards. The relative standard deviation (RSD) of the analytical method was approximately 1.0 percent in the 40- to 100-micrograms arsenic per milliliter range. The stability of both simulated sample types (impinger and filter) for potential use as audit materials for EPA Proposed Method 108 was also evaluated over a six-month period. Stability as a function of sample type, concentration level and time was evaluated. Changes in concentration level and time was evaluated. Changes in concentration were not found to be statistically significant over a six-month period for filter type materials except at the highest loading (25 mg). For impinger materials there were no significant losses over the same time period.

Two field tests to validate proposed Method 108 at different sites were conducted. The first field test was conducted at a primary copper smelter (Plant No. 1) and the second test was conducted at a glass manufacturing facility (Plant No. 2). During the field test series, PEDCo conducted a total of 14 tests of proposed Method 108 (seven paired runs) at Plant No. 1 and a total of 36 tests of proposed Method 108 (nine quad-train runs) at Plant No. 2 to determine the precision of the methodology for measuring arsenic concentrations. A comparison of the statistical results for total arsenic from Plant No. 1 indicates that the within-run RSD for the seven sample runs ranged between 3.9 and 22.8 percent with the value for precision of the Method at 15.7 percent. Standard deviations of paired runs had a low value of 0.36 mg/dNm^3, a high of 4.06 mg/dNm^3, and a pooled mean of 1.90 mg/dNm^3. The mean arsenic concentration of paired runs ranged from 3.08 to 18.3 mg/dNm^3 based on total arsenic, and the overall mean value was 10.5 mg/dNm^3. Considering the sampling site constraints and variable process operation, the results indicate that an acceptable degree of precision was achieved at this source.

The standard deviations of the quad run (Plant No. 2) had a low value of 0.10 mg/dNm^3, a high value of 0.51 mg/dNm^3, and a pooled mean value of 0.37 mg/dNm^3. The RSD values ranged from 0.95 to 5.5 percent with the value for the precision of the Method at RSD value of 3.85 percent. The mean arsenic concentration of the individual quad runs ranged from 9.18 to 10.55 mg/dNm^3 with an overall mean of 9.67 mg/dNm^3, which indicated a generally consistent process operation throughout the test period. Once again, the results indicated that an acceptable degree of precision was achieved. The detailed results of all tests are presented in the project report.

Conclusions and Recommendations

Several conclusions and recommendations have been made regarding the proposed EPA Method 108 for the determination of arsenic emissions from stationary sources. These include: (1) the method is relatively straight-forward and is reasonable with respect to time and cost; (2) greater care of the sample during preparation than the proposed method requires, should be exercised, including avoidance of bumping and spattering during the evaporation process; (3) filter and impinger audit samples were found to be stable over a six-month period; and (4) an acceptable degree of precision of Method 108 is achieved from the field tests. Graphite furnace atomic absorption techniques have an improved analytical range over hydride techniques, are more rapid and therefore are recommended to be an adequate measurement substitute.

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The complete report, entitled "Validation of an Emission Measurement Method for Inorganic Arsenic from Stationary Sources: Proposed Method 108—Laboratory and Field Test Evaluations," (Order No. PB 85-115 160; Cost: $11.50, subject to change) will be available only from:

National Technical Information Service
5285 Port Royal Road
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