DEVELOPMENT OF A FIELD SCREENING TECHNIQUE FOR DIMETHYL MERCURY IN AIR

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Many forms of organic and inorganic mercury are pervasive in the environment; with both natural and industrial sources contributing to the total environmental mercury burden. Mercury can be biologically metabolized to form various organomercurials. One of these, Dimethyl Mercury (DMM) represents a potential health risk via air exposure because of its high volatility and toxicity.

Mercury contaminated soils and sediments are frequently biologically active and have been demonstrated to contain DMM. If left undisturbed, emissions of DMM will be related to the biological generation rate of DMM as well as the emission rate through the soil or sediments as regulated by porosity, temperature, pressure, and other physical-chemical factors. However, when the soils are disturbed, the potential for elevated emissions of DMM increases.

Research conducted by the USEPA's Environmental Response Team (ERT), with the support of Roy F. Weston, Inc. through the Response, Engineering, and Analytical Contract (REAC), has resulted in a potential real-time monitoring technique.

BACKGROUND INFORMATION PROMPTING RESEARCH

The Army Corps of Engineers had been conducting a cleanup of mercury contaminated soils; however, site remediation was suspended due to the potential for DMM emissions and the lack of a real-time air monitoring method.

A preliminary investigation conducted by ERT and Weston/REAC at the request of the Army Corps of Engineering and USEPA Region I, indicated that DMM could be present in the soils, especially in areas where anaerobic activity was prevalent.

REVIEW OF REAL-TIME PORTABLE INSTRUMENTS FOR DETECTING DMM

The criteria established for selecting a real-time instrument for monitoring DMM were quite restrictive. First, the instrument had to be portable and permit operation by non-technical personnel. Second, it had to have real-time or semi-real-time monitoring capabilities.

The third requirement was that it be specific to organomercurials.
A literature review indicated that the primary methods for detecting mercury were atomic adsorption, gas chromatograph, infra-red analyzers, and gold film technology. Atomic Adsorption instruments are generally not portable, require technical expertise to operate and provide only semi-real-time results. Gas chromatography requires technical expertise and provides semi-real-time results. Infra-red analyzers have too many interferences from organic compounds. Gold film detectors are cross-sensitive to sulfide compounds, however, the use of an internal sulfide trapping pre-filter negates this cross-sensitivity. The gold film technology thus appeared to have the greatest potential for the required application, and a gold film mercury vapor analyzer was selected for detailed review.

GOLD FILM TECHNOLOGY

The Arizona Instruments Model 411, Gold Film Mercury Vapor Analyzer was selected as the instrument of choice. The Model 411 was originally developed for monitoring elemental mercury in air, and operates on the principal that mercury will form an amalgam when it contacts a gold film.

The Model 411 detects the presence of mercury by passing a stream of air across a thin gold film. As the mercury in the air contacts the film an amalgam is formed. The amalgamation causes an increase in the electrical resistance of the film proportional to the mass of mercury in the sample. The change in resistance is compared to a sealed reference gold film and processed by a microprocessor to provide a digital read-out in milligrams of mercury per cubic meter (mg/m^3).

To eliminate the necessity of thermally desorbing the gold film after each use, the Model 411 employs a microprocessor which allows the instrument to operate over a wide range of resistances while remaining balanced with the reference film. Heating the film to approximately 250°C, and subsequently passing a stream of mercury free air across the film desorbs the mercury and restores the film to its baseline resistance.

EXPERIMENTS WITH SILVER-COATED CHROMOSORB

Since DMM may be metabolized from elemental mercury, the hypothesis was made that both DMM and elemental mercury might be present during air monitoring. Elemental mercury would interfere with the detection of DMM in monitoring air, therefore a means to remove the elemental mercury from the sample without affecting the DMM concentration was required. Silver-coated Chromosorb was tested for this purpose.

The first test involved monitoring for elemental mercury with the Model 411 using a silver-coated Chromosorb tube pre-scrubber within a test vessel containing elemental mercury in which the vapor pressure had reached equilibrium. Thirty samples of the mercury-saturated air were collected without breakthrough occurring from the silver-coated Chromosorb tube.

The second test of the silver-coated Chromosorb pre-scrubber involved determining if DMM would pass through it. This was accomplished by preparing a DMM standard and measuring the concentration with and without the silver-coated pre-scrubber. As Table 1 indicates, the test results for the analysis with and without the pre-scrubber are essentially the same.

PREPARATION OF DMM STANDARDS

DMM standards are not commercially available , therefore, it was necessary to prepare them in-house in Summa passivated canisters by injecting a measured volume of DMM and methanol solution into the canister. Due to uncertainties in this procedure, DMM standards were confirmed by select ion gas chromatography and mass spectra analysis.

USE OF THE MODEL 411 FOR DETECTION OF DMM

Initial experiments conducted with the Model 411 (configured as per manufacturer's specifications) provided erratic results and an inadequate detection limit for DMM.

The Arizona Instrument's Model 411 was therefore modified as follows:

1.The detector resistance was increased from approximately 60 ohms to approximately 98 ohms.
2.The instrument's sample flow rate was increased from 720 cubic centimeters per minute (cc/m) to 866 cc/m.
3.The sampling duration was doubled from 10 seconds to 20 seconds.

TABLE 1. COMPARISON OF ARIZONA INSTRUMENTS MODEL 411 RESPONSE WITH AND WITHOUT A SILVER-COATED CHROMOSORB PRE-SCRUBBER TO 4.8 ppb-V and 24.6 ppb-V STANDARDS OF DMM

DMM Standard Concentration ppb-V	Date Run	Model 411 Response (unitless) without Pre-Filter	Model 411 Response (unitless) with silver-coated Chromosorb Pre-Filter
4.8	7/25/89	0.003	0.003
4.8	7/25/89	0.003	0.002
4.8	7/25/89	0.003	0.002
4.8	7/25/89	0.003	0.003
4.8	7/25/89	0.003	0.002
4.8	7/25/89	0.003	0.003
4.8	7/25/89	0.004	0.003
4.8	7/27/89	0.003	0.003
4.8	7/27/89	0.004	0.003
4.8	7/27/89	0.004	0.003
4.8	7/28/89	0.002	0.002
4.8	7/28/89	0.001	0.002
4.8	7/28/89	0.002	0.002
4.8	7/28/89	0.002	0.003
4.8	7/28/89	0.002	0.002
4.8	7/28/89	0.002	0.002
4.8	8/01/89	0.002	0.002
4.8	8/01/89	0.002	0.002
4.8	8/01/89	0.003	0.002
4.8	8/01/89	0.002	0.002
4.8	8/03/89	0.002	0.002
4.8	8/03/89	0.002	0.002
4.8	8/03/89	0.002	0.002
4.8	8/03/89	0.002	0.003
24.6	7/25/89	0.012	0.016
24.6	7/25/89	0.011	0.012
24.6	7/25/89	0.010	0.009
24.6	7/25/89	0.015	0.011
24.6	7/25/89	0.016	0.011
24.6	7/25/89	0.014	0.011
24.6	7/25/89	0.012	0.011
24.6	7/27/89	0.013	0.013
24.6	7/27/89	0.013	0.011
24.6	7/27/89	0.012	0.011
24.6	7/27/89	0.011	0.011
24.6	7/28/89	0.011	0.009
24.6	7/28/89	0.009	0.009
24.6	7/28/89	0.009	0.008
24.6	7/28/89	0.010	0.008
24.6	7/28/89	0.008	0.008
24.6	8/01/89	0.010	0.010
24.6	8/01/89	0.011	0.010
24.6	8/01/89	0.011	0.010
24.6	8/01/89	0.010	0.009
24.6	8/03/89	0.009	0.008
24.6	8/03/89	0.008	0.008
24.6	8/03/89	0.008	0.008
24.6	8/03/89	0.009	0.009

4.A silver-coated Chromosorb tube was utilized as a pre-scrubber to remove elemental mercury.
5.The calibration switches were adjusted to calibrate the instrument to a known concentration of DMM.

SENSOR STATUS DRIFT IN THE MODEL 411

It was observed during method development that the Model 411's sensor status would first increase after the instrument detected DMM, then decrease after a period of time. The sensor status is an indication of the percent gold film saturation. The increase and subsequent downward drift in sensor status was not encountered with elemental mercury. Sensor status drift resulted in the instrument indicating readings lower than actual concentrations and was corrected for by allowing the instrument to balance the Wheatstone bridge between the sample gold film and the reference film prior to monitoring another sample. This was accomplished by drawing four 20-second samples into the instrument through a iodized charcoal filter. The filter effectively adsorbs organic and inorganic mercury resulting in mercury free sweep air. The number of mercury free air sweeps required to permit the instrument to re-establish baseline resistance was determined empirically to be four.

LINEAR RANGE OF THE MODEL 411 FOR THE DETECTION OF DMM

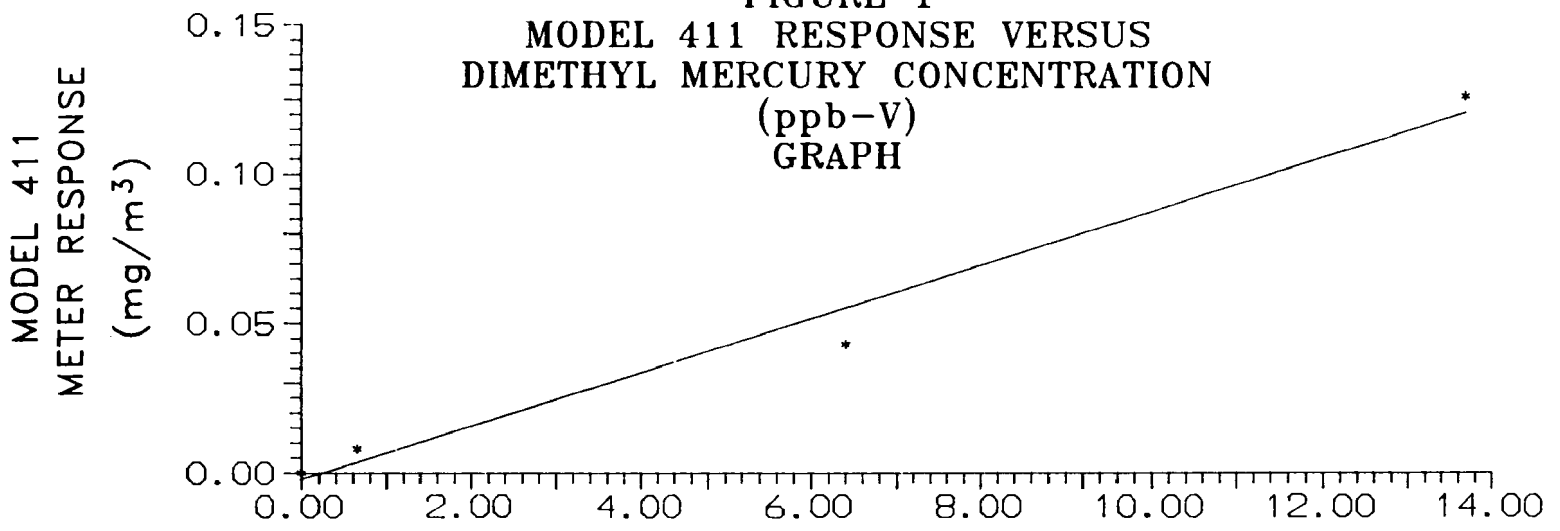
The linear range of the Model 411 for the detection of DMM was determined by diluting a 13.70 ppb-V DMM standard down to approximately one half the Threshold Limit Value (TLV) of 0.01 mg(Hg)/M^3. Dilutions were made to 0, 0.64, 6.40, and 13.70 ppb-V and were validated by GC/MS analysis.

The DMM dilutions were measured with the Model 411 and the data utilized to generate a calibration curve (Figure 1). The calibration curve was found to be linear, with a critical correlation coefficient (R^2) of 0.98. This was deemed an acceptable linear range for this work effort.

DISCUSSION AND CONCLUSIONS

This study indicates that gold film mercury vapor detectors have definite potential in monitoring for DMM. The Model 411 appears promising because of its simplicity, stability and effectiveness as a screening tool. However, as with any screening device, it should not be relied upon exclusively; rather, it should be incorporated into a multi-tiered sampling and monitoring program.

FIGURE 1
MODEL 411 RESPONSE VERSUS DIMETHYL MERCURY CONCENTRATION (ppb-V) GRAPH



Note: 1ppb-V is approximately 0.01 mg/m³ for DMM

DMM CONC. (ppb-V)	METER RESPONSE (mg/m³)
0	0
0.64	0.008
6.40	0.043
13.70	0.126

LINEAR REGRESSION VALUES:

R^2 = 0.98
y Intercept = 0.00220
Standard error of y = 0.010048
Slope = 0.008959
Standard error of x = 0.000911

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