

DETERMINATION OF LEWISITE OXIDE IN SOIL USING SOLID PHASE MICROEXTRACTION FOLLOWED BY GAS CHROMATOGRAPHY WITH FLAME PHOTOMETRIC OR MASS SPECTROMETRIC DETECTION

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Lewisite oxide (*syn.* 2-chlorovinylarsonous oxide or CVAO, CAS Registry No. 3088-37-7) is a readily-formed hydrolysis product of the chemical blister agent Lewisite (*syn.* 2-chlorovinylchloroarsine, CAS Registry No. 541-25-3). CVAO is frequently observed in the soil of United States Department of Defense installations where Lewisite was manufactured, and is therefore an indicator of legacy Lewisite production. For this reason, highly-reliable and rigorously-tested analytical methods for CVAO are required to measure its soil concentration during site remediation, and to ensure that the existing levels are at or below regulatory-mandated values. Traditional analytical methods for Lewisite or CVAO involve degradation of the analyte with strong base to produce acetylene. These procedures are time-consuming, generate considerable quantities of chemically hazardous waste, and are somewhat insensitive (0.5-5 $\mu\text{g/g}$ soil). The purpose of the current work is to investigate newer procedures, which would be more sensitive, easier to perform, faster, and more environment-friendly than those currently available.

CVAO and a candidate surrogate, phenylarsine oxide (PhAsO), were added to 2-g samples of standard soil at concentrations from 0.05 to 5 $\mu\text{g/g}$ soil, then extracted (30 min) with 0.66% (w/v) ascorbic acid containing 100 μL 1,3-propanedithiol (PDT)/L. Each sample was centrifuged; the supernatant was passed through a 0.45 μm porosity nylon syringe filter. The filtered supernatant was then sampled using a solid phase microextraction fiber (100 μm polydimethylsiloxane) for 20 min with vigorous stirring. The collected derivatives of CVAO and PhAsO were then thermally desorbed from the fiber into the injection port of a gas chromatograph, separated using a fused-silica column (Rtx®-5 or Rtx®-35 bonded phase). The products were detected using either a flame photometric detector (FPD) in its sulfur-selective mode or a mass spectrometric detector in its selective-ion monitoring mode (MS-SIM).

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The detection limits and recoveries of CVAO and PhAsO were calculated for the FPD-based method using two independent calculation procedures. The procedure was evaluated intensively for three independent certification days according to the protocol described in the *Program Manager Rocky Mountain Arsenal Chemical Quality Assurance Plan*. The Method Reporting Limit (MRL) values calculated for CVAO using the Rtx®-5 (primary) and Rtx®-35 (confirmatory) columns were 0.49 and 0.20 µg/g soil, with estimated recoveries of 51 and 75%, respectively. The MRL for PhAsO was 1.1 µg/g soil with an estimated recovery of 15% on both columns. The Method Detection Limit (MDL) values for both analytes were also calculated using the protocol developed by the U. S. Environmental Protection Agency. The MDL values for CVAO using the Rtx®-5 and Rtx®-35 columns were 0.30 and 0.14 µg/g soil, respectively, with an estimated recovery exceeding 60%. The corresponding values for PhAsO were both approximately 0.05 µg/g soil with an estimated recovery of approximately 15%. Approximately 16 samples (eight standards and eight unknowns) could be processed manually in an eight-hour working day. The figures of merit using the MS-SIM analytical method are expected to be similar to those given above.