



Effects of sonication time variations on extraction efficiency of chemical warfare agent simulants in soil

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Introduction

In 1997, the Chemical Weapons Convention (CWC) entered into force. The United States, along with 86 other nations, ratified and signed the CWC, agreeing to destroy chemical weapons production facilities and set regulations and prohibitions surrounding the production and use of chemical weapons. To assist in detecting dangerous chemical compounds in soil and set a national standard, the Environmental Protection Agency (EPA) created EPA SW-846 Method 3550C (2007). To make the EPA method more efficient, the Army Public Health Center developed a miniaturized version of the EPA method to test for organophosphorus compounds. The purpose of this study was to reduce the previously used sonication time of 90 minutes, while maintaining efficient extraction of chemical warfare agents (CWA's) simulants from soil. It was hypothesized that sonication time has no significant effect on extraction efficiency.

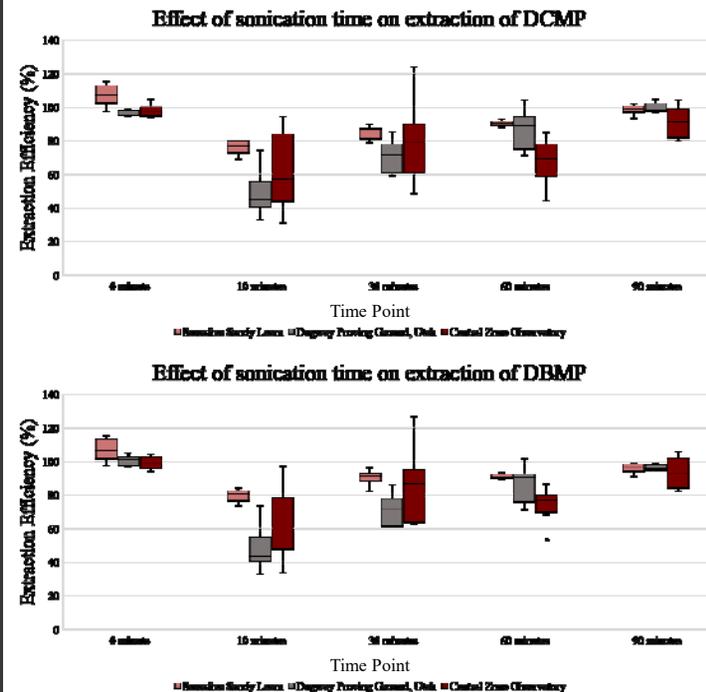
Methods and Materials

Six compounds were used to determine the extraction efficiency of each sonication time. Two organophosphorus compounds, malathion and methyl parathion (MPT), were used as surrogate compounds, while CWA simulant compounds deoxycytidine monophosphate (DCMP), dibutyl methylphosphonate (DBMP), bis(diphenylphosphanyl)methyl-phenylphosphane (DPMP), and O,S-dibutyl methyl phosphonothioate (OSDIBMP) were used as compounds of interest. The organophosphorus compound chlorpyrifos (CPF) was used as an internal standard. Sassafras Sandy Loam (SSL), Dugway Proving Ground, Utah (DW), and Central Zone Observatory (CZO) soils were used for this. A 100 μ L aliquot of a 1 mg/mL simulant and surrogate cocktail solutions were spiked into a 5 g soil sample. Following the spiking, 10 mL of a 1:1 acetone/hexane solvent mixture was added to the soil. A total of nine replicates were prepared for each sample set, along with a negative control, which was spiked with only the 1 mg/mL of the surrogate cocktail solution. These samples were then sonicated for a designated amount of time (90, 60, 30, 10, or 0 minutes) before being gravity filtered using filter paper. For the 0 minute sonication, samples were shaken using a vortex machine for 60 seconds. A positive control sample was also prepared for each sample set, by spiking 10 mL of the acetone/hexane solvent mixture with 100 μ L each of the 1 mg/mL surrogate and simulant cocktail solutions. A gas chromatograph (GC) equipped with a flame photometric detector (FPD) was calibrated using reference standards of 0.5, 1.0, 5.0, 10.0, and 15.0 μ g/mL concentration of the surrogate and stimulant

Methods and Materials (cont.)

compounds. A 900 μ L aliquot of the sample extracts, the control samples, and reference standards were spiked with 100 μ L of a 100 μ g/mL solution of the internal standard in a GC vial prior to analysis by GC/FPD. Each GC sequence included a 0.5 μ g/mL sensitivity verification solution (SVS) and a 5.0 μ g/mL continuing calibration verification (CCV) solution at the beginning and end of every run to monitor instrument performance. A 15–20% deviation from the expected calibrated CCV concentration was permitted. Internal standard area counts for each sample were compared to those of the CCV to ensure instrumental precision.

Results



Graph 1 (top) and Graph 2 (bottom): A box and whisker plot displaying the extraction efficiencies across the five time points for DCMP (top) and DBMP (bottom) for the SSL, DW and CZO soils. Recoveries above 100% may be attributed to the evaporation of the extraction solvent during extraction or analysis while the vials were sitting at the GC.

Results (cont.)

Extraction efficiency was calculated by dividing the reported amount of each compound by the expected amount and multiplying by 100. Extraction efficiency decreased as the sonication time decreased, excluding the 0 minute sonication time. The graphs are of two CWA simulants, chosen to represent the other CWA simulants. Using the Mann-Whitney Test for Comparing Medians, comparing all other sonication times to the 90 minute sonication for each soil and compound combination, no sonication time achieved a p -value above 0.05, except the 60 minute sonication time for extracting malathion and methyl parathion from DW soil. This means that no other sonication type, soil and compound combination produced similar results to the 90 minute sonication. The high recoveries reported for the 0 minute sonication may be due to insufficient contact between the soil and the spike, making these recoveries non-representative of good recoveries. Recoveries exceeding 100% may be attributed to evaporation of the extracts or to an internal standard error affecting the calculation on the ECBC GC.

Conclusion

The goal of my study, to reduce the sonication time previously used while maintaining efficient extraction of CWA simulants from soil, was not accomplished for CWA simulants in any of the soils. Using the Mann-Whitney Test, it was determined that the 60 minute sonication is sufficient for malathion and methyl parathion when extracted from DW soil only, however these compounds are surrogates and only used for comparison. Due to uncertainty as to whether the 0 minute sonication method allows enough interaction with the soil before extraction, the 0 minute sonication method cannot yet be confirmed as a viable method. The overall conclusion for this study is that 90 minute sonication is necessary for proper extraction of CWA simulants from SSL, DW and CZO soil, while 60 minute sonication is sufficient for the extraction of malathion and methyl parathion from DW soil. In the future, a study on the reasoning behind the high extraction efficiencies of the 0 minute sonication method may be necessary. If the sonication time necessary for proper extraction can be lowered, soldiers and those in the field detecting CWA's will be able to respond more swiftly.

References

(2007). Method 3550C: Ultrasonic Extraction. *Test Methods for Evaluating Solid Waste, Physical/Chemical Methods*. Retrieved from <https://www.epa.gov/hw-sw846/sw-846-test-method-3550c-ultrasonic-extraction>