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Matrix-effect-free determination of BTEX in variable soil compositions using room temperature ionic liquid co-solvents in static headspace gas chromatography mass spectrometry

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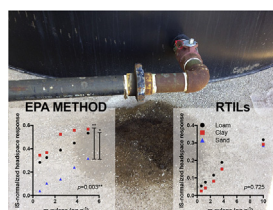
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HIGHLIGHTS

- Varying soil composition affects the quantification of BTEX in soil HS analysis.
- Hydrophilic RTILs as HS solvents normalized response for BTEX compounds from varying soil compositions.
- Soil samples were obtained from areas associated with UD activities.
- Quantifiable amounts of BTEX were detected in 2 of the 5 samples collected.

GRAPHICAL ABSTRACT



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ABSTRACT

Concerns about the environmental impact of shale energy exploration (i.e., hydraulic fracturing and other well stimulation techniques) have risen due to its rapid expansion in the United States and other countries. Soils in shale basins engaged in unconventional oil and gas development can become contaminated by volatile organic compounds (VOCs), such as benzene, toluene, ethylbenzene, and xylenes (BTEX) through mishandling of chemical additives, products, and/or waste fluids. In this study, room temperature ionic liquids (RTILs) were evaluated as solvents in an effort to increase sensitivity and to reduce and normalize matrix effects associated with varying soil compositions during analysis. Headspace gas chromatography mass spectrometry (HS-GC-MS) experiments demonstrated that hydrophilic RTILs 1-ethyl-3-methylimidazolium ethyl sulfate [EMIM][ESO₄], 1-ethyl-3-methylimidazolium diethyl phosphate [EMIM][DEP], and tris(2-hydroxyethyl) methylammonium methylsulfate [MTEOA][MeOSO₃] normalized the response for BTEX compounds between 2 different soils, sandy loam and sandy clay loam. Furthermore, the optimization of the HS equilibration time to 30 min resulted in the reduction of matrix effects in certified reference soils of sand, clay, and loam textures. Limits of detection and limits of quantification were in the sub- to mid- pg g^{-1} level in soil. For determination at 1 g of certified BTEX reference soil, the relative standard deviation was within 10% and percent recoveries were above 80% for toluene, ethylbenzene, and xylenes. This method reduces the need to characterize and matrix-match soil texture for calibration purposes. It also reduces the analysis time and increases

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precision and accuracy for the quantification of BTEX in variable soil matrices relative to standard methods.

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1. Introduction

Due to the continued growth of hydrocarbon extraction in the United States and in other countries, unconventional oil and gas development (UD) is expected to become more common near residential and urban areas. This growth has increased public concern about the human health and environmental implications associated with such industrial activities. The potential for the release of pollutants into the air,^{1,2} groundwater,^{3–6} and soil⁷ exists within many phases of the hydrocarbon extraction process. More specifically, soil can become contaminated by hazardous volatile organic compounds (VOCs), such as benzene, toluene, ethylbenzene, and xylene isomers (BTEX) as a result of spills and pipeline leaks. BTEX compounds have a high pollution potential, attributed to their solubility in water and other matrices.

Soil, as a matrix, is very complex. It is an extremely variable mixture of mineral and organic particles of various sizes that also carry diverse microbial communities, which collectively interact

with the surrounding ecological framework.^{8–9} An important descriptor of soils is soil texture, which parameterizes the different sizes of particles that make up a soil in terms of the percentage of sand, silt, or clay, as shown in Figure 1. Soil texture and the abundance of organic carbon are the primary contributing factors to the relative sorption of VOCs like BTEX.¹⁰ Furthermore, soils with high organic matter can affect the sorption and limit the extraction efficiency of target analytes in analytical procedures, in this case, such that the accurate quantification of BTEX in soil can be a significant challenge.

Various analytical methods for the determination of VOCs in multiple environmental matrices have been based on gas chromatography – mass spectrometry (GC-MS), using either static or dynamic headspace (HS), or HS solid phase microextraction (HS-SPME), as sample introduction modules.^{11–15} Other techniques, like liquid chromatography, supercritical fluid extraction or near infrared spectroscopy, have also been used.^{16–19} HS sampling has been used successfully in qualitative and quantitative analysis of VOCs in soils. However, difficulties arise when using HS methods for quantitative analysis of VOCs in soil, because these methods rely on equilibrium partitioning of the analyte of interest between the soil sample and the gas phase in the vial. Many studies have shown that the equilibrium partitioning can be altered by changing the heating temperature, time, and co-solvents used. These are indicated as possible approaches to overcome matrix dependency in HS analysis of soils.^{12,13,20}

Here, we explore the use of room temperature ionic liquids (RTILs) as solvents for HS-GC-MS quantification of BTEX from contaminated soils. RTILs are liquid organic, molten, or fused salts; they are a class of molecular ionic solvents with low melting points.²¹ Ionic liquids (ILs) have garnered significant attention for their use in general analytical chemistry, in separation techniques, and in sample preparation methodologies.^{21–28} RTILs can be ideal HS solvents due to their physiochemical properties, including negligible vapor pressure, wide liquid range, high viscosity, and tunable thermal stabilities.

The aim of this work was to evaluate the use of three hydrophilic RTILs (1-ethyl-3-methylimidazolium ethyl sulfate ([EMIM][ESO₄]), 1-ethyl-3-methylimidazolium diethyl phosphate ([EMIM][DEP]), and tris(2-hydroxyethyl) methylammonium methylsulfate ([MTEOA][MeOSO₃])) and one hydrophobic RTIL (1-ethyl-3-methylimidazolium bis(trifluoromethanesulfonyl)imide ([EMIM][NTf₂)]), as solvents for homogenization of soil samples prior to HS

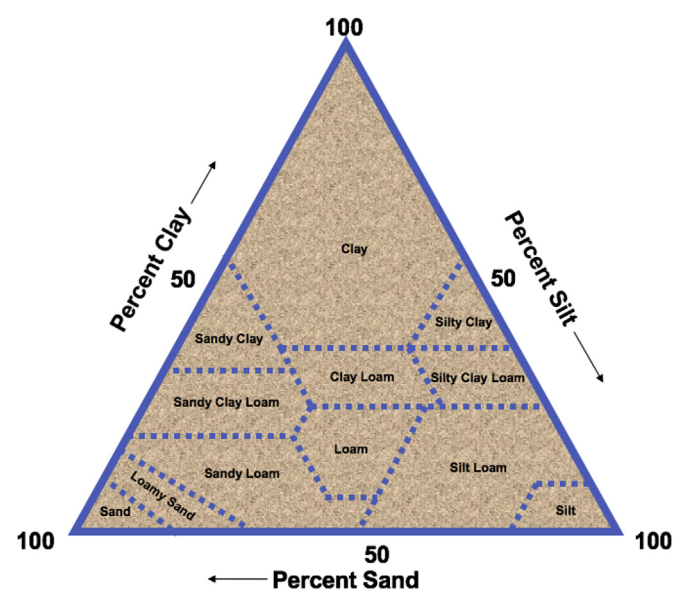


Figure 1. Soil texture is classified by the percent sand, silt, and clay in relation to the soil texture triangle.^{7,32}

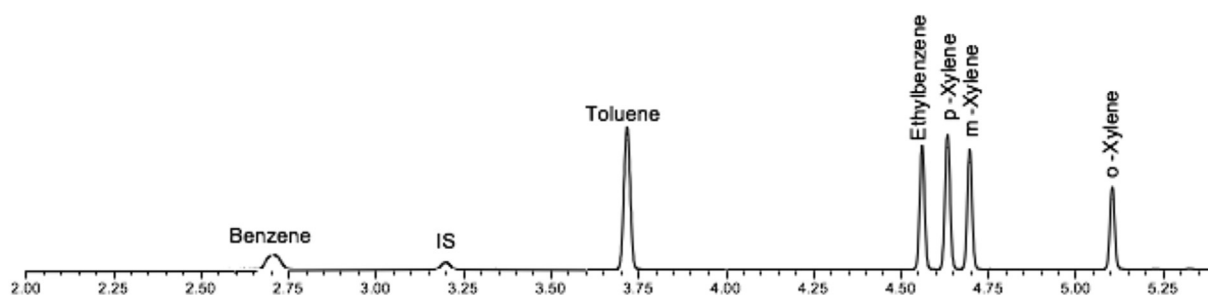


Figure 2. Chromatogram of sample # 5, with complete separation of xylene isomers.

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