

Characteristics and Performance of Supercritical Fluid Extraction (SFE) in the Analysis of Petroleum Hydrocarbons in Soils and Sludges

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PURPOSE AND MAJOR FINDINGS OF THE RESEARCH

This project was designed to evaluate and improve supercritical fluid extraction (SFE) methods and instrumentation for the analytical-scale extraction from soils and sludges of petroleum hydrocarbons ranging from benzene, toluene, ethylbenzene, and xylene (BTEX) to polynuclear aromatic hydrocarbons (PAHs) and heavy crudes. The primary goals of this two-year study were to:

- Determine which types of petroleum industry environmental samples and wastes can be extracted using SFE, by:
 - Quantitative comparisons to standard (Soxhlet) methods;
 - Qualitative descriptions on SFE performance (primarily restrictor plugging);
- Evaluate when presently-available SFE methods are viable alternatives to conventional liquid solvent extraction;
- Determine development needs for SFE extraction and collection conditions, and develop extraction conditions for a wide range of petroleum-based hydrocarbons and PAHs. This effort included:
 - Development of two SFE methods that can yield quantitative extraction and recovery of gasoline- to diesel-range organics from soils, allowing BTEX and total petroleum hydrocarbons (TPH) to be determined using a single extraction method;
 - Development of quantitative extraction conditions for PAHs and heavier hydrocarbons including heavy crudes and heavy resids;
- Determine hardware development needs based on problems encountered with real-world samples, and identify commercially available instrumentation to meet those needs.

Commercially available instrumentation and standard SFE approaches, such as the proposed Environmental Protection Agency (EPA) method for TPH, were used. Comparisons were made to standard liquid solvent

extraction methods. Good comparability for gasoline- and diesel-range TPH was demonstrated between conventional Soxhlet extraction and SFE at conditions similar to the proposed EPA SFE method, using both infrared (IR) and gas chromatograph/flame ionization detector (GC/FID) quantification of extracted hydrocarbons.

For the more volatile (e.g., BTEX and light alkane) components, SFE yielded lower extraction losses and higher efficiencies than Soxhlet extraction. Compared to SFE and conventional Soxhlet extractions performed in the laboratory, field SFE gave good agreement for gasoline- and diesel-range TPH with IR determination. Commercial instruments using both solvent trapping (ISCO®) and sorbent trapping (Hewlett-Packard®) yielded quantitative recoveries (>90%) of BTEX and gasoline- and diesel-range alkanes as volatile as C_6 (for sorbent) and C_7 (for solvent trapping), demonstrating that BTEX and TPH determinations can be performed with a single extraction.

Also developed was an on-line supercritical fluid extraction/gas chromatography (SFE/GC) method for gasoline- and diesel-range organics that allows species as volatile as n-butane to be extracted and collected at approximately 100% efficiency. In addition to allowing quantitative determinations of very volatile species, the SFE/GC method allows sensitive detection limits (e.g., < 10 ppb for benzene) for samples as small as 1 gram. However, the on-line method is more difficult to perform than the standard SFE methods, and requires modifications to existing SFE and GC instruments.

SFE methods were also developed utilizing high-temperature SFE and the addition of organic modifiers for components that were not efficiently extracted using standard SFE conditions (e.g., heavy hydrocarbons and PAHs). With the combined use of either high SFE temperatures (e.g., 150°C) and/or organic modifiers, the recoveries of heavy hydrocarbons (e.g., heavy resids > C_{40}) were higher than those achieved using Freon-

113® Soxhlet extraction as determined by IR. In general, contaminated soils could be extracted as received without drying or other sample preparation, although soils and waste sludges contaminated with high levels of heavy hydrocarbons often caused plugging of some types of SFE flow restrictors. In nearly every case, heating the restrictor and mixing such samples with dispersants and/or drying agents eliminated restrictor plugging.

Practical advantages of SFE included typical extraction times of 30-40 minutes, compared to 4 hours or greater for Soxhlet extraction; and typical total solvent use of less than 10 ml, compared to 150 ml for Soxhlet extraction. In nearly all of the samples studied, SFE yielded efficiencies similar to or higher than Soxhlet extraction; however, elevated temperature and/or organic modifiers were often needed to obtain high extraction efficiencies for organics beyond the gasoline- and diesel-range. It should be noted that SFE instruments continue to evolve, especially in the areas of improved restrictor and collection system designs, as well as systems offering automated extraction of up to 20 samples without operator intervention. Such developments should further increase reliability and speed of SFE for petroleum hydrocarbon extractions from soils and sludges.

GASOLINE-RANGE TPH, DIESEL-RANGE TPH, AND BTEX BY ON-LINE SFE/GC

On-line SFE/GC methodology was developed to allow extraction and analysis of organics as volatile as n-butane from solids at part-per-billion (ppb) detection limits (Burford *et al.*, 1994a). A solid-based calibration standard, consisting of several n-alkanes and aromatic hydrocarbons spiked onto Tenax-TA®, was successfully used to optimize the chromatographic parameters for coupled SFE/GC. A simple and reliable split SFE/GC system was developed utilizing a septumless injector installed on a split/split-

less injection port. The high gas flow rate generated inside the injection port during the SFE step was accommodated for by using the correct split ratio, so that high (1 ml/min liquid CO₂) SFE flow rates could be used. The use of thick-film (5 µm film thickness) columns and cryogenic trapping temperatures in the GC oven as low as -50°C allowed efficient trapping of species as volatile as n-butane, acetone, and methylene chloride. The chromatograms obtained using the optimized SFE/GC technique showed good peak shapes (comparable to those obtained using a conventional split injection) and typical peak area reproducibilities of <5% relative standard deviation.

The SFE/GC method was used for the quantitative extraction and analysis of gasoline- and diesel-range organics from real-world environmental samples (Burford *et al.* 1994b). Petroleum contaminated samples containing gasoline, kerosene, diesel or motor oil (total hydrocarbon contents of 168, 2, 26, and 10 mg/g, respectively) were quantitatively extracted by a 15 minute SFE/GC extraction using 400 atm, 60°C CO₂. The SFE/GC hydrocarbon recoveries were comparable to those obtained by sonicating the samples in methylene chloride for 14 hours. Gasoline recovery was higher by SFE/GC analysis, due to the more efficient collection of volatile analytes. Gasoline- and diesel-range organics could be quantitatively retained during the SFE step of the SFE/GC analysis using a thick-film (30-m x 0.32-mm I.D., 5-µm film thickness) DB-1® column operated at a cryogenic trapping temperature of -25°C. Using split SFE/GC operated at a high split ratio (100:1), relatively large (1 g) sample sizes could be investigated; and by using a drying agent (molecular sieve 3A), very wet (25 wt% water) samples could be analyzed without extracted water freezing in the GC column during the SFE step.