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Extraction of hydrocarbon contamination from soils using accelerated solvent extraction

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Abstract

Accelerated solvent extraction was studied as a method for the extraction of hydrocarbon contamination from wet and dry soils. Temperatures from 125 to 200°C and six different solvents were investigated. Nonpolar solvents could not achieve complete recovery from wet soils at the temperatures studied. Optimum conditions were found to be 175°C with dichloromethane–acetone (1:1, v/v) with 8 min heat-up time and 5 min static time. Quantitative recoveries for diesel range organics (DROs) and waste oil organics (WOOs) were obtained using the optimized conditions. The recovery of DROs and WOOs from three matrices at two concentrations (5 and 2000 mg/kg) averaged 115%. These results show that accelerated solvent extraction can generate results comparable to those obtained using Soxhlet or sonication. © 2000 Elsevier Science B.V. All rights reserved.

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1. Introduction

Accelerated solvent extraction (Dionex trade name ASE), also known as pressurized fluid extraction (PFE) or pressurized liquid extraction (PLE), was first described in 1995 [1,2]. Accelerated solvent extraction uses organic or aqueous solvents at elevated temperatures and pressures to obtain complete extraction of analytes from solid and semi-solid samples in short periods of time and with small quantities of solvents, as compared to conventional extraction procedures. A recent review considered the state of the art for accelerated solvent extraction technology and applications [3].

One of the most common uses of accelerated solvent extraction is in the determination of en-

vironmental contaminants in solid waste samples. Accelerated solvent extraction is accepted by the United States Environmental Protection Agency (US EPA) as Method 3545A for the extraction of nearly all of the organic compounds covered by the Resource Conservation and Recovery Act (RCRA) [4]. However, the technique has not been validated for the extraction of hydrocarbons such as diesel range organics (DROs), waste oil organics (WOOs) or total petroleum hydrocarbons (TPHs). Data have been generated from TPH-containing samples as part of the original development of accelerated solvent extraction [5]. Additional data have been reported on the recovery of benzene, toluene, ethylbenzene and xylenes (BTEXs) from soils using accelerated solvent extraction [6]. However, these results were not part of complete and thorough studies that used completely optimized conditions.

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Bruce reported on a relatively extensive study using accelerated solvent extraction for TPH determination [7]. He compared accelerated solvent extraction using perchloroethylene to Soxhlet extraction using chlorofluorocarbon-113 (CFC-113). Infrared (IR) spectroscopy was used as the determinative step. He found that high temperatures (200°C) were necessary to get complete extraction of the hydrocarbons from wet clay-soil samples when using accelerated solvent extraction. However, many states agencies have or will be moving away from using IR methods in favor of gas chromatography (GC) due to more complete speciation of hydrocarbon contamination offered by GC.

The objective of this study was to develop an accelerated solvent extraction method that would be equivalent to standard extraction procedures and compatible with a GC determinative step. Temperatures from 125 to 200°C with six different solvents were studied on both wet and dry soil samples. After the accelerated solvent extraction method was optimized, data were collected on three soil types and at two concentrations for submission to the US EPA SW-846 Work Group for incorporation in Method 3545A. The data obtained in this study, for the first time, demonstrate that accelerated solvent extraction is equivalent to standard extraction methods for the recovery of DROs and WOOs from soil samples.

2. Experimental

2.1. Chemicals and reagents

Dichloromethane (DCM), hexane (hex), heptane (hept) and acetone (ace) were all analytical grade or better (Fisher Scientific, Fair Lawn, NJ, USA). HPLC-grade water (Fisher Scientific) was used to produce wet soil samples from dry soils. Motor oil (30 W) was purchased from a local automobile parts store. A hydrocarbon window defining calibration standard (C_8 to C_{40}), a diesel standard (No. 2 fuel), and surrogate spiking solutions (*n*-tricosane or *ortho*-terphenyl) were purchased from AccuStandard (New Haven, CT, USA). Sodium sulfate was obtained from Fisher Scientific. Hydromatrix (pelletized diatomaceous earth) was purchased from Varian Sample Preparation (Harbor City, CA, USA). Chromatographic

silica gel (Davisil, grade 634) was obtained from Fisher Scientific.

2.2. Soil samples

For accelerated solvent extraction method development, certified soil samples were purchased from Environmental Resource Associates (ERA, Arvada, CO, USA). This soil was designated as TPH Standard 1 and contained no fatty acids. The hydrocarbon material present on the soil was vacuum pump oil (WOO range) and was in the concentration range of 250–3000 mg/kg.

For the validation portion of the study, custom prepared soils were purchased from ERA. Concentration levels ranged from near the quantitation limit (5 mg/kg of both diesel and 30 W motor oil) to 400-times this low level (2000 mg/kg of both diesel and 30 W motor oil). The three matrices provided by ERA were designated as clay (topsoil consisting of approximately 60% clay and 40% sand), loam (90% topsoil mixed with Ottawa sand) and sand (80% topsoil mixed with 20% Ottawa sand). All soils were stored at 4°C until they were extracted.

2.3. Sample preparation and extraction

For the extraction of dry samples, the soils were weighed out directly into the extraction cells. Dry sample mass ranged between 10 and 15 g. A 1-ml aliquot of surrogate solution was added to the top of all soil samples prior to closing the extraction cells and placing them in the extractor. For wet samples, 5 to 7.5 g of soil were weighed into a 50-ml beaker. HPLC-grade water was added to obtain a sample that was 50% (w/w) water. The soil and water were thoroughly mixed and allowed to stand for 5 to 10 min. Diatomaceous earth was added to the beaker and mixed to produce a powder that could be easily placed into the extraction cells. Care was taken to ensure that all of the soil was removed from the beaker. Wet samples were prepared in this fashion because it was felt this represented a worse case scenario. Water that came in contact with a previously contaminated soil would shield the hydrocarbon compounds from being extracted using nonpolar solvents.

All extractions were performed using a Dionex

(Sunnyvale, CA, USA) ASE 200 accelerated solvent extraction system. Either 11- or 22-ml stainless steel cells were used for the extractions. Glass fiber filters were placed in the outlet of each cell prior to being loaded with sample. Extractions were performed at 125, 150, 175 and 200°C with the following solvents: DCM, hexane, heptane, DCM–acetone (1:1, v/v), hexane–acetone (1:1, v/v), and heptane–acetone (1:1, v/v). Heat-up times were 6, 7, 8 and 9 min for the temperatures listed, respectively. Extraction pressure was 1500 p.s.i., static time was 5 min, flush volume was 70%, and purge time was 60 s with 150 p.s.i. nitrogen gas for all samples (1 p.s.i.=6894.76 Pa). The extracts were collected in pre-cleaned 40- or 60-ml glass vials (I-Chem, New Castle, DE, USA).

For method development, extractions were repeated three times at each set of conditions. For the method validation portion of the study, seven replicates at each concentration (low and high) and from each matrix (sand, loam and clay) were performed. In addition, matrix blank, matrix spike and matrix spike duplicate extractions were performed for each matrix at the low level. A blank for each matrix was also extracted along with the high-level samples to check for carry-over.

The extracts collected from all samples, whether wet or dry, were treated in the same manner. Upon collection, 10 ml of DCM, hexane or heptane was added to facilitate phase separation. Then, 5 g of dry sodium sulfate was added to each glass vial. The vials were shaken to ensure excess water was removed from the extracts. The extracts were then passed through 10-ml serological pipettes containing sodium sulfate (5 g) on top of silica gel (5 g) held in place with silanized glass wool. Approximately 20 ml of the appropriate solvent (DCM, hexane or heptane depending on which solvent was used for the extraction) was used to rinse the vial and to elute the hydrocarbons from the clean-up columns. The extracts were then taken to 1.0 ml using a Turbo Vap II (Zymark, Hopkinton, MA, USA). The concentrated extract was loaded in an autosampler vial for analysis.

2.4. Gas chromatography

Analyses of the extracts were performed on a HP 6890 (Hewlett-Packard, Little Falls, DE, USA) gas

chromatograph. Separations were performed using a 30 m×0.32 mm I.D., 0.25 μm film, Rtx-1 column (Restek, Bellefonte, PA, USA). A 2-μl volume was injected in the splitless mode (0.75 min) at 300°C. The oven temperature program was as follows: initial temperature 40°C (held for 5 min), programmed at 12°C/min to 330°C and held for 12 min. A ramped flow program was also used. The flow remained at 1 ml/min for 20 min, then it was increased at 0.5 ml/min per min to 6.0 ml/min and held there for 12 min. The flame ionization detector was maintained at 350°C, and helium was the carrier gas. DROs were assigned as the sum of the area from 12.25 to 25.7 min (C_{10} to C_{28}). WOOs were assigned as the sum of the area from 25.71 to 41.0 min (end of C_{28} to end of C_{40}). For this study, TPHs were defined as the sum of the DROs and WOOs. Calibration curves with five data points for DROs and WOOs were generated using the appropriate standard solutions. The concentration range used corresponded to between 2 and 3000 mg/kg for a 10-g sample. Fig. 1 shows a typical chromatogram obtained from the extract of a soil contaminated with hydrocarbons. The respective areas of the chromatogram used to quantify DROs and WOOs are marked.

The analyses of all extracts from the validation portion of the study were performed by an outside laboratory (Mountain States Analytical, Salt Lake City, UT, USA). The conditions used were in compliance with US EPA SW-846 Method 8015 and were similar to those listed above. Aliquots of the same solutions used to prepare the custom soils (solutions contained diesel and 30 W motor oil) were used for the GC calibration for this part of the work. The results from the seven replicates at the low concentration level were used to calculate the method detection limit (MDL) and the reliable quantitation limit (RQL). To determine RQL, the MDL was first calculated from the low concentration standard deviation (σ) determined from the seven replicate measurements (six degrees of freedom, 95% confidence interval):

$$\text{MDL} = 3.143\sigma$$

The RQL was calculated using the following equation:

$$\text{RQL} = 4\text{MDL}$$

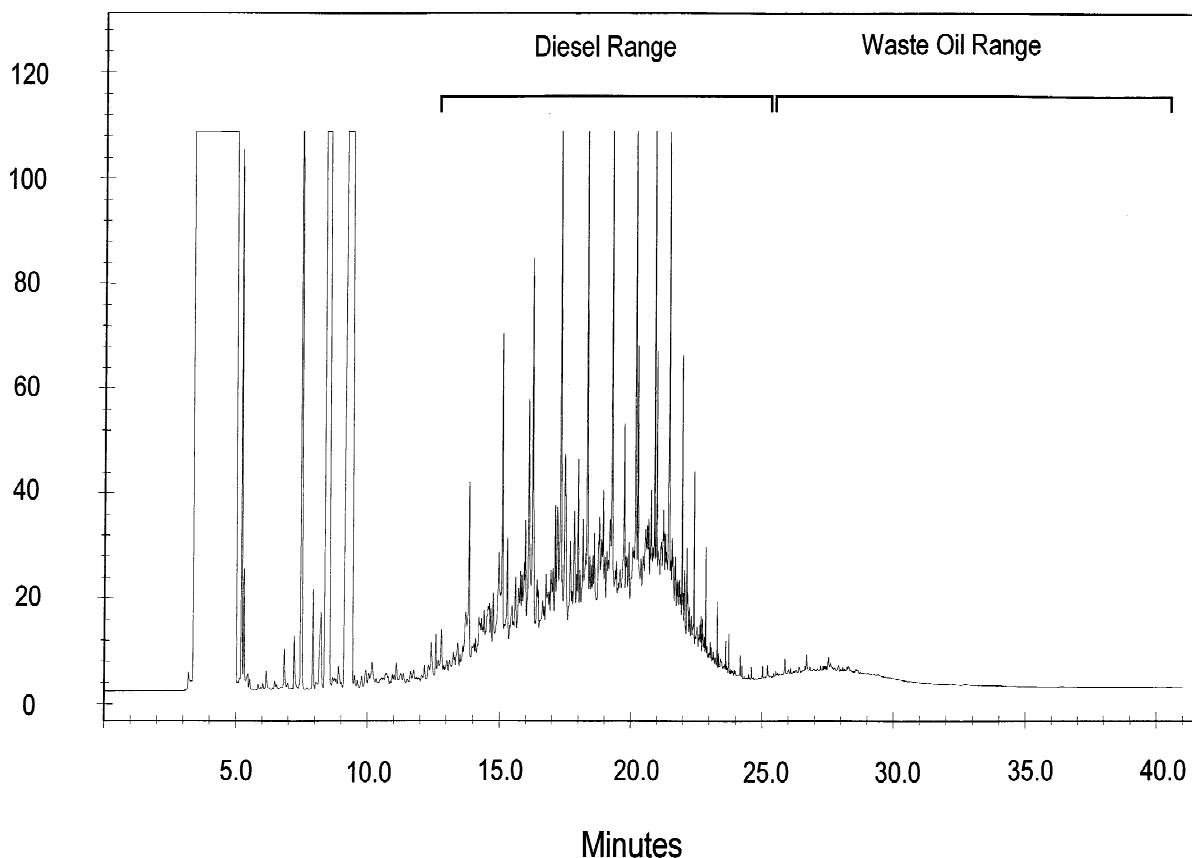


Fig. 1. Typical chromatogram from the extract of a soil contaminated with hydrocarbons. The conditions used to obtain these results are given in the text.

3. Results and discussion

3.1. Method development

Fig. 2 shows the results from the experiments performed to investigate the effect of temperature and solvent on the recovery of TPHs from dry and wet soils. Hexane and heptane gave essentially equivalent results from the dry soils. A recovery over 100% of the certified value probably indicates a high level of background material was extracted from the soil. It was somewhat surprising that DCM gave a lower recovery than either hexane or heptane. Even more surprising was the dramatic effect that water had on the extraction efficiency of the hydrocarbons using a single solvent. As can be seen, the best

recovery achieved was still less than 30%, even at 200°C with DCM.

Fig. 3 shows the results from dry and wet soils when acetone was added to increase the polarity of the extraction solvent. DCM–acetone, hexane–acetone and heptane–acetone (all 1:1, v/v) seemed to give essentially equivalent results at all temperatures from dry soils. When extracting wet soils, DCM–acetone and hexane–acetone gave a lower recovery than heptane–acetone at 125°C. Quantitative recoveries of the hydrocarbons were achieved using any of the solvents at temperatures higher than 150°C. Based on these results, the optimized conditions were determined to be 175°C, 8 min heat-up time, 5 min static time, 70% flush and 60 s nitrogen purge. Any of the mixed solvents would work for this extraction, but DCM–acetone was chosen be-

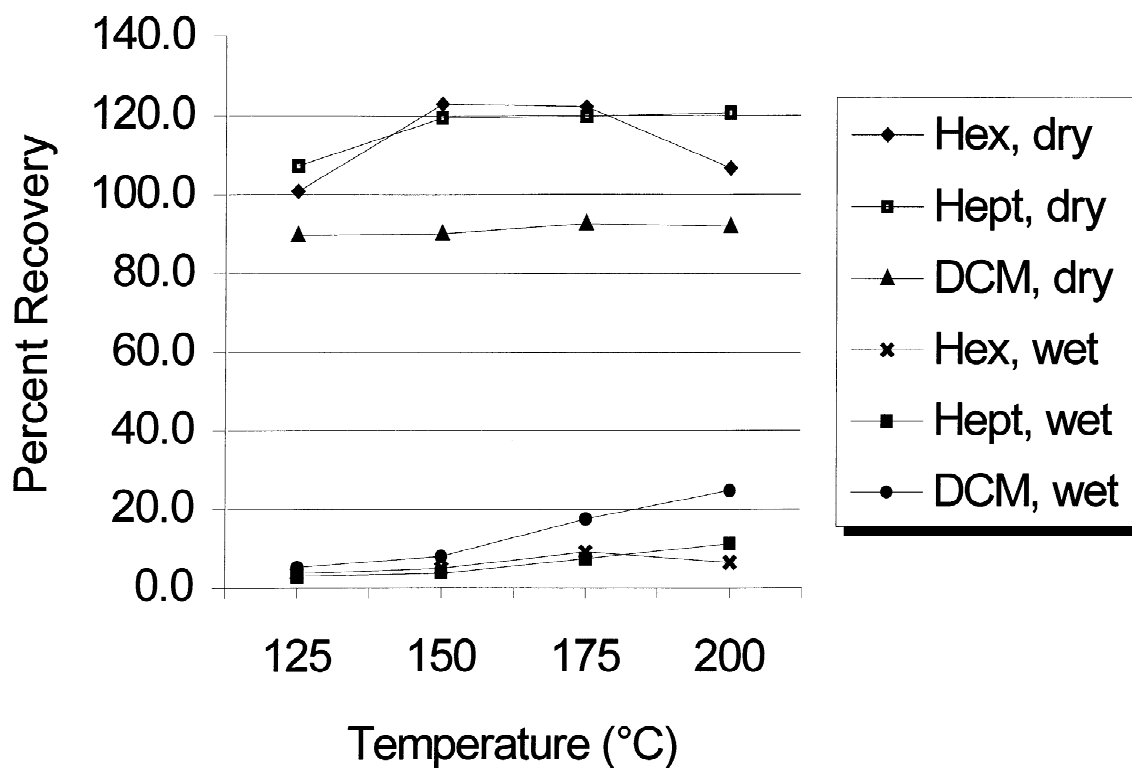


Fig. 2. Effect of temperature on the recovery of hydrocarbons from wet and dry soils using single-component solvents.

cause this solvent evaporates more quickly than the other two solvents, and many laboratories are already using DCM as the extraction solvent for the hydrocarbons. It is interesting to note that with the exception of the higher temperature (175°C versus 100°C) the conditions for the hydrocarbons are the same as those currently stated in US EPA Method 3545A.

As a test of these conditions, eight replicates of ERA TPH Standard 1 (1840 mg/kg) were extracted. The extracts underwent the same clean-up and concentration procedure before analysis as the other samples. The average recovery was 117% with a 3.6% RSD.

3.2. Method validation

Table 1 summarizes the results obtained from the validation portion of the study. These data demonstrate that the optimized conditions give good values

for recovery, and precision. Tables 2 and 3 compare the average recovery and precision results as a function of matrix and concentration. These data indicate that the recovery of the hydrocarbons is not dependent on matrix or analyte concentration. The higher recovery at the low concentration level indicates that there might be some residual background even after silica gel column clean-up. These data show also that the precision from the loam matrix was slightly better than sand or clay. The precision of DROs from clay was slightly worse than the others. In general, no adverse trends were seen. As expected, the precision values at the high concentration level were better than for the low-level concentration samples.

Table 4 gives a comparison of the MDL values for some existing methods for the determination of hydrocarbons from soils. These state methods use either sonication or Soxhlet extraction coupled with the GC analysis of the extracts. Since the GC

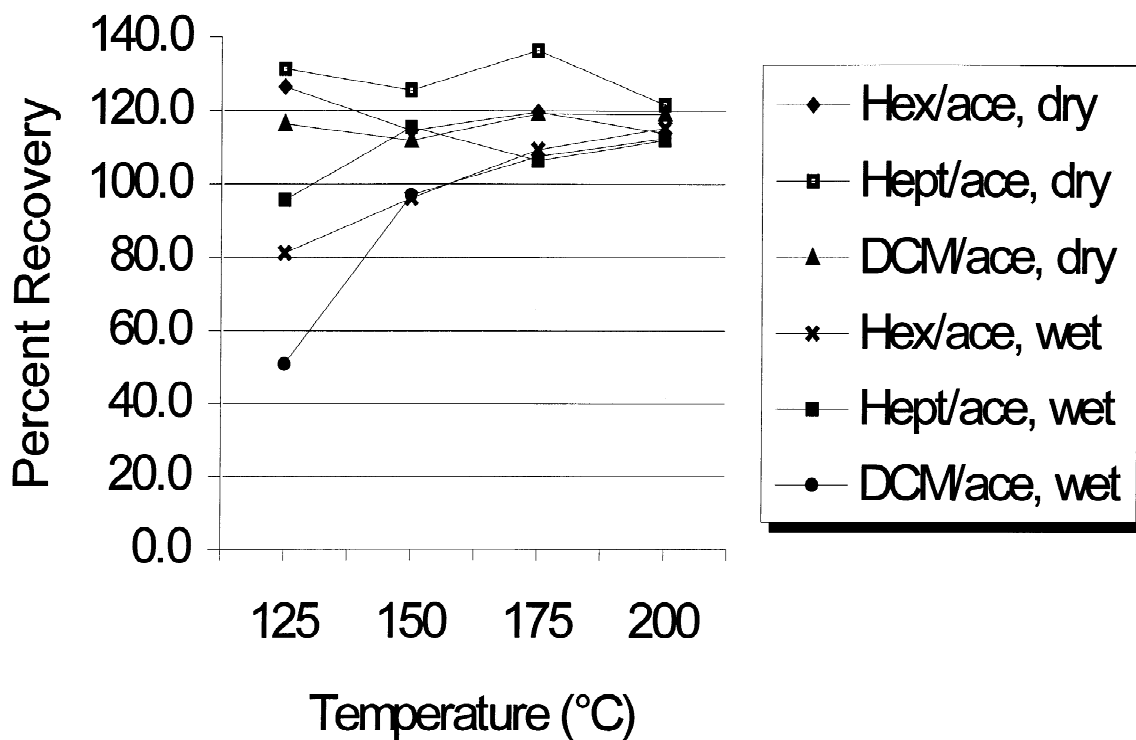


Fig. 3. Effect of temperature on the recovery of hydrocarbons from wet and dry soils using mixed solvents.

methodology is the same as used in this study, the MDL values can be used as a good comparison of the performance of the accelerated solvent extraction method to these established extraction methods. As can be seen, the optimized accelerated solvent extraction conditions along with GC analysis give results similar to Soxhlet and sonication extraction combined with GC analysis in terms of MDL values. The action level for all states for hydrocarbon groups such as DROs, WOOs and TPHs are in the range of 50–100 mg/kg. The control limits for all state methods currently are 75–125% recovery for the hydrocarbon groups and 50–150% recovery for the surrogate compounds. In this study, the average recovery of all hydrocarbon groups at both concentration levels from all three matrices was 115%. The recovery of the surrogates ranged between 88% and 148%. These data indicate that the accelerated solvent extraction method gives results that meet

these acceptance criteria for hydrocarbon contamination from soils.

4. Conclusions

Accelerated solvent extraction has been shown to give results comparable to established techniques when extraction hydrocarbon contamination from wet and dry soils. High temperature (175°C) along with a polar solvent (DCM–acetone) were found to be necessary to extract the hydrocarbons quantitatively from wet clay soils. Clean-up of the extracts using sodium sulfate to remove water and silica gel to remove interfering coextracted compounds was found to be necessary. In comparison to established methods such as sonication and Soxhlet, accelerated solvent extraction offers the advantage of faster extraction times and lower solvent consumption.

Table 1
Results summary for TPHs, DROs and WOOs

Matrix, concentration	Bias ^a	Precision ^b	MDL ^c	RQL ^c
<i>TPH</i>				
Clay, low	123.8	17.6	6.9	27.4
Clay, high	111.0	18.1	NA ^d	NA
Loam, low	124.6	20.3	8.0	32.0
Loam, high	100.8	7.8	NA	NA
Sand, low	123.6	16.1	6.3	25.1
Sand, high	108.6	12.2	NA	NA
TPH average	115.4	15.3	7.0	28.2
<i>DRO</i>				
Clay, low	127.8	23.6	4.8	19.0
Clay, high	111.8	19.2	NA	NA
Loam, low	137.5	20.7	4.5	17.9
Loam, high	94.2	4.6	NA	NA
Sand, low	127.2	25.4	5.1	20.4
Sand, high	108.6	10.7	NA	NA
DRO average	117.8	17.4	4.8	19.1
<i>WOO</i>				
Clay, low	119.8	17.9	3.4	13.5
Clay, high	110.3	18.2	NA	NA
Loam, low	111.8	23.8	4.2	16.8
Loam, high	107.3	11.3	NA	NA
Sand, low	120.1	23.0	4.4	17.5
Sand, high	108.6	13.8	NA	NA
WOO average	113.0	18.0	4.0	15.9

^a Bias was calculated as the percent recovery of the certified concentration by accelerated solvent extraction.

^b Precision was calculated as the RSD (%) of accelerated solvent extraction recovery.

^c Expressed as mg/kg.

^d NA designates not applicable.

Table 2
Comparison of average recovery as a function of matrix and concentration

	Average recovery (%)				
	Clay	Loam	Sand	High	Low
TPHs	117.4	112.7	116.1	106.8	124.0
DROs	119.8	115.9	117.9	104.9	130.8
WOOs	115.1	109.6	114.4	108.7	117.2

Table 3
Comparison of precision values (RSDs) as a function of matrix and concentration

	RSD (%)				
	Clay	Loam	Sand	High	Low
TPHs	17.9	14.1	14.2	12.7	18.0
DROs	21.4	12.7	18.1	11.5	23.2
WOOs	18.1	17.8	18.4	14.4	21.6

Table 4
Reported MDL values for selected state hydrocarbon methods

State	MDL (mg/kg)	Analyte
Arizona	30	DRO
	50	WOO
	100	TPH
Connecticut	10	TPH
Florida	4	TPH
Oregon/Washington	50	DRO
	100	WOO
Texas	50	DRO
API Method 4599	12–20	DRO
Results from this study	4.8	DRO
	4.0	WOO
	7.0	TPH

Method 3545A will be expanded to include DROs and WOOs as part of Update IV based on the data presented here which have been submitted to the SW-846 Workgroup.

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