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The analytical parameters were optimized with respect to acid type, base type, extraction solvent, reagent amounts, and heating time. Parameter selection was based on that value which gave a maximum absorbance and a minimum relative standard deviation. Examples of optimization experiments will be presented. In addition, results from experiments evaluating spiking procedure, response of method to other alkylating agents, and stability of reaction product will also be presented.

The method was validated by spiking and analyzing seven replicates at each of four spike levels. All four spike levels were performed in simulated matrix, and one spike level was also performed in an actual sample. There was not a significant difference in percent recoveries when the spike was performed in simulated matrix or an actual sample. The average percent recovery at 537 μ M alkylating capacity was 102% ($n=14$, $CV = 11.7\%$). The method limits of detection and quantitation will be discussed.

The method was used to evaluate three independent reactor runs, and gave consistent patterns for each kinetic series within a reactor run. In addition, a sample was monitored for approximately 90 hours after reactor drain to follow the continued breakdown of HD. Parallel analyses using the standard GC/MSD methods were also conducted. Results from both sets of analyses will be presented and compared.

DETERMINATION OF OIL CONTENT OF CONTAMINATED SOILS AND SLUDGES

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ABSTRACT

This paper reports potential applications of liquid phase agglomeration techniques in the removal of oil from contaminated soil and sediment samples for subsequent quantitative measurements. The use of liquid phase agglomeration techniques greatly improves the efficiency of solids-solvent separation. As a result, better contaminant recoveries were achieved in a shorter period of time compared with the conventional Soxhlet - Dean and Stark solvent extraction method. Quantitative determination of the contaminant was carried out using gas chromatographic and spectrophotometric methods. Two case studies are discussed. The first deals with the quantitative determination of diesel fuel from a contaminated diesel invert drilling mud sample. The second evaluates the extraction and subsequent quantification of heavy oil from a contaminated soil sample.

The objective of this study was to develop a quick and efficient procedure for the extraction and subsequent quantification of total petroleum hydrocarbons in contaminated wastes. The proposed method can be adapted to the extraction and subsequent quantification of a variety of hydrocarbon pollutants from contaminated soils and sediments.

INTRODUCTION

Both the design and planning of a soil reclamation program and the evaluation of disposal, reprocessing or reclamation options for sludges, oily wastes and tailings depend upon a reliable and accurate means of evaluating the total oil content of polluted soils. A precise estimate of the amount of hydrocarbons is essential to determine the extent of contamination and the success of the reclamation program. Treatment technologies and site remediation progress lean heavily on analytical techniques that are accurate, reproducible and of real time value. Current analytical methods are inadequate because of the following concerns:

- The recovery of oil from contaminated samples is influenced by the sample preparation method and the oil extraction methods.
- The solvent extraction methods, used to remove oil from contaminated samples for subsequent measurements, have limitations with respect to the water content of the sample and the particle size distribution of the matrix. Usually these methods are less efficient for fine textured materials. Also, water is known to reduce the extraction efficiency of organic solvents because of the formation of oil-in-water

- emulsions¹⁻².
- Loss of volatile organics, during solvent removal for sample concentration, results in significant bias.
- Spectroscopic determination of contaminants has the disadvantage that degradation of pollutants in the soil results in altered spectral characteristics. Absorbance at certain wavelengths may increase with time even though the total amount of oil in the soil would be decreasing. Also, in clay soils where oil components may be absorbed, spectral properties of the extracted oil may also change¹.
- A wide variety of laboratory techniques used to measure TPH provide data of varying quality.

In our previous work we demonstrated the potential applications of proton NMR in the quantitative determination of bitumen and solvents extracted from oil sands and fine tailings³⁻⁴. The NMR method can be used to estimate the amount of any residual solvent in the oil. The retention of low boiling components, normally lost during solvent removal, produces a more representative sample of the oil for calibration purposes.

Liquid phase agglomeration techniques, in combination with solvent extraction have been successfully used for the removal of hydrocarbon contaminants from fine textured, organic contaminated soils⁵. Agglomeration of fines with the coarse particles is achieved by the addition of water to a vigorously mixed slurry of soil in the selected solvent. Water acts as a solids bridging liquid and dense soil agglomerates are formed under appropriate conditions. The bridging liquid remains in the agglomerate pores where interfacial tension provides the forces holding the aggregates together. Judicious selection of agglomerate size, by controlling water content, greatly improves the efficiency of solids-solvent separation.

The objective of this study was to explore the use of liquid phase agglomeration techniques in the development of a more efficient solvent extraction procedure. Two hydrocarbon contaminants, one associated with a fine textured soil and the other with a coarser matrix, were selected for subsequent quantitative measurements.

EXPERIMENTAL

Samples. One of the samples used for this study was a used Diesel Invert Drilling Mud (DIDM) from Alberta. This sample contained over 70 w/w% of solids < 41 μm diameter. The diesel content of this sample was estimated by extraction with toluene using the Dean and Stark Soxhlet method⁶. The extract was characterized and subsequently quantitated by GC. The GC chromatogram of the extract was a good match with the chromatogram for a sample of diesel obtained from a local gas station in the summer of 1995. This commercial diesel sample was used for preparing calibration standards.

The second sample used in this study was a highly saline soil sample provided courtesy of Newalta Corporation, Calgary, Alberta. It was a mixture of tank bottoms, frac sand and spill material containing a range of organic and inorganic contaminants. The organic contaminant in this sample was a high boiling heavy oil.

Proton NMR measurements. Proton NMR measurements were performed on a Bruker AM-400 NMR spectrometer (400 MHz); 500 μL of solution in a 5 mm outer diameter tube was used in each case. A repetition time of 2 seconds was selected. Each spectrum was the Fourier transform of 1000 free induction decay curves. Once adjusted all parameters were kept constant for subsequent measurements.

GC determination of diesel. The extract was analyzed employing a Varian Model 3300 GC equipped with an FID detector and a temperature gradient program: A DB-5, megabore, capillary column, 30 meters in length with a 0.53 mm internal diameter and a 1.5 micron film thickness (J & W Scientific) was used. The initial operating temperature was 50 degrees Celsius with an initial hold-time of 5 minutes. The temperature was then increased at the rate of 10 degrees per minute to a final temperature of 300 degrees Celsius where it was held for 5 minutes. Calibration curves were prepared using the purchased sample of #2 Diesel Fuel.

Soxhlet Dean and Stark Method. The extraction of heavy oil from the Newalta sample was carried out for 20 hours using the Soxhlet-Dean and Stark method⁶. Both toluene and methylene chloride were used separately for extraction.

Spectrophotometric estimation of heavy oil. The quantitation of the oil component was carried out using a spectrophotometric method⁷ based on the linear relationship between the absorbance at 530 nm and the concentration of oil in solution.

For calibration purpose oil samples were obtained from a methylene chloride extract of the soil. Non-filterable solids were removed from the oil extract by centrifugation. The solvent was removed at 40°C in a Brinkmann rotary evaporator under reduced pressure. The amount of residual solvent in the oil was quantitatively measured using proton NMR⁴. A correction for solvent content was applied to the amount of oil used in the preparation of standard solutions. For spectrophotometric measurements, absorbances at 530 nm were determined for toluene solutions of the oil for concentrations ranging from 0.01 - 0.4 w/w%. Plots of the percent oil vs. absorbance produced a straight line passing through the origin.

Liquid Phase Agglomeration Procedure. In a typical test a polypropylene Waring Blendor Jar (500mL), equipped with Teflon washers and a plastic cover, was accurately weighed. To the jar were added: contaminated solids (20g), and solvent (50mL). The contents were agitated at high shear for 1 minute. The solution was carefully drained into another 500 mL polypropylene jar. About 1w/w% of an additive (sodium meta phosphate, calcium hydroxide or scrubber sludge), additional water and fresh solvent (50 mL) were added to the original Blendor jar still containing the extracted solids from the primary extraction. The contents were agitated-at high shear for 1 minute followed by 5-10 minutes at low shear until the slurry became clear as discrete agglomerates were formed. The supernatant solution from the second treatment was drained into the polypropylene jar containing solution from the primary extraction. The procedure was repeated three more times and all extracts were combined. The extracted solids were surface washed and the washings were added to the solution in the polypropylene bottle. The contents of the bottle were centrifuged and the clear solution was transferred to a 500 mL glass measuring flask. The residue in the polypropylene bottle was agitated with fresh solvent and then centrifuged. The solution was combined with the solution in the measuring flask. The procedure was repeated until the washings became colorless. The solution in the measuring flask was made up to the mark. The amount of oil was estimated in this solution using the spectrophotometric method.

RESULTS AND DISCUSSION

The Amount of Extractable Oil from Contaminated Solids

The extraction of diesel from a used diesel invert mud sample and a heavy oil from Newalta contaminated soil sample were carried out using both the conventional Dean & Stark Soxhlet and Solvent Extraction Soil Agglomeration (SESA) methods. Subsequent quantification was carried out using GC/FID for the diesel and spectrophotometric method for the heavy oil. The results are summarized in the Table. It is obvious from the results that not only better recoveries of the contaminants were obtained using the SESA method but the total turn around time was also much reduced.

Method	Extraction plus analysis turn around time (Hrs)	Amount of oil extracted (g/100g of wet solids)*	
		DIDM***	NEWALTA
Dean & Stark Soxhlet Method	21	4.84 ± 0.1 (5)	12.9 ± 0.2 (5)
SESA**	2	4.99 ± 0.22 (3)	13.38 ± 0.49 (3)

* Figures in parenthesis represent number of tests carried out.

** Solvent Extraction Soil Agglomeration process.

*** Diesel Invert Drilling Mud sample

CONCLUSION

Liquid phase agglomeration has potential for use as a quick and efficient analytical procedure for the extraction and subsequent quantification of a variety of petroleum contaminants from contaminated wastes.

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IMPROVED EXTRACTION EFFICIENCY OF POLYCHLORINATED BIPHENYLS FROM CONTAMINATED SOIL USING A TOTAL HALOGEN SCREENING METHOD

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ABSTRACT

Polychlorinated biphenyls (PCBs) are strictly regulated on the state and federal levels. Responsible parties must determine the concentration and extent of contamination to make appropriate decisions regarding remediation of PCB contaminated soils. Gas chromatography (GC) analysis has been traditionally used to delineate PCB contamination in soil. On-site, field screening techniques have been developed within the last decade to reduce the number of samples requiring laboratory confirmation. All field screening methods require the use of organic solvents to extract the contamination from soil. Soils sampled for analysis frequently contain water which, with some solvents, may result in poor extraction efficiencies and can subsequently produce false negatives. In this study, GZA GeoEnvironmental, Inc. (GZA) utilized a total organic halogen (TOX) screening kit to characterize complex, multi-component PCB contaminated soil at an industrial property located in the midwest. Furthermore, the results demonstrated the effectiveness of two novel solvent systems to extract PCBs from wet clay soil for reliable quantification with a portable field analyzer. Preliminary GC analyses indicated that the soil was contaminated with Aroclor 1248 as well as diesel range organics. The excavated soil consisted of wet, red clay. Two types of field test methods are available for PCB screening, both of which may exhibit lower extraction efficiencies for wet clay soils. One method relies on immuno-assay chemistry, and the second method involves chemical dehalogenation of the PCBs followed by analysis with a colorimetric reaction or chloride-specific electrode. Immuno-assay PCB kits suffer severe negative interferences in the presence of hydrocarbon co-contaminants and are not suitable for this site. Dexsil Corporation's L2000[®] PCB Analyzer (U.S. EPA SW-846 Draft Method 9078, "Screening Test Method for Polychlorinated Biphenyls in Soil") is not adversely affected by the presence of the aforementioned co-contaminating fuels and oils and was therefore selected to quantify the PCBs. Aroclor 1248 concentrations were determined in over 71 wet samples by extracting the contaminated wet soil samples with a new, two-step, ozone-friendly solvent system followed by analysis using the L2000. An additional, modified aqueous-organic solvent extraction method with a Florisil cleanup column was also used to determine the PCB content of 42 of the same wet samples. The second method was designed to quantify PCBs in the presence of some non-PCB halogenated solvents. A portion of each wet soil sample was then dried and reanalyzed. Ten percent of the nondetected samples along with all samples testing positive (>2 ppm) for PCBs were analyzed using U.S. EPA Method 8080 (gas chromatography with Soxhlet extraction) to establish the extraction efficiencies of each new two-step solvent system. The L2000 results of wet soil samples were adjusted for water content and compared to the values generated by Method 8080 (GC). Both solvent systems demonstrated the ability to efficiently extract (>73%) PCBs from wet and dry lacustrine red clay soil. Data generated by L2000 analysis of PCBs extracted into both new solvent systems exhibit excellent correlation to the data produced by the more sophisticated laboratory (GC) technique. This information lends confidence in PCB field screening data for field engineers.



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