

Quantitative determination of oil films/slicks from water surfaces using a modified solid-phase extraction (SPE) sampling method

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Abstract

We have developed a procedure using solid-phase extraction (SPE) for the quantitative determination of oil films and slicks floating on water surfaces. During Phase One of this study, nine oil loadings (Exxon #6 fuel oil: 3 to 38 mg/cm²) were sub sampled with C₁₈-SPE disks in replicates (n = 2-4) from the surface of 1L beakers. Sonication and accelerated solvent extraction (ASE) were both tested as extraction procedures and quantification was determined gravimetrically (Total Extractable Material or TEM) and following a laboratory procedure employing extraction of samples with dichloromethane and analysis using gas chromatography-mass spectrometry (Total Petroleum Hydrocarbon or TPH). Based on these two quantification methods, the recovery efficiency of oil from the SPE pads was 95±6% and 98±14%, respectively, and no significant difference was observed between sonication and ASE extraction procedures. Moreover, a strong linearity was observed throughout the whole range of loadings with a precision of ±7% and a 1:1 sampling efficiency of TEM and TPH per unit area. In Phase Two, the method was tested on a controlled surface oil slick (9.5±1.1 m²) in a salt-water mesocosm and using multiple SPE disks (n = 12). Although the TEM-based approach slightly overestimated the overall amount of spilled oil (127±41%) it suggests that the present sampling method can be used as a first approximation to the quantification of oil on water surfaces. Total Petroleum Hydrocarbon results, on the other hand, showed a much stronger potential for resolving the source of overestimation obtained using TEM (i.e. emulsification of oil/water and/or incorporation of non-oil products in the oil slick) as well as reducing the variability. Using this method the estimates of spilled oil ranged 105±25% suggesting that the SPE/TPH combined procedure can be used to quantify meso-scale to large-scale spills in experimental or natural settings with the added advantage of recovering material for oil fingerprinting.

1.0 Introduction

Oil spills are as pervasive as our need for energy. Maybe more so when we realize that natural oil seeps in certain regions of the world Oceans, such as in the Gulf of Mexico, contribute substantial amounts of oil to marine environments that are comparable to large-scale accidental spills due to transport or drilling activities (MacDonald, 1998). However, although the quantities may be roughly equivalent, the rates are not. The case of the *Exxon Valdez* in Alaska or the *Erika* recently in South Brittany (France), are vivid examples of how anthropogenic influences impact coastal environments at a hurried pace. Rapid detection, and eventually quantification, of natural or anthropogenically-derived hydrocarbon slicks floating on water is crucial to reduce the consequences on safety and the environment. Although certain systems exist for detection of

such slicks/films (MacDonald et al., 1993; MacDonald, 1998; Brown and Fingas, 1998, 1999; Seureau, 1999), there still exists a need for a method to evaluate slicks in a quantitative manner and simultaneously provide material for fingerprinting. More specifically, a method such as this one would provide a strong tool to assess the effectiveness of methods for clean-up of coastal substrates affected by oil spills. Chemical surface washing agents (shoreline cleaners) are formulated and used to help release stranded oil from shoreline substrates (rocky shores, sandy beaches, wetlands, mud-flats, etc.). The main role of the cleaner is to coalesce with the oil, strip it from the substrate and rise to the water surface where the mixture can be collected by mechanical procedures (booming or skimming). The objectives of this project were thus to test a modified solid-phase extraction (SPE) procedure using C-18 disks to determine 1) if surface sampling of oil slicks using this procedure is linear, precise, and consistently yields quantitative recoveries of oil per unit area, and 2) if this method can be used to quantify meso- to large-scale oil slick on water surfaces. Solid-phase extraction is now well recognized as a method for isolating hydrophobic organic compounds from aqueous solutions in preparation for subsequent analysis, and is used in a variety of applications (Donat et al., 1986; Jandera et al., 1994; Snyder et al., 1999; Louchouart et al., 2000). We have applied this method in a new fashion to quantitatively recover oil for water surfaces. A related objective of this project was also to assess the effectiveness of oil removal from a sandy beach in meso-scale wave tanks using different shoreline cleaner products. The results of this selected work is presented in a companion paper appearing in these proceedings (Page et al., 2000).

2.0 Methods and Materials

2.1 The Oil Mixture

The oil used in this experiment was Exxon #6 fuel oil since it is a common fuel oil in South Texas Bays and the Houston Ship Channel and it was selected in the related meso-scale shoreline cleaner study. Due to the density and viscosity issues, the oil was blended into a 1:1 mixture with CytoSol[®]. This latter product is described by its formulator (CytoCulture International, Inc., Point Richmond, CA, USA) as a “biosolvent formulation based on vegetable oil methyl esters in combination with bioremediation enhancers” commonly used as a shoreline cleaner. In addition, this shoreline cleaner was one of two products tested in the same oil-to-product ratio in our meso-scale study (Page et al., 2000).

2.2 Beaker Experiment

A series of 1L beakers were filled with deionized water in preparation for replicate applications ($n = 2-4$) of known volumes of oil mixture to their surface. Seven loadings of oil mixture were chosen to cover a one order of magnitude range in mixture mass per unit area (3 to 40 mg/cm²). The upper limit was also chosen to cover that highest values expected to be used in slick experiments (≈ 30 mg/cm²). The oil/CytoSol mixture spread rapidly to form a uniform layer over the whole water surface of the beakers. Sampling of the water surface (Figure 1) involved placing a C-18 solid-phase extraction disk (SPE Empore[®], Filtration Products, St. Paul, MN) on a fritted funnel that was attached to a small pump. A slight vacuum was applied to hold the disk in place while sampling the slick. The disk was carefully placed on the oiled surface, and then removed quickly. The disks were then stored in 4-ounce jars, and refrigerated until processing.



Figure 1. Sampling Procedure during Beaker Experiment.

2.3 Wave Tank Experiment

Approximately two liters of a 1:1 oil/CytoSol mixture was prepared and spilled on the water surface of a meso-scale wave tank located at the Shoreline Environmental Research Facility (SERF) in Corpus Christi, Texas. A more detailed discussion of the wave tanks available at SERF is presented by Kitchen et al. (1997) and companion papers in these proceedings (Fuller et al., 2000; Page et al., 2000). Briefly, the oil mixture was introduced in the middle of the wave tank and the surface slick was contained within a 9 m² area using “air booms” (industrial fans) at both ends of the tank (Figure 2). Sampling of the surface (n = 12) involved the same fritted funnel/pump procedure developed initially for the Beaker Experiment. During the wave tank

experiment, eight SPE disks were sampled in the fuller, thicker portion of the slick and four SPE disks were used to collect oil from the thinner, filmy edge of the slick (fringe). Each disk was then stored separately in a 4-ounce jar, and refrigerated until processing.



Figure 2. Wave Tank with Air Booms.

2.4 Analytical Methods

The SPE disks were extracted either by Accelerated Solvent Extraction (ASE, Dionex Corp., Salt Lake City, UT) according to the method of Bauguss (1997) and using dichloromethane (DCM) as the solvent, and/or by sonicating three times the disks in 25 ml of warm DCM. The DCM extracts were reduced by evaporative concentration (TurboVap II Concentration Workstation, Zymark Corporation, Hopkinton, MA), reconstituted to a final volume of 5-10 ml, and then refrigerated until analysis. All samples were preserved in pre-cleaned glass container (EPA grade) to insure no residual hydrocarbon contamination. All solvents were HPLC-grade or better.

Total Extractable Materials (TEM) were determined gravimetrically using replicate aliquots of the DCM extracts according to standard gravimetric Oil and Grease methods (USEPA, 1983, 1986) and slight modifications by Mills et al. (1999). Briefly, a 100-250 μ l aliquot of concentrated extract was added to a tared pre-combusted glass-fiber filter, the solvent evaporated, and the filter weighed. Total Petroleum Hydrocarbon (TPH) concentrations were acquired by GC-MS analysis (EPA SW846, modified method 8270b) by injecting a 1 μ l aliquot of DCM extract into a Hewlett-Packard (HP) 5890 Series II gas chromatograph (GC) interfaced to a 5972 mass selective detector (MS) and operated using HP MS ChemStation software (Hewlett-Packard Corporation, Palo Alto, CA, USA). Total Petroleum Hydrocarbon (TPH) concentrations are defined as the sum of the total resolved hydrocarbons (including n-C10 through n-C34) and the unresolved complex mixture. To insure the accuracy and precision of the method, Quality

Assurance/Quality Control (QA/QC) measures were incorporated in the method. During extractions, blank extraction samples, duplicate samples, and standard reference materials (SRMs) were processed along with the samples of interest. The GC-MS system was calibrated with a seven-point curve and based on relative response factors (RRF) derived from target analyte standards or nearest homologues. More details of the analytical technique for the determination of TPH have been outlined in Mills et al. (1999).

3.0 Results

We first evaluated the recoveries of oil mixture by adding known amounts of oil (□240 mg; n = 3) on SPE disks and subsequently extracting these disks under sonication. Based on TEM and TPH quantification methods, the recovery efficiency of oil was 95±6% and 98±14%, respectively, indicating that oil was recovered with high efficiency from the pads. When we tested sonication vs. ASE as extraction procedures on a series of oil concentrations adsorbed to SPE disks, no significant difference was observed for both TEM and TPH values. Although these results indicate that both extraction methods can be used to extract oil materials from SPE disks, each provide singular advantages and disadvantages. The sonication method does not require high-end and costly equipment but is more time-consuming and uses more solvent. On the other hand, the ASE method uses less solvent, is more automated, but requires more expensive equipment.

Using both TEM and TPH to quantify recoveries, we observed that the sampling of oil mixture per unit area of the SPE disks was strongly correlated to the amount of oil mixture per unit area on the beakers with a sampling efficiency of 1:1 and an average variability for replicate samples of □7% (Figure 3a-b).

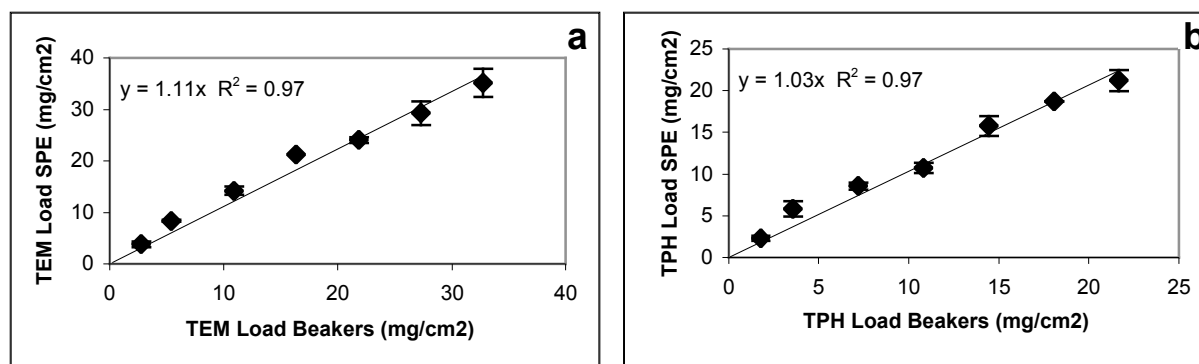


Figure 3. Solid-Phase Extraction Disks Sampling Efficiencies. **a.** Sampling efficiencies (mass per unit area on SPE vs. mass per unit area on beakers) calculated using TEM. **b.** Sampling efficiencies calculated using TPH.

The SPE method was then used in a meso-scale wave tank to test for applicability of this sampling/quantitating method to environmental settings. Estimated values for oil mixture at the surface of a controlled surface slick (9.5±1.1 m²) are presented in Table 1. The area of the slick was divided into two sub-areas: 1) the fuller, thicker portion of the slick (Full) which represents about 74% of the total slick, and 2) the thinner, filmy edge of the slick (Fringe) which comprises the remaining 26% of the total slick. The estimates of the Full and Fringe surface areas vary by

12% and 25%, respectively. Using the TEM and TPH quantification methods, the total estimated values for oil at the surface of the water vary by 32% and 23%, respectively, and account for 128% and 105% of the actual oil added to the tank. Both methods indicated that the vast majority of the oil was present in the Full slick (95-98%) with minimal amounts in the Fringe (2-5%).

Table 1. Oil Recoveries from a Controlled Spill on a Meso-Scale Wave Tank.

	TEM	TPH
Area - Full (m ²)	9.1±1.1	9.1±1.1
Area - Fringe (m ²)	3.2±0.8	3.2±0.8
Total Slick (Kg)	2.29±0.75	0.99±0.23
% Full	95.3	98.0
% Fringe	4.7	2.0
Oil Added (Kg)	1.78	0.95
% Recovery	128.4	105.1

1.0 Discussion

As stated earlier, to test for the effectiveness of shoreline cleaners in removing oil from hard substrates (rocky shores, sandy beaches, wetlands, mud-flats, etc.), we needed to quantitatively assess the transfer of oil from the initial substrate to the water surface. Water samples taken in bottles would not be appropriate since they would not discern between oil-present in vs. on the water, and that discrimination is critical for testing the effectiveness of the shoreline cleaners. During a preliminary test, using C-18 SPE disks and low loadings of Arabian crude oil on small beakers (range of oil loadings: 0.05-0.55 mg/cm²), we observed a strong sampling efficiency of oil per unit area (TEM based: $y = 0.89x + 0.02$ $r^2 = 0.97$). These result suggested that the SPE method would be appropriate for a quantitative assessment of oil in surface slicks. However, before we could apply it to field measurements, we first needed to assess its potential for quantitatively sampling higher loadings of oil on water surface under controlled conditions (laboratory and meso-scale calibrations). When the method was applied to a higher range of oil loadings (3 to 40 mg/cm²), we obtained similar results regardless if we used TEM or TPH to quantify recoveries (Figure 3a-b). In both cases, the sampling efficiency of oil mixture per unit area was 1:1 between the SPE disks and the beakers over the whole range of loadings tested and the average variability was lower than 10%.

When this method was applied to a controlled spill in a meso-scale setting, our estimates were highly concordant with the original amount of spilled oil when the total mass was calculated using TPH values (105%) and slightly overestimated (128%) when TEM values were used. From the data obtained from the laboratory (“beaker”) experiment, it seems that the variability observed in the meso-scale experiment may be related more to slick heterogeneity than to the sampling or analytical variability. By increasing the numbers of samples, we could obtain a direct estimate of the slick heterogeneity independent of sampling and analytical variability. A true estimate of the uncertainty of oil mass quantification, could further be obtained by replicating

this sampling in either one slick or replicate slicks in multiple wave tanks and then by comparing the respective total mass estimates.

Typically, the gravimetric analysis is rapid, but it represents a gross measurement of spilled oil in addition to any material from organic and inorganic interferences that is soluble in the extraction solvent, especially strong solvents such as DCM. In contrast, the GC-MS derived TPH value is target specific and thus reduces the interferences associated with the gravimetric analysis. In any extent, in view of the relatively good estimate given by the TEM values, the gravimetric method could still be taken in consideration for quick turnover of samples and rapid estimates of oil on surface slicks. The same extracts can then be prepared for treatment under GC-MS and provide a better estimate of the oil amount as well as additional information on the source and degradation state of the oil(s) comprised in the slick.

2.0 Conclusion

Controlled experiments in the laboratory showed that a modified solid-phase extraction (SPE) method using C-18 SPE disks allows for quantitative recoveries of oil from surface slicks/films. The sampling efficiency was strongly linear over the whole range tested, the variability was below 10%, and the oil was collected by the SPE disks in a 1:1 ratio relative to the water surface loadings. The application of this method to a meso-scale salt water wave tank showed a strong potential for this method to be used for the quantification and fingerprinting of oil present in meso-scale to large-scale slicks/films in experimental or natural settings

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4.0 References

- Bauguss, J.L. *Accelerated Solvent Extraction of Petroleum Contaminated Sediments*. M.Sc. Thesis. Texas A&M University. College Station, TX. 1997.
- Brown, C.E. and M.F. Fingas "Oil Spill Remote Sensing in Marine and Coastal Environments Using Lase-Based Sensors" *Proceedings of the Twentieth Canadian Symposium on Remote Sensing*, Canadian Aeronautica and Space Institute, Ottawa, Ontario, pp. 15-18, 1998.
- Brown, C.E. and M.F. Fingas "Oil Spill Surveillance, Monitoring and Remote Sensing: A Global Review" *Proceedings of the Twenty-Second Arctic and Marine Oilspill Program (AMOP) Technical Seminar*, Calgary, Alberta, Canada, Vol. 1, pp. 387-401, 1999.
- Donat, J.R.; P.J. Statham and K.W.Bruland, "An Evaluation of a C-18 Solid-Phase Extraction Technique for the Isolation of Metal-Organic Complexes from Central North Pacific Ocean Waters", *Marine Chemistry*, Vol. 18, pp. 85-99, 1986.
- Fuller C., J. Bonner, S. Dellamea, S. Ussery, P. Tissot, P. Louchouart, C. Page and T.J. McDonald, "Comparative Ecological Effects of Sandy Shoreline" *Proceedings of the Twenty-third Arctic and Marine Oilspill Program (AMOP) Technical Seminar*, Environment Canada, Ottawa, Ont., (this volume), 2000.
- Jandera, P., K. Ventura, R. Hladonikova and J. Churacek, "Comparison of Various Sorbents for the Enrichment of Samples of Aliphatic Amines Using Solid-Phase Extraction Prior to the

- Determination by HPLC With Fluorimetric Detection" *Journal of Liquid Chromatography*, Vol. 17, pp. 69-95, 1994.
- Kitchen, R.B., J.S. Bonner, R.L. Autenrieth, K.C. Donnelly, and A.N.S. Ernest. "Introducing COSS: A New and Unique Oil Spill Research Facility." *Proceedings of the Twentieth Arctic and Marine Oilspill Program (AMOP) Technical Seminar*, Vancouver, British Columbia, Canada, Vol. 2: 1327-1407, 1997.
- Louchouart, P., S. Opsahl and R. Benner, "Isolation and Quantification of Dissolved Lignin from Natural Waters Using Solid-Phase Extraction (SPE) and GC/MS Selected Ion Monitoring (SIM)", *Analytical Chemistry*. In Press, 2000.
- MacDonald, I.R. "Natural Oil Spills", *scientific American*, November 1998, pp. 56-61.
- MacDonald et al., "Natural Oil Slicks in the Gulf of Mexico Visible from Space" *Journal of Geophysical Research*, Vol. 98 No. C9, pp. 16351-16364, 1993.
- Mills, M.A., T.J. McDonald, J.S. Bonner, M.A. Simon, and R.L. Autenrieth. "Method for Quantifying the Fate of Petroleum in the Environment." *Chemosphere* Vol. 39.14, pp. 2563-2582, 1999.
- Page, C.A., P.L. Sumner, R.L. Autenrieth, J.S. Bonner, and T.J. McDonald. "Materials Balance on a Chemically-Dispersed Oil and a Whole Oil Exposed to an Experimental Beach Front." *Proceedings of the Twenty-Second Arctic and Marine Oilspill Program (AMOP) Technical Seminar*, Calgary, Alberta, Canada, Vol. 2, pp. 645-658, 1999.
- Page, C., J. Bonner, P. Louchouart, P. Tissot, C. Fuller, T.J. McDonald and R. Autenrieth, "Materials Balance on an Oil Washed from a Sandy Substrate Using Shoreline Cleaners", *Proceedings of the Twenty-third Arctic and Marine Oilspill Program (AMOP) Technical Seminar*, Environment Canada, Ottawa, Ont., (this volume), 2000.
- Seureau, J.J. "Detection of Hydrocarbon Films on the Surface of Water" *Proceedings of the Twenty-Second Arctic and Marine Oilspill Program (AMOP) Technical Seminar*, Calgary, Alberta, Canada, Vol. 1, pp. 403-415, 1999.
- Snyder, S.A., T.L. Keith, D.A. Verbrugge, E.M. Snyder, T.S. Gross, K. Kannan and J.P. Giesy, "Analytical Methods for Detection of Selected Estrogenic Compounds in Aqueous Mixtures" *Environmental Sciences and Technology*, Vol. 33, pp. 2814-2820, 1999.
- USEPA, *Methods for Chemical Analysis of Water and Wastewater*, Environmental Protection Agency, 1983.
- USEPA, *Organic Analytes*, Chapter 4 in *Test Methods for Evaluating Solid Wastes*, Document SW-846, Environmental Protection Agency, Office of Solid Waste and Emergency Response, Washington D.C. 3rd Ed., 1986.