Survey of Portable Oil Detection Methods

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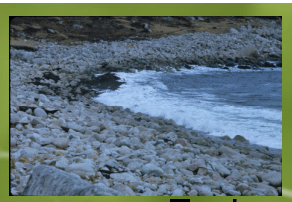

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ABSTRACT

When oil is spilled into the marine environment, it may be found on the water's surface, in the water column, in the sediment, or on the shoreline. When delineating the extent of contamination, it is important to be able to differentiate the spilled oil from other components that may appear to be oil. There are established methods for detecting oil-in-water, such as fluorometry, that allow in situ measurements to be made. In this study, we investigate both established methods and potential technological advancements that could provide a means for a site investigator to gather meaningful on-site information regarding the presence of oil. The primary focus will be usefulness to a shoreline application, but application to other types of samples is addressed. The degree to which an oil could be identified using these portable methods, such as the ability to differentiate petrogenic from biogenic oils, is also discussed. Method comparisons are discussed, with relevance to portability, selectivity, relative cost, and ability to process multiple samples.

INTRODUCTION

Determining the extent of oil contamination from a spill is complex. The oil may be seen on the surface, in the water column, in sediment, and on the shoreline. In addition, some portion of the spilled oil is not visible, such as evaporated components and that which is taken up by biota. The properties of the oil or oil product that is spilled vary widely and those properties, along with the conditions, determine the fate of the oil. In some cases, the contamination is extensive and obvious. In others, the contamination is localized and needs to be assessed by a ground team. The ground team can also provide confirmation of aerial surveys.

When doing an assessment and delineating the extent of contamination, it is important to be able to differentiate the spilled oil from other components that may appear to be oil. Visual inspection can be foiled by naturally occurring components that appear, behave, and smell similar to petroleum hydrocarbons. Presence of blackened vegetation, sheen from plant rot, bacterial films, lichen cover, peat, mud, oxidized surfaces, and banding caused by layers of coloured sand (mineral sand) could all contribute to false positives for oil. If portable instruments can differentiate between petrogenic and biogenic oil sources, it would be helpful. Also of value would be a means to differentiate oil types at the scene. Traditionally, an assessment team would use visual cues and collect samples for laboratory analysis for confirmation. There are portable technologies that could provide results in situ. In some cases, these technologies are already used for assessment of oil in some fashion, either in the petroleum industry or in the food products industry, for quality measurements of olive oil, for example. Emerging technologies may provide additional information for the site assessment team.

Other studies have been undertaken in the past that address this question, in whole or in part. Some of the emerging technologies were not viable at the time of those studies or were overlooked. This review contains a summary of portable methods that have merit in assessing oil content, though, in some cases, these may not be currently suited to shoreline assessment.

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OBJECTIVES

1) Review previous work related to field methods and detection of oil
2) Review existing products and product literature for potential applications
3) Review emerging technologies and research initiatives to identify potential field measurement strategies.
4) Compile information to prepare for future lab. and field studies.

Courtesy of Thermo Scientific

FINDINGS

In each case, the oil type determines the fate. The fate of individual oils is not within the scope of this study, but overall the oil and/or its components will be found in the following states:
- Stranded oil on shoreline. If fresh, there may be volatiles that can be detected in air or headspace. A liquid sample of fresh oil or oil residue could be available. In the event of heavy weathering and/or buried oil, a solid sample may be available
- Floating oil. Again, there may be volatiles detected from evaporation. Depending on thickness, a composite liquid sample could vary from mostly oil to mostly water.
- Oil in the water column. An aqueous sample would capture a representation of this, but potentially this could also be sorbed onto a solid sorbent and the sorbent analyzed.
- Oil in sediment. A sediment sample would likely be a composite water/soil matrix.

Some portable instruments are scaled versions of laboratory instruments. There is no single standard method used for determination of all petroleum hydrocarbons. Different methods are used for different carbon ranges as follows:
- Purgeable/Volatile/Gasoline: Analyzed by Modified ASTM 8015, Purge and Trap, GC
- Diesel Fuel/Middle Distillates: Analyzed by Modified 8015, Extraction, GC
- Lube/Motor Oil, Grease: ASTM 418.1, Modified 418.1, Extraction, IR

Summary of potential portable oil detection methods are listed below:

Method	Potential Use	Strengths	Weaknesses
PID	VOC (Air)	Continuous No consumables	Non-specific Only for fresh oil
FID	VOC (Air)	Continuous Sensitive to alkanes	Also detects methane
Electrochemical	Water	Continuous monitor "lab-on-a-chip"	Currently only available as fixed detector
Portable GC/MS	VOC (Air)	Better differentiation than simple detector	Sample extraction required at minimum Portability and cost
Fluorometer	Water/beach/sediment	Continuous monitor Good for positive ID	Hard to calibrate to quantitative use
Test Strip	Water	Very inexpensive	Often many false positives
Immunoassay	Water/sediment	Good differentiation from biogenic	High consumables Temperature sensitive
IR	Water	Quantitative with good MDL	Solvent extraction Not a hand-held method
FTIR	Beach/sediment	Spectral matching Direct contact with sample	Need to build libraries More water=lower sensitivity
UV/Vis	Water	Quantitative	Not very portable
TLC	Sediment	Differentiates from biogenic	Not commercially available
Raman	Water/beach/sediment	Used currently for differentiation of biogenic oils	Need to build libraries
XRF	Sediment	Spectral signature	Metals only

NEXT STEPS

Laboratory and Field Studies are ongoing in the following areas:

Courtesy of Turner Designs

Fluorometry - This is a common method used for in situ detection of oil. Some flow-through systems were tested for oil-in-water determination in past studies. Newer models offer simultaneous detection at multiple wavelengths. Using this feature, there will be efforts to attempt to differentiate oil types and/or extent of weathering

IR/FTIR - IR is one of the standard methods used to determine concentration of some oils. In the standard method, a specific wavelength is used. New handheld FTIR instruments use direct contact with sample – no extraction required. Since it is a full spectrum scan, the spectral signature may help in matching samples to stored spectra and/or the source oil. Water causes a significant interference in these samples, so neat or solid samples may be best suited to this method.

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