

Development of a fast analytical tool to identify oil spillages employing infrared spectral indexes and pattern recognition techniques

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Received 16 March 2007; received in revised form 23 May 2007; accepted 23 May 2007

Available online 3 June 2007

Abstract

A fast analytical tool based on attenuated total reflectance mid-IR spectrometry is presented to evaluate the origin of spilled hydrocarbons and to monitor their fate on the environment. Ten spectral band ratios are employed in univariate and multivariate studies (principal components analysis, cluster analysis, density functions – potential curves – and Kohonen self organizing maps). Two indexes monitor typical photooxidation processes, five are related to aromatic characteristics and three study aliphatic and branched chains. The case study considered here comprises 45 samples taken on beaches (from 2002 to 2005) after the *Prestige* carrier accident off the Galician coast and 104 samples corresponding to weathering studies deployed for the *Prestige*'s fuel, four typical crude oils and a fuel oil. The univariate studies yield insightful views on the gross chemical evolution whereas the multivariate studies allow for simple and straightforward elucidations on whether the unknown samples match the *Prestige*'s fuel. Besides, a good differentiation on the weathering patterns of light and heavy products is obtained.

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Keywords: Oil spill; Infrared spectroscopy; Attenuated total reflectance; Spectral index; Pattern recognition

1. Introduction

The *Prestige* oil tanker breached her hull during a heavy storm on November 12, 2002. On Tuesday, November 19, the vessel splited in two halves and sank off the Galician coast (North-west of Spain). The tanker transported around 77,000 tonnes of a heavy fuel oil and most of it spilled out during that period. Nevertheless, the wreckage was estimated to contain still *circa* 20,000 tonnes of fuel oil when it sunk, of which ca. 6000 tonnes leaked out during the subsequent weeks. The Spanish government estimated that around 63,000 tonnes were spilled on the marine ecosystem.

The somewhat erratic navigation of the ship before her wreck-age caused different, successive major oil slicks affecting the Galician coast (ca. 900 km length), North of Spain and South-West of France, giving rise to huge ecological problems. This

was the fifth large oil spillage which occurred at the Galician coast since 1970. The *Prestige*'s oil was a heavy fuel oil (score 2, AFNOR scale or score 6, English scale, or M-100, Russian scale) whose high specific gravity (0.99) and viscosity (615 and 30,000 cSt at 50 and 15 °C, respectively) made it fluid only after heating it. This makes such a fuel to be long-persistent into the environment, difficult to recover and difficult to degrade. Despite its acute toxicity is lower than other fuels [1], medium-long term impact might occur due to the release of heavy metals, sulphur and cancerigenous aromatic compounds [2]. Good news is that the *Prestige*'s fuel is hardly water-soluble and this would reduce its final impact on the ecosystem.

When oils enter the environment a plethora of processes occur. They are collectively known as weathering and include evaporation, dissolution, dispersion, photooxidation and biodegradation [3]. The long-term weathering processes at the sea are dominated by photooxidation [4,5] although the long-term fate of hydrocarbon spills that occur close to the coastline is usually determined by the stranding pattern of the oil as it ashores and how and where it pools in low energy coastal waters [6].

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Studying oil spills requires analytical techniques capable of characterizing the original fuel and its evolution on time. Moreover, since many vital decisions have to be taken on the hours subsequent to the spillage, the analytical procedures should be fast and, if possible, applicable on portable devices.

A wide range of analytical techniques are available to analyze hydrocarbons. They can be divided grossly in specific and non specific [7]. The former are based on measuring specific chemicals and recalcitrant molecules that can be used as reference species (e.g. biomarkers, hopanes, etc.) [8,9]. This is termed oil “fingerprinting” and gas chromatography–mass spectrometry (GC–MS) has been applied typically for this purpose (see Ref. [7] for a review). Main drawbacks are that it is expensive, time-consuming, labor-intensive, needs skillful analysts and it is not suited to field measurements.

Non-specific techniques are fast, inexpensive, simple to use and can be deployed on the contaminated areas thanks to portable equipments. In general they do not provide information on individual components nor can distinguish between highly similar products, but they do determine an overall sample profile and identify groups of functional groups/compounds. They include spectroscopic techniques like FTIR, UV and fluorescence. Two previous papers [10,11] demonstrated that attenuated total reflectance (ATR) mid-IR spectrometry is a reliable and simple-to-apply methodology to monitor the *Prestige*'s oil weathering and differentiate it from other products. Multivariate studies were carried out on the spectra although a fine chemical interpretation of the abstract factors was difficult mainly because of the high complexity of the mid-IR spectral profiles ($1600\text{--}400\text{ cm}^{-1}$). On the other hand, Kister and co-workers analyzed complex mixtures of asphalts and monitored their weathering using a reduced set of simple band ratios instead of the full spectra [12–15].

In this paper a new, fast, simple to use, cheap and reliable analytical tool is presented to evaluate the origin of spilled hydrocarbons. It is based on measuring their ATR mid-IR spectra and analysing some spectral ratios by multivariate pattern recognition techniques (namely, principal components analysis, cluster analysis, potential curves and Kohonen neural networks). To the best of our knowledge, this is the first time spectral indexes are considered in a multivariate way to ascertain hydrocarbon pollution and to monitor weathering of oil slicks.

2. Experimental

2.1. Apparatus and reagents

A 16PC Perkin-Elmer mid-IR spectrometer (beamsplitter Ge-KBr, DTGS detector, 4 cm^{-1} nominal resolution, Beer–Norton apodization) with a horizontal, fixed path, ATR device (ZnSe, trapezoidal, 45° , 12 reflections) was used throughout (50 scans, $4000\text{--}600\text{ cm}^{-1}$ measuring range, wavelenght penetration was corrected for using proprietary functions and spectra were baseline corrected). Weekly and monthly quality assurance tests were carried out to verify the S/N ratio, wavenumber accuracy by means of standard polystyrene bands, laser performance and transmittance accuracy [16].

The ATR crystal, glassware and plasticware were thoroughly cleaned. Special attention was placed on cleaning the ZnSe ATR plate as it tends to adsorb materials. First, fuel oil was released using kerosene (aviation jet fuel); second, dichloromethane (Super Purity, Romil, Cambridge, UK) was used to remove kerosene; third, the plate was washed using temperate water with soap, tap water and rinsed with propanone (Panreac, Barcelona, Spain); finally, the crystal was sequentially rinsed with temperate water, clean water (MilliQ-type water, Millipore, Barcelona, Spain) and dried very gently with cotton. This process yielded clean IR backgrounds.

Other devices were: a 5804 Eppendorf centrifuge (Eppendorf, Germany), a Seta Oil Test thermostated centrifuge (Wehingen, Germany), a sand thermostatic bath (Selecta, Spain), and a polyethylene glycol thermostatic bath (2L Precisterm, Selecta, Spain).

2.2. Samples and sample pretreatment

Two main types of samples are considered throughout: (i) controlled spillages of several products in special containers and whose weathering processes were monitored on time, and (ii) samples obtained directly from oil slicks beached at the shoreline, they will be referred to as “beaches”.

Four crude oils (Maya, Ashtart, Brent and Sahara Blend), a “Marine Fuel Oil” (briefly IFO) distributed by the Spanish Government to the scientific community as “similar” to the *Prestige*'s oil, and the original fuel oil from the *Prestige* tanker were studied. The Maya crude oil is very heavy, Ashtart is intermediate, and Brent and Sahara Blend are very light crude oils. The *Prestige*'s and IFO fuel oils are heavy residues of the crude oil distillation processes. In addition, 45 samples were taken at several beaches located along the province of A Coruña on different sampling seasons (2002–2005) to ascertain if they came from the *Prestige* tanker and to seek out if the weathering patterns followed those observed at the laboratory (see Fig. 1 and Table 1 for more details). Each “type of sample” (i.e. “controlled spillage” or “beach”) required differentiated sample pretreatments:

- (i) Around 500 mL of each oil were released on metallic containers containing sea water and weathered under atmospheric conditions. Continuous shaking was performed using air pumps (more details about controlled spillages can be found elsewhere [10,11]) and aliquots were sampled at preset intervals, less spaced during the initial days than during the final ones [17]. The organic phase was transferred to 50 mL Pyrex centrifuge tubes where approximately 1 g of anhydrous sodium sulphate (Merck, 99.0%, Damstard, Germany) was added, and centrifuged at 3000 rpm during 30 min. Whether emulsions appeared, NaCl (Panreac, 99.5%, Barcelona, Spain) and another gram of sodium sulphate were added until they broken down. To avoid excessive handling of stable emulsions, it was found satisfactory to thermostate them at $50\text{--}60^\circ\text{C}$ ($\pm 1^\circ\text{C}$) while centrifuging at 3000 rpm for 30–40 min.
- (ii) Samples from beaches were collected systematically. Care was placed on avoiding debris and sand but this was only

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