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Screening the origin and weathering of oil slicks by attenuated total reflectance mid-IR spectrometry

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Abstract

The combination of attenuated total reflectance–fourier transform mid-infrared spectrometry (ATR–FTMIR) and multivariate pattern recognition is presented as a fast and convenient methodology to ascertain the source product an oil slick comes from and to evaluate the extent of its weathering. Different types of hydrocarbons (including crude oils, several heavy distillates and the Prestige's heavy fuel oil) were spilled on metallic containers designed ad hoc and their fate monitored by ATR–FTMIR. Not only environmental conditions were considered for weathering but artificial IR- and UV-irradiation. Pattern-recognition studies revealed that the different hydrocarbons clustered at different locations on the score plots and that the samples corresponding to each oil became ordered according to the extent of their weathering. Among them, fuel oil samples coming from the recent disaster of the Prestige tanker off the Galician shoreline showed a distinctive behaviour. Comparison of natural-, IR- and UV-weathering of a crude oil showed that IR solar radiation can be important in oil-weathering, in addition to broadly-reported UV degradation.

Keywords: Fuel oil; Crude oil; Prestige; ATR; Mid-IR; Oil spill; Weathering; Galicia

1. Introduction

Although crude oil is worldwide distributed on the earth crust, there are only some few strategic geographical areas, where its accumulation gave rise to huge deposits. There, benefits justify the deployment of special facilities to extract the crude oil. So far, the most important discovered oil deposits are located on a relatively small number of very large oil fields. Only ca. 300 large oil fields contain about three-quarters of the world's discovered oil. The primary concentrations are in the Persian Gulf, North and West of Africa, the North Sea and the Mexican Gulf. Further, only five nations out of ca. 990 oil-producing ones contain around two-thirds of current, known oil reserves. Noteworthy, main consumers are in developed (and developing) countries, where most refineries are sited [1]. Transport of crude oil and its distillates is, therefore, a strategic and main economic issue. Several general routes exist for oil tankers and super-tankers crossing the oceans, being the so-called "Galician International Corridor for Hazardous Goods" among the most important ones. It directs all tankers carrying oil from the Persian Gulf, Africa and (partly) the Mediterranean to Northern Europe throughout the Fisterra Cap (Galicia, NW of Spain), only 25 miles off the Galician shoreline.

As recent Erika's and Prestige–Nassau's accidents demonstrated, large oil spill accidents and their inherent pollution are an international affaire, since huge areas will be affected. Some data will reveal how serious the situation is on the Galician International Corridor. Out of the 10 most important tanker accidents occurred in the world in the last years, up to seven occurred along the maritime triangle depicted by Fisterra (Galicia, NW of Spain)–Bretagne (W of France)–North Sea (UK), namely Urquiola (1976, A Coruña, Galicia), Aegean Sea (1992, A Coruña, Galicia), collision amongst Mexican tanker Teoatl and Bahamas-registered carrier Bona

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Fulmar (1977, UK), Braer (1993, Shetland Islands, UK), Sea Empress (1996, UK), Erika (1999, Bretagne) and now, Prestige (2002, Galicia). Not to mention other accidents also along the Galician coast: Polycommander (1970), Andros Patria (1978) and ships containing chemicals as Cason (1987).

Main sea routes for tankers are of huge environmental concern because although it is true that ship accidents occur (due to as many reasons as incompetence, bad weather and heavy sea, lack of staff training, shipping activities, etc.), many spills are deriverately made to release ballast, cleanup of the cargo deposits and so on. This causes an almost continuous presence of oil slicks and oil lumps on the sea, as well as water in oil emulsion lumps and tar balls reaching the coast and chronically damaging the environment and the food chain (see, Peña et al. [2] for a similar problem on the Canary Islands). Following, there is a real need for fast and reliable analytical techniques to easily evaluate, monitor and control such pollution episodes as well as to follow their remediation.

There are well-established analytical methods and protocols to determine specific chemicals, their ratios, the persistence of several species used as reference values (e.g., study of the prystane–fytane ratio; biomarkers; hopanes), etc. [3–6]. Almost all of them rely on gas chromatography and mass spectrometry, being their main disadvantage that this hyphenated technique is expensive, quite slow, labour-consuming and not too suited to field measurements. On the contrary, general-purpose analytical techniques, as mid-infrared (IR) spectrometry, are fast, inexpensive and can be deployed on the contaminated area thanks to recent portable equipments (see, e.g., www.spectroscopy.co.uk/ftir, for several examples). Although IR spectroscopy will seldom be of use whenever the fate of a particular chemical has to be monitored or when a substance has to be quantified (studies typically associated to chromatography), it is so fast, well-established, robust and stable that it can be used as a screening method before applying more fine techniques. Furthermore, chemometric tools can extract so many information that IR methodologies can be of real use in many complex situations. Thus, IR spectrometry can well be employed as a "first analytical weapon" on the battlefield against hydrocarbon pollution, and it is a reliable analytical aid to decision-making during the initial (critical) moments of the spillage.

Despite these advantages, IR spectroscopy has so far scarcely been employed (relevant works will be referred to in the next sections), and so, the main aim of this work is to show that attenuated total reflectance–fourier transform mid-IR spectrometry (ATR–FTMIR) is a very simple, fast and useful analytical tool to evaluate the origin of an oil slick, sampled either offshore and/or the shoreline. Further, it will be employed to monitor the weathering processes undergone by several laboratory-controlled oil spillages under natural conditions, IR- and UV-irradiation. Due to the complexity of the spectra, chemometric techniques will be employed to ascertain main patterns on the data sets and differentiate among different hydrocarbons.

2. Experimental

2.1. Apparatus

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 interferograms were averaged to obtain the final spectrum, 4000–600 cm^{-1} measuring range, a function was applied to correct for wavelength penetration 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 [7,8], laser characteristics and transmitance accuracy [9], among others.

The ATR crystal, glassware and plasticware were thoroughly cleaned. First, fuel was released using kerosene (aviation jet fuel); second, dichloromethane (Super Purity, Romil, Cambridge, UK) was used to cleanup kerosene; third, the plate was washed using temperate water with soak, 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. It was verified that this process yielded IR backgrounds without signals of organic compounds. Note that cleaning a ZnSe ATR plate is not trivial as it has a real trend to adsorb materials [10].

Other devices were: a 5804 Eppendorf centrifuge (Eppendorf, Germany), a polyethylene glycol thermostatic bath (2 L Precisterm, Selecta, Spain). A 250 W Tob8 IR lamp (Osram, Slovakia) and a VL 6LC UV lamp (Vilber Lourmat, France), were used to induce fuel-weathering, the latter operating at 254 nm, where the C=C bonds and aromatic structures absorb UV-radiation strongly.

2.2. Samples and sample pretreatment

Different types of hydrocarbons were characterised by ATR–FTMIR and weathered. They were selected to model those products more likely to be spilled along the coast of A Coruña (NW Spain). The industrial activities in this area explain why several products were considered here. No doubt that this database has to be updated from time to time with more crude oils and some other refined products, although this is a common issue for any identification/monitoring scheme of oils spills: the best (most useful) database should be as comprehensive as possible.

Used crankcase oil, fuel oil for domestic calefaction (score 1, AFNOR scale), fuel oil from the recent environmental disaster of the Prestige tanker (score 2, AFNOR scale or score 6, English scale or M-100, Russian scale), automotive gasoil and six different crude oils (Ekofisk, Flotta, Syrian, Sharara, Duc and Maya) were considered. The Maya crude oil is very heavy, whereas Ekofisk and Flotta are very light, the others have intermediate behaviours.