

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.

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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 pristane–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, $4000\text{--}600\text{ cm}^{-1}$ 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 transmittance 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.

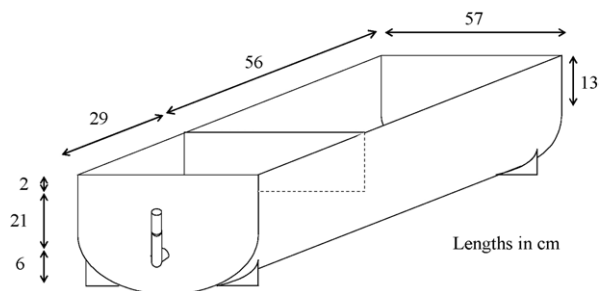


Fig. 1. Metallic containers prepared to perform controlled spillages. The oil is spilled on the large compartment, as the lower one is used to agitate and avoid overflow.

All products were spilled (500 mL) on a two-compartment special metallic container (see Fig. 1) filled with seawater (50–60 L) and weathered under atmospheric conditions during, at least, 2 months. The smaller compartment was used to agitate, make works and avoid overflow, it did not contain oil slicks. Because of a limited amount of space and resources (we only had three containers), not all products were simultaneously spilled, and therefore, atmospheric conditions and air and water temperatures were registered for each aliquot being sampled. Manual shaking (3 min, once a day) was performed on the containers and one aliquot was sampled at preset intervals (the same for all products), less spaced during the initial days than during the final periods, as suggested [11]. Briefly, samples were taken after 2, 8 h and 1, 2, 3, 4, 7, 8, 10, 14, 18, 22, 28 and 30 days. Although sampling was scheduled to be at the same time periods for all products (and it was maintained as far as possible), their different behaviour strongly determined the final number of samples of each product (for instance, crankcase oil was sampled after 56 days and the Prestige's fuel was sampled 63 and 85 days after being spilled, because of their very slow evolution). Samples were included in the statistical studies only when their spectra were different from their previous counterparts (determined by visual observation). In total, 114 samples were included in this study: 9 from Flotta oil (rainy weather, 10–15 °C), 12 from Maya oil (sunny, 22–27 °C, and rainy, 10–15 °C, periods), 6 from Ekofisk oil (sunny, 22–27 °C, an accident impeded us to get more samples), 13 from Duc oil (sunny, 22–27 °C, and rainy, 10–15 °C, periods), 12 from gasoil (windy, rainy and cloudy, 16–18 °C), 13 from Sharara oil (windy, rainy and cloudy, 16–18 °C), 12 from calefaction fuel oil (windy and cloudy, 16–18 °C, and rainy, 12–18 °C, periods), 13 from Prestige fuel (sunny, 27–31 °C, and cloudy and rainy, 12–18 °C, periods), 12 from Syrian oil (sunny, 27–31 °C, and cloudy and rainy, 12–18 °C, periods) and 12 from crankcase oil (windy and rainy, 11–18 °C).

In addition, fuel oil samples from the Prestige wreckage, were taken on different beaches located along the province of A Coruña. Besides, weathering studies were made on a medium-volatile crude oil (Amna) using IR and UV-radiation in order to simulate different ageing processes.

Samples taken along the coastline required some pre-treatment before their IR measurement as seawater, debris and sand cannot be fully avoided when sampling. Following ASTM D3326 [12], sample aliquots (2–4 mL, withdrawn either with disposable graduated plastic Pasteur pipettes or 10-mL cylinders, for very viscous samples) are transferred to Pyrex centrifuge tubes (50 mL capacity), where ca. 10 mL of dichloromethane and 1 g of anhydrous sodium sulphate (Merck, 99.0%, Damstard, Germany) were added. The mixture is placed on a thermostatic bath at 60 °C until the two phases separate (2 h minimum or up to getting a good separation). The organic phase is transferred to another tube, where sodium sulphate is added again and centrifuged at 3500 rpm during 30 min. Whether stable emulsions are seen, NaCl (Panreac, 99.5%, Barcelona, Spain) and another gram of sodium sulphate are added until the emulsion is broken. Samples yielding stable emulsions were transferred to PPT centrifuge tubes and centrifuged at 9000 rpm. Samples weathered in the metallic containers did not require elimination of debris or sand but the final treatment (water separation). As the Amna crude oil had been previously dissipated, the IR- and UV-weathered samples did not suffer any pre-treatment. All ATR-FTMIR spectra were baseline corrected, digitized (1 datum each 3 cm⁻¹) and exported to ASCII files, and then, introduced on Matlab ©. Statistical studies were made with in-house and built-in routines.

3. Results and discussion

Factor analysis (principal-component analysis, PCA; with and without Varimax rotation) and cluster analysis were carried out to extract the main patterns latent on the datasets. Different spectral regions were studied, namely 1850–600, 1851–1547 and 924–650 cm⁻¹, along with different data scaling (mean centring, autoscaling, scaling 0–1 and some of their combinations). To simplify the study, the spectral dataset was divided in two “epochs”: samples belonging to the first fortnight and samples corresponding to the final weathering period. The results summarised here correspond to the overall 1850–600 cm⁻¹ region, scaled from 0 to 1; results from other spectral regions will be referred to only when new relevant information was obtained. Neither dendrograms nor Varimax rotation added insights and they will not be presented here.

Preliminar studies (not detailed in this work) considered edible oils because at the ria of A Coruña (*ria* is a geological term, similar to the *fjörds*) there are shellfish cultivars, which, sometimes, suffer pollution by superficial oil slicks. This is a sensitive area since it can be affected by nearby shipping activities and/or an edible-oil refinery. As expected, the spectra of edible oils became so different from petroleum-related products that they can be immediately identified, regardless of their degree of weathering. Although expected, this evidence is relevant to immediately and definitely elucidate the main cause of the oil slick. All the following studies will, accordingly, focus on the petroleum-related products.

3.1. Natural weathering, first fortnight

In total, 64 samples were considered for this initial weathering period: 4 from Flotta, 7 from Maya, 4 from Ekofisk, 8 from Duc, 7 from gasoil, 8 from Sharara, 7 from calefaction fuel, 5 from Prestige fuel, 6 from Syrian and 8 from crankcase oils.

Three principal components (PC) explained up to 90.8% of the initial variance (PC1, 66.5%; PC2, 16.2%; PC3, 8.1%) and they revealed interesting patterns as the PC1–PC2–PC3 subspace score plot separates the different types of hydrocarbons (see Fig. 2A). Clearly, PC1 and PC2 discriminate fuel samples (Fig. 2B). Calefaction (“domestic”) fuel gets separated along PC1, whereas the Prestige’s fuel oil is clearly differentiated by PC2. Note also that unknown samples taken at different beaches cluster around a central core (samples of the Prestige’s fuel oil weathered on our facilities), pointing towards a common origin. Their scatter has to be attributed, mainly, to different weathering stages (samples were taken on different beaches along different days, as the oil slicks or lumps arrived at the intertidal areas). Noteworthy, some samples do not correspond to the immediate days after the wreckage but to oil slicks beaching several months after the main accident (once the bow and the stern of the Prestige sunk they continued releasing fuel) and despite this difficulty, the ATR–FTMIR–PCA methodology demonstrated their common origin. PC1 is also useful to differentiate two “opposite” types of crude oils, Maya and Sharara plus Syrian. The former is quite heavy (only 0–20% losses by evaporation), whereas the others are light (40–50% losses by evaporation).

The PC1–PC2–PC3 score subspace (Fig. 2A) leads to different clusters for automotive gasoil, crankcase oil and the Sharara and Syrian crude oils. Nevertheless the Duc and Ekofisk crude oils cannot be differentiated. They are similar (>50% losses by evaporation) and suffered a quite sunny and hot weather, which, likely, caused large evaporation rates and a very similar weathering pattern.

Interestingly, when each product is considered alone, its samples are ordered according to the extent of its weathering or “age” (see arrows on Fig. 2B). The general pattern is that older samples (more-weathered) are characterised by lower PC1- and PC2-scores. Samples belonging to the Prestige’s fuel oil do not show any trend, as it degrades very slowly (as expected).

Study of the main loadings will clarify these trends. PC1-loadings describe the calefaction fuel oil, although participation from the Prestige and from the Maya heavy crude oil spectra cannot be disregarded (see Fig. 3A). Accordingly, PC1 roughly differentiates between heavy (calefaction fuel oil, Maya crude oil, and to some extent, Prestige’s fuel oil) and light products (PC1-scores < -0.1 discriminate heavy products). Its chemical interpretation can be: the 1600 cm⁻¹ region is mainly related to the C=C stretching vibration (either in linear and aromatic structures), whereas the 1460 and 1373 cm⁻¹ bands are typically associated to the symmetric and asymmetric CH bending (CH₃ and/or CH₂ structures)

[13]. The 950–650 cm⁻¹ region is more complicated because it constitutes the typical IR fingerprint region and because the products we are dealing with are very complex, and so, there is not a unique species nor a unique type of substituted aromatic rings. Typically, these bands are attributed to the CH out-of-the-plane bending vibration in benzene rings, although CH out-of-plane bending vibration in thiophene rings cannot be disregarded (see next section for more details). Interpretation of the high loading at 780 cm⁻¹, is not straightforward as it can appear with different benzene substitutions; nevertheless, it is mostly assigned to mono-substituted; 1,3 di-substituted and/or 1,2,3 tri-substituted aromatic rings [14,15].

The most relevant PC2-loadings appeared at 1619, 1028, 866 cm⁻¹ and (opposite sign) 1460 and 1373 cm⁻¹ (Fig. 3B). The latter (also relevant in PC1) characterise, again, CH₃ and/or CH₂ groups, whilst the former three seem more related to aromatic/olefinic structures, and noteworthy, they increase as product-weathering progress. The broad band at 1619 cm⁻¹ can be related to C=C stretching vibrations (olefins and/or aromatic rings), whereas the 866 cm⁻¹ peak points to the CH out-of-the-plane bending on 1,3,5 tri-substituted rings [13,16]. The loading at 1028 cm⁻¹ has broadly been attributed to the S=O stretching in sulphoxide-type structures [15,17,18], which increases with hydrocarbon ageing (as S enters the structures), although it could also correspond to the C–O–C bending vibration. These findings agree with previous reports about fuel oil-weathering [17,19].

PC3 discriminates basically samples from the Prestige’s fuel oil, see Fig. 3B. Relevant loadings are: 1643 cm⁻¹ is a common wavenumber either for the C–N stretching (amines or amides, C=N) and esters or ketones [13,14]. The 1457 and 1373 cm⁻¹ bands seem related to the CH bending vibration in CH₃ and/or CH₂ groups in aliphatic chains (as for PC2). Noticeably, the 782, 734 and 695 cm⁻¹ loadings have opposite signs (their absorbances decrease with ageing) to the previous bands as they are related to the CH out-of-the-plane bending vibration in mono-substituted, 1,3 di-substituted and/or 1,2,3 tri-substituted rings. Also interesting is that the 695 cm⁻¹ peak can be attributed to the C–S stretching vibration, pointing, again towards the photo-oxidation of the sulfur compounds within the hydrocarbons to more oxidised forms as sulfoxides, sulfones, sulfonates and/or sulfates, as explained elsewhere [19].

Studies using other IR regions were carried out. They confirmed the previous findings, and sometimes, gave additional insights. As an example, a PCA study on the 1850–1547 cm⁻¹ region discriminated nicely the products in the PC1–PC2 subspace (see Fig. 2C).

3.2. Natural weathering, final weathering period

In total, 50 samples were included in the final weathering period: 5 from Flotta, 5 from Maya, 2 from Ekofisk (an accident caused loss of the oil slick), 5 from Duc, 5 from gasoil, 5 from Sharara, 5 from calefaction fuel, 8 from Prestige fuel,

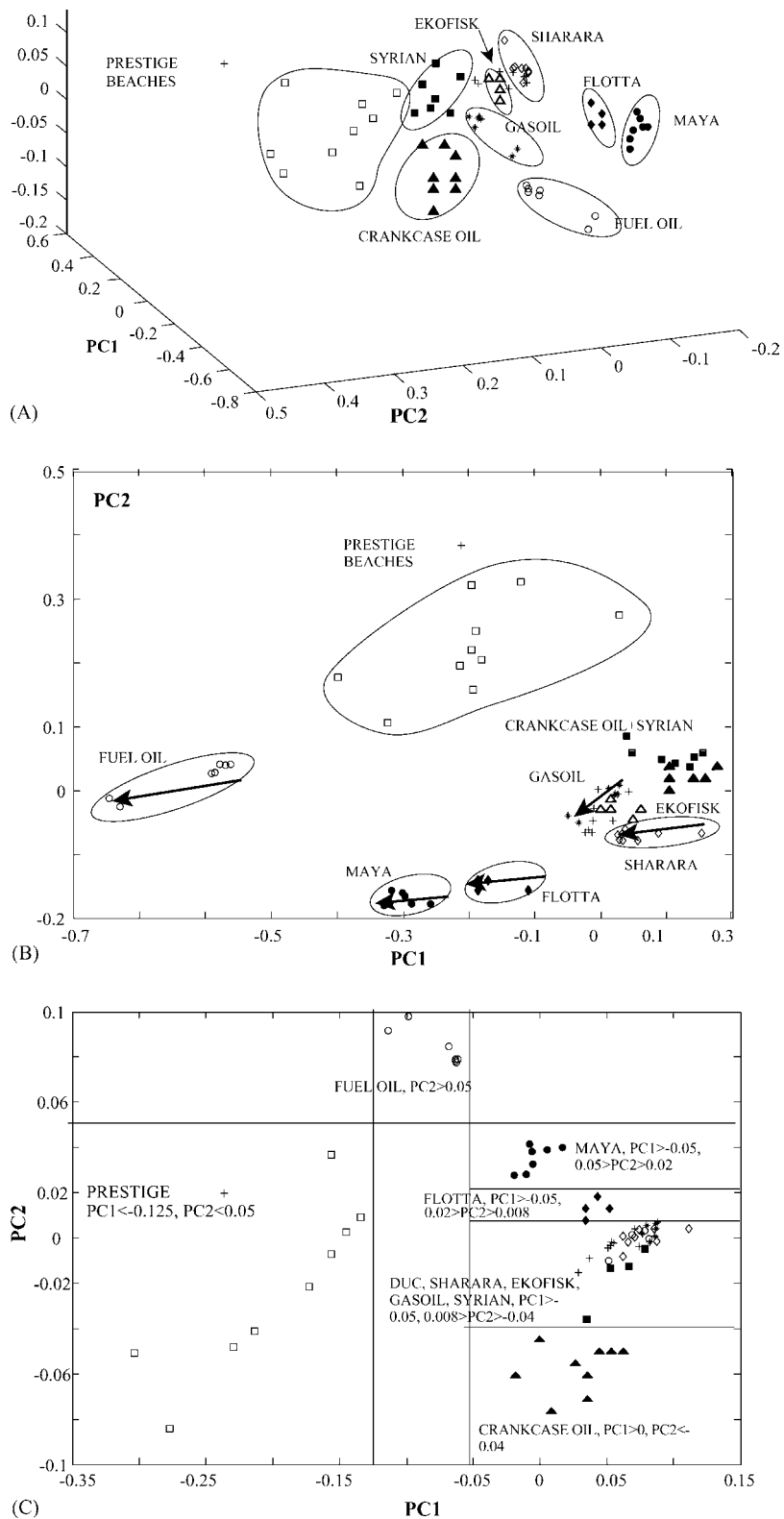


Fig. 2. (A) PC1–PC2–PC3 and (B) PC1–PC2 scores subspaces differentiating all products. Weathering under natural conditions, first fortnight, $1850\text{--}600\text{ cm}^{-1}$ (the arrows point the evolution of the products from less-weathered to more-weathered, see text for details). (C) The same study but on the $1850\text{--}1547\text{ cm}^{-1}$ region.

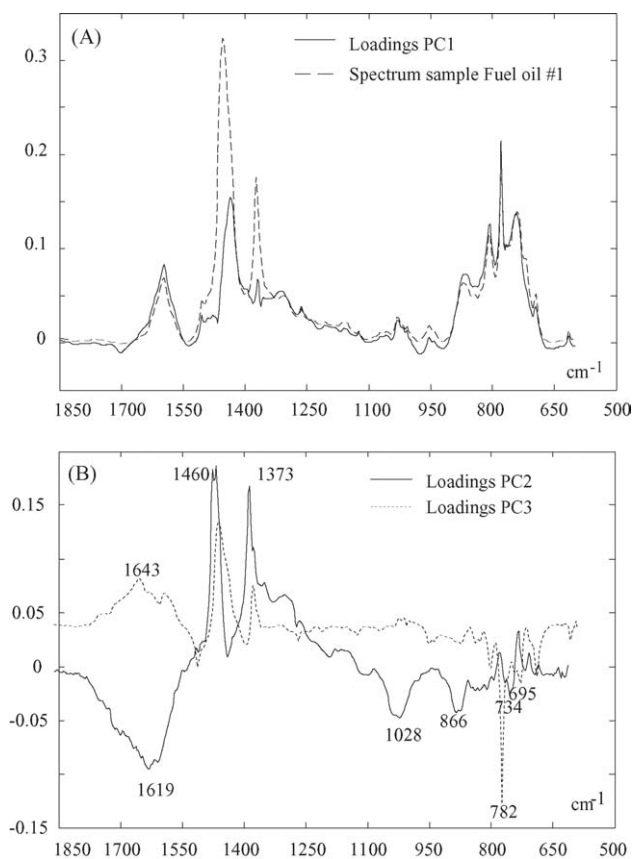


Fig. 3. Loadings associated to the first PCs, natural conditions, first fortnight, 1850–600 cm^{-1} : (A) 1st PC (loadings and an overimposed original spectrum) and (B) 2nd and 3rd PCs.

6 from Syrian and 4 from crankcase oils. The most weathered samples (taken from the containers from the 15th day onwards, up to approximately the 60th day plus the 63th and 85th ones for Prestige's fuel and the 85th day for Syrian) were included in this subset along with samples taken on beaches and rocks several months after the Prestige's wreck.

Three PCs (81% of the variance) allowed for a good separation between the products (see Fig. 4), despite the gasoil and Sharara crude oil samples partially overlap. PC1 (48.7% of the variance) differentiates between samples with an intense and well-defined peak at 1595–1600 cm^{-1} (plus a complex structure on the 920–700 cm^{-1} region, e.g., calefaction fuel, Prestige's samples and the two most weathered Duc samples) and those without it (nor such spectral characteristics, e.g., crankcase oil and Syrian crude oil), see Fig. 5A. Its chemical interpretation is similar to that of the previous section, suggesting that the main weathering patterns do not changed highly. The most remarkable differences are the lower importance of the 780 cm^{-1} peak (pointing that once the most volatile aromatic compounds are gone, the band does not discriminate the products) and that the sulphoxides (1028 cm^{-1}) show higher loadings.

PC2 (25.4% of the variance) is characterised by the carbonyl peak ($\text{C}=\text{O}$, 1703 cm^{-1}) and differentiates the

calefaction fuel oil from any other product (see Fig. 5B), because this peak is not present on it. Recall that increase of this peak has typically been associated to the photo-oxidative processes [13,15,16,20–22]. This PC is clearly different from that extracted for the first fortnight (Fig. 3B, PC2), where the $\text{C}=\text{O}$ peak had not appeared. Opposed to the calefaction fuel samples, all the other products, particularly the Prestige's samples showed intense and well-defined peaks at 1703 cm^{-1} (two Duc samples, extensively weathered after a dry and sunny period, reported the highest increase). The loading of the 780 cm^{-1} peak is only associated to calefaction fuel oil samples and it decreases with weathering. Despite the most typical interpretation for the 780 cm^{-1} peak is the CH out-of-plane vibration (1,3- and/or 1,2,3-substituted benzene rings), the facts that this peak is only clearly resolved for calefaction fuel samples, that it decreases with ageing and that its loadings oppose to the 1028 and 1703 cm^{-1} ones, suggest that it could also be related to thiophene rings. Heavy distillates have only trace amounts of mercaptans and light molecules containing sulfur, and therefore, this means that sulfur would be mainly present in the form of thiophene rings. The exact band-structure relationship is far from straightforward but there is enough evidence that thiophene rings give strong bands on the same region as typical CH out-of-plane benzene-like structures. It was demonstrated [23–25] that the ca. 795 cm^{-1} peak corresponded to out-of-plane deformation of CH at beta-positions of thiophene rings. This finding is in good agreement with the fact that thiophenes evolve towards more oxidised forms, sulfoxides and/or sulfones, which make the 1028 cm^{-1} peak to increase with ageing. Even if the 780 cm^{-1} peak were partially due to substituted benzenes, its diminution with time would be consistent with the fact that benzene structures evolve towards highly substituted/polymerised structures under photo-oxidation [6,17,26].

PC3 (12.8% of the variance) is defined by several peaks attributed typically to the carbonyl group ($\text{C}=\text{O}$ stretching vibration, 1703 cm^{-1} and the combination of $\text{C}-\text{O}$ stretching plus $\text{O}-\text{H}$ bending, 1250 cm^{-1}), aliphatic groups (CH_3 and/or CH_2 , 1450 and 1375 cm^{-1}) and, slightly, the $\text{C}=\text{C}$ groups (1604 cm^{-1}), with opposite sign (see, Fig. 5C). Further explanation of this PC is not easy.

For each particular product, older (more extensively weathered) samples located at higher PC1- and PC2-scores (Fig. 4). Prestige's fuel oil, calefaction fuel oil and Maya crude oil did not follow this trend because they are heavy and their ageing processes are much slower. Although the Prestige's fuel oil was monitored for 3 months all its samples formed a random group.

3.3. Weathering of a crude oil

An interesting issue when studying hydrocarbon weathering is whether the natural processes can be simulated (at least, to some extent) into the laboratory, and thus, if the fate an oil would suffer under natural weathering can be advanced in

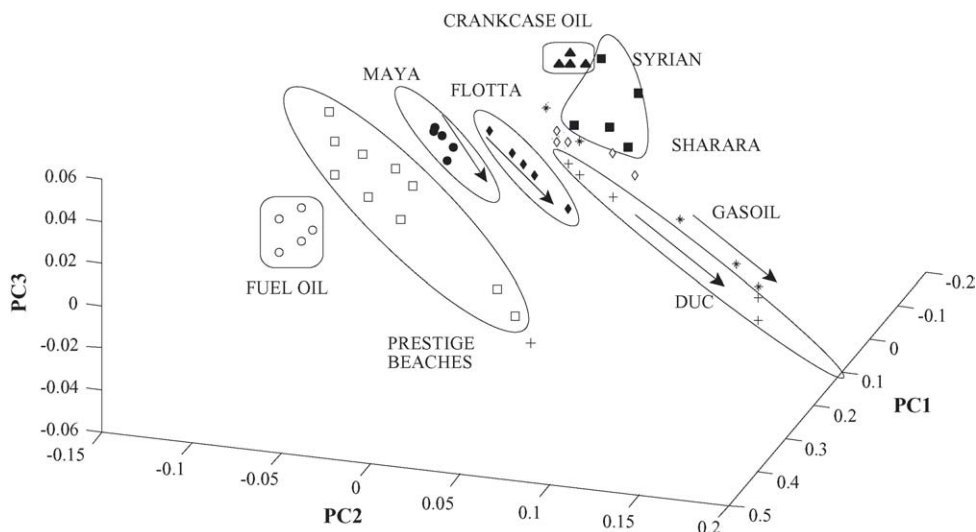


Fig. 4. PC1–PC2–PC3 scores subspace discriminating all products (weathering under natural conditions, more-weathered samples, $1850\text{--}600\text{ cm}^{-1}$). The arrows point the evolution of the products from less-weathered to more-weathered (see text for details).

order to draw useful information for decision-making, when the spillage is being attacked. ASTM D3326 [12] gives a convenient alternative to hydrocarbon ageing, not difficult to implement and whose concept has been broadly applied. The study presented here considers a typical crude oil instead of a heavy distillate because preliminary assays made with the Prestige's fuel oil revealed highly complex (this fuel is currently being studied in our laboratory). Four aliquots of an Amna crude oil (density, 36.8 API degrees) were placed on a special metallic container and three Petri dishes (glass, 10 cm diameter), respectively. The crude oil on the metallic device suffered natural weathering, whilst each Petri dish was irradiated with IR, UV and IR + UV-radiation by separate. The IR and UV lamps were set 20 cm above the Petri dishes. Samples were withdrawn at 1, 4, 8, 24 and 32 h; then, on the 3rd, 5th, 8th, 10th, 12th, 15th, 17th, 19th, 23rd and 29th days (at the same hour). Different spectral regions and scaling modes were studied. All the experimental conditions were as those on the experimental section.

Natural weathering of the Amna oil confirmed most of the findings discussed previously. A PCA of the overall spectra yielded a sample distribution on the scores subspace not simple to explain. The samples do not follow a simple trend (Fig. 6A), not only because minor analytical errors can occur but (mainly) because natural weathering is so complex that little can be predicted, as discussed elsewhere [11]. Recall that solar irradiation, winds, temperatures, rainfalls, etc. vary during the day, night, from day to day, etc., and so, natural weathering is far from a steady process. Nevertheless some trends are relatively clear, when the loadings are analysed.

PC1-loadings (99.89% of the initial variance) resemble the average spectra, and therefore, it orders the samples according to the intensity of the spectral bands. PC2-loadings are mainly defined by the 1700, 725 and

716 cm^{-1} bands (Fig. 6B). The first band corresponds to the typical photo-oxidative formation of C=O (acids, ketones, esters and ethers). Here, it is thought that it corresponds to ketones (not conjugated with aromatic rings), esters or RCOOAr structures [13]. Carboxylic acids and ethers are, in principle, discarded because no broad bands appeared on the $1300\text{--}1000\text{ cm}^{-1}$ region. The 725 and 716 cm^{-1} bands might be related to 1,3-, 1,2,3- or 1,3,5-benzene substitutions. Although the 725 cm^{-1} peak may also be related to typical $(\text{CH}_2)_n$ rocketing, the facts that (i) it increases slightly with ageing, (ii) its loading has the same sign as the 1700 cm^{-1} peak and (iii) other peaks associated to typical CH stretching vibrations ($1450, 1375\text{ cm}^{-1}$) do not participate in this factor, suggest that its variation is, essentially, caused by changes on the aromatic structures. The more intense these bands, the older the product.

UV-irradiation led to somewhat surprising results because the rate of crude oil ageing was very slow, as the absence of substantial changes on the spectral profile evidenced (Fig. 7A). This can be explained either because the UV lamp was not intense enough (compared to other studies) or because the chemical processes UV-radiation causes are kinetically slow. Note that although a low-power UV lamp was used it emitted at 254 nm, where double bonds absorb strongly. Despite different authors reported UV lamps of different power their conclusions agreed (e.g., [13,17,19]).

Only the out-of-the-plane CH bending region ($800\text{--}650\text{ cm}^{-1}$) varied clearly during the Amna UV-weathering. Important enough, UV light alone do not caused the C=O band to appear, which agree with previous results showing that UV-irradiation do not affect alkanes [19]. Besides, it seems that not even evaporation was too relevant, since none of the typical bands associated to linear aliphatic chains varied. The multivariate study of the spectra showed that two

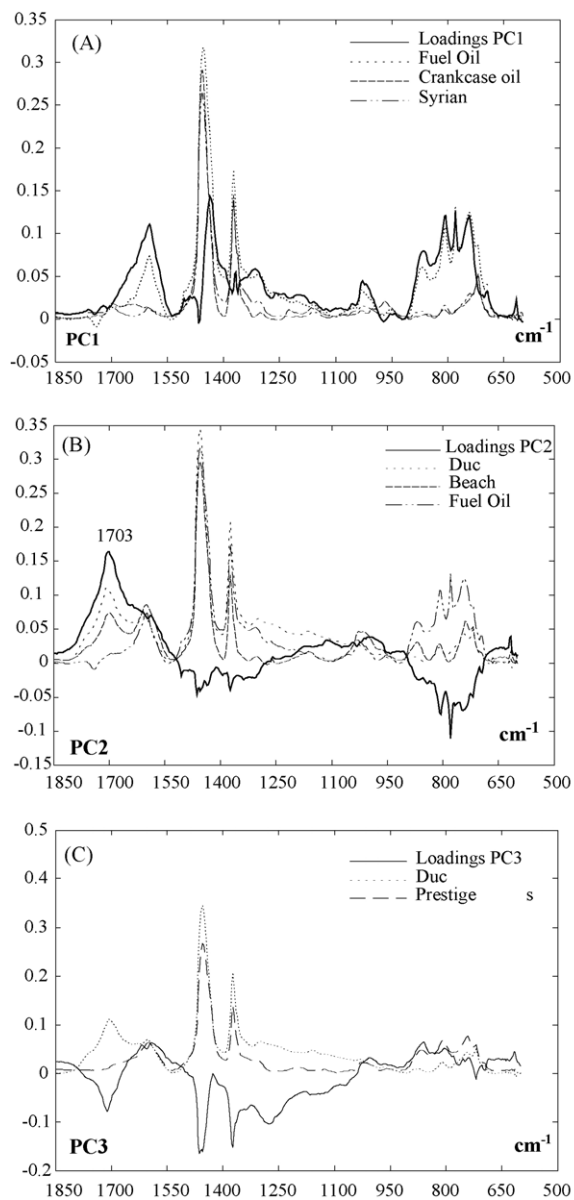


Fig. 5. Loadings associated to the first PCs (overimposed to several original spectra) natural conditions, more-weathered samples, 1850–600 cm^{-1} : (A) 1st PC; (B) 2nd PC; (C) 3rd PC.

PCs explained most variance (99.96%). Sequential samples are ordered towards higher PC1- and PC2-scores (Fig. 7B), being the PC1, again the average spectra but without any participation of the C=O band. PC2 does not match the behaviour of other weathering modes presented in previous sections (arrows without peaks on Fig. 7C) and only the 716 and 810 cm^{-1} bands suggest that 1,3-di-substituted rings might be being formed.

Opposed to UV light, IR radiation caused the fuel to evolve quite fast (Fig. 8A). PC1 is defined by bands whose intensities increase with time: 1703, 1601, 725 and 716 cm^{-1} ; they correspond to the C=O (carbonyl) and C=C stretching and the aromatic CH (out-of-the-plane) bending vibrations, re-

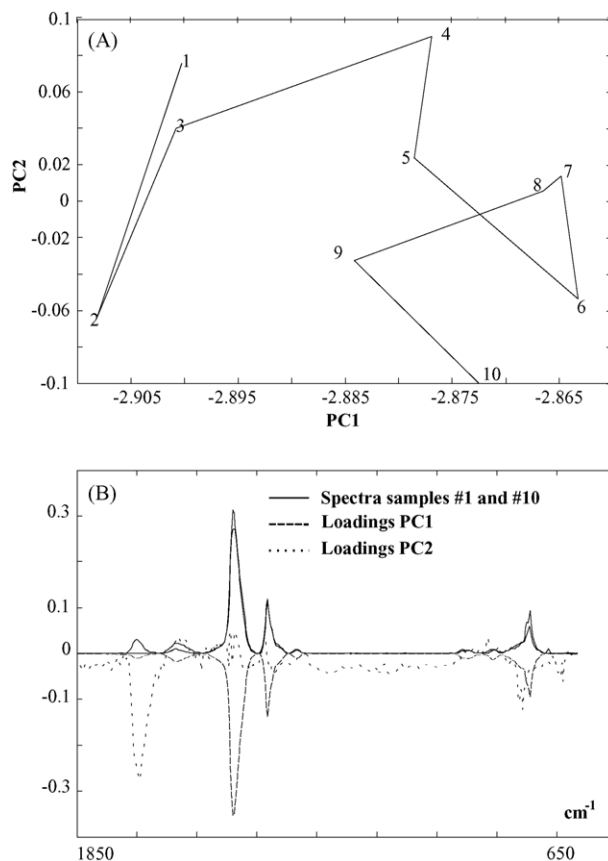


Fig. 6. Natural weathering of Amna crude oil: (A) scores subspace depicting sample evolution (1 = original sample, 10 = last sample); (B) PC1-loadings and two extreme samples.

spectively. The increase on the 810, 725 and 716 cm^{-1} bands points to the increase on 1,3-di-substituted aromatics. PC2 is mainly defined by the 1700 cm^{-1} band (plus a peak around 1769 cm^{-1} , corresponding to the most weathered sample) and the 716 cm^{-1} region (Fig. 8B). The former reveals that Amna weathering by IR radiation undergoes formation of ketones, esters and/or RCOOAr groups [13]. The latter has several interpretations: the typical CH out-of-plane bending, CH_2 rocking or S–C stretching in R–S– CH_3 groups [15,27]. Noteworthy, the intensity of the 716 cm^{-1} band is around twice that of 725 cm^{-1} , more intense than in any other study. This poses the hypothesis that formation of 1,3-di-substituted aromatic benzene rings (716 cm^{-1} band) might be favoured over tri-substituted rings (725 cm^{-1}), when only IR radiation is used.

It can be concluded that IR light caused the Amna crude oil to weather fast and extensively because of a higher evaporation rate (part of the IR radiation is converted to heat) and a more efficient photo-oxidation. This means that IR radiation might had played an important role on the very fast degradation of a heavy crude oil pipeline spill in Bolivia (ca. 4.6 million liters), which occurred in a desertic area. The authors [28] attributed such very fast degradation to a very good

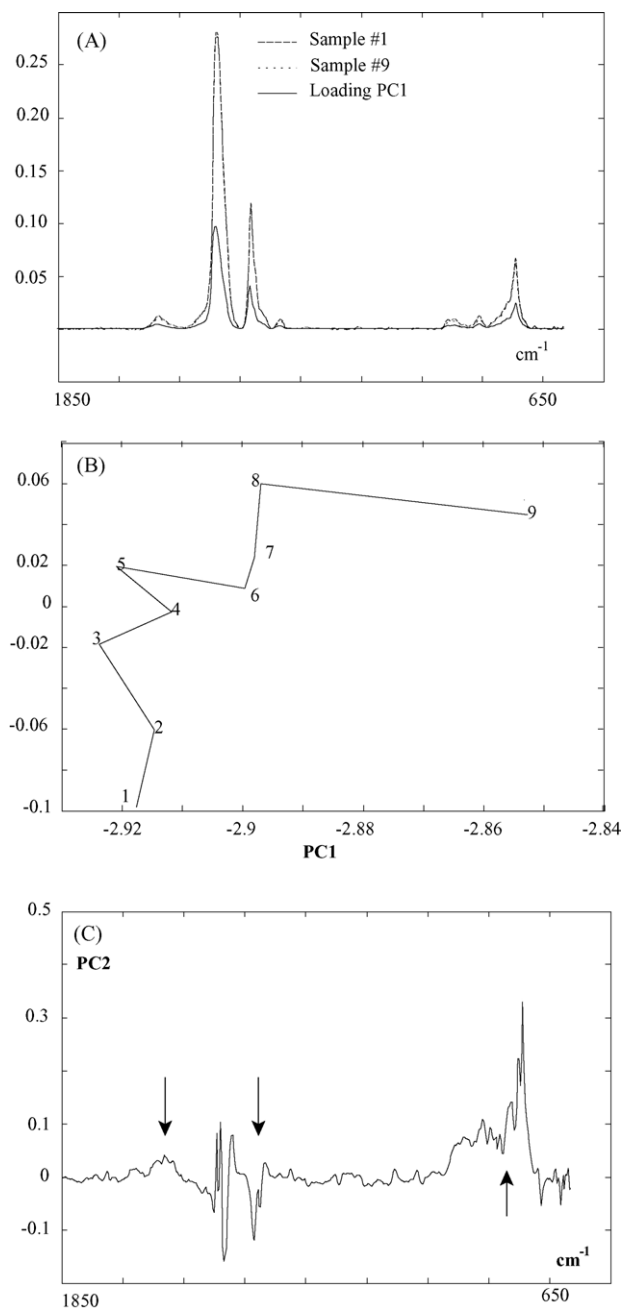


Fig. 7. UV-weathering of Amna crude oil: (A) PC1-loadings and two extreme spectra (the original and last ones) registered during weathering, 1850–600 cm^{-1} ; (B) scores subspace depicting sample evolution (1 = original sample, 9 = last sample); (C) PC2-loadings. The arrows show differences with other weathering modes (see text for details).

mixing of the crude oil with river water (which enhanced solubilization, dispersion and bioavailability), evaporation and UV photo-degradation (IR light was not mentioned). Note also that IR-weathering resembled very well the general patterns the Amna crude oil suffered under natural conditions (but faster).

Simultaneous use of IR and UV-radiations on one Petri dish revealed similar patterns to those observed using each

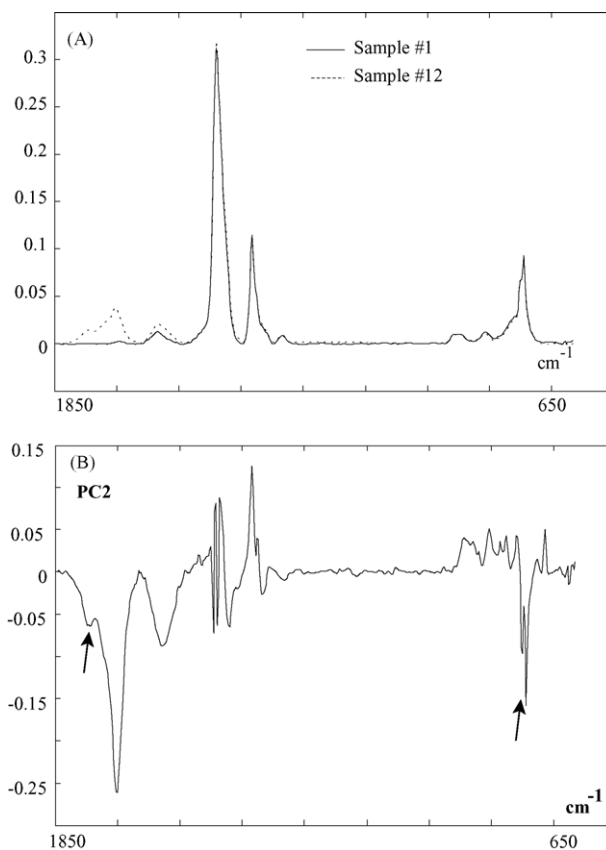


Fig. 8. IR-weathering of Amna crude oil: (A) spectra of two different samples (1 = original sample, 12 = last sample) registered during weathering, 1850–600 cm^{-1} and (B) PC2-loadings showing a typical photo-oxidative pattern.

radiation by separate. The most remarkable spectral characteristics were related to the IR-type weathering.

4. Conclusions

The combination of ATR-FTMIR and principal-component analysis revealed as a useful methodology to monitor the fate of spilled hydrocarbons. It constitutes a convenient methodology (fast, cheap and simple-to-apply) to identify the original source product an oil slick comes from, even when the slick suffered a relatively important weathering. The fact that different products became separated in a three-dimensional factor scores subspace (sometimes even in a two-dimensional one) allowed for the clear elucidation of the origin of oil slicks at the ria of A Coruña and unknown samples taken at different beaches. Besides, chemical interpretation of the loadings of the first principal components revealed weathering patterns in good agreement with current literature. Finally, it was seen that laboratory weathering using IR radiation can be a good tool to predict how a crude oil will evolve under natural conditions and that solar IR-irradiation can play an important role in natural oil-weathering.

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