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Monitoring photooxidation of the Prestige's oil spill by attenuated total reflectance infrared spectroscopy

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Abstract

The recent release of ca. 70,000 tonnes of a heavy fuel oil from the Prestige-Nassau carrier along the Spanish northern coast, mainly along Galicia, was monitored using attenuated total reflectance—mid IR spectrometry. The fuel was characterized and differentiated from 10 products commonly transported along the Galician coast (and their series of weathered samples) using factor analysis. The Prestige's fuel was weathered under natural conditions and under infrared radiation to study its evolution on time. A correlation was established using the 1690–1700 cm^{-1} carbonyl peak, where from it was deduced that IR radiation weathered the product two times faster than natural conditions. The use of 10 weathering indexes was carried out to confirm the main patterns given by factor analysis and to seek out which main functional groups and structures increased or decreased during weathering. It was found that the carbonyl and sulphoxide indexes varied greatly, as well as the total aromaticity and long chains ones. The substitution-related indexes pointed out that highly substituted aromatic structures increased although the total amount of isolated CH groups in aromatic structures reached a plateau.

Keywords: Fuel oil; Prestige; Oil spill; Galicia; Photooxidation; Infrared spectrometry; Attenuated total reflectance

1. Introduction

Petroleum (crude oil) and its distilled products are, undoubtedly, the main source of energy worldwide. Although renewable sources are increasingly gaining importance (mainly electricity from solar and eolic facilities), fossil fuels continue to be a cornerstone in our society.

Crude oil is a complex mixture of thousands of hydrocarbons which are naturally accumulated under very special geological conditions. Despite such deposits exist throughout the overall Earth's crust, it is only some special geographical areas where its accumulation gave huge reservoirs and, so, where it is economically profitable to extract it. As crude oil itself is not useful at all some sort of "refining" (sequential distillations) is needed to separate main families of compounds (e.g. from C_4 to C_{12} to obtain automotive gasolines, and from C_{19} to C_{36} to get diesel fuel).

Considering the common situation, where main consumers and petroleum refineries are in developed (developing) countries, extensive transportation of petroleum by ocean-going tankers is vital. As not only transport but handling is required, there are a large number of environmental risks associated to this good. Besides, as oil-consuming industries and refineries are frequently located in coastal areas, marine and shoreline environments are particularly vulnerable to pollution by petroleum-related products. Unfortunately, coastal areas are polluted also by other industries and increasingly large populations which settle down there. It is a disappointing view that these problems will increase unless severe political and social decisions are taken (accompanied by strict national and international surveillance programs).

There are two important issues which have to be addressed scientifically: to identify the source(s) of a spillage (i.e., to ascertain the parent material and, may be, the facility where it came from) and to determine its fate, either for environmental care and liability cases [1].

Spilled crude oils and related products undergo a variety of weathering processes [2] including evaporation, dissolution,

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dispersion, photochemical oxidation, flushing due to wave energy, emulsification, microbial biodegradation, adsorption to suspended matter and deposition on the seabed [1,3]. The major weathering processes, together with the chemical nature of the oil, determine its fate and degradation rate.

Photooxidation is considered the most important factor involved in hydrocarbons' transformation when they are released into the environment [4]. It is a rapid process which occurs at the surface of the oil slick. Petroleum oils can be oxidized either by sunlight radiation (photooxidation) or by marine microorganisms which utilize them as food source (biooxidation or biodegradation). Both take place at the oil–water interface and produce a large variety of oxidation products which are generally more water soluble than the parent oil [1]. The former oxidation is faster although there are huge differences in the rates at which the different components oxidize. It is worth note that, to some extent, photooxidation and biodegradation are "complementary" since photooxidation is relevant for many chemicals which are not easily degraded by microorganisms, and vice versa [4].

The chemical mechanism includes direct photolysis and the reaction of reactive oxygen species produced by solar radiation and/or humic substances [5–7]. The precise mechanism is not fully well understood but is thought to result in the loss of about 1% of the oil volume per day. The portion of the solar spectrum responsible for photooxidation (eventually, phototoxicity) is, primarily, the ultraviolet region, which is composed of 5% UV-B (280–315 nm) and 95% UV-A (315–400 nm) at the Earth's surface [7]. The main results are an increase on the asphaltenes content, viscosity and density, together with a decrease in the sulphur content.

Photooxidation of an oil slick is not homogeneus and it depends on the climatic conditions. For instance, Tjessem and Aaberg [8] showed that high molecular weight resin/asphaltene fractions of an Ekofisk crude oil were considerably influenced by irradiation, changing both its chemical and physical characteristics. Photooxidation of Blend Arabian Light (BAL) crude oil asphaltenes showed that light exposure increased carbonyl, phenolic, sulfoxide and carboxylic groups, without significant alterations of the hydrocarbon skeletons of polyaromatic and alkyl compounds associated with the asphaltene matrix [9–11]. Lee [7] studied the appearance of oxidized compounds, including aliphatic and aromatic ketones, aldehydes, carboxylic acids, fatty acids, esters, epoxides, sulfoxides, sulfones, phenols, anhydrides, quinines and aliphatic and aromatic alcohols.

In general photooxidation will: (i) increase the amount of the carbonyl group and form carboxylic groups, (ii) oxidize sulphur to thiophenes and, then, thiophenes to sulphoxides, which evolve to sulphones, sulphonates and sulphates [4], and (iii) oxidize the alkyl chains and aromatic rings to quinone structures [11]. It can be affirmed that the highest the solar irradiation, the larger and faster the photodegradation of the parent product. Two good examples are the rapid destruction of a 2.5 μm Kuwait oil slick, in 100 h [7,12] (presumably such destruction was due to a combination of microbial degradation and photooxidation) and the huge degradation of around 4.6 tonnes of a heavy crude oil in the Atacama dessert (Bolivia) [13], showing that IR radiation had also an important role on photooxidation.

Although artificial weathering cannot be identical to the processes the oils undergo on the environment, still their changes will reflect those occurring under natural conditions [14]. In the present work a comparison between the natural evolution and artificial ageing of the Prestige's fuel oil using IR radiation will be presented.

Currently, many scientific efforts are spent on characterising spilled hydrocarbons by chromatographic methods [7,15,16]. Nevertheless, chromatography is slow, expensive, needs cleanup steps and it is hardly portable. On the contrary, mid infrared spectroscopy is fast, cheap, simple to apply, requires limited or not at all sample preparation (specially if attenuated total reflectance, ATR, is employed), and can be portable. IR spectra can yield not only "general" information on the sample but also particular knowledge on chemical species and functional groups (providing some characteristic wavenumber can be monitored) although, of course, overlap of the spectral bands of compound classes can be considerable. Hence, IR spectroscopy has been applied to seek out information related to the general evolution of an oil slick and important conclusions have been derived [11,17]. As an example, a matching criterion was established by ASTM [18].

In this paper a study is presented by which a fast and convenient methodology based on mid-IR spectroscopy (ATR-IR) is used to monitor photooxidation of an oil spill into the marine ecosystem. The case study will center around the fate of Prestige's heavy fuel oil which was released on December 2002 (around 70,000 tonnes). The direct spillage affected the Galician coast (NW Spain) but it spread soon throughout all the North of Spain and, even, beached at Southwest France. Some months after the disaster there were still oil slicks floating around the Gulf of Viscay. The Prestige's oil was a heavy fuel oil (score 2, AFNOR scale or score 6, English scale, or M-100, Russian scale) intended to produce asphalt, coke or be burnt in power stations and furnaces to get electricity and move large vessels. Its viscosity was around 615 and 30,000 cSt (at 50 and 15 °C, respectively) and it was fluid only after heating it (as it was on the tanker while it was being transported).

Some results are given from a principal components analysis (PCA)-based comparison carried out between the natural weathering patterns of several crude oils (Ekofisk, Flotta, Maya, Syrian, Sharara and Duc), refined products (calefaction fuel oil, gasoil, crankcase oil) and the Prestige's oil itself [19].

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 scans, 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, laser characteristics and transmittance accuracy [20,21].

The ATR crystal, glassware and plasticware were thoroughly cleaned. Special attention was payed on cleaning the ZnSe ATR plate as it tends to adsorb materials [22]. 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 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 IR backgrounds without signals of organic compounds.

Other devices were: a 5804 Eppendorf centrifuge (Eppendorf, Germany), a polyethylene glycol thermostatic bath (2L Precisterm, Selecta, Spain), and a 250 W Tob8 IR lamp (Osram, Slovakia) to induce fuel weathering.

2.2. Samples and sample pretreatment

Prestige's fuel oil was studied in three ways:

(i) Around 500 mL of the bulk fuel were released on a special metallic container filled with sea water (50–60 L) and weathered under atmospheric conditions during 3 months. Manual shaking was carried out on the container from time to time and aliquots were sampled at preset intervals, less spaced during the initial days than during the final periods, as suggested [23]. Atmospheric conditions and air and water temperatures were registered for each aliquot being sampled.

(ii) Fifty mililiters of the fuel oil were put on a Petri dish (glass, 10 cm diameter) and they were irradiated with IR radiation. The lamp was set 20 cm above the Petri dish. Samples were withdrawn at 0 h, 2nd, 3rd, 4th, 6th, 8th, 12th, 16th, and 20th days.

(iii) Finally, hydrocarbon samples were taken on different beaches located along the province of A Coruña on different sampling seasons in order to ascertain if they were originated on the Prestige's wreck and to seek out if the weathering patterns followed those observed in the laboratory.

Samples taken along the coastline required some pretreatment before their IR measurement to eliminate seawater, debris and sand. Sample aliquots (2–4 mL) were transferred to Pyrex centrifuge tubes (50 mL capacity) where ca. 10 mL of dichloromethane and 1 g of anhydrous sodium sulphate (Merck, Damstard, Germany) were added [24]. The mixture was placed on a thermostatic bath at 60 °C until the two phases separated. The organic phase was transferred to another tube, sodium sulphate was added again, and centrifuged at 3500 rpm during 30 min. Whether emulsions persisted, NaCl (Panreac, 99.5%, Barcelona, Spain) and another gram of sodium sulphate were added and centrifuged again. Those samples forming stable emulsions were transferred to PPT centrifuge tubes and centrifuged at 9000 rpm. Samples weathered in the metallic device required only the final treatment. The Prestige's oil on the Petri dish had been previously dissicated and, therefore, its aliquots did not required any pretreatment. All ATR-IR spectra were baseline corrected, digitized (1 datum each 3 cm^{-1}) and exported to ASCII files and, then, introduced on Matlab© (Matlab v. 4.2c.1, The Mathworks Inc., Natick, MA, USA). Statistical studies were made with in-house and built-in routines.

3. Results and discussion

3.1. Differentiating fuel oil samples from other products

In order to get a preliminar overview of the weathering pattern of the Prestige's fuel under natural conditions, some unpublished results of a previous comparative study [19] are to be presented briefly, just to understand its singular behaviour. Several crude oils and distillates were spilled on special metallic containers filled with sea water and weathered under natural conditions (due to a lack of containers not all products were studied simultaneously). In total, 121 samples were taken (see [19] for more details): 9 from Flotta oil, 12 from Maya oil, 6 from Ekofisk oil, 13 from Duc oil, 12 from gasoil, 13 from Sharara oil, 12 from calefaction fuel oil, 20 from Prestige fuel (13 from natural weathering and 7 from beaches), 12 from Syrian oil and 12 from crankcase oil. The general appearance of their spectra is presented at Fig. 1, where several samples have been overlaid, along with a simplified chemical interpretation. More detailed discussions will be given in next paragraphs.

A principal components analysis, PCA (spectra were scaled from 0 to 1) revealed that the two fuel oils separated from the remaining products and also among one another (Fig. 2a). Most products are found in different groups, only gasoil, Duc and Ekofisk mixed to some extent (although this can be partially corrected for dividing the overall weathering period in two different epochs [19]). For each product, less weathered samples appear at lower PC2 and PC3 scores. As Fig. 2a is hard to visualize, Fig. 2b was obtained from another PCA study where both fuel oils were omitted in order to improve visualization of the crude oils, gasoil and crankcase oil. The distribution is clearer now (PC1–PC3 subspace), as well as the weathering patterns. The most different one is that corresponding to Maya crude

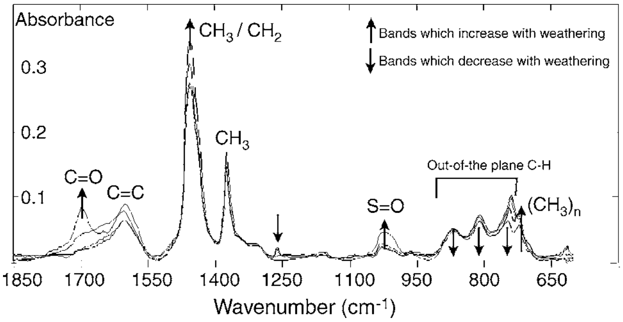

Fig. 1. ATR-FTIR spectra of Prestige's fuel oil, basic chemical interpretation and main regions where changes are visible with weathering (the arrows show the direction of increase/decrease).

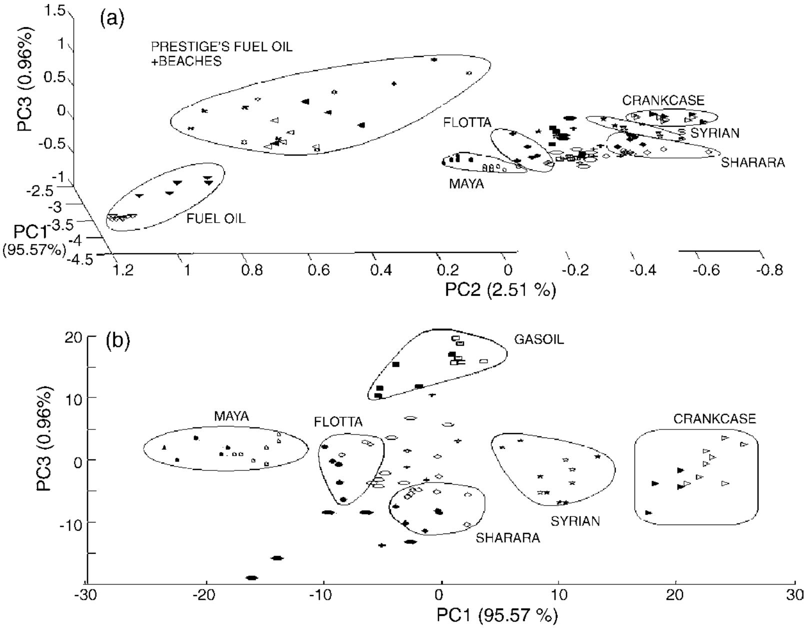

Fig. 2. Comparison among the Prestige's fuel oil and some other crudes and distillates. (a) PC1–PC2–PC3 score subspace, and (b) PC1 and PC3 scores subspace without the Prestige and calefaction fuel oils (see text for details). The variance explained by each PC is given between brackets. (◁), Prestige's fuel oil; (✡), beaches, natural weathering, first fortnight; (✖), beaches, natural weathering, latest samples; (▽), fuel oil for domestic calefaction; (◇), Sharara crude oil; (☆), Syrian crude oil; (▷), Crankcase oil; (▯), Maya crude oil; (⬡), Flotta crude oil; (□), automotive gasoil; (⬭), Duc crude oil; (✙), Ekofisk crude oil. Filled symbols depict more weathered samples.

oil (a quite heavy crude and, so, difficult and slow degrading oil).

Chemical interpretation of the loadings considering all products gives some interesting clues about the major processes the products undergo. PC1 loadings resemble a typical sample spectrum (see Fig. 3a) and this means that PC1 orders the samples according to the intensity of their bands (PC1 is proportional to the population mean spectrum maximizing the spectral variance). Noticeably, the calefaction fuel oil do not present the typical 1690–1700 cm^{-1} carbonyl band throughout the weathering process, while the other products do (see Fig. 4). Of particular interest is the Prestige's behaviour since this band increased

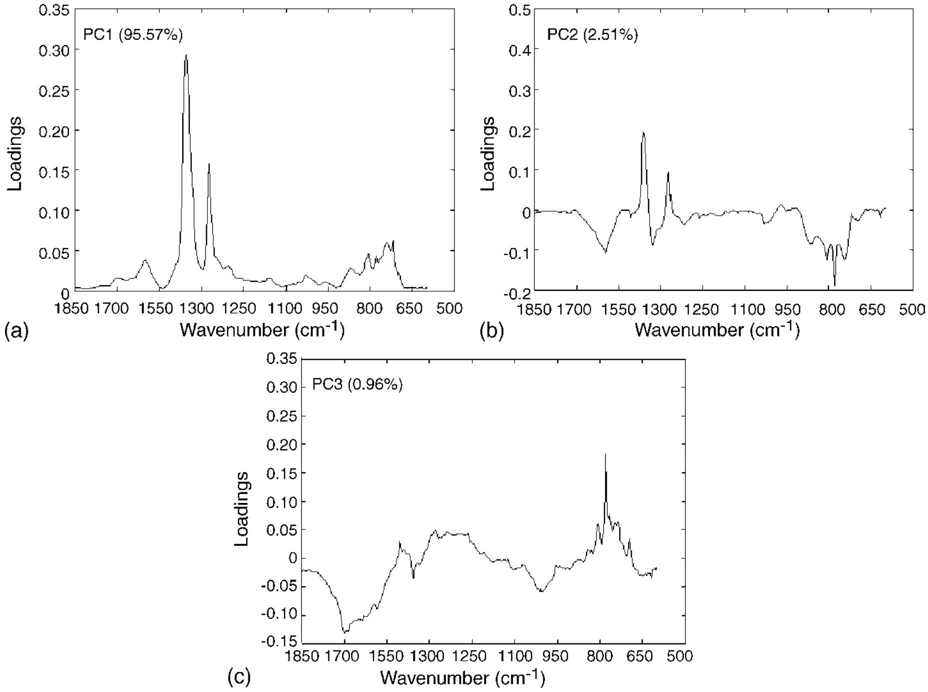

Fig. 3. PC loadings associated to a PCA study considering the overall set of products: (a) PC1 loadings, (b) PC2 loadings, and (c) PC3 loadings. The variance explained by each PC is given between brackets.

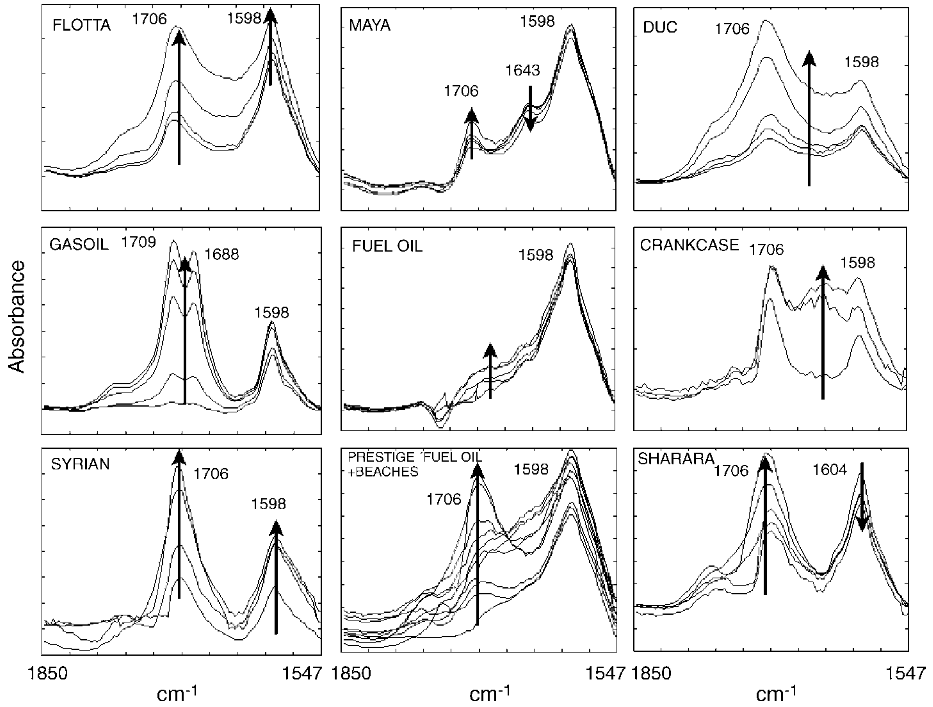

Fig. 4. Simplified view of the 1850–1547 cm^{-1} region showing evolution of the C=O and C=C stretching bands during ageing. The arrows point the increasing/decreasing trends with time (weathering).

largely throughout the weathering process. The crankcase oil is on the opposite side of PC1 as it always showed the carbonyl band (even the initial sample) and, although it was slightly modified, the main change occurred on the 1600 cm^{-1} area (likely because of the polymerization processes this kind of products undergo). The bands between 900–600 cm^{-1} decreased their intensities along the weathering process.

PC2 loadings oppose, essentially, the two fuel oils to all other products. Both Prestige's and calefaction fuels have a complex aromatic structure characterizing the different vibrations of the C–H bonds (out-of-plane) in different substituted rings: 869, 812 and 746 cm^{-1}. The fingerprint structure of the other products is less complex, with a quite different spectral shape. The sharp loading at 780 cm^{-1} (Fig. 3b) corresponds to the calefaction oil, which has a characteristic sharp, pronounced peak at this wavenumber (C–H out-of-plane bending in 1,3- and 1,2,3-substituted rings), neither the Prestige's fuel nor the other products present such a peak. The signal observed at 1457 and 1375 cm^{-1} can be assigned to CH_2 and/or CH_3 groups. The loading at 1602 cm^{-1} is the typical C=C stretching.

PC3 loadings (Fig. 3c) are clearly defined by the 1707 and 780 cm^{-1} peaks. The first (C=O stretching) does not exist on the original samples (except for the crankcase oil) but it increases on weathered samples. It constitutes the most typical indication of the photooxidative process the hydrocarbons undergo [9–11] and it is very clear on heavily weathered Prestige's samples, taken long after the wreck (see next sections for more details). The 900–650 cm^{-1} region discriminates fuel oil samples from the other products, mainly the intense peak at 780 cm^{-1} (characteristic of the calefaction fuel). PC3 loadings are important in the sense that they order samples (within the region where each product lyes) from less-weathered to more-weathered aliquots, except for Maya samples (which PC1, to lower scores). Note that the PC3 scores in Fig. 2a and b are rotated but this is not critical because Fig. 2b was made without fuel samples; the important thing is the capability of PC3 to discriminate weathered samples.

3.2. Weathering patterns of the Prestige's fuel oil

Once the distinctive behaviour of the Prestige's fuel oil was verified (and, so, that none of its samples can be confounded with any other of the studied products), it is worth to study it specifically. Artificial weathering using UV lamps has been performed quite frequently to assess how a product evolved with time [4,11,15] and, despite conclusions are only approximate because it is almost impossible to mimic natural conditions in the laboratory, results were consistent. Artificial weathering of a typical crude oil under natural conditions, UV radiation, IR radiation, and UV + IR radiations was accomplished [19] where from it was concluded that IR radiation induced a fast and pronounced weathering process, very similar to the natural evolution. Accordingly, irradiation of the Prestige's fuel with a IR lamp was carried out in the present study, along with its weathering under natural conditions ("natural weathering").

Two portions of a Prestige's sample were weathered under natural conditions (on a special metallic container, 80 days) and under a IR lamp (20 days). A preliminar conclusion is that there are three main spectral areas which change clearly (Fig. 1): the 1700 and 1028 cm^{-1} regions, where the C=O and S=O stretching bands appear, respectively, and the 900–600 cm^{-1} fingerprint region, where the out-of-plane C–H bending vibrations dominate (these bands decrease with ageing).

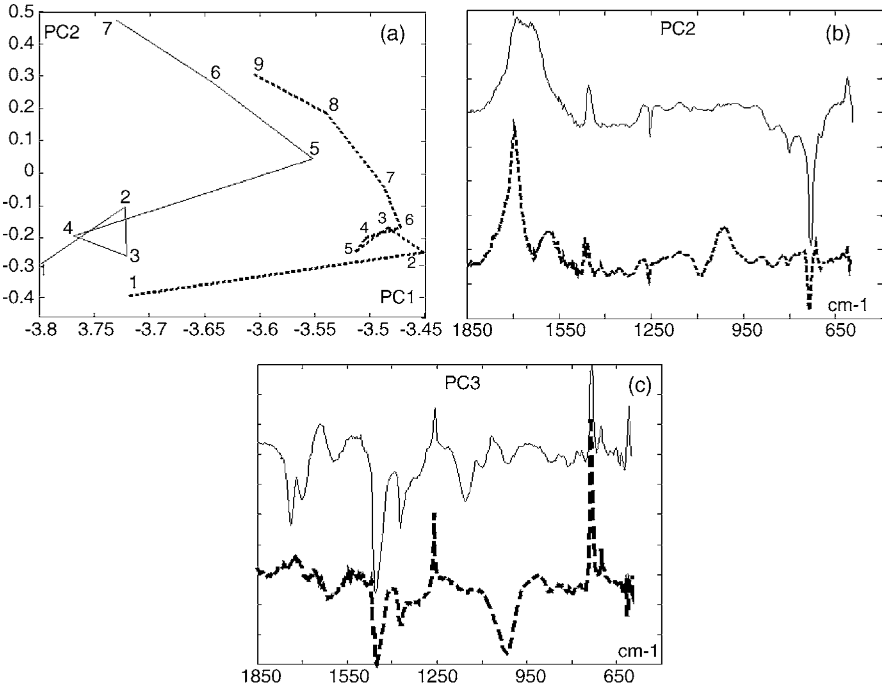

Fig. 5. PCA study of the Prestige's weathering under natural conditions (continuous lines) and IR-exposition (dotted lines): (a) PC1–PC2 scores for both treatments, (b) PC2 loadings, and (c) PC3 loadings.

Then, the series of samples from the two weathering modes were analyzed by PCA. Fig. 5a presents simultaneously both studies. The plot shows that 20 days of IR irradiation yielded approximately the same final result than the natural evolution and, so, that IR weathering resembles well the natural processes (but faster). This fact is in good agreement with ASTM D3326 [24] (although ASTM considered lighter products). The somewhat erratic behaviour shown by several aliquots was attributed to the various complex and simultaneous processes the samples suffer during photooxidation (this was also observed elsewhere [22,23]). Both ageing modes show that the evolution is initially more clear along the PC1 and, then, it proceeds mainly along PC2.

The loadings for PC1 have the same profile for both ageing modes and they order samples according to the intensity of their spectra and, particularly, to the absorbances on the C=O and S=O region.

PC2- and PC3-loadings are also very similar for both ageing modes despite there are some differences that may be attributed to the different velocities of the reactions involved on the weathering processes. These loadings are complex (recall that the fingerprint region cannot always be fully interpreted, even for rather simple mixtures) although they allow to draw some conclusions. PC2 is, basically, defined by (see Fig. 5b):

(i) The 1697 cm^{-1} C=O stretching in ketones and/or esters (a broad band ca. 1100 cm^{-1} was not visualized and, so, carboxylic acids were discarded). The band depicted by the loadings is very well defined for IR-irradiated samples but broader and noisier for natural weathering, which might be a consequence of the more complex natural processes the sample undergo (including natural sunlight, rain, wind, etc.) and the larger variety of photooxidation products due to the existing UV-radiation.

(ii) The 1460 cm^{-1} band, typically attributed to the CH asymmetric vibration in CH_3 and CH_2 structures (symmetric vibration). Although alkanes do not suffer important variations during photooxidation [4] it has also been stated that the 1460 cm^{-1} band would increase thanks to branched or linear aliphatic structures which get included as substituents with weathering [25]. In our samples, we observed that this band increased only for the most weathered samples. Since the 1605 cm^{-1} band increased also, we think that these two bands point towards the formation of either condensed aromatic structures or alkenes along the photooxidative process, in both cases the structures would include aliphatic substituents (this will be elucidated calculating some indexes, see next section).

(iii) The 1028 cm^{-1} band revealed important for IR-exposed samples (natural weathered samples present this band on PC3). It is currently associated to the S=O stretching of sulphoxide-type structures and, so, this peak reveals photooxidation of sulphur structures [7,17,25]. Noteworthy, 2.3% of sulphur in the Prestige's oil was reported by the Spanish government during the accident, and around 1320 $\mu\mathrm{g\,g}^{-1}$ (referred to the fuel) were of thiophene-like structures; this means that up to 1150 and 66 tonnes of sulphur and thiophene-like structures, respectively, could be released to the environment.

(iv) The 900–600 cm^{-1} region, which has been attributed mainly (but not only) to the out-of-plane C–H bending vibrations in C=C–H structures either in alkenes and aromatic structures. Interpretation here is difficult, specially for a highly complex product as the Prestige's one, with hundreds of different species. The most important loading here (almost the unique one for IR-irradiated samples) corresponds to the 752 cm^{-1} band. Noteworthy, its mathematical sign opposes to the other peaks, except for the small band at 1262 cm^{-1}, with the same sign. Three main interpretations can be foreseen: (a) monosubstituted rings (although its 690–700 cm^{-1} counterpart is not observed); (b) disubstituted benzene rings, particularly 1,2- and/or 1,3- disubstituted rings (whose ca. 700 cm^{-1} counterpart was not seen) [26]; (c) *cis*-dialkyl substituted C═C–H bending, although this would imply that the band should increase and not decrease, according to consideration (ii) above. Overall, the negative sign of the band means that it decreases (the total amount of the functional groups causing it diminishes) while the other bands increase. Taking this fact into account, it can be hypothesized that this band (mainly) corresponds to the most volatile species present into the Prestige's oil and, particularly, to disubstituted rings (mainly, of the "1,2- type"). This would agree with the fact that 1,6-, 1,8- and 2,3-dimethylnaphthalene (the most volatile species measured on Prestige's fuel oil) present two absorption bands around 750 and 1260 cm^{-1}. Other volatile compounds present in this fuel oil, like 1,4-, 1,5- and 1,3-dimethylnaphthalene; indene, acenaphthene, acenaphthylene and 1-methylnaphthalene present a strong band on the 750–780 cm^{-1} range [27], which might participate on the 754 cm^{-1} loading (they disappear with ageing).

PC3 loadings (Fig. 5c) are similar to the PC2 ones although they have specific details:

(i) The 1716 cm^{-1} C═O stretching band is quite well indicated for the naturally-weathered samples, in conjunction with the 1200–1150 cm^{-1} band (also clear for IR-treated samples), it means that carboxylic acid groups might be being formed.
(ii) The 1460 and 1375 cm^{-1} bands are typically attributed to the CH asymmetric and symmetric vibration in CH_3 and CH_2 structures. The same considerations can be made here as above. These bands increased only on the most weathered samples.
(iii) The 1028 cm^{-1} band (S═O stretching) is important both for IR-weathered samples and (less) for the naturally treated ones.
(iv) The 900–600 cm^{-1} region shows an outstanding 752 cm^{-1} band, with the same considerations as above (the loading at 600 cm^{-1}, naturally-treated samples, is an artifact caused by a sample).

To sum up, two bands describe the overall photooxidative weathering quite well: the C═O stretching band (ca. 1700 cm^{-1}), revealing the formation of carboxylic groups and/or ketones, and the S═O stretching band (ca. 1028 cm^{-1}) showing oxidation of the atoms of sulphur. Besides, a general diminution on the bands associated to the CH aromatic bending is seen, except for two shoulders at 729 and 755–759 cm^{-1} which grow up slightly during the weathering processes.

3.3. Weathering indexes

Pieri et al. [28] and Permanyer et al. [17] defined several indexes ratioing different mid-IR peak (band) areas against the total area under the spectral peaks or sums of several areas. Here, some of those indexes are applied to visualize how samples evolved and to assess whether they could confirm our previous discussions. Thus, the carbonyl (A_{1697}/A_{tot}), sulphoxide (A_{1028}/A_{tot}), aromaticity (as a measure of the total amount of C═C bonds, A_{1600}/A_{tot}), aliphaticity ($A_{1450+1375}/A_{tot}$), long chains ($A_{724}/A_{1450+1375}$), substitution 1 (as a measure of the number of isolated CH groups in multisubstituted aromatic rings, $A_{864}/A_{864+814+743}$), substitution 2 (as a measure of the number of 2 or 3 adjacent CH groups in substituted rings, $A_{814}/A_{864+814+743}$), substitution 3 (as a measure of the number of 3 and 4 adjacent CH groups in aromatic rings ($A_{743}/A_{864+814+743}$), aromatic condensation ($A_{864+814+743}/A_{tot}$) and branched chains ($A_{1375}/A_{1450+1375}$) indexes [25,29] were calculated. Samples whose weathering periods extended from several hours to 2 years in two Galician beaches were also included.

Both the carbonyl and sulphoxide indexes (Fig. 6a) increase steadily with ageing; the larger the indexes, the older the samples. The parallel behaviour of the two series (natural and IR weathering) suggests that the underlying processes should be similar, although faster when the IR radiation was employed. Regression of the peak height absorbance at 1697 cm^{-1} (measured using valley-to-valley baseline correction) for the IR- and natural-treatments yield "natural = 0.0034 + 0.5359IR" ($r = 0.9571$) which means that, grossly speaking, each day of IR exposure is equivalent to 2 days of natural weathering, in good agreement with ASTM D3326 [24].

Samples taken at the beaches became satisfactorily ordered according to the long period they stayed at the oil lumps on the beach (recall the Prestige leakage started on 13 November 2002). Note that the two more weathered Cayon samples showed a larger evolution on the S═O peak than on the C═O one. They were sampled on a site affected by tides and waves and, therefore, might be affected by some additional natural processes. The Muxia samples were sampled on rocks were the sea seldom arrives.

The aromaticity index increases with ageing. Note the steady evolution of the natural series compared to the IR exposed one, which affected the fuel largely (Fig. 6b). Aliphaticity does not show a clear trend; although it decreases for the IR weathering and the long-weathered Muxia samples (from December 2002 to December 2004, see Fig. 6b). Noteworthy, the IR treatment seems to emulate quite well the natural degradation suffered by Prestige samples not affected by seawater.

The aliphaticity versus long-chains index plot (Fig. 6c) reveals that the number of "long" chains (four or more CH_2 groups) increases with ageing. Nevertheless, the two series of samples have a different behaviour since natural weathering evolves steadily whilst the IR radiation causes a sudden, large increase on these substituents (the index increases from ca. 0.005 for the original untreated sample to ca. 0.025, the first irradiated one), then, a plateau is obtained. Natural weathering reaches

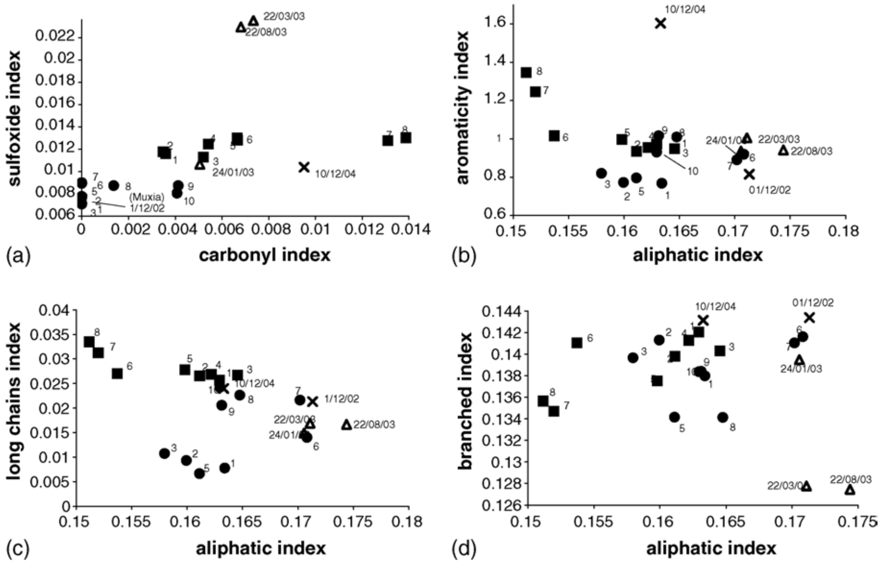

Fig. 6. Weathering indexes calculated for the Prestige's fuel: (a) carbonyl vs. sulphoxide, (b) aromaticity vs. aliphaticity, (c) aliphaticity vs. long chains, and (d) aliphaticity vs. branched chains. (■), IR-weathered series; (●), natural-weathered series; (△), samples from Cayon Beach; (×), samples from Muxia Beach. The sampling date for beaches is displayed (dd/mm/yy).

also those values (samples #8–10, circles) and, finally, the most IR-weathered samples increase the index again (samples #6–8, squares). Regarding the Muxia and Cayon samples, their evolution is less clear as they remain around the central cluster of the graph. This suggests that the (total) amount of long chains would increase only during the first stages of weathering and, then, do not evolves too significantly (in this fuel). Only the IR treatment leads to higher ratios after more than 12 days of irradiation.

Fig. 6d reveals that the branched chains index is not very helpful in characterising the Prestige evolution. Neither the natural nor the IR weathered series show trends. The most significant fact is the clear diminution of this index for the Cayon samples. As suggested above, these samples would reflect other processes than photooxidation, maybe induced by sea washing or, even, biological degradation.

Study of the three substitution indexes confirm the main ideas drawn in the previous sections. First, the total amount of aromatic structures (characterized by the C–H out-of-plane bending, aromatics condensation index) decreases (Fig. 7a), even although the total amount of C=C groups increases (aro-

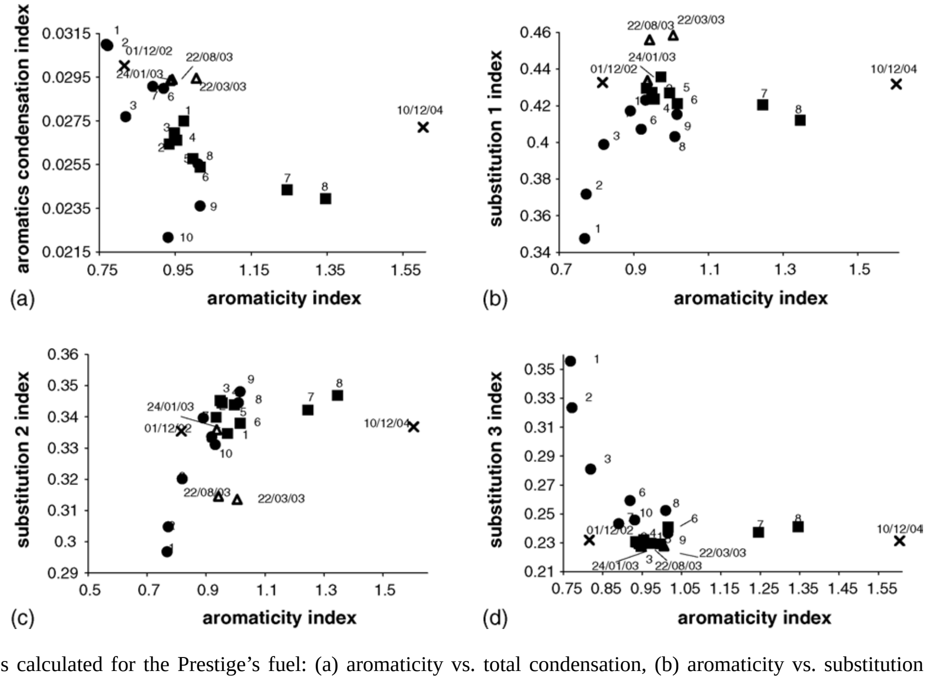

Fig. 7. Weathering indexes calculated for the Prestige's fuel: (a) aromaticity vs. total condensation, (b) aromaticity vs. substitution type 1, (c) aromaticity vs. substitution type 2, and (d) aromaticity vs. substitution type 3. (■), IR-weathered series; (●), natural-weathered series; (△), samples from Cayon Beach; (×), samples from Muxia Beach. The sampling date for beaches is displayed (dd/mm/yy).

maticity index). This fact suggests evaporation of the more volatile components, that some cyclanes get broken and/or that unsaturated substituents are being included on the aromatic structures.

Substitution type 1 (isolated CH groups in highly substituted rings) increased clearly for natural weathering (Fig. 7b) and, after 15 days (sample #6), they reached the values of IR-weathered samples (which in turn, do not vary; after the first 48 h) and remained around a 0.43 index.

Substitution types 2 and 3 (Fig. 7c and d, respectively) are very interesting in the sense that substitution type 3 (three/four adjacent CH groups) decreases whilst substitution type 2 (two/three adjacent CH groups) increases. This appears very clear on the Muxia samples. This fact confirms the previous hypothesis about the diminution on the amount of disubstituted rings in favour of trisubstituted ones (also observed for an Amna crude oil weathered under different conditions [19]). Besides, this agrees with Lee's discussions about photooxidation pathways involving formation of complex aromatic structures and polymerization [7] and the higher resistance of complex PAHs to be degraded [30]. Lamontagne et al. [25] reported also about the evolution of simpler to more complex substituted structures. Note that the larger variation is observed for the natural series (maybe because of the larger variety of compounds and/or processes induced by UV-radiation), although it reaches a plateau around the index of IR-weathered samples and those from beaches.

4. Conclusions

The ATR-mid IR analytical technique combined with factor analysis allowed for a fast, simple, cheap and satisfactory differentiation between several petroleum-related products and crude oils. There, main conclusions were: (i) Prestige's weathering was much slower than those of the other products (except for the calefaction fuel oil and Maya crude oil—a heavy crude oil); (ii) its weathering pattern got always distinct from the other products; (iii) the weathering processes of the Prestige samples were characterized by the appearance and subsequent increase at 1703 cm^{-1} (C=O streteching, attributed to—mainly esters and/or ketones) and 1028 cm^{-1} (S=O stretching, mainly of sulfoxides coming from thiophene degradation). Some changes were observed at the 900–600 cm^{-1} region which suggested that ring structures evolved towards more substituted/polymerized structures.

Comparison of natural weathering and in-laboratory IR exposition of the Prestige's fuel revealed similar patterns, faster when the latter option is employed. The use of peak ratios allowed for a simple interpretation of the main photooxidation processes this fuel undergo. Here, it is worth draw attention on: (i) the faster evolution of the IR-exposed sample, two times faster than that under natural conditions; (ii) the increase of the aromaticity index given by the total amount of C=C bonds; (iii) the diminution on the total amount of aromatic structures; (iv) the increase on trisubstituted aromatic rings.

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References

[1] Z. Wang, M. Fingas, Mar. Poll. Bull. 47 (2003) 423.

[2] J.R. Payne, C.R. Phillips, Acta Chromatogr. 11 (1985) 25.

[3] S. Ezra, S. Feinstein, I. Pelly, D. Bauman, I. Miloslavsky, Org. Geochem. 31 (2000) 1733.

[4] R.M. Garrett, I.J. Pickering, C.E. Haith, R.C. Prince, Environ. Sci. Technol. 32 (1998) 3719.

[5] T. Mill, D.G. Hendry, H. Richardson, Science 207 (1980) 886.

[6] R.G. Zepp, G.L. Baughman, P.F. Schlotzhauer, Chemosphere 10 (1) (1981) 109.

[7] R. Lee, Spill Sci. Technol. Bull. 8 (2) (2003) 157.

[8] K. Tjessen, A. Aaberg, Chemosphere 12 (1983) 1373.

[9] A. Boukir, M. Guiliano, L. Asia, A. El Hallaoui, G. Mille, Analusis 26 (1998) 358.

[10] A. Boukir, M. Guiliano, P. Doumenq, A. El Hallaoui, G. Mille, CR Acad. Sci. Série IIc 1 (10) (1998) 597.

[11] A. Boukir, E. Aries, M. Guiliano, L. Asia, P. Doumenq, G. Mille, Chemosphere 43 (2001) 279.

[12] M. Freegarde, C.G. Hatchard, C.A. Parker, Lab. Pract. 20 (1) (1971) 35.

[13] G.S. Douglas, E.H. Owens, J. Hardenstine, R.C. Prince, Spill Sci. Technol. Bull. 7 (3–4) (2002) 135.

[14] K. Urdal, N.B. Vogt, S.P. Sporstol, R.G. Lichtenthaler, H. Mostad, K. Kolset, S. Nordenson, K. Esbensen, Mar. Poll. Bull. 17 (8) (1986) 366.

[15] R.C. Prince, R.M. Garret, R.E. Bare, T.T. Grossman, T. Townsend, J.M. Suflita, K. Lee, E.H. Owens, G.A. Sergy, J.F. Braddock, J.E. Lindstrom, R.R. Lessard, Spill Sci. Technol. Bull. 8 (2) (2003) 145.

[16] R.M. Garret, S.J. Rotlenburger, R.C. Prince, Spill Sci. Technol. Bull. 8 (3) (2003) 297.

[17] A. Permanyer, L. Douifi, N. Dupuy, A. Lahcini, J. Kister, Fuel 84 (2005) 159.

[18] ASTM 3414, Annual Book of ASTM Standards, vol. 11.02, 2004.

[19] R. Fernández-Varela, D. Suárez-Rodríguez, M.P. Gómez-Carracedo, J.M. Andrade, E. Fernández, S. Muniategui, D. Prada, Talanta 68 (2005) 116.

[20] F.M. Garfield, Quality Assurance Principles for Analytical Laboratories, 3rd ed., AOAC, 2000.

[21] D. Barnes, G. Dent, Spectroscopy (Europe) 6 (2) (1994) 3.

[22] B. Innawong, P. Mallikarjunan, J. Irudayaraj, J.E. Marcy, Lebensm. Wiss. U.-Technol. 37 (2004) 23.

[23] Li, S. Fuller, J. Cattle, C.P. Way, D.B. Hibbert, Anal. Chim. Acta 514 (2004) 51.

[24] ASTM D3326, Annual Book of ASTM Standards. vol. 11.02, 2002.

[25] J. Lamontagne, P. Dumas, V. Mouillet, J. Kister, Fuel 80 (2001) 483.

[26] R. T. Conley, Espectroscopia Infrarroja. Edit. Alhambra S.A. (Madrid), 1979.

[27] Ch.J. Pouchert (Ed.), The Aldrich Library of FTIR Spectra, Aldrich Chemical Company Corp., Wisconsin, USA, 1989.

[28] N. Pieri, J.P. Planche, J. Kister, Analusis 24 (1996) 113.

[29] A. Permanyer, L. Douifi, A. Lahcini, J. Lamontagne, J. Kister, Fuel 81 (2002) 861.

[30] Z. Wang, M. Fingas, L. Sigouin, J. Chromatogr. A 909 (2001) 155.