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## Pyrolysis of asphaltenes and biomarkers for the fingerprinting of the *Amoco-Cadiz* oil spill after 23 years

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## ABSTRACT

The geochemical technique of asphaltenes pyrolysis was successfully applied to the long-term monitoring of the *Amoco-Cadiz* oil spill 23 years after the wreck in the salt marshes of Île Grande, Northern Brittany, France. This method allows the reconstitution of the saturated fraction of the original oil from the asphaltenes fraction of severely degraded oil residues. The results showed that the oil reached a degradation rate of 60% relatively to the initial oil. The asphaltenes pyrolysis generated a gas chromatographic profile very similar to the original *Amoco-Cadiz* oil. In the biomarkers fraction, gas chromatographic/mass spectrometric (GC-MS) analyses demonstrated that terpanes were conserved whereas steranes were partly degraded. We also showed that the class of seco-hopanes biomarkers are conserved and can be used in the long-term monitoring of oil pollutions.

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## R É S U M É

La technique géochimique de pyrolyse des asphaltènes a été appliquée avec succès pour le suivi à long terme de l'évolution chimique du pétrole de l'*Amoco-Cadiz* après 23 ans dans les sédiments des marais salants de l'Île Grande en Bretagne nord. Cette méthode permet la reconstitution de la fraction saturée du pétrole initial à partir de la fraction asphaltènes de résidus pétroliers très dégradés. On montre que le taux de dégradation du pétrole de l'*Amoco-Cadiz* s'élève à 60 % par rapport au pétrole d'origine. La pyrolyse des asphaltènes a permis de générer des hydrocarbures dont le profil chromatographique est identique à celui du pétrole initial. L'analyse par *gas chromatography/mass spectrometry* (GC-MS) des marqueurs biologiques du pétrole résiduel dans les sédiments a montré que les terpanes étaient bien conservés, tandis que les stéranes étaient partiellement altérés. On montre aussi que la classe nouvellement identifiée dans une étude environnementale des séco-hopanes est bien conservée et qu'elle peut également être utilisée dans le suivi à très long terme des pollutions pétrolières.

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### 1. Introduction

The chemical composition of the petroleum products accidentally or deliberately released in the environment varies considerably with time under the action of

biological (biodegradation) and physicochemical (photo-oxidation) processes. It becomes more and more difficult to trace the origin of the oil spilled. The simple analytical techniques like conventional gas chromatography with flame ionisation detection (GC-FID) reach rapidly their limits, due to the biological and physicochemical weathering of oils [1]. In the course of the process, most compounds initially identifiable by GC-FID vanish, in the saturated as in the aromatic fractions of oil [2]. Gas

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chromatographic/mass spectrometric (GC-MS) techniques then become very useful, as they can trace degradation-resistant compounds. This is the case for the biomarkers terpanes (hopanes) and steranes [3,4] which were widely used in geochemical as well as in environmental studies. The geochemical technique of pyrolysis of asphaltenes is used in oil-source rock and oil-oil correlations, and helps follow the secondary evolution process of reservoir oils [5–7]. Asphaltenes are considered to be remnants of the fossil kerogen. The pyrolysis of asphaltenes under carefully controlled conditions mimic the process of generation of oil from the kerogen that occurred in geologic times and hence regenerate saturated hydrocarbons similar to the original oil.

In the present work, we used biomarker analysis and, for the first time in an environmental study, the pyrolysis of asphaltenes to characterise the residues of the *Amoco-Cadiz* oil stranded in sediments of northern Brittany coasts 23 years after the wreck.

The accident occurred on 16 March 1978, and the 223,000 tons of Arabian light crude oil polluted about 360 km of shoreline. Numerous studies were carried out after the grounding [8]. Conversely, few researches have been conducted over a long period of time after an oil spill [1].

## 2. Materials and methods

Samples were collected in March 2001 in the salt marshes of the Île Grande, where *Amoco-Cadiz* oil was shown to persist by places [9]. The sediments were kept frozen ( $-20^{\circ}\text{C}$ ) until analysis. To evaluate the total weathering of the oil in these sediments, the chemical composition of the residual oil was compared to the original *Amoco-Cadiz* oil that had been collected a few days after the wreck and kept frozen from this time.

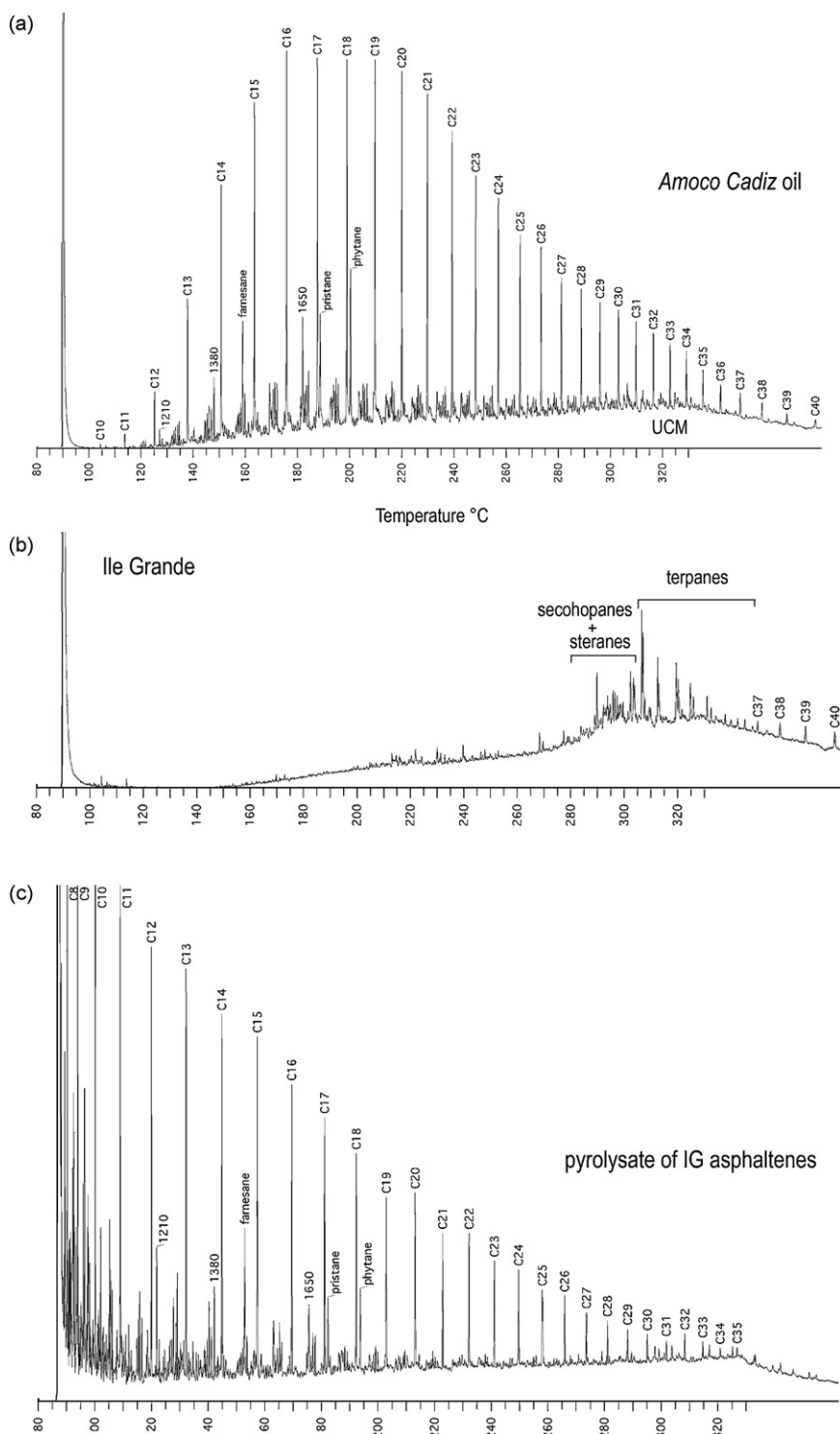
Total residual hydrocarbons (HC) were extracted from defrost sediments by Soxhlet extraction with dichloromethane (DCM) during 8 hours. Their concentration was 3.14% wet weight. After solvent evaporation, the hydrocarbons of the initial oil (AMC) and those extracted from the sediments (IG) were separated with a SARA protocol into saturated, aromatic, resin and asphaltene fractions [2,10]. Briefly, asphaltenes were precipitated in hexane and retained on glass microfiber filters. The filtrate (maltenes) was separated in saturates, aromatics and resins by liquid–solid chromatography. After evaporation of the solvents, each fraction was weighed. The saturated and aromatic fractions of AMC and IG were submitted to GC-FID analyses [10]. The saturated fractions were also analysed by GC-MS in the SIM mode to detect and quantify the biomarkers terpanes ( $m/z$  191), steranes ( $m/z$  217) and, for the first time in an environmental study, the secohopanes ( $m/z$  123). The asphaltenes of IG were washed and pyrolysed as follows:

The asphaltenes of the total residual oil extracted from IG sediments were precipitated at room temperature in hexane during a time contact of 12 hours. The hexane that contained insoluble asphaltenes and soluble maltenes was filtered on Whatman GF/F glass microfiber filters that retained the asphaltene fraction. The filters were then

washed with boiling hexane in a Soxhlet apparatus for 8 hours. Preliminary trials showed that this purification step is essential to remove metabolic byproducts resulting from HC biodegradation like fatty acids, esters and ketones that co-precipitate with true asphaltenes and generate artifacts during pyrolysis. The washed asphaltenes were Soxhlet extracted from the filters for 2 hours with DCM and about 20 mg were transferred dried in glass tubes ( $100 \times 6$  mm in diameter) for closed mild pyrolysis [11,12]. The tubes were sealed with a flame under nitrogen, then placed in a gas chromatograph oven at  $320^{\circ}\text{C}$  for 48 hours. The temperature and time of the pyrolysis were fixed after a series of trials conducted with a view to obtain the most similar chromatograms between original AMC oil and pyrolysate. After the heating period, the tubes were cooled at room temperature, opened and the pyrolysis products were recovered with hexane by ultrasonication (40 kHz, 20 mn). The hexane soluble pyrolysate was passed on a 100–200 mesh activated silicagel microcolumn so that only the saturated fraction of the pyrolysate was collected. This saturated pyrolysate fraction was analysed by GC-FID.

## 3. Results and discussion

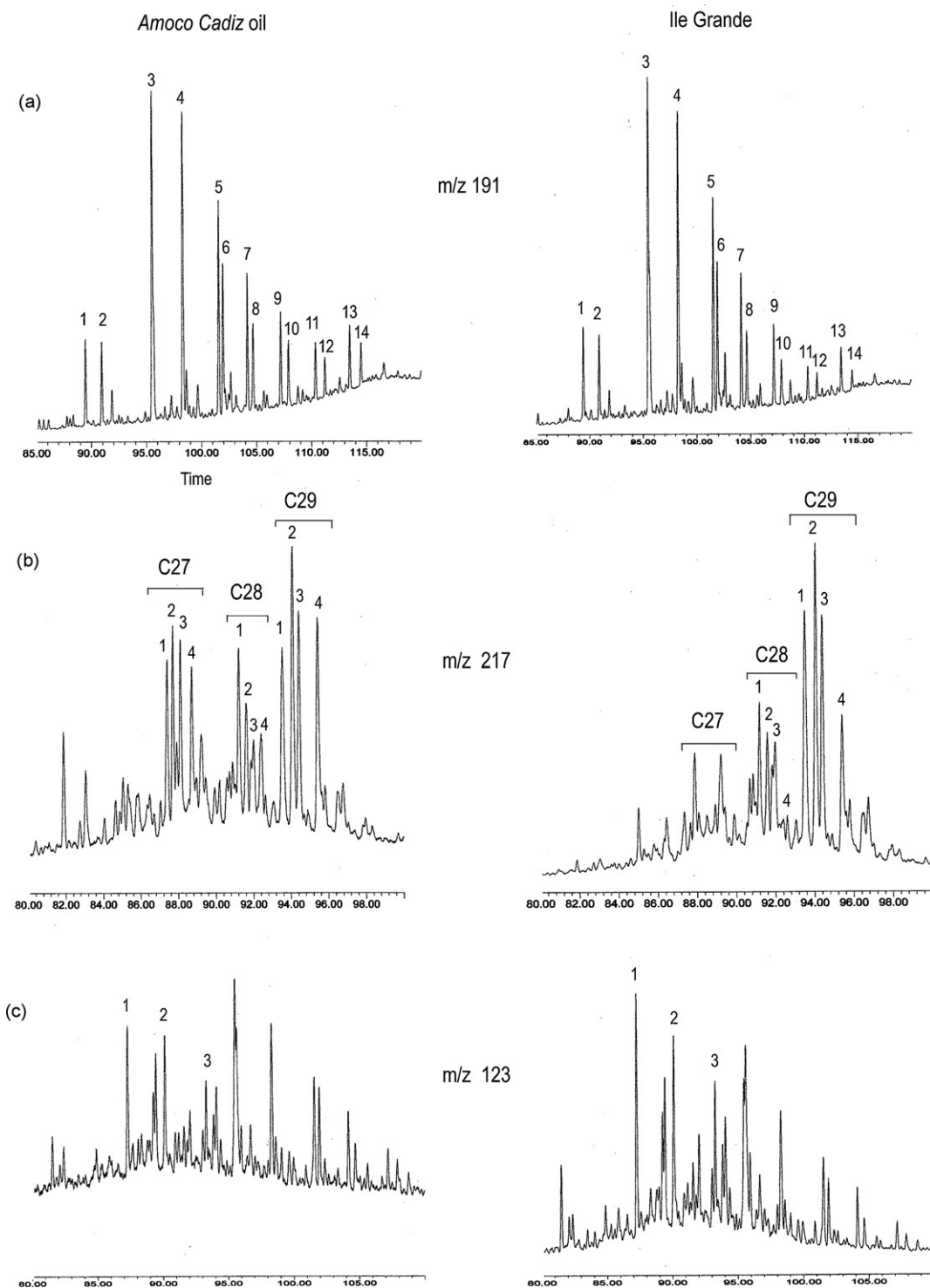
The Fig. 1 a shows the GC-FID chromatogram of the saturated fraction of the original *Amoco-Cadiz* oil. The typical distribution of n-alkanes from nC11 to nC40 was observed, together with the isoprenoids farnesane, norpristane (1650), pristane and phytane, and was characteristic of an Arabian light crude [8]. The lightest compounds below C13 had been lost by evaporation in the environment since the oil had been collected several days after the wreck. The unresolved complex mixture (UCM) contains alicyclic saturated hydrocarbons. The Fig. 1b shows the composition of the residual saturated HC in the Île Grande sediments after 23 years of weathering. Almost all GC-resolvable HC were eliminated, which indicates that biodegradation of these compounds was achieved. The removal was yet not total since part of the UCM still remains. These degradation-recalcitrant compounds constitute a stable form of organic matter and will be removed from the environment at an extremely slow rate [2]. Also visible on the chromatogram are the biomarkers steranes and hopanes that were further studied by GC-MS (Fig. 2). The most salient point is the chromatogram of the Fig. 1c that shows the distribution of HC released by pyrolysis of the asphaltenes of IG. When virtually no compound can be distinguished in Fig. 1b, all saturated HC from the initial AMC oil were regenerated by the pyrolysis, giving a fingerprint nearly identical to the saturated fraction of the original oil of Fig. 1a. Even light compounds below C8 were generated. The characteristic ratios C17/pristane and C18/phytane were similar in the initial oil (2.46 and 1.80) and in the pyrolysate (2.37 and 1.87). This indicates that pyrolysis of asphaltenes can be used most successfully in environmental studies of ancient crude oil pollutions. The GC-FID analysis of the aromatic fraction of IG showed that almost all GC-resolvable compounds were removed, with the exception of some monoaromatic steroids and benzohopanes (data not shown).



**Fig. 1.** Gas chromatography with flame ionisation detection (GC-FID) analyses of the saturated fractions. a: initial *Amoco-Cadiz* oil; b: hydrocarbons extracted from the *Ile Grande* sediments after 23 years; c: pyrolysate of the *Ile Grande* asphaltene. Ci refer to the number of carbon atoms in the n-alkane chain, intermediate peaks are iso- and branched alkanes. UCM: unresolved complex mixture.

Concerning the saturated heavy biomarkers, the Fig. 2a shows that the terpanes were not affected by long-term weathering, since their distribution is nearly identical in AMC and IG. This confirms the validity of using these

compounds as conserved markers in long-term oil pollution monitoring [13]. A less cited fact in oil pollution tracking is that steranes were not as stable as currently expected. It can be seen in Fig. 2b that C27 steranes were



**Fig. 2.** Gas chromatographic/mass spectrometric (GC-MS) analyses of the biomarkers [17] (abbreviated nomenclature). a: terpanes. 1: Ts; 2: Tm; 3: C29  $\alpha\beta$  norhopane; 4: C30  $\alpha\beta$  hopane; 5 and 6: C31  $\alpha\beta$ , 22S and 22R; 7 and 8: C32  $\alpha\beta$ , 22S and 22R; 9 and 10: C33  $\alpha\beta$ , 22S and 22R; 11 and 12: C34  $\alpha\beta$ , 22S and 22R; 13 and 14: C35  $\alpha\beta$ , 22S and 22R; b: steranes. 1:  $\alpha\alpha\alpha$  20S; 2:  $\alpha\beta\beta$  20R; 3:  $\alpha\beta\beta$  20S; 4:  $\alpha\alpha\alpha$  20R; c: secohopanes. 1: C29 8–14 secohopane; 2: C30 8–14 secohopane; 3: C31 8–14 secohopane.

highly altered as well as the  $\alpha\alpha\alpha$  20R isomers of C28 and C29 steranes. As a result, these compounds should be used with caution in long-term oil pollution studies. In the geological field, steranes were already known to be less resistant to biodegradation than terpanes [14]. The class of seco-hopanes (Fig. 2c) is here tracked for the first time in an environmental study. These compounds [15,16] appear to be very stable and could be useful in researches on the topic.

According to the SARA protocol, the initial composition of the *Amoco-Cadiz* oil was: 37.3% saturates, 34.7% aromatics, 15% resins and 13% asphaltenes. The composition of the Île Grande residual oil was: 6.8% saturates, 14.6% aromatics, 29.5% resins and 49% asphaltenes. If it is considered that resins are globally resistant to biodegradation at the time scale concerned [2,10], they can be used as stable internal standard. Consequently, the biodegradation rates of the different fractions of *Amoco-Cadiz* oil after 23 years were 93% for saturates, 82% for aromatics, 0% for resins when an increase of 50% of asphaltenes was observed. This is highly compatible with previous data on the biodegradation of oil components [2] that gave very similar results. The persistent compounds are heavy polycyclic saturates and aromatics, and the totality of the resins. The asphaltenes concentration increased as a result of the production of stable metabolites resulting from the oxidation of degradable HC that are pooled with the true asphaltenes in the hexane precipitation procedure (see above). Overall, the total biodegradation rate of the *Amoco-Cadiz* oil in the Île Grande sediments was 60% after 23 years. This shows that crude oil degradation is not complete and that some oil compounds and stable metabolites can persist on the very long term in the environment. The potential ecological impact of these persistent compounds is not yet known. Further degradation will

proceed only very slowly, at the time scale of at least tens or hundreds years.

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