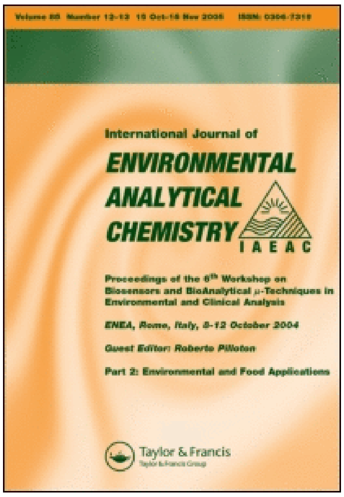

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SOURCES OF TAR BALLS AND OIL SLICKS ON THE COASTS OF THE CANARY ISLANDS

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Tar balls and oil slicks were sampled on several beaches in the Canary Islands and analyzed, along with reference crude oils, for *n*-alkanes and polycyclic aromatic hydrocarbons by gas chromatography and spectrofluorimetry, respectively. Statistical treatment of the data including intercorrelations, Factor Analysis and Cluster Analysis allow the identification of most of source-crudes.

KEY WORDS: Tar balls, oil slicks, *n*-alkanes, PAHs, factor analysis, cluster analysis.

INTRODUCTION

Tar balls and oil slicks, according to their densities, the prevailing temperature and their degree of weathering, can be observed in the marine environment as floating, sinking, or stranded onto the beaches. Field studies have shown the wide distribution of tar balls in the world's oceans, from the Artic to the Antarctic[1,2]. However, the most recent study of Coles and Gunay[3] indicates that over the last few years there has been a certain tendency towards a decrease in this kind of marine pollution probably due to the strengthening of international environmental protection laws as well as to the better design of pumping stations and tankers.

The Canary Islands due to their geographical situation, are in an area of high tanker traffic. Furthermore, The Canary Islands Stream and Trade Winds carry over the pollution which originates far from the Island's coasts. De Armas *et al.*[4] showed that more or less degraded oil slicks and tar balls in the sea near Canary Islands mostly belong to tank washings and ballast water and to accidental oil spills.

On 19 December 1989 the Iranian tanker Khark-5 was disabled 150 miles off the Moroccan coast and by the beginning of January it had lost a total of 60,000 t of heavy Iranian crude oil. About 220,000 t of oil remained on the tanker which was towed along the north of the Canary Islands down to Cape Varde Islands to discharge the cargo and effect repairs. Later, on 30–31 December 1989 the damaged Spanish tanker Aragon spilled 25,000 t of Maya crude oil off Madeira and was towed into the port of Santa Cruz de Tenerife (Canary Islands) to discharge the cargo.

A new approach in discerning significant trends of environmental concern among the massive number of acquired data, is the application of computer assited mathematical

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analysis techniques. These techniques have been succesfully applied in a wide variety of analytical chemical studies involving inorganic[5–11] as well as organic contaminants[12–14].

As a part of a continuous research program on the pollution of the marine environment of the Canary Islands, a study on oil slicks and tar balls carried to their coasts was started aiming at their identification by methods of Factor Analysis and Cluster Analysis.

MATERIAL AND METHODS

Analytical reagent grade chemicals and Milli-Q water were used throughout with no further purification. *n*-Hexane was first distilled, treated with concentrated sulfuric acid, washed with water until neutral, dried over anhidrous sodium sulfate and redistilled with a 1:1 reflux ratio. Random sampling was carried out on three selected beaches in the Tenerife coast and samples kept in polyethylene bags or wrapped in aluminium foil at –20°C until analyzed. Samples and reference crude oils (Maya, heavy Iranian, and heavy and medium Arabian) were extracted with *n*-hexane for 30 min and after centrifugation aliquots were cleaned up and fractionated on a silica-alumina chromatographic column, eluting with 30 ml *n*-hexane (aliphatic fraction) and 30 ml *n*-hexane-dichloromethane 4:1 (aromatic fraction). Both fractions were concentrated at low temperature under vacuum, and the aliphatic fraction analyzed by gas chromatography (Varian 3300, split-splitless, injector at 220°C, SPB-5 0.32 mm × 15 m column: 90°C for 2 min, up to 280°C at 8°C/min, held for 30 min), and total polycyclic aromatic hydrocarbons quantified by spectrofluorimetry as chrysene equivalents (λ_{ex} = 310 nm, λ_{em} = 360 nm, slits 6 nm) (Perkin Elmer MPF-44A ratio recording spectrofluorimeter).

Samples and reference crude oils were also analyzed for nickel and vanadium by flame atomic-absorption spectrophotometry (Varian SpectrAA. 10 Plus) after acid mineralization[15].

Statistical treatment of the data was carried out using the Statgraphics *Plus* V.5 program (STSC, Inc., USA).

RESULTS AND DISCUSSION

Our study on the composition of tar balls and oil slicks arriving on the coast of the Canary Islands, specially in Tenerife's coast, started on October 1989 and was pursued until September 1990, with a monthly sampling in three beaches of this island. At the same time we had samples of oil slicks and tar balls arriving to Lanzarote and La Graciosa, the northern islands of the Canaries nearer to the West African Coast (Figure 1).

During the sampling period tar balls were visually classified according to their viscosity from grade 1 (jelly-like) to grade 5 (solid) as a qualitative indication of their weathering stage, and it can be seen in Figure 2 that they present a normal distribution centered on grade 3 which indicates that most of the oily residues arriving on these coasts show a similar weathering stage while highly weathered or very fresh samples are less often encountered.

As an example of what was encountered along the sampling period one can take Candelaria Beach, to the E-SE of the island, for which Table 1 summarizes monthly data for the total concentration of *n*-alkanes and PAHs as well as various geochemical correlation parameters which have been used to characterize oil spills and tar balls[16–19]. It can be seen that while Ni/V and Pristane/Phytane (Pr/Ph) ratios remain almost constant

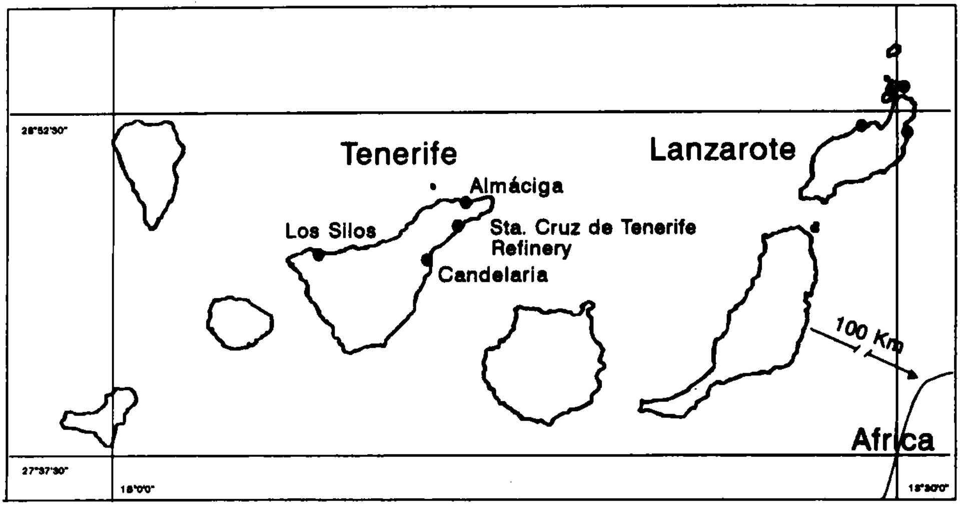

Figure 1 Sampling stations in the coast of the Canary Islands.

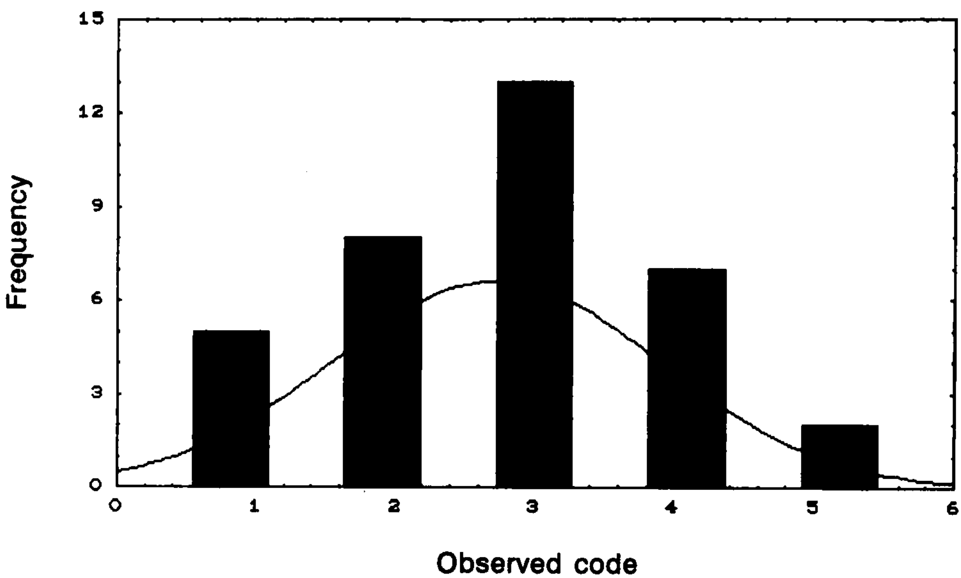

Figure 2 Qualitative weathering stage distribution of tar balls and oil slicks.

along the sampling period suggesting that the tar balls washed onto these beaches belong to the same or to very similar kind of oils, the C_{17}/Pr and C_{18}/Ph ratios are more irregular with a minimum for the sampling carried out on January 1990. The chromatograms of the aliphatic fraction for the overall samples were very similar to each other and showed the presence of the well known unresolved complex mixture underlying the views of C_{15}–C_{35} *n*-alkanes, which indicate the petrogenic origin of the analyzed samples.

Table 1 Monthly values for some parameters of tar balls collected on Candelaria Beach.

Month	*n-alkanes* *mg/g*	*PAHs* *μg/g*	*Pr/Ph*	C_{17}/Pr	C_{18}/Ph	*Ni/V*
Oct. 89	63.94	16.6	0.64	4.37	3.28	0.22
Nov. 89	59.64	36.3	0.69	4.73	3.01	0.45
Dec. 89	55.07	36.6	0.73	3.51	2.65	0.41
Jan. 90	28.71	55.1	0.81	0.70	0.65	0.52
Feb. 90	36.60	31.2	0.63	4.08	2.65	0.58
Mar. 90	1.84	32.5	0.74	–	–	0.06
Apr. 90	14.86	22.5	0.65	1.79	2.11	0.55
May 90	26.91	62.2	0.70	2.89	2.10	0.34
Jun. 90	12.03	40.8	0.74	3.15	2.21	0.29
Jul. 90	5.40	25.1	0.74	2.78	1.74	0.02
Aug. 90	18.92	88.8	1.52	2.34	3.45	0.29
Sep. 90	8.93	65.8	0.59	4.60	3.41	0.22

Differences among the data set based solely on the visual examination of the variables does not unequivocally demonstrate that the samples were the same or different, because of the small differences between the respective values and the large number of samples.

Pattern recognition techniques have been succesfully applied in a wide variety of analytical chemical studies and application to petroleum pollution monitoring was first undertaken by Duewer *et al.*[20] to identify sources of oil spills using its elemental composition when the field sample had undergone weathering. Several other authors have also used statistical methods such as Principal Components Analysis and Soft Independent Modelling of Class Analogy in order to classify crude and degraded oil samples[21–24].

In order to ascertain the possibility of identifying the crude oil from which the samples come, firstly Factor Analysis (FA) was applied to the data without reference to environmental conditions or restraint on the data, that is to say FA was conducted blind. Only when FA was completed, the results were assessed with regard to sample location, proximity to petroleum sources and actual spills, seasonal variations and/or oceanographic conditions in the sampling areas. The FA was carried out directly on the untransformed experimental data.

As there were a large number of descriptors being generated, some of them were likely to be intercorrelated, thus, before Factor Analysis could be performed the variables used must be selected as the presence of intercorrelations can severely affect the efficiency of the variable selection procedure. Therefore, it was necessary to discard some of these descriptors before the data could be submitted to factor analysis and cluster analysis. From the correlation matrix of the 23 variables for the 39 samples of tar balls and oil slicks and the four reference crude oils we observed that the concentration of every *n*-alkane can be discarded as their total centration must give the same information. This is shown in Table 2. Furthermore, the high correlation found between C_{17}/Pr and C_{18}/Ph ratios indicates that both ratios are equally affected by weathering and thus either one can be used to characterize the samples, thus the C_{17}/Pr ratio was slected. In addition, as the concentrations of Ni and V are also well correlated to each other $\{[Ni] = (5.509 \pm 2.496) + (0.195 \pm 0.035)[V]$, c.c. 0,656, $P > 0{,}000\}$, and of course to the Ni/V ratio, we selected the latter for trial.

Then for the first trial variables (1) total *n*-alkane concentration, (2) total PAHs concentration, (3) Pr/Ph ratio, (4) C_{17}/Pr ratio and (5) Ni/V ratio were selected, and (6)

Table 2 Correlation matrix

	n-alkanes	*PAH's*	*Pr/Ph*	C_{17}/Pr	C_{18}/Ph
C_{11}	0.3855	0.5202	0.2078	0.2523	0.1692
C_{12}	0.4236	0.4523	0.1796	0.3420	0.2475
C_{13}	0.4396	0.4578	0.2559	0.3639	0.3085
C_{14}	0.6511	0.3253	0.2059	0.4532	0.4596
C_{15}	0.7895	0.3056	0.2506	0.5145	0.5547
C_{16}	0.8958	0.1362	0.1584	0.4797	0.5631
C_{17}	0.9258	0.1188	0.0391	0.5214	0.5402
C_{18}	0.9112	0.0042	0.0043	0.4847	0.5302
C_{19}	0.9259	0.0769	0.0210	0.4879	0.5149
C_{20}	0.8614	0.0132	0.0512	0.3331	0.3436
C_{21}	0.8915	0.0829	0.0215	0.4424	0.4673
C_{22}	0.9027	0.0664	0.0386	0.4661	0.4981
C_{23}	0.8885	0.0459	0.0329	0.4686	0.4986
C_{24}	0.8551	0.0092	0.0517	0.3936	0.4521
C_{25}	0.7210	0.0448	0.0408	0.1331	0.1832
C_{26}	0.7186	0.0007	0.0766	0.1444	0.1829
C_{28}	0.6257	0.0258	0.1574	0.0439	0.0566
C_{30}	0.1618	0.0166	0.1073	0.3392	0.3724
n-alkanes	1.0000	0.2013	0.0653	0.4643	0.4846
PAH's		1.0000	0.4988	0.0170	0.4803
Pr/Ph			1.0000	0.2450	0.0876
C_{17}/Pr				1.0000	0.8260
C_{18}/Ph					1.0000

total *n*-alkane/C_{16} ratio was included as it has been used as a good indication of petroleum pollution in the case of mussels exposed to No 2 fuel oil spills[21,25]. The six starting descriptors were subjected to Factor Analysis and the results are shown in Table 3. If the number of factors is chosen with the ordinary rule of selecting the > 1 eigenvalue, three factors are extracted which account for the 74.4% of the total variance.

Confirming the results of the factor analysis, the Varimax rotated matrix in Table 4 show that variables 3,4 and 5 have strong factor loadings on factors 1,2 and 3, respectively. Thus, one can select only three factors and reject three out of the six variables considered in the first trial. The rejected variables will be the total aliphatic and total aromatic concentrations and the C_{16} ratio which is a concordant result confirming that they are strongly intercorrelated and give similar information, and are likely to be more influenced by weathering and by the sand mixed into the tar balls while remaining on the beach.

Consequently, further study was carried out with variables 3, 4 and 5 and three factors and as one can see in Table 5 every variable has the strongest loading on one factor.

Then using these variables and factors a cluster analysis was carried out whose result is shown in Figure 3, where five clusters can be observed. The largest cluster encloses 23 samples (59%) together with the heavy Iranian reference crude oil; a second cluster encloses the medium Arabian reference crude oil and two samples (5.1%), while only one sample (2.6%) is related to the Maya reference crude oil, this sample comes from Candelaria beach in Tenerife, to the south of the pumping station where the Aragon tanker discharged its cargo; 6 (15.4%) samples are enclosed into two other clusters associated to no reference crude oils, and no sample is related to the heavy Arabian reference crude oil; another 7 (18%) samples are not clasiffied into any cluster, these samples belong equally to every visual grade of weathering.

Table 3 Factor analysis of the five selected variables.

Variable	*Factor*	*Eigenvalue*	*% Cummulative variance*
n-alkanes	1	1.89603	31.4
PAHs	2	1.55466	57.5
Pr/Ph	3	1.01293	74.4
C_{17}/Pr	4	0.81715	88.0
Ni/V	5	0.48205	96.0
C_{16} ratio	6	0.23718	100.0

Table 4 Varimax rotated matrix of the five variables on three factors.

Variable	*Factor:*	*1*	*2*	*3*
n-alkanes		0.17715	0.75669	0.28633
PAHs		0.74875	0.03819	0.08063
Pr/Ph		0.91507	−0.11044	−0.04060
C_{17}/Pr		−0.18774	0.89363	−0.07024
Ni/V		−0.01689	0.07728	0.93994
C_{16} ratio		−0.56940	−0.48629	0.26212

Table 5 Varimax rotated final factor matrix of the three selected variables on three factors.

Variable	*Factors:*	*1*	*2*	*3*
Pr/Ph		−0.01742	0.99222	−0.12327
C_{17}/Pr		0.02086	−0.12330	0.99215
Ni/V		0.99965	−0.01707	0.02044

These results suggest that at the begining of our study there already were tar balls belonging to heavy Iran crude oil and this kind of tar balls, including those arriving on Lanzarote and La Graciosa islands, carried on arriving until May 1990, the months after the Karhk 5 spill. On the contrary, only one sample of tar balls belonging to Maya crude oil, appears on the sampling area (to the south of the pumping station where the Aragon tanker discharged its cargo), and that no pollution generated from heavy Arabian crude could be detected during the sampling period.

However, the presence of clusters associated with none of the crude oils we used as references, and of samples associated with any cluster, suggests they belong to crude oils from a different origin than the reference crudes used here.

It can be concluded, according to the high relevance given by Factor Analysis and Cluster Analysis, that the quantitative determination of the C_{17}/Pr (or C_{18}/Ph), Pr/Ph and Ni/V ratios together with the use of factor analysis and cluster analysis allow the classification of most of the tar balls and oil slicks appearing on the coast and to relate them to the original crudes. This method can be considered as an alternative to the comparative study of the fingerprints of both tar balls and original crudes[26].

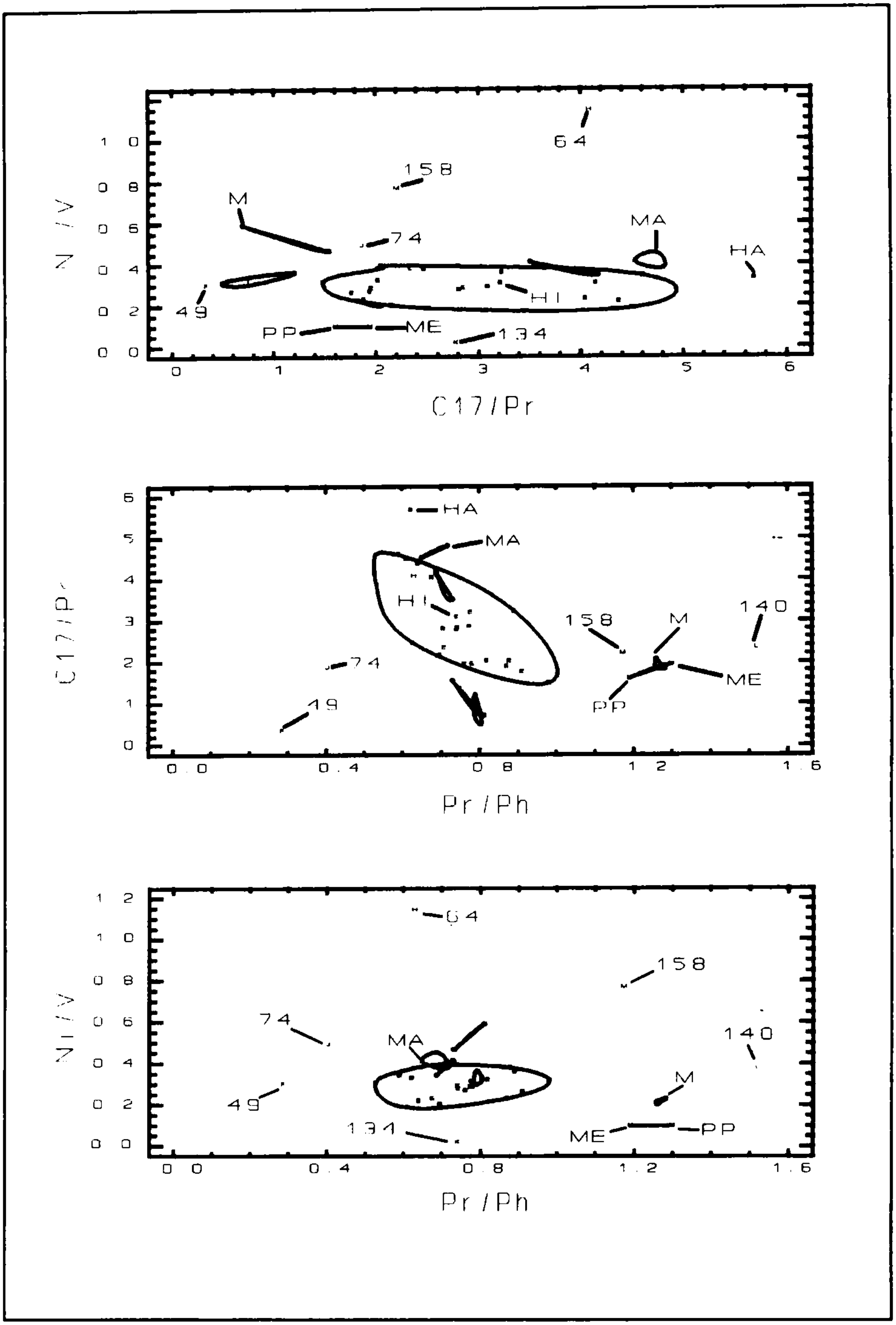

Figure 3 Bidimensional plot of the result of the cluster analysis (M = Maya crude oil, HI = heavy Iranian, HA = heavy Arabian, MA = medium Arabian, ME: Egean Sea tanker crude, PP = Perbes Beach; Numbers identify samples not enclosed in clusters).

Note added in revision

When this paper was under revision we could have a sample of sand coming from Perbes Beach (La Coruña, Spain) and of crude oil similar to the cargo of the *Aegean Sea* tanker stranded 1993 near Hércules Tower in La Coruña. Both samples were analyzed only for Ni/V (0.1 and 0.1, respectively), C_{17}/Pr (1.65 and 1.93) and Pr/Ph (1.17 and 1.25) and these data introduced in the data matrix for Cluster Analysis. As one can see in Figure 3 both sand and crude oil samples are clustered together and well appart from the previous clusters and isolated samples, this fact confirms the conclussions previously established.

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