Full Length Article

Characterization of petroleum-based products in water samples by HS-MS

Marta Ferreiro-González, María José Aliaño-González, Gerardo F. Barbero, Miguel Palma*, Carmelo G. Barroso

Department of Analytical Chemistry, Faculty of Sciences, IVAGRO, University of Cadiz, Spain Campus de Puerto Real, 11510 Puerto Real (Cádiz), Spain

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ABSTRACT

In forensic and environmental sciences, the identification of petroleum-based products is an important task to establish not only the origin of a given residue but also the hazard level or the appropriate cleanup procedure. A new strategy for the fingerprinting of petroleum-based products (PP) in water samples (seawater and freshwater) for rapid and easy fuel spill identification has been developed. For this purpose, an HS-MS has been used in combination with chemometric tools such as linear discriminant analysis (LDA). A set of 70 samples from seven types of PPs (aromatic products, alcohols, normal alkanes, gasoline, diesel, lubricants and naphthenic-paraffinic products), all of which were added to water (seawater and freshwater), were analyzed. 100% of the samples were discriminated according to the type of petroleum-based products used regardless the nature of the water. Furthermore, a fingerprint was obtained for each petroleum product by plotting the m/z values selected by the LDA and this allowed the rapid identification of the petroleum products. The repeatability and intermediate precision were evaluated for both types of water samples and good values were obtained (RSD < 10%). The applicability of the method for the detection of lower proportions of PP was assessed and the same fingerprints were obtained for each PP, even when the volume was decreased down to 0.05%. The results demonstrate the potential of HS-MS in this field.

1. Introduction

The characterization of petroleum-based products is an important area with respect to forensic and environmental problems. Oil and fuel spills (accidental or illegal) are commonplace, but the identification of the source is not always straightforward. The main sources of accidental oil spills include tanker vessels for petroleum products, pipeline spills, coastal facility spills, offshore oil production platform spills, and freighter (fuel) spills, amongst others [1–3], whereas intentional discharges are related to spills from vessels, cargo hold washings or water discharges from offshore platforms [4,5].

Petroleum-based products come from crude oil. As they have a common source, these products will have similar compositions. It is the refining processes and the use of different additives that make one product different from another and these processes define the composition of the product. The toxicity of crude oil depends of its final composition and this is characteristic of each sample. The diversity of petroleum-based products on the market – together with the fact that new products are continuously being developed – has made it necessary to investigate fast and reliable analytical methods for the characterization of petroleum products to allow the discrimination of fuel spills in water and enable the source to be identified. Identification of the petroleum product allows the environmental damage caused by the spilled oil to be easily assessed and facilitates the selection of the appropriate cleanup treatment [6]. For this reason, one of the most important analytical tasks is the development of methods to obtain chemical fingerprints for each type of product in order to distinguish one from another, even when they are very similar, and to establish a conclusion rapidly in order to initiate the correct cleaning process as soon as possible.

A large number of research and review articles have been written concerning the different methods used for the determination and discrimination of petroleum-based products, which include gasoline, diesel or kerosene [7–9]. The majority of the methods that have been developed are based on gas chromatography (GC) [10–12]. GC–MS-based methods are usually employed to characterize fuel-related products and sample preparation steps such as headspace concentration or other concentration techniques are required [13–15].

The data treatment employed to identify the petroleum-based product on using GC–MS includes matching performance by visual inspection of the total ion chromatogram (TIC) and extracted ion chromatograms [16] combined with target compound analysis [17]. This methodology works well but it does suffer from some drawbacks [18] as the results are highly dependent on the analyst's experience,

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automation is not possible, some information from the analytical results is not used and the method is time consuming.

The application of chemometric tools has provided a solution to the problems outlined above. Chemometric tools allow the classification of the data, the extraction of useful information and enable conclusions to be drawn, including discrimination between different groups of samples, in an almost automatic procedure [19]. Some of the chemometric tools commonly used in the discrimination of petroleum-based products are covariance mapping [20,21], principal components analysis (PCA) [22], linear discriminant analysis (LDA), artificial neural networks [23], soft independent modeling of class analogy (SIMCA) [24], cluster analysis, self-organizing feature map [24], and fuzzy rule-building expert system classification.

In several studies, the compounds that produce chromatographic peaks are not identified and only the chromatographic information without detailed identification is used. This approach has a drawback in that the procedure cannot be applied in different laboratories without obtaining a variance in the results due to differences in the retention times. One strategy that has been employed to solve this problem is the use of the total ion spectrum (TIS), which is independent of time; "it is the average mass spectrum across the chromatographic profile" [25]. The TIS has been widely applied in the discrimination and classification of ignitable liquid residues in burned samples, with good results obtained and the prediction of classification error rates also possible [26].

For this reason, non-separative techniques such as HS-MS (headspace mass spectrometry) are good alternatives for rapid identification when it is sufficient to obtain a signal profile or fingerprint of the sample formed by all of the components [27]. The HS-MS has been successfully optimized and validated for the analysis of ignitable liquids in fire debris [28,29] and for the discrimination of gasoline samples with different RON (Research Octane Number) [30,31]. However, this technique has never been applied for the identification of fuel products in aqueous media. The HS-MS provides a mass spectrum (MS) without any chromatographic separation and this is equivalent to the TIS and is characteristic of each sample being analyzed. Consequently, suitable chemometric treatment of the signal could readily provide a fingerprint for each sample and this in turn could be used to identify the fuel spill quickly in a real case. The HS-MS presents several advantages over the more commonly used techniques: it is a green technique, it does not require the use of any solvents and does not contaminate the environment, it is rapid and easy to use for routine analysis, and has a low cost.

The aim of the work described here was to develop a new strategy to fingerprint petroleum-based products in water samples (seawater and freshwater) to achieve rapid and easy fuel spill identification by using the HS-MS combined with chemometric tools.

2. Experimental

2.1. Samples

Fuel spill samples were prepared in the laboratory. For this purpose, a total of 35 petroleum-based products of different types were used to spike both freshwater (FW) and seawater (SW) samples. All of the PPs were liquids and they were purchased from local Spanish petrol stations and stores. Fuel spill samples are denoted by the water code followed by the PP code; For example, SWGas1 is seawater spiked with type 1 gasoline. The relevant information for the PPs and the corresponding classes and codes are shown in Table 1. Fuel spill samples were simulated by adding a 20 μL aliquot of petroleum product to the 10 mL HS-MS vial containing 1 mL of seawater or freshwater.

2.2. HS-MS acquisition

Analysis of the fuel spill samples was performed on an HS-MS Alpha Moss (Toulouse, France) system consisting of an HS 100 static headspace autosampler and a Kronos quadrupole mass spectrometer (MS).

Table 1

Petroleum Products used to simulate fuel spills in freshwater and seawater samples.

PP class	Class code	Products
Normal alkanes	Na	2 heptane and 2 hexane solvents
Aromatics	Ar	2 xylene, 2 toluene and 1 naphthalene based solvents
Alcohols	Al	2 commercial ethanol 96°, 1 commercial ethanol 76° and 1 propanol
Gasoline	Gas	5 commercial gasoline samples (RON 95)
Diesel	Die	5 commercial diesel samples
Lubricants	Lu	2 commercial 2 T motor lubricant and 1 commercial diesel lubricant
Naphthenic-paraffinic products	Np	3 commercial charcoal starters, 3 commercial lamp oils and 2 commercial paraffinic products

The samples were contained in 10 mL sealed vials (Agilent Crosslab) and these were placed into the autosampler oven to be heated and agitated in order to generate the headspace. Headspace was taken from the vial using a gas syringe and injected into the mass spectrometer. The gas syringe was heated above the sample temperature (+5 °C) to avoid condensation phenomena. Between each sample injection, the gas syringe was flushed with carrier gas (nitrogen) to avoid cross-contamination.

The optimized experimental conditions for the headspace sampler were as follows: incubation temperature 145 °C, incubation time 10 min, agitation speed 500 rpm, syringe type 5 mL, syringe temperature 150 °C, flushing time 120 s, fill speed 100 μL/s, injection volume 4.5 mL and injection speed 75 μL/s. The carrier gas was nitrogen. The total time per sample was approximately 12 min.

The components in the headspace of the vials were passed directly to the mass detector without any chromatographic separation or sample pre-treatment. In this way, for any given measurement, the resulting mass spectrum gives a fingerprint of the PP. Ion electron impact spectra were recorded in the range *m/z* 45–200. Instrument control was achieved using RGA (Residual Gas Analysis software package) and Alpha Soft 7.01 software.

2.3. Data analysis and software

The mass spectra were normalized by assigning one unit to the maximum intensity. Multivariate analysis of the data, which included hierarchical cluster analysis (HCA) and linear discriminant analysis (LDA), was performed using the statistical computer package SPSS 17.0 (SPSS Inc. Chicago, IL, USA).

The HCAs were applied by using all of the *m/z* (45–200) values obtained from HS–MS as a variable to form clusters. All spectra were normalized by assigning one unit to the maximum intensity. The results of the HCAs are represented in the dendrograms, in which all of the samples are listed, and the level of similarity (dissimilarity) at which any of the two clusters were joined is indicated. For all HCAs the Ward method was used for cluster preparation and square Euclidean distance was used to measure distances between clusters.

In an effort to obtain a more robust discrimination in the LDA, for each study a cross validation method was used. Furthermore, 75% (n = 26) of the samples were randomly selected as a training set in order to obtain discriminant functions and the remaining 25% (n = 9) of the samples were then used as a validation set. A stepwise discriminant analysis was applied in order to identify whether there are specific *m/z* values in the mass spectra that are more significant than others when classifying the PPs in water samples.

3. Results and discussion

In order to simulate real fuel spills, 20 μL samples of PP were added to 1 mL of both seawater and freshwater. The reason for using two types