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Total petroleum hydrocarbons (TPH) determination in surfactant stabilized marine water emulsions

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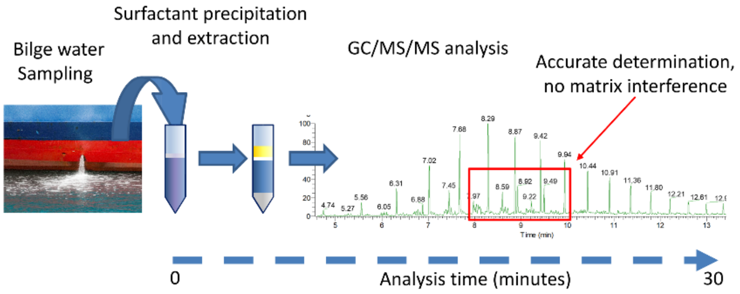
Abstract

Bilge waters are wastewaters produced on boats during navigation and usually contain hydrocarbons and oils. They cannot be released into the sea if not below certain hydrocarbon concentration limits set by current legislation. Surfactants are often used to improve the solubility of petroleum hydrocarbons in water and in this work, the analytical approach proposed is suitable to determine accurately the concentration of hydrocarbons in surfactant-rich waters, as found in bilge water or similar wastewater. The method relies on the surfactant precipitation by addition of potassium and calcium salts, which also promote TPH extraction through a "salting out" effect. This allows for an accurate determination of total petroleum hydrocarbons (TPH) by a GC-MS/MS approach, which reduces any matrix/surfactant interference to a negligible extent.



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Introduction

Hydrocarbons are released to the environment through several ways: accidents, managed releases or as unintended by-products of industrial, commercial or private actions. The result is that, today, it is practically impossible to avoid exposure to hydrocarbons and generally to petroleum products, as they even originate from petrol fumes at the pump, oils from the asphalt and pesticides that use petroleum products as solvents or carriers. For this reason, several concerns with the long- and short-term exposures for humans, fish and shellfish to petroleum hydrocarbons have arisen. In addressing public health issues for total petroleum hydrocarbon (TPH) exposure, it is therefore advisable to understand the changes that take place over time in the composition of petroleum hydrocarbons in environmental matrices such as air, soil and water.

TPH components that have densities less than that of water, generally pose less potential for water pollution with respect to most chlorinated solvents that are denser than water. On the other hand, for surface water, petroleum fractions characterized by a low density can pose major short-term concerns, especially for fish and wildlife. These low-density fractions float in water and form thin surface films 0.1 millimeter or less in thickness.[1,2] For this reason, very small amounts of gasoline, diesel or other common fuel oils, when spilled into water, can spread over a very large area. Some denser petroleum fractions, that include the dangerous polycyclic aromatic hydrocarbons (PAHs), show neutral buoyancy or may even be heavier than water. Such compounds, found in motor oils or as byproducts of combustion components, can accumulate in substrates and can lead to stress for bottom feeding fish, benthic organisms and shellfish. As for the human health risk associated with exposure to TPH, most of the literature information is linked to the cancer risk due to long-term exposure to PAHs,[3,4] or to the risk associated with the acute exposure to the aromatic xylene and toluene fractions of TPH.[5] The most dangerous of these effects are neurological diseases that can culminate in death.[5,6]

Another important source of TPH pollution is due to bilge water disposal. Such water is essentially an emulsion of oils and hydrocarbons in water, be it fresh or salty water, in the presence of substances with emulsifying properties (surfactants) and are the result of routine operations taking place on water-faring vehicles.[7,8] The current legislation, Marpol 73/78[9], stipulates a maximum concentration limit of 15 ppm for TPH. Bilge water having hydrocarbon concentrations below this limit can thus be pumped directly into the sea.[5] To reduce pollutant levels in bilge water prior to the transfer, the Marpol 73/78 legislation suggests the adoption of specific water treatment systems to minimize the amount of hydrocarbons being released into the environment.

To determine TPH levels, different techniques including GC, turbidity measurement and fluorescence detections, are used. In this latter case TPH levels are indirectly determined. Indeed, the measured signal due to the presence of PAHs (which constitute the fluorescent moieties) is converted into TPH concentration using appropriate calibration functions and some approximations that consider a fixed TPH/PAH ratio. On the other hand, several equilibria are connected to TPH levels in an open environment (as for instance, marine water), that could lead to severe discrepancies with respect to the assumed TPH/PAH amount ratios involved. Two aspects should therefore be considered: TPH volatility and PAHs precipitation.

Volatility is defined as “the propensity of a chemical to partition to air and migrate as a vapor”[10] and is a function of the vapor pressure of the volatile compounds. A consistent fraction of TPH thus tends to volatilize and enters the vapor phase, since petroleum products are complex mixtures of hundreds of compounds, with several characterized by relatively high vapor pressures. For gasoline, taken as an example, the compounds that are preferentially volatilized are propane, butane, benzene, toluene, ethylbenzene and xylene.[11] The transfer of such compounds from the liquid phase to the vapor implies that their concentration in liquid phase will decrease, as the concentration in the air phase increases.

Another point to consider is TPH water solubility; this aspect generally decreases with increasing molecular weight of the hydrocarbons. In general, the aromatic fraction is the most water soluble and it follows the straight-chained aliphatic fraction, while branched hydrocarbons are the least water-soluble.

The PAHs in water partition between dissolved and particulate fractions depending upon the solubility of the individual PAH and the availability of binding substrates as suspended particulate matter. The distribution of PAH in the environment is thus largely controlled by their solubility and hydrophobicity. Sediments represent their primary repository, while their content in water (fresh and marine) can vary due to the aforesaid tendency to bind particulates and precipitate, or in the case of the most volatile fraction, to be volatilized.

Both these aspects limit the usability of TPH/PAH ratios to an indirect determination of TPH in extracts (stabilized with surfactants) obtained from soils or other solid samples.[12] To accurately determine the TPH fraction in water (fresh and marine), it is therefore advisable to follow a more time-consuming liquid/liquid extraction procedure, that, in part, has other disadvantages. In this case, the most annoying behavior is formation of emulsions due to the presence of the high levels of surfactants often characterizing bilge water and other wastewater. These surfactants could be present in the pristine sample but, in some cases, are just added to the samples to stabilize hydrocarbons levels.[13] For this reason, in this work we aimed to solve this aspect by developing an analytical approach involving minimal sample treatment, leading to a simple surfactant analysis, with few or no residual interferences.

Results and Discussion

Among surfactants classes, those containing an anionic polar head are the most widespread, and include sodium decyl sulfate, sodium *N*-lauroyl-*N*-methyltaurate, sodium tetradecyl sulfate and especially sodium dodecyl sulfate (SDS).[14] A related class of surfactants is that of the linear alkylbenzenesulfonates (LAS), compounds also found in waste water systems and river water[15] Among LAS, sodium dododecylbenzenesulfonate (SDBS) is the surfactant used in the preparation of test fluids employed in oil water testing, as required by the current legislation.[5]

It is important to note that surfactants are capable to form large supramolecular aggregates in both condensed and gas phase.[16-24] In condensed phase, the aggregation occurs above a critical concentration (critical micelle concentration, CMC) and leads to the formation of aggregates named micelles. In polar media micelles are organized with a hydrophobic "core" and a hydrophilic outer shell constituted by polar heads. Micelles can ease hydrophobic hydrocarbon dissolution within their hydrophobic core, increasing their apparent aqueous solubility. In turn, this latter capability depends on the type and dose of the surfactant and its hydrophobicity.[25-27] These features are also the fundament of Surfactant-Enhanced Remediation (SER), a promising technology with the aim of hydrophobic pollutant removal from water and soil.[28]

For remediation of hydrocarbons from soil and aqueous media, some synthetic surfactants have been used.[29] Several studies have been performed with a single surfactant,[30] while some others adopt a synergistic approach, i.e., using several surfactants. Of note is that SDS and SDBS are the most widespread agents adopted. From an analytical point of view, the presence of surfactant(s) constitutes a complication of the sample treatment procedure. Indeed, the presence of surfactant(s) increases the hydrocarbons' dispersion and hinders the separation processes. For this reason, the extraction procedure requires removal of the surfactants from the aqueous media or at least to reduce their levels in the sample. To accomplish this task, two approaches are possible. The first approach is to reduce the formation of micelles in the aqueous media, which can be achieved by the addition of divalent cations to the sample solution.[31] The second method reduces the solubility of the SDS and SDBS surfactants by means of potassium salts.[32]

In the development of the proposed method, several experimental trials were followed to ascertain whether the addition of divalent cations (as calcium or magnesium salts) could be, alone, capable of removal of the surfactants from the samples. The addition of calcium salts has proven to be more effective since the magnesium salt addition still gave opalescent suspensions, even after prolonged centrifugation. The treatment with potassium salts alone was also quite effective in the precipitation of surfactant salts, but the synergistic effect of both calcium and potassium salts gave the best results. For this reason, most of the optimization efforts were aimed at determining the best calcium/potassium amounts ratio.

Adopting both these strategies, we were able to precipitate most of the surfactant present in surfactant-fortified tap and marine waters (surfactant at 2.5 mg/mL). Our studies were performed in simulated marine water samples containing surfactants (SDS or SDBS) at 0.25% and variable (5 to 50 ppm) concentrations of two differing refined petroleum products: a gasoline range organic (RGO) fuel certified standard (Agilent RGO-616) and a Marine Gas Oil (MGO) fuel standard sample for boats (DMA type, ISO 8217:2017).[33] This latter compound is not obtainable as a pure reference standard, but was received from a local dealer of marine gas oil.

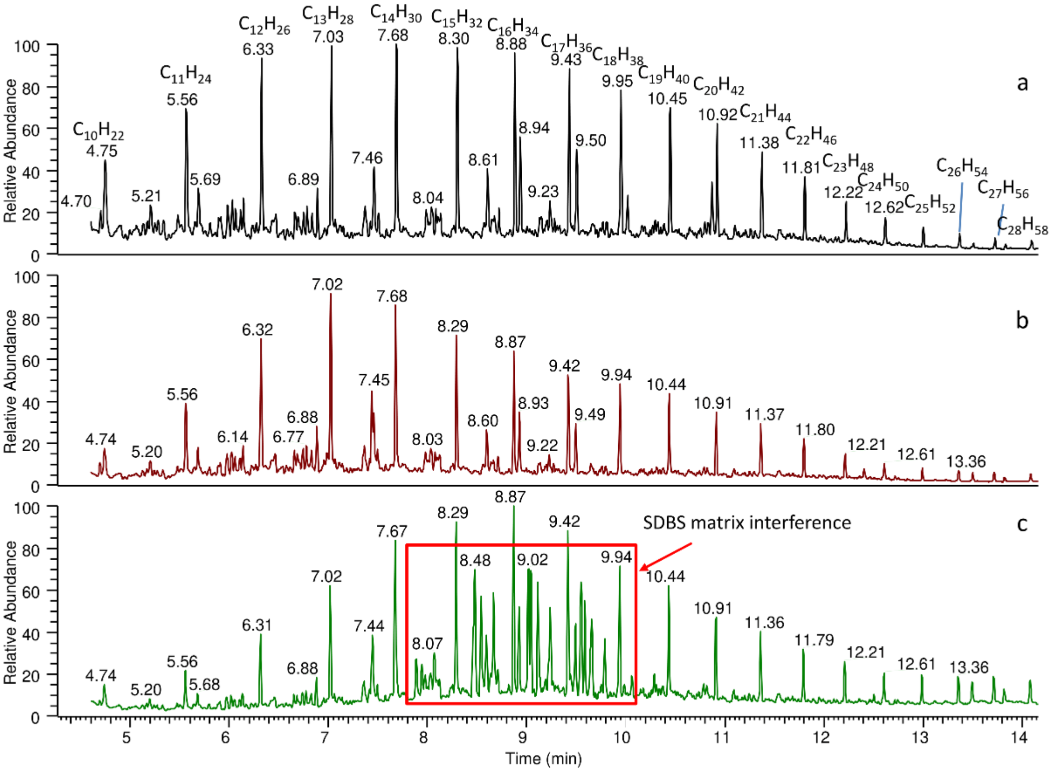

Figure 1. SIM (*m/z* 55; *m/z* 57) chromatograms of DMA, a) in hexane, b) extracted from tap water fortified with SDS and DMA, c) extracted from tap water fortified with SDBS and DMA.

In terms of the procedure followed, the protocol involved initially measuring contaminated water samples (5 grams) into 10 mL glass test tubes. After the addition of an internal standard (6 µL of perdeuterated eicosane, 100 ppm), samples were rapidly treated with fixed amounts of KCl and anhydrous $CaCl_2$ (0.7 g and 0.5 g respectively); this was followed by the addition of a single pearl (about 20 mg) of KOH. Hexane (1.5 mL) was then added to the samples, which were then sealed with a phenolic/PTFE screw cap and gently shaken to dissolve the KOH pearl. This was followed by vigorous vortex-assisted mixing (30 sec) to effectively mix the organic and the aqueous layers. The slurry obtained was then centrifuged (5000 rpm for 5 minutes) to separate the solid precipitate, the aqueous phase and the upper organic layer. The upper layer was recovered, and the residual extracted sample treated with a further aliquot (1.5 mL) of hexane to improve extraction efficiency, again repeating the vortex, centrifugation and upper layer collection steps. To the combined extracted organic phases was then added a small amount of anhydrous granular sodium sulphate (0.5 g) to remove any residual water. The anhydrous samples were then transferred into a 300 µL vial and injected (2 µL) into the GC-MS/MS apparatus. The chromatograms, acquired in Selected Ion Monitoring (SIM) mode, of the ions at *m/z* 55 and 57, are reported in Figure 1 (a, b, c). In figure 1c it is possible to observe a strong matrix interference. These chromatograms indicate that the ions are indeed characteristic of the electron ionization mass spectra of low and high molecular weight hydrocarbons[34] and that they can be used as quantification and confirmation ions in the determination linear, branched, and oxygenated hydrocarbon species.[35-37] The interference observed in the SIM traces at *m/z* 55 and *m/z* 57 is due to the presence of the surfactant SDBS, as it disappears in DMA-fortified tap water samples subjected to the same extraction procedures. To overcome this drawback, the development of a more selective MS/MS method was deemed necessary.[38,39]

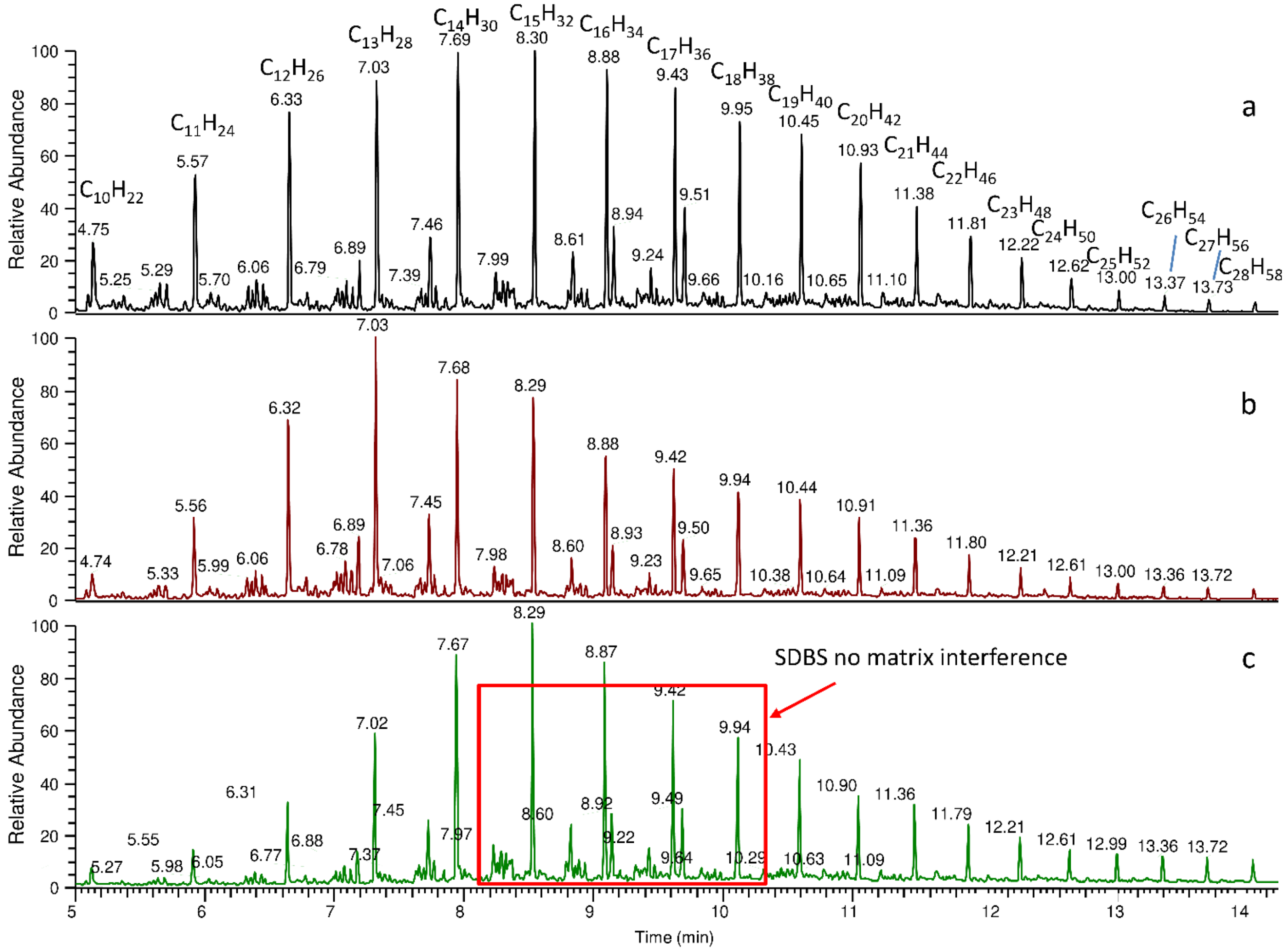

Figure 2. SRM (*m/z* 85 to *m/z* 43) chromatograms of DMA a) in hexane, b) extracted from tap water fortified with SDS and DMA, c) extracted from tap water fortified with SDBS and DMA.

In Figure 2 (a, b, c) the signals due to the SRM transitions from the precursor ion at *m/z* 85 to the fragment ion at *m/z* 43 (used as quantification ion) and from the precursor ion at *m/z* 98 to the fragment ion at *m/z* 50, (used as quantification ion for the internal standard) were obtained with a collision energy of 10 eV using argon as collision gas, are reported for the DMA-fortified samples. The choice of the ion at *m/z* 85 was to reduce the extent of the interferences due to the lower abundance of this moiety in the spectra of the alkyl benzene sulfonic acids, which in turn were dominated by the fragment at *m/z* 91 (benzylic ion). In the spectra of both the linear and branched hydrocarbons, the ion at *m/z* 85 is always very abundant if not the base peak. The fragmentation of the peak at *m/z* 85 leads to the formation of the ion at *m/z* 43, through the loss of C_3H_6. This approach granted a marked reduction of the surfactant interference signal to an acceptable extent.

The parameters tested for the method validation included linearity, limits of detection and quantification, intra-day laboratory repeatability, reproducibility and analyte recovery. Fortified matrix samples preparation for the determination of all the validation parameters are detailed in the experimental section. The linearity was evaluated in terms of correlation of determination (R^2) in a concentration range from 2 to 80 ppm. Two sets of six samples of standard solutions containing respectively RGO 616 and DMA were prepared at 2, 4, 8, 20, 40 and 80 ppm and injected in triplicate. In terms of the data obtained, the following regression equations have been calculated:

$Y=0.0686X+0.0839$ and R^2 was 0.995 for RGO 616 fuel
$Y=0.0726X+0.0444$ and R^2 was 0.998 for DMA fuel

The limit of detection (LOD) and the limit of quantification (LOQ) of the method were obtained using the following equations:

$$LOD=SB+3\cdot\sigma\_SB \qquad (\mathbf{1})$$

Eq.2) $$LOQ=SB+8\cdot\sigma\_SB \qquad (\mathbf{2})$$

where "SB" is the blank signal and σ_SB is the blank signal standard deviation calculated based on eight independent extracted samples (four samples were obtained from tap water fortified with 0.25% SDS and the internal standard and four samples obtained from tap water fortified with 0.25% SDBS and the internal standard).

It should be pointed out that the above limits have been determined on the total TPH content of the fortified matrices, because TPH and the corresponding reference material is a mixture of several hundreds of hydrocarbons that must be quantified as whole. Therefore, it is not feasible to calculate LOD and LOQ for each individual component, and this also could lead to unreliable results. The LOD and LOQ values calculated adopting both the regression curves were practically superimposable, and respectively 0.1 ppm and 0.3 ppm. To remove internal standard compensation during the extraction step, the TPH recoveries determination required a slightly different matrix treatment (as detailed in the experimental section). The TPH recovery, calculated on fortified blank samples as the ratio of determined amount to fortification one, was 86% (ranging from 69% to 102%) for DMA samples, while it was 102% (ranging from 93% to 110%) for RGO 616 fortified samples. Precision of method was evaluated as relative standard deviation for repeatability and reproducibility. The intra-day laboratory repeatability was considered as percentage relative standard deviation (RSD r %) of multiple injections of internal standard solution at 200 µg/L within the same analytical session. The reproducibility was calculated as percentage relative standard deviation (RSD R %) of multiple injections of internal standard solution at 200 µg/L obtained by several analytical sessions in different days (inter-days) and by several operators. For DMA fortified samples, the average intra-day laboratory repeatability was 8.6 (RSD r %), and the reproducibility was 29.1 (RSD R %). For RGO 616 fortified samples the average intra-day laboratory repeatability was 9.2 (RSD r %), and the interday reproducibility was 18.8 (RSD R %).

The effect of the surfactant nature was evaluated using two anionic surfactant solutions (SDS and SDBS) at the same concentration (0.25%). Similar results in terms of recovery were observed. It must be noted, however, a different behavior in the respective chromatograms, (see Figure 1). Chromatograms of DMA obtained after the extraction of the fortified solutions treated with SDBS surfactant, show some moderate intensity peaks due to the matrix interferences in the SIM traces at *m/z* 55 and *m/z* 57. The same does not apply with extracts obtained from solution treated with SDS. Also, the general appearance of the MS/MS chromatograms are different, as both the lowest and highest MW TPH fractions in SDBS treated samples seem to be extracted with a lower efficiency. This reflects in slightly lower recovery. The SDS treated samples show a chromatographic profile that more closely follows the trend of untreated DMA solutions. For this reason, the SIM traces at *m/z* 55 and 57, traditionally employed to enhance the sensitivity of TPH analysis, have been discarded in this study, as they showed too much inconsistency at lower TPH levels.

Conclusions

Surfactants are often used to improve the solubility of total petroleum hydrocarbons (TPH) in water; in addition, they represent a common interference in bilge water samples. The effect of surfactants is exerted by micelle formation and their capability to solubilize hydrocarbons have been extensively investigated.[40] On the other hand, surfactants do have an impact when an accurate determination of TPH is required, since their extraction becomes more difficult. The analytical approach here proposed synergistically adopts a separation of the surfactants from the aqueous matrix, followed by selective MS/MS determination of the hydrocarbons that dramatically reduces to a negligible extent the residue surfactant interferences, even at the lowest TPH levels. Recoveries ranged from acceptable to good levels, while the sample treatment remains very simple and straightforward. A perdeuterated internal standard has been used as it grants the best performances for a MS based instrumentation. However, it could be easily replaced with less pricey substances that could resist the strongly alkaline extraction procedure. In perspective, this approach could give a sufficient support for TPH determination, even in surfactant rich aqueous samples.

Experimental Section

General. Synthetic bilge water was prepared dispersing hydrocarbons in water with surfactants. A MGO fuel for boats (DMA type, in agreement to ISO 8217:2017 standard requests, and provided by a local dealer) was used as prototype of hydrocarbon mixture. In addition, for qualitative and quantitative comparison, the following certified reference material RGO 616 at 50000 ppm (Agilent) was also used.[33] The surfactants alternatively used in the emulsion preparation were SDS, (Sigma, ≥ 98%) and SDBS, (Aldrich, technical grade). Perdeuterated eicosane (Cambridge Isotope Laboratories inc. atomic purity 98%), KCl (Sigma Aldrich 99 %), $CaCl_2$ anhydrous (Supelco 98%), KOH (Sigma Aldrich >85 %), hexane (VWR > 95%, Pestinorm) and anhydrous granular sodium sulphate (Merck EMSURE > 99%) were used in extraction-based GC-MS/MS method.

TPH determination in simulated bilge water was performed after extracting hydrocarbons with hexane. To reduce surfactant interference during the liquid/liquid extraction procedure the following method was applied: About 5.00 ± 0.05 g of simulated bilge water (accurately weighed on a Sartorius TE412 technical balance) was placed into a threaded 10 mL test tube. To the sample, 6 µL of a solution of perdeuterated eicosane (Cambridge Isotope Laboratories inc. atomic purity 98%), at a concentration of 100 ppm, was added. This constituted the internal standard adopted to increase accuracy and measure the method recovery. To this amount of water were then rapidly added 0.7 g of KCl (Sigma Aldrich 99 %), 0.5 g of anhydrous $CaCl_2$ (Supelco 98%) and about 20 mg (a single pearl) of reagent grade KOH (Sigma Aldrich >85 %) and finally with a first aliquot of 1.5 mL of hexane (VWR > 95%, Pestinorm). The test tube was then closed with a PTFE sealing cap to avoid any volatile compound loss and gently shaken with hands, to allow the dissolution of the KOH pearl. Finally, the tube was vigorously shaken in a vortex mixer for 60 seconds to allow the complete and effective mixing of the aqueous and organic layers. The suspension obtained was the centrifuged for 5 minutes at 5000 rpm on a Thermofisher SL16 centrifuge to separate the phases. After the centrifugation step, most of the upper organic layer was then carefully taken (by a glass Pasteur pipet) from the test tube and deposed into a sealed vial. To the residue aqueous sample in the tube, a further aliquot of 1.5 mL of hexane was then added, and the extraction procedure repeated. The hexane layers, reunited, were then treated with 500 mg of anhydrous granular sodium sulphate (Merck EMSURE >99%) to remove the residual water. This sample treatment leads to a final analyte concentration that is slightly higher than the initial one (1.67-fold), thus increasing sensitivity. Finally, 0.3 mL of the resulting anhydrous solutions was then deposed in vials and analysed on a Thermofisher Trace GC 1300, equipped with a programmable temperature vaporizer (PTV), and coupled with a Thermofisher TSQ 8000 triple quadrupole mass spectrometer. The instrument was also equipped with NIST 2015 mass spectral database.

To calculate TPH recoveries, a slightly different procedure was adopted. The addition of the internal standard (used as syringe internal standard) was performed after the liquid-liquid extraction. The procedure involved the preparation of several fortified blank samples: three samples for each type of surfactant and for each type of fuel (RGO 616 and DMA), all fortified at 50 ppm. The fortified samples (5 g), after salt addition, were extracted (as above detailed) with two aliquots of 1.5 mL of hexane. A portion (1.5 mL) of dried extract was finally spiked with the appropriate volume internal standard (3 µL) just before the GC/MS analysis. This approach also led to a final analyte concentration that is slightly higher than the initial one (1.67-fold), and it allowed for the calculation of the real recovery of the fuel extracted, avoiding the compensation of the internal standard during the extraction procedure.

The instrumental parameters were the following: GC column: poly(dimethyl siloxane), Supelco SPB-1, 30 m length, 0.25 mm I.D.; film thickness 0.25 µm. PTV injector parameters: PTV mode = splitless; splitless time 2 minutes; split flow 12 mL/min; septum purge flow 5 mL/min; injection temperature = 60 °C, injection time = 0.05 minute, evaporation temperature = 60 °C, evaporation time = 0.5 minutes; transfer temperature = 320 °C; ramp rate °C/sec = 14.5; transfer time = 2 minutes; cleaning temperature = 320 °C; time 10 minutes at 50 mL/min flow rate, carrier gas Helium at 99.9995% purity; gas flow program 1 mL/min held for 14.5 minute, switch to 1.5 mL/min held for 5 minutes. GC oven program parameters were the following: initial temperature 80 °C, held for 2 minutes, thermal gradient at 20 °C/min up to 310 °C, held for 5 minutes. The mass spectrometer, equipped with an EI source that was set with an ionization potential of 70 eV, operated in SIM mode monitoring the following ions at *m/z* 55, *m/z* 57, *m/z* 66, *m/z* 91, additionally the SRM transitions *m/z* 85 → *m/z* 43 (with a collision energy of 10 eV) and *m/z* 98 → *m/z* 50 (with a collision energy of 12 eV) were followed, to reduce matrix interferences and increase sensitivity for both TPH and IS detection. Collision energies and SRM transitions were chosen and optimized adopting the automated software available on the mass spectrometer.

Acknowledgements

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