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TECHNICAL NOTE

Natural and artificial markers of gasoline detected by membrane introduction mass spectrometry

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A few hydrocarbons in gasoline display relatively high solubility in water and may function therefore as its characteristic set of natural markers. These markers are detected from an aqueous gasoline extract *via* membrane introduction mass spectrometry (MIMS) producing characteristic chemical profiles. MIMS adds a second selectivity criterion detecting only the water soluble hydrocarbons that most easily permeate through a silicone membrane. MIMS screening and the use of artificial markers for gasoline with similar chemical properties (high water solubility and membrane permeability) as those of its natural markers is proposed. MIMS provides a reliable screening method for natural and artificial markers in gasoline for its typification and to monitor adulteration and origin.

Introduction

Automotive gasoline consist of a complex hydrocarbon (HC) mixture of mostly C4 to C12. The composition varies significantly depending on the type of crude oil, the refinery processes, the overall balance of product demand, and product specifications. Additives and blending agents such as anti-knock agents, anti-oxidants, metal deactivators, lead scavengers, anti-rust agents, anti-icing agents, upper-cylinder lubricants, detergents, and dyes are also added to the gasoline to improve performance and stability. At the end of the production process, the finished gasoline typically contains more than 150 constituents and as many as 1,000 constituents have been identified.[1,2]

Due to its high value and widespread use and importance, gasoline is a major target for adulteration and illegal commercialization. A common adulteration procedure is the addition of cheaper petrochemical solvents (white spirit, naphtha and raffinates, for instance), paint thinner, turpentine, rubber solvent, diesel oil and kerosene. The addition of such solvents to gasoline may cause engine malfunction, rubber corrosion, environmental hazards and tax evasion.[3–8] Because these solvents have HC compositions similar to gasoline, their identification in gasoline has been a challenging analytical task. To help detect solvent addition to gasoline, for instance, the Brazilian National Agency of Petroleum, Natural Gas and Biofuels (ANP) has implemented a program that determines the addition of artificial markers in all petrochemical solvents commercialized in Brazil.[9] Their detection requires, therefore, selective and sensitive analytical methods. Marked solvents illegally added to gasoline are usually screened by gas chromatography (GC) using non-selective detectors such as flame ionization detection (FID).[9]

Membrane introduction mass spectrometry (MIMS)[10–14] is a well established technique for the direct trace analysis of volatile organic compounds (VOCs) or semi-volatile organic compounds (SVOCs) in aqueous solutions.[10] The introduction of analyte into the mass spectrometer in MIMS occurs by permeation through a hydrophobic polymeric membrane, which is selective for relatively small and apolar (or less polar) organic molecules. The extraction and pre-concentration of the analytes by the membrane is performed rapidly and simultaneously. MIMS analysis has also been applied to the on-line monitoring of gases dissolved in water employing miniature mass spectrometers.[15,16] Such systems are highly desirable for *in situ* chemical analysis.[17,18] MIMS coupled to a hand-held mass spectrometer has been applied to the quantitation of aqueous polycyclic aromatic hydrocarbons (PAHs), environmentally relevant analytes, with limits of detection in the ppb range for naphthalene and anthracene.[19] A mini-MIMS system for field analysis of both aqueous and organic solutions has been demonstrated.[20] Whereas MIMS has been extensively used for the detection of compounds dissolved in water, the use of the technique for the selective detection of compounds dissolved in organic liquids has received less attention.[21] In this study, we have investigated the applicability of MIMS to the detection of natural and artificial markers in aqueous extracts of gasoline.

Experimental

All chemicals were of analytical-reagent grade and Milli-Q water was used throughout. The standard gasoline samples used in the MIMS solubilization experiments were provided by Petrobras (Brazil). Ethanol and additive-free gasoline samples, ethanol-containing additive-free gasoline samples of the Brazilian

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"comum" type (*ca.* 22% ethanol), ethanol and additive containing gasoline samples of the "aditivada" type (*ca.* 22% ethanol and variable amounts of additives) and higher octane ethanol and additive containing gasoline samples of the "premium" type (*ca.* 22% ethanol and various amounts of octane enhancers) were used. Methyl *tert*-butyl ether (MTBE) was used as a proof-of-principle artificial marker for MIMS monitoring. To simulate an adulteration procedure, kerosene spiked with the MTBE marker was added to gasoline samples, resulting in a final concentration of MTBE in the range of 50–1000 mg L^{-1}.

A single-quadrupole ABB Extrel (Pittsburgh, PA, USA) mass spectrometer using 70 eV electron ionization (EI) and a standard MIMS probe[22–25] with a 125 μm silicone sheet membrane (Silastic 500-3 from Dow Corning) was used. Solubilization of natural and artificial markers of gasoline in water was monitored by mixing 10 mL of one of the gasolines or of the kerosene-adulterated gasolines with 110 mL of deionized water. The mixture was stirred for 60 min and the lower aqueous phase was then pumped continuously through the standard MIMS probe using a peristaltic pump at a flow rate of 2 mL min^{-1} (Fig. 1). All experiments were performed at room temperature (22 ± 2 °C) with constant stirring. Markers were monitored *via* selective ion monitoring (SIM) of characteristic ions formed by 70 eV EI; that is, the ion of *m/z* 73 for MTBE (the artificial marker) and that of *m/z* 74 for gasoline. The *m/z* 74/73 ratio is proposed to function as an adulteration alert.

Results and discussion

A "chemical signature" for gasoline by MIMS

Fig. 2A shows a typical MIMS profile (using 70 eV EI) of the aqueous extract of a typical sample of "pure" gasoline produced by crude oil refining. Despite the high diversity of its composition, MIMS provides a relatively simple profile for gasoline that functions therefore as a "chemical signature" with a unique combination and proportion of natural marker ions. As Fig. 2 exemplifies, many gasoline samples produced from crude oil
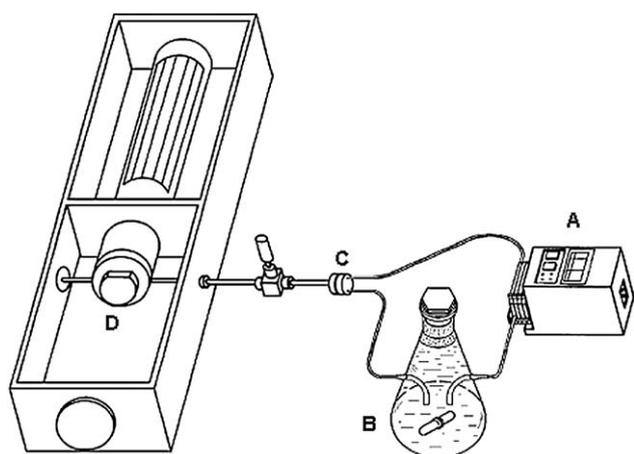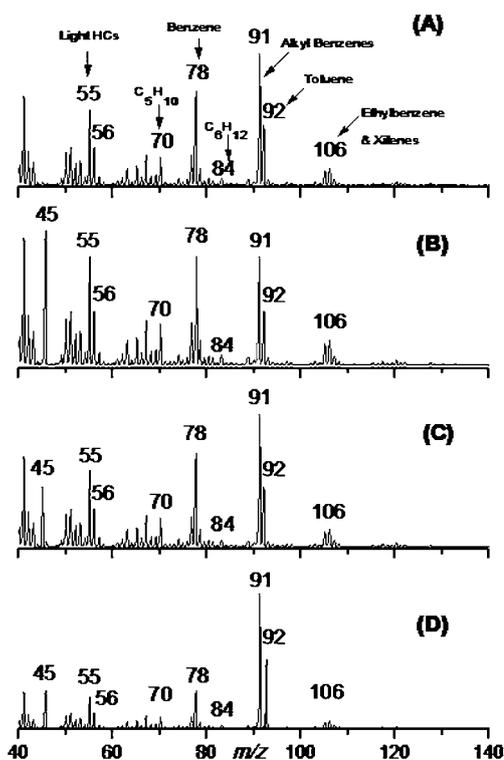
Fig. 2 Typical "chemical signatures" obtained by MIMS (70 eV EI) from samples of (A) ethanol and additive-free gasoline, (B) 22% ethanol-containing additive-free gasoline, (C) 22% ethanol and additive-containing gasoline and (D) 22% ethanol and higher octane gasoline.

refining from different sources and types were analyzed and reproducible MIMS profiles were observed. Repetitions with pure gasoline and 22% ethanol-containing gasoline samples[26] show a deviation in the relative ion abundance of less than 5%. This result indicates therefore that MIMS is able to provide reliable chemical fingerprints for gasoline. The simplicity and selectivity of the MIMS gasoline profile results from double filtering *via*: (a) selective extraction by water of the most polar, water-soluble gasoline HCs, and (b) selective permeation through the silicone membrane of the lightest and least polar HCs. The "survivor" HCs with properties compatible with both "filters" (best water solubilization and most efficient membrane permeation) form, therefore, the characteristic MIMS chemical signature for gasoline.

The ions in the typical MIMS spectra of Fig. 2 are due to molecular or fragment ions of known gasoline constituents[26] such as benzene (*m/z* 78), toluene (*m/z* 92), alkyl benzenes (*m/z* 91), ethylbenzene and the xylenes (*m/z* 105, 106). The ethanol-containing Brazilian gasolines (Fig. 2B–D) show a characteristic ion of *m/z* 45 (H loss from EtOH$^+$). Two other minor but still characteristic marker ions indicate solubilization of alkenes and/or cyclic alkanes of C_5H_{10} (*m/z* 70) and C_6H_{12} (*m/z* 84) compositions, whereas *m/z* 55 is a common and often abundant fragment ion in the 70 eV EI mass spectra of these HCs.

Note that gasolines produced from different types of crude oils or from different processes would be expected to display wide variations in HC composition but the double MIMS selectivity seems to assure that a characteristic set of gasoline natural

Fig. 1 Experimental set-up used for MIMS monitoring of artificial and natural markers of gasoline. A: peristaltic pump; B: water extraction (lower layer) of the markers from the gasoline sample; C: silicone membrane probe and D: ion source of the mass spectrometer.

markers is detected. Distinct MIMS profiles would only be observed for gasoline with much disturbed HC compositions. Such unusual profiles would therefore indicate fraud or, for instance, a different origin other than crude oil refining. A typical case would be of gasolines produced from blends of synthetic solvents.

Quantitative changes in the MIMS profile are also informative. For instance, gasolines with high octane numbers are known to contain higher levels of aromatic HCs such as toluene. The MIMS profile of a sample of such high octane gasoline (Fig. 2D) displays the same set of natural markers but with a higher abundance of the ions of the "aromatic ions" of m/z 92 and 91.[26] Additives that would fulfill the double selective requirements enforced by water solubilization and membrane permeation would also be detected and therefore appear in the gasoline MIMS signature. Ethanol is one such additive and is therefore detected as a prominent ion of m/z 45 in gasoline–ethanol blends (Fig. 2B–D).[26]

Artificial markers for gasoline: MTBE

An efficient artificial marker for gasoline should therefore fulfill the two selective criteria for MIMS detection. Many molecules were considered as potential markers but MTBE was selected as a proof-of-principle example since it displays high water solubility and high permeability through the silicone membrane.[26] In addition, MTBE has also been used for decades as a gasoline additive with no major influence on gasoline performance. Actually, MTBE is known to be beneficial to gasoline and to increase its anti-knocking properties. Environmental concerns about the use of MTBE as an artificial gasoline marker should not be too high since only trace amounts are needed for MIMS detection (*ca.* 50 mg L^{-1}). For the screening of gasoline adulteration with solvents, MTBE could then be added to the solvents and, for instance, the intensity of its main EI ion could be monitored using a background ion such as the natural marker (Fig. 2) ion of m/z 74 as an internal standard.

Fig. 3 shows MIMS data in the m/z 71–75 range. This range was selected since it is, for pure gasoline, nearly free from
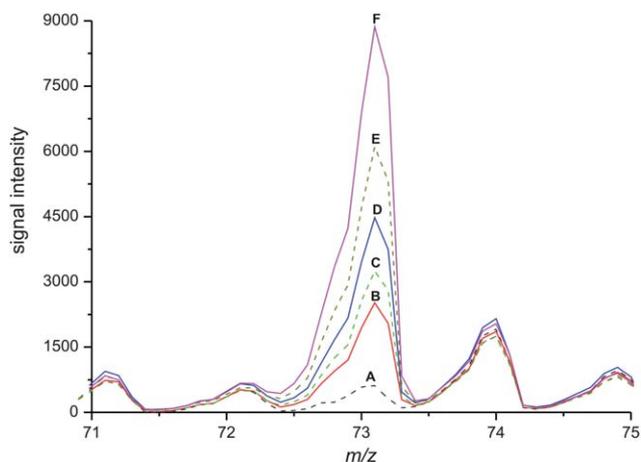
Fig. 3 MIMS in the m/z 71–75 range for (A) pure gasoline and (B–F) gasoline adulterated with kerosene marked with MTBE to final MTBE concentrations of (B) 50, (C) 100, (D) 200, (E) 500 and (F) 1000 mg L^{-1}.

natural marker ions (Fig. 2). The very minor, background ion of m/z 74 was used as a reference ion. To mimic adulteration, MTBE was spiked into kerosene, which was then added to gasoline resulting in final MTBE concentrations of 50 to 1000 mg L^{-1} (Fig. 3B–F). Note that with as little as 50 mg L^{-1} of MTBE, the artificial marker ion of m/z 73, the most intense ion in the 70 eV EI-MS of MTBE, is clearly perceived and its abundance increases linearly with the level of MTBE. In the linear range tested (50–1000 mg L^{-1}), a correlation coefficient of 0.98 ± 0.01 was obtained, which demonstrates good linearity of MIMS quantitation of MTBE in gasoline samples. A signal to noise ratio of 3 was used as the criterion for detection limit. MIMS detection of 25 mg L^{-1} of MTBE in the aqueous extract was easily attained. Method repeatability was tested by comparing the responses for 10 consecutive injections of 200 mg L^{-1} of MTBE. The relative standard deviation was about 5% in all cases. For all gasoline samples tested, the m/z 73 : 74 ratio of pure gasoline as compared to 1000 mg L^{-1} addition of MTBE was found to be quite constant, that is 0.27 ± 0.03 *versus* 4.0 ± 0.4.

MTBE has been used as an example of an efficient artificial marker for gasoline. But adulteration of gasoline as well as other petrofuels could be screened by MIMS *via* the use of a variety of artificial markers that, as for MTBE, are found to fulfill the double selectivity criteria of favored MIMS detection. These molecules would most likely include light ethers, esters, halobenzenes such as fluorobenzene as well as alkyl benzenes, ketones, and haloalkenes.

Conclusions

MIMS provides double selectivity for the detection of natural or artificial markers in gasoline. Simple but characteristic chemical signatures of gasoline are provided by MIMS due to the detection of a unique set of natural markers. Gasoline screening by MIMS for adulteration or to certify production sites (for instance different refineries, petrochemical plants or brands) could also be performed *via* the use of specific artificial markers selected from a variety of suitable molecules, as demonstrated herein for MTBE. To increase selectivity and minimize the chance for false positives (which should be confirmed by additional analysis), MS/MS experiments, easily performed for instance in miniature ion trap mass spectrometers, could be done. Miniature mass spectrometers[17,18,27,28] able to perform selective ion monitoring of the marker ions could be used in portable MIMS devices for the *in situ* and/or on-line monitoring of gasoline. On-site MIMS devices could be designed, and optimized to operate directly connected to gasoline pumps in fuel stations. A water reservoir could be directly connected, in a proper orientation and design, to the input gasoline line. A small pump would circulate the water through the system with the mass spectrometer set to monitor the artificial marker ion. Green and red lights could then be used to indicate gasoline quality. If the intensity of the artificial marker ion, as compared to a background ion, is lower than a threshold value, the green light is turned on. But if the artificial marker is present and the artificial marker intensity goes beyond a pre-established threshold value, the red light would trigger an alert for adulteration.

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