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Analysis of hydrocarbon contamination with membrane-assisted solvent extraction: Comparison of agitation and sonication methods

Z. Szekeres[a,*], Zs. Eke[a,b], T. Rikker[b], K. Torkos[a]

[a] Eötvös Loránd University, Joint Research and Training Laboratory (EKOL), H-1117 Budapest, Pázmány Péter sétány 1/A, Hungary
[b] Wessling International Research and Educational Centre Nonprofit Co., H-1047 Budapest, Fóti út 56., Hungary

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ABSTRACT

Membrane-assisted solvent extraction (MASE) coupled to large volume injection was applied to the determination of (gasoline-type) hydrocarbon contamination in water samples. Hexane was used as acceptor phase. 50 μL extract was injected in the programmed temperature vaporizer injector using combined split–splitless evaporation. The extraction conditions were optimized both for MASE with agitation and for MASE with sonication. In the course of optimization the effect of extraction time, extraction temperature, agitation speed, solvent volume, pH, ionic strength and the addition of methanol were tested. Over 75% recovery was accomplished in the range of diesel oil hydrocarbons (n-C_9–n-C_{24}). The developed method was validated. Linearity, accuracy and precision were tested. The method showed excellent linearity between 1 and 1000 μg L^{-1} for n-alkanes and between 0.05 and 50 mg L^{-1} for gasoline. The method was tested with comprehensive GC × GC as well and found to be non-discriminative to all major compounds of diesel oil.

1. Introduction

Oil is still the world's main energy source. Its distillates are used in every corner of our planet. No wonder that assessing oil spills and hydrocarbon contamination is one of the main branches of environmental analysis. Oil contaminations are commonly characterized by their extractable petroleum hydrocarbon content.

In April 2004 the European Committee for Standardization (CEN) presented an European Standard for the quantitative determination of total petroleum hydrocarbons (TPH) by gas chromatography [1]. The method applies simple liquid–liquid extraction for the assessment of hydrocarbons within the boiling range of n-nonane (C_9H_{20}) and n-tetracontane ($C_{40}H_{82}$). But, as in every field of analytical chemistry, faster analysis, lower detection levels, environmentally friendly and cost-effective methods are called for in hydrocarbon analysis as well. Sample preparation methods like liquid–liquid extraction (LLE) and solid-phase extraction (SPE) are recently amended by newer, solvent-free or solvent-reduced methods [2]. Techniques like solid-phase microextraction (SPME), stir bar sorptive extraction (SBSE) have become widely accepted [3,4].

Attempts were made to enhance laboratory throughput in the field of environmental hydrocarbon analysis as well. Microwave-assisted extraction [5,6] was applied successfully to reduce solvent demand and extraction time, while supercritical fluid extraction [7] and pressurized liquid extraction [8] omitted completely the use of organic solvents. Among the new techniques several types of membrane extraction have been developed during the past decade [9]. Membrane extraction methods are very effective in reducing solvent consumption and offer the possibility of the exclusion of matrix components that result in clearer spectra and reduced matrix effect.

Membrane-assisted solvent extraction (MASE) is a promising technique in this field. It has been introduced by Hauser et al. [10]. MASE is performed with dense polypropylene membrane bag attached to a metal funnel with a Teflon ring. The funnel can be crimped to the top of the common 20 mL headspace vial together with the cap. The vial is filled with 15 mL of sample and the membrane bag is immersed in the liquid. The membrane bag is filled with the extraction solvent and the compounds in the sample diffuse through the membrane and accumulate in the solvent according to their distribution coefficient. If the vial contains 15 mL of sample and the membrane 500 μL of solvent then, theoretically, 30-fold concentration can be reached in the organic phase. Since that is usually not enough for environmental applications, MASE is often combined with large volume injection [11–16]. By injecting 50 μL or more extract the achieved overall enrichment can surpass that of conventional LLE methods.

MASE has the possibility to replace LLE in various applications. It is cost-effective, solvent-sparing and fully automatable. MASE has been successfully applied to the analysis of various organic compounds (including phenols [12], pesticides [13,17],

* Corresponding author. Tel.: +36 304093809; fax: +36 12090602.
E-mail address: zoltan.szekeres@gmail.com (Z. Szekeres).

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polychlorinated biphenyls [14], polycyclic aromatic hydrocarbons [15] and (in miniaturized version) for volatile organic hydrocarbons [18] as well) from different aqueous matrices [9]. In comparison studies MASE proved to be superior to SBSE in the analysis of pesticides in point of recovery and automatability [15].

MASE is used mainly for the extraction of target compounds. In fuel contamination analysis, however, the concurrent extraction of a wide range of compounds (aliphatic, aromatic, unsaturated, carboxylic. . ., etc.) is necessary. The aim of the present work was to explore the capabilities of MASE in this field and develop a method that is able to substitute LLE in the analysis of petroleum hydrocarbon contaminants in water samples. MASE is usually performed with a multipurpose sampler. Though, the versatility of the device allows one to achieve extraction by an ultrasonic bath and sample introduction by a simple liquid autosampler. This is an expedient method for laboratories that do not dispose of a multipurpose sampler. In our work, both methods were optimized, evaluated, compared and validated for the extraction and analysis of petroleum hydrocarbons from water samples.

2. Experimental

2.1. Chemicals and standards

The alkane stock solution was prepared in acetone and contained the following n-alkane standards: C_9, C_{10}, C_{12}, C_{13}, C_{14}, C_{15}, C_{16}, C_{18}, C_{20}, C_{22} and C_{24} at concentrations of 200 μg/mL each. The n-alkane standards were purchased from Sigma–Aldrich (Steinheim, Germany) and were of at least 99% purity. Acetone and hexane were from Merck (Darmstadt, Germany) and were of SupraSolv® quality. NaCl was obtained from Merck and was of at least 99% purity. HCl (30%) was obtained from Merck and was of Suprapur quality. Diesel oil was obtained from a local petrol station.

2.2. GC conditions

The work was performed on an Agilent 6890N gas chromatograph (Agilent Technologies, Santa Clara, CA, USA) equipped with a flame ionisation detector (FID), a CTC Pal autosampler (CTC Analytics, Zwingen, Switzerland), a Cooled Injection System 4 (CIS 4) type injector provided with Peltier cooling and glass wool filled-insert (Gerstel, Mühlheim, Germany). The column was an Agilent HP-1 15 m × 0.25 mm i.d. column coated with cross-linked methyl silicone with a film thickness of 0.1 μm. The oven temperature program was a follows: 40 °C (held for 2.5 min), increased at 20 °C/min to 250 °C, increased at 35 °C/min to 300 °C (held for 3 min). Hydrogen 5.0 was used as carrier gas at a constant flow of 2 mL/min. The FID was maintained at 300 °C.

The GC × GC measurements were performed on an Agilent 7890 gas chromatograph equipped with a FID, an automatic liquid sampler (ALS) and a CFT Flow Modulator. The first column was a J&W DB5-MS 30 m × 0.25 mm i.d. column with a film thickness of 0.25 μm and the second column was an Agilent HP-Innowax 5 m × 0.25 mm column with a film thickness of 0.15 μm. Hydrogen 5.0 was used as carrier gas. The inlet temperature was 250 °C, splitless time was 1 min. The oven was kept at 40 °C for 1 min, then heated at 8 °C/min to 260 °C which was maintained for 20 min. The modulation cycle was 1.5 s with 0.1 s injection time. The first column flow was 0.8 ml/min and the second column flow was 20 ml/min. The column combination and GC × GC parameters were set as suggested by the corresponding Agilent Application Brief [19].

2.3. Membrane-assisted solvent extraction

The membrane-assisted solvent extraction devices were obtained from Gerstel. Before application the membrane bags underwent a preconditioning step in order to remove interfering compounds such as alkanes and phthalates, which can be coextracted from the membrane material. Twofold extraction with hexane was performed at room temperature. As it was shown in a former work the membrane bags can be reused at least seven times without losing efficiency [13]. In the optimized method extraction was performed as follows: 15 mL of water sample was filled in a 20 mL headspace vial. The vial was equipped with the membrane bag attached to its metal funnel with a polytetrafluoroethylene (PTFE) ring. The vial is closed with a metallic crimp cap. Two MASE methods were tested in our work: extraction with agitation and extraction with sonication. The optimized MASE with agitation method was performed the following way: the vial is placed on the tray of the autosampler. The autosampler injects 700 μL of hexane into the membrane bag, then the vial is transported into the agitator and stirred for 120 min at 40 °C and 750 rpm. After the agitation, the vial is transferred back onto the tray. Then, the autosampler aspirates 50 μL extract from the membrane bag and injects it directly into the CIS 4 injector. In the optimized MASE with sonication method 15 ml of water sample was filled in a 20 ml headspace vial, 500 μL of hexane was filed in the membrane which was inserted in the vial as above. The vials were put in an ultrasonic bath and sonicated for 50 min. 200 μL aliquots of the extracts were filled in 2 ml GC vials equipped with a microvolume insert and placed on the autosampler tray. For the optimization distilled water was spiked at the 0.05 μg/mL level by 20 μL of the stock solution.

2.4. Large volume injection

To ensure the appropriate recovery in the whole TPH range (C_9–C_{40}) a combined split–splitless evaporation method [20] was used for the introduction of the analytes into the GC This method allows the introduction of analytes over a wide boiling point range without discrimination. The injection was carried out with a CTC Pal autosampler and a temperature-programmable injector (CIS 4) provided with a glass wool filled-insert. 50 μL of the extract were injected with a 100 μL syringe. The injection speed was 2.5 μL/s. During the injection the inlet temperature was maintained at 10 °C by cooling with the Peltier cooling system. The injection was performed in stop-flow mode with a vent flow of 200 mL/min. The initial 10 °C was maintained for 0.4 min, then the split went was closed and the inlet was heated at a rate of 10 °C/s to 60 °C. This temperature was maintained for 1 min, then the inlet was heated at a rate of 10 °C/s to the final temperature of 300 °C and maintained for 10 min. The split vent was opened at 2.5 min.

3. Results and discussion

3.1. Optimization of agitation parameters

3.1.1. Extraction time

For optimizing the extraction time the agitation rate was set to 750 rpm and the extraction temperature to 40 °C. The extraction time was varied between 30 and 120 min. Extraction yields are showed in Fig. 1. With the increase of the extraction time the area of the analytes increased considerably up to 120 min. Therefore 120 min was chosen as the optimal extraction time. This does not lead to elongated analysis time, as the instrument is capable of preparing multiple samples simultaneously.

3.1.2. Agitation rate

In comparison to liquid–liquid extraction in MASE the phase boundary between the sample and the extraction solvent has a definite, relatively small area. Therefore the effective mixing of the sample is very important to facilitate the transfer of analytes through the membrane by furnishing the boundary layers with new analytes from the bulk of the sample. For optimization, the agitation rate was varied between 250 and 750 rpm. The extraction yield increased almost linearly with the agitation rate hence, the agitation speed of 750 rpm was used for all further experiments.

3.1.3. Solvent volume

The sample/extraction solvent ratio is an important factor when measuring low concentrations, as lower organic phase volume (higher sample to acceptor phase ratio) may lead to increasing concentration in the acceptor phase. The effect of solvent volumes 500, 700 and 900 μL was tested. The solvent volume did not have significant effect on the amount of hydrocarbons extracted. However, as the analytes were concentrated in different volumes, the smaller extraction volumes gave proportionally larger peak areas. At the solvent volume of 500 μL the injection process became insecure, as the solvent level in the membranes was sometimes too low for the syringe to reach and in these cases no valuable injection was performed. With 700 μL solvent this problem was no longer observed. This amount of solvent was used for all further agitation experiments.

3.1.4. Extraction temperature

Elevation of temperature shortens extraction time in most of the cases. The upper limit is determined by the boiling point of the extraction solvent. The extraction should be carried out 10–20 °C under the boiling point of the extraction solvent in order to avoid evaporation, or excessive increase of pressure that can damage the membrane bag. The lowest temperature, that the sampler can provide is 30 °C. Considering these limits, the extraction temperature was tested at 30, 40 and 50 °C (Fig. 2). The efficiency of the extraction increased in the whole temperature range. At 50 °C decrease in the reproducibility of the extraction was observed, supposedly, due to partial evaporation of the solvent. This leads to changes in the concentration of the extracts and, in some cases, to 'empty injections' as the needle could not reach the dropped surface of the solvent in the membrane bag. Consequently, the extraction temperature of 40 °C was used in all following experiments.

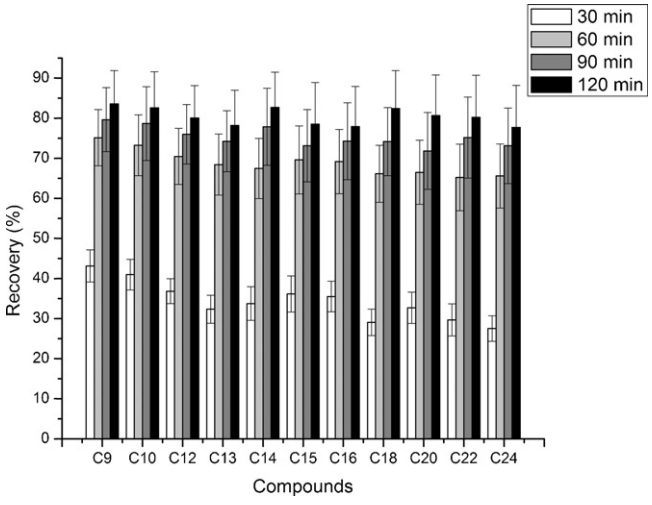

Fig. 1. Optimization of the extraction time (agitation with 900 μL hexane, at 40 °C and 750 rpm without salt or pH adjustment).

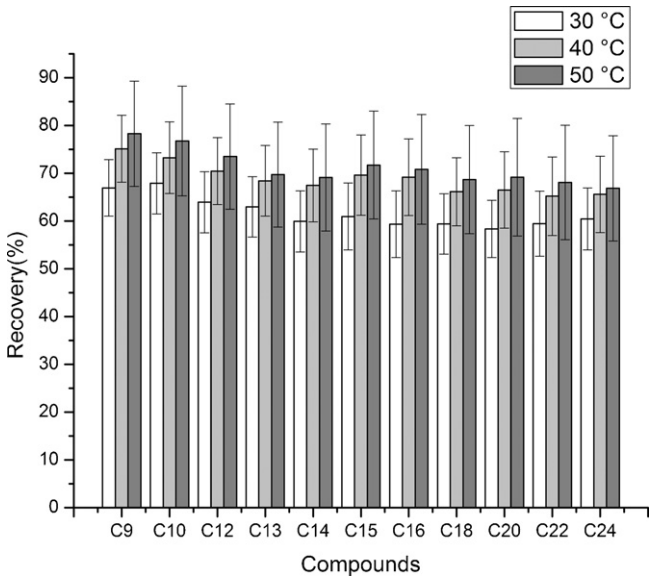

Fig. 2. Optimization of the extraction temperature (agitation with 700 μL hexane for 60 min at 750 rpm without salt or pH adjustment).

3.1.5. Ionic strength, pH and methanol content

Increased ionic strength usually facilitates the extraction of organic compounds from aqueous media. In the case of MASE several different observations were reported. Some of them indicate positive 'salting-out' effect, mostly for polar analytes [10,12,13], but there are observations where ionic strength had no or negative effect on the extraction efficiency [17,14,15]. Solutions with different concentrations of NaCl were prepared to examine the effect of ion strength on recovery. The concentration of salt was varied between 0 and 25% (m/m) on 5 levels. The increased ionic strength had no positive effect on the extraction efficiency. On the contrary, the recoveries decreased slightly with the increasing ionic strength. With 25% (m/m) NaCl the extraction yields were 7–18% lower than the ones without NaCl. The effect of pH was tested at pH 2 and 11. No significant effect on the recovery was observed, the differences are comparable to the deviation of the results. The effect of methanol was tested with spiked water samples containing 2 and 5% (v/v) methanol. No difference could be observed between the samples with 0 and 2% methanol content. With 5% methanol, the extraction yield decreased considerably. In the developed method, therefore, no pH adjustments were made and no methanol was added to the sample.

3.2. Optimization of sonication parameters

3.2.1. Optimization of the extraction time

The sonic bath was operated at room temperature. The extraction time was varied between 5 and 50 min at 4 levels. The yields at different extraction times are shown in Fig. 3. It can be seen from the yields, that the extraction goes about two times faster with sonication owing to the more effective mixing of the extracted boundary layers with the bulk of the sample. The extraction time of 50 min yielded the best recovery and was chosen as optimal.

3.2.2. Ionic strength, pH and methanol content

The experiments with ionic strength and pH showed no significant differences from the results obtained with agitation. This matches expectations as the principles of the extraction process do not change with the type of the mixing. In further experiments no salt or methanol was added to the samples and the pH was not adjusted.

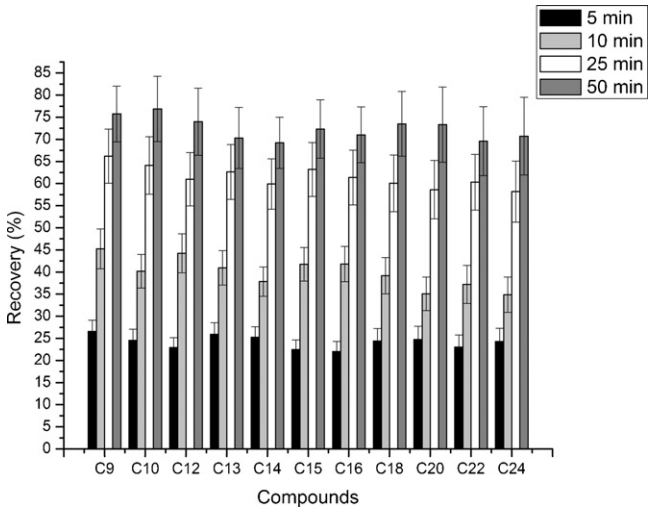

Fig. 3. Optimization of the extraction time (sonication with 700 μL hexane, at RT without salt or pH adjustment).

3.2.3. Solvent volume

After the extraction with sonication 200 μL of the solvent was transferred from the membrane bag into a GC microvial which was then placed on the GC sample tray. Large volume injection was performed with an Agilent 7683 automatic liquid sampler. The sampling from the membrane bag was performed by hand with a finnpipette. There was no limitation owing to the length of the syringe, nevertheless, handling solvent volumes under 500 μL was impractical. Thus, the volume of the extraction solvent was varied between 500 and 900 μL. 500 μL that gave the larges peak areas was chosen as the optimal solvent amount.

3.3. Validation of the methods

3.3.1. Carryover

MASE is cost-effective because the membranes can be reused several times. To reuse the membranes, however, one has to be sure, that no cross-contamination occurs. For testing the effect water samples were spiked with alkane standards and with diesel oil as well to concentrations corresponding to the highest calibration points. Following the extraction the membrane bags were cleaned by two times 10 min sonication in hexane. Then, pure water samples were extracted with the purified membrane bags. The resulting chromatograms showed no sign of cross-contamination in the case of normal alkanes, and lower than 0.1% cross-contamination in the case of diesel oil.

3.3.2. Calibration, linearity, precision

The results concerning linearity, precision, recovery, detection limits, and calibration data (for n-alkanes) are summarized in Table 1. MASE is a non-exhaustive extraction method. To make the analysis quantitative, either an internal standard has to be applied or the whole sample preparation process has to be included in the calibration. In an EPH analysis no distinct peaks are determined but the whole area of the corresponding retention-time window must be integrated. In such circumstances no internal standard can be separated from the analytes reliably. Therefore we used external calibration with sample preparation included. The methods proved to be linear between 1 and 1000 μg/L with both extraction methods. It can be seen from Table 1 that there is no significant difference in the performance of the two types of extraction.

3.3.3. Testing discrimination with 1D and comprehensive 2D GC

The method is designed for the assessment of hydrocarbon contaminants in water where not only n-alkanes are present but also several other aliphatic and monoaromatic compounds. Since the method was developed using normal alkanes we had to make certain, that it does not discriminate against other (either unsaturated, cyclic, or monoaromatic) compounds present in a typical hydrocarbon contamination. All the compounds cannot be tested. To study discrimination we choose a mixture that most closely represents the range of molecules we intend to measure. Our choice fell upon diesel oil, being one of the most frequent contaminant and rich in unsaturated and aromatic compounds in the studied boiling point range. Discrimination was tested by comparing the chromatogram of a water sample contaminated with diesel oil and the chromatogram of the same amount of diesel oil diluted in hexane. The comparison of the chromatograms showed no significant discrimination. Both the low- and the high-boiling compounds are extracted in equal proportions and all peaks are present in the chromatogram of the extracted diesel oil (Fig. 4). To see if the method discriminates to unsaturated or aromatic compounds, we tested it with comprehensive GC × GC as well. The chromatograms of extracted and diluted diesel oil were compared as seen in Fig. 5. On the GC × GC chromatogram 8 compound groups were chosen in a way that they cover all major compound classes present in diesel oil. The volumes of the groups were compared in the two chromatograms and no discrimination was found. Even the recovery of the fatty acid methyl ester (FAME), or diaromatic group does not differ significantly from the general recovery calculated from the

Table 1
Validation data for n-alkanes. S: MASE with sonication, A: MASE with agitation. LOD and LOQ: $S/N \geq 3$ and $S/N \geq 10$ respectively, calculated from pure water samples spiked at 1 μg/mL level.

Analyte	Recovery (%)[a]		Linearity (R^2)[b]		Precision[dm] RSD (%)[a] ($n=5$)		Precision[sm] RSD (%)[a] ($n=5$)		LOD (μg/L)		LOQ (μg/L)	
	S	A	S	A	S	A	S	A	S	A	S	A
n-C_9	76	84	0.9927	0.9995	8.1	8.6	4.9	4.0	0.089	0.071	0.47	0.41
n-C_{10}	77	83	0.9965	0.9993	9.8	9.7	3.1	5.1	0.090	0.069	0.44	0.36
n-C_{12}	74	80	0.9986	0.9989	10.4	6.9	5.7	2.3	0.093	0.089	0.46	0.39
n-C_{13}	70	78	0.9997	0.9994	9.2	12.1	4.4	4.3	0.10	0.072	0.43	0.35
n-C_{14}	69	81	0.9963	0.9990	10.6	10.0	5.4	2.4	0.11	0.061	0.48	0.46
n-C_{15}	72	79	0.9954	0.9988	8.7	13.1	3.1	3.8	0.10	0.062	0.56	0.34
n-C_{16}	71	78	0.9971	0.9989	9.6	11.8	2.9	3.9	0.097	0.086	0.67	0.69
n-C_{18}	73	82	0.9990	0.9976	10.0	12.2	4.5	4.6	0.10	0.078	0.69	0.39
n-C_{20}	73	81	0.9986	0.9972	11.3	11.5	4.7	5.0	0.10	0.058	0.57	0.54
n-C_{22}	70	80	0.9980	0.9956	11.4	14.2	3.8	5.3	0.098	0.064	0.63	0.51
n-C_{24}	71	78	0.9987	0.9953	12.3	10.3	5.3	3.9	0.10	0.066	0.62	0.46

[dm] Reproducibility using different membrane bags. [sm] Reproducibility using the same membrane bag.
[a] Calculated from water samples spiked at 50 μg/mL level.
[b] Seven point calibration from 1 to 1000 μg/mL.

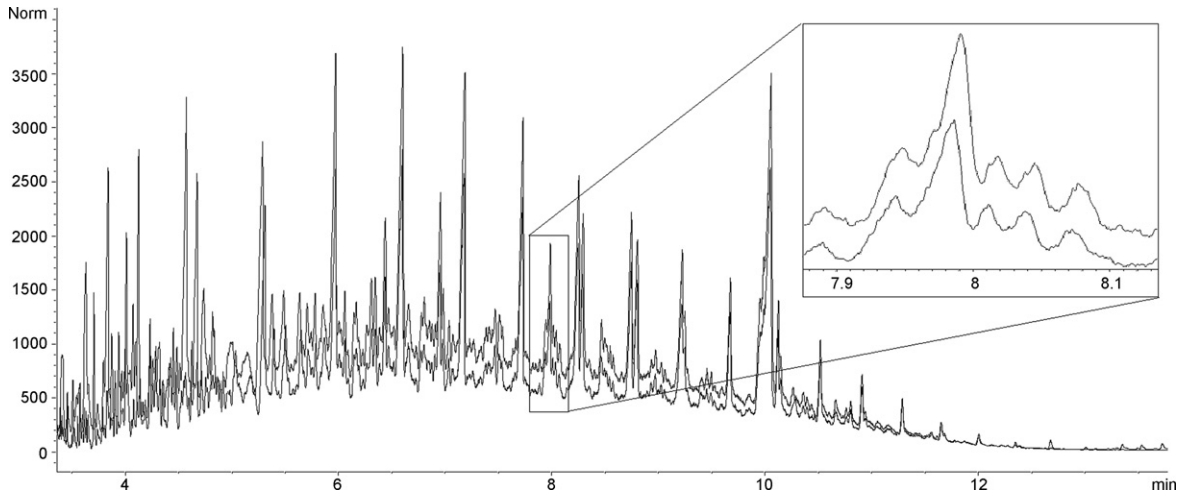

Fig. 4. Part of the overlayed chromatograms of diesel oil diluted in hexane (upper line) and diesel oil extracted from water by MASE with agitation (lower line). The water was spiked at the 2 μg/ml level with diesel oil.

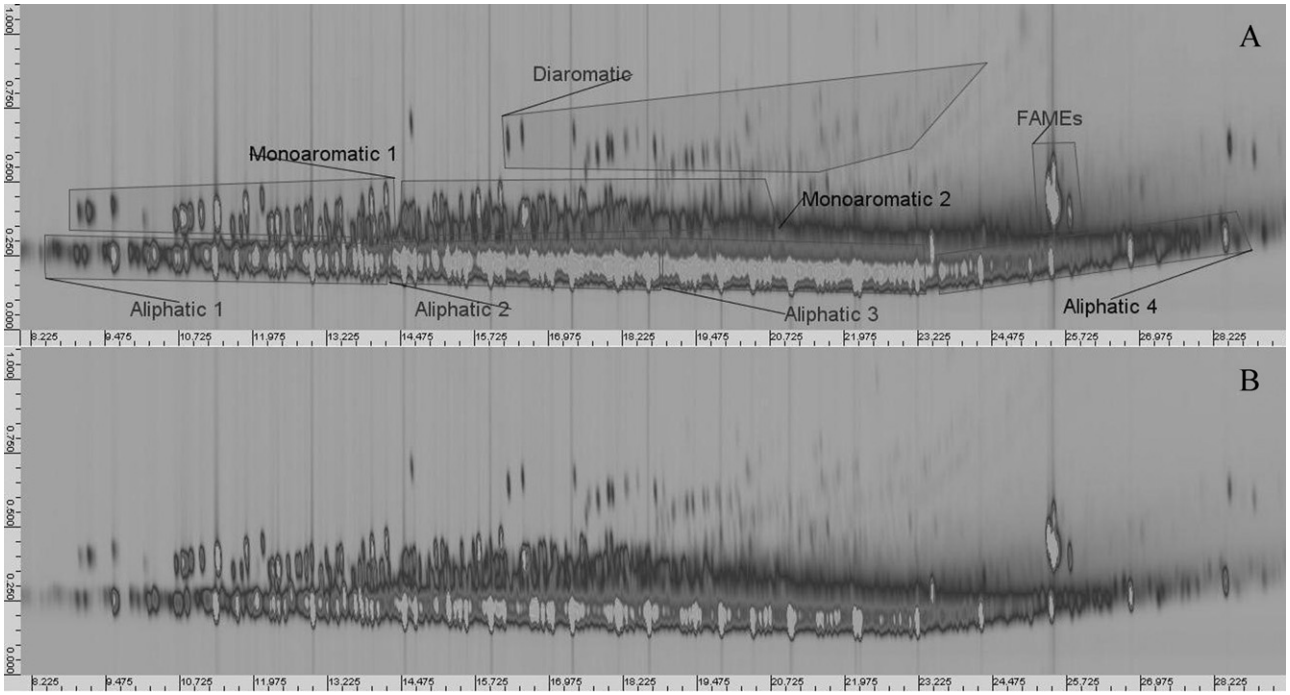

Fig. 5. Comparison of the 2D chromatograms of diesel oil diluted in hexane (A) and diesel oil extracted from water (B) by MASE with sonication. The areas used to compare the recovery of the different compound groups in Table 2 are shown on chromatogram A.

Table 2
Recovery data of the major compound groups of diesel oil, measured by GC × GC. All recoveries are within the 95% confidence interval of recovery of the diesel oil measured by the one-dimensional method.

Area name	Recovery	
	Agitation	Sonication
Aliphatic 1	79.2%	75.7%
Aliphatic 2	80.9%	74.2%
Aliphatic 3	77.1%	71.9%
Aliphatic 4	78.6%	71.1%
Monoaromatic 1	80.1%	73.3%
Monoaromatic 2	81.3%	72.8%
Diaromatic	79.2%	71.6%
FAMEs	72.8%	69.5%

conventional GC chromatogram by integrating the whole diesel oil range (Table 2). Thus, GC × GC corroborated the 1D GC results that the method does not discriminate significantly to the compounds of diesel oil. Therefore, it is better to calibrate it with diesel oil, because it is closer to the nature of the expected contamination than normal alkanes. If calibrated with n-alkanes the difference in the integration process can lead to false estimation of the performance of the

Table 3
Validation with diesel oil. LOD: three times the blank value. The values were rounded up for convenience. LOQ: the lowest calibration point, over 10 times the blank value.

	Recovery (%)	Precision (RSD% $n = 5$)	LOD (μg/L)	LOQ (μg/L)	Linearity (R^2)
Agitation	81	12.6	15	50	0.9986
Sonication	73	11.3	15	50	0.9997

method. Consequently, the calibration and LOD, LOQ data obtained from diesel oil measurements represents more accurately the overall performance of the method. Both MASE methods were calibrated with diesel oil. Validation data can be found in Table 3.

4. Conclusions

MASE proved to be a practical technique for the assessment of hydrocarbon contamination in water. The developed method offers non-discriminative, effective enrichment of diesel oil type contamination from water samples.

The method is robust: neither differences in pH (acidic or basic sample), nor high electrolyte concentration can significantly deteriorate the analysis. The range of linearity spans over 3 orders of magnitude from 1 to 1000 μg/L for alkanes and from 0.05 to 50 mg/L for diesel oil. The method can be used in fingerprinting or age dating studies where polar, unsaturated or aromatic hydrocarbons are of special concern and must not be excluded. Combination with GC × GC can provide detailed analysis of hydrocarbon contamination in a wide polarity range.

MASE can be performed with agitation or with sonication as well. Sonication is faster but needs more manual work, while agitation can be completely automated. In the discrimination, linearity or reproducibility of the two methods no significant difference was found. The occasional differences are more due to differences in the membrane bags. The possibility, that MASE can be performed not just with multipurpose sampler but manually as well, makes it a versatile technique for differently equipped laboratories. Applied with a multipurpose sampler it offers fast, fully automated analysis.

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