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COMBINATION OF SOLID PHASE EXTRACTION WITH SUPERCRITICAL FLUID EXTRACTION FOR THE DETERMINATION OF CONTAMINANTS IN WATER

M. Adam, K. Ventura, P. Jandera, J. Churáček

Department of Analytical Chemistry
Faculty of Chemical Technology
532 10 Pardubice, Czech Republic

ABSTRACT

The applicability of supercritical fluid extraction was studied for the determination of mineral oil contaminants in the presence of non-ionic surfactants in water after a prior preconcentration on a solid sorbent. The species representative of the two types of contaminants were retained first on a solid sorbent Separon SGX C18. Under optimized conditions supercritical fluid extraction (SFE) with carbon dioxide was used in the first step to extract selectively mineral oil, to be determined by FTIR in a carbon tetrachloride solution. In the second step, SFE with carbon dioxide modified with 5 % (v/v) of methanol yielded a selective and quantitative separation of a non-ionic surfactant into methanol with UV spectrometric finish. A new design of column for retention of species from SFE with the use of a solid sorbent was also developed and tested.

INTRODUCTION

In determinations of most pollutants in waters classical extraction techniques, namely liquid-liquid extractions or microextractions, are very often used for separations of analytes. These extraction procedures require, however,

relatively great amount of solvents and a long time for the separation. At present, a typical trend of chemical analysis is represented by combining a sample treatment, which allows a prior separation of substances into different fractions or groups, with the application of methods allowing determination of very low concentrations. Often the development of new extraction techniques is also inspired by the need to reduce consumption of organic solvents in order to minimize environmental risks.

Hence new extraction techniques have been introduced, e.g., such as solid-phase extraction (SPE),^{1,2} in which a sample of water is passed through a column packed with such kind of sorbent that can retain the analyte under investigation.^{3,4} Reversibility of the retention and an easy and quantitative desorption of the analyte into a suitable solvent represent criteria for the choice of sorbents. Direct supercritical fluid extraction (SFE) is another technique suitable for isolation of pollutants from water samples.^{5,6} This extraction method is based on a low solubility of water (<1 mol%) in carbon dioxide at supercritical conditions, which is due to a low polarity of CO₂. However, even such low solubility of water in supercritical CO₂ increases the polarity of the supercritical phase to such extent that some moderately polar substances are extracted with a fair efficiency, in contrast to a high recovery achieved with nonpolar substances. Routine SF extractors are designed only for extraction of solid samples; thus a special adaptation of the apparatus is required for direct SFE of a water matrix. A simple answer to this problem is to introduce a prior step of solid-phase extraction (SPE), which is then followed by actual SFE,^{7,8} allowing elution of the retained analyte from the sorbent with the aid of supercritical CO₂ into a solvent suitable for subsequent analytical finish. The problems of preconcentration of analytes by means of SFE are treated in the literature^{9,10} in more detail.

These extraction techniques can be used for the determination of the content of mineral oil pollutants and non-ionic surfactants. In recent years, the two kinds of pollutants represent a frequent cause of environmental hazards. The contamination with mineral oil may be brought about not only by human activities but also by a natural cause, for example, by leakage of crude oil close to an oil field. In the case of non-ionic surfactants the contamination is always caused by man, because these substances represent products of organic synthesis, i.e. oxyethylation leading to adducts of ethylene oxide and an organic compound with active hydrogen (primary and secondary alcohols, alkylated phenols, etc.). The two types of pollutants have several common properties:

- a) toxicity
- b) high persistence
- c) tendency to accumulation

They are found in soils, and above all in waters, where their presence is not harmful by itself but gradual accumulation causes formation of a thin film on water surface, which prevents access of atmospheric oxygen to water.¹¹ Thus anaerobic processes occur with formation of toxic products which are the actual cause of gradual harmful pollution of water.¹² In addition to that, bacteria present in water bring about decomposition of the two kinds of contaminants, which results in formation of further decomposition products, such as polyethylene glycol, which is a typical decomposition product of a nonionic surfactant: it helps to monitor the contamination of environment by this type of pollutant.

For determination of a total amount of mineral oil products and non-ionic surfactants spectrophotometric methods in the ultraviolet and infrared are suitable after a prior separation and preconcentration.¹³ However, these methods cannot provide more detailed information about individual components of mineral oil and surfactant pollutants. For this purpose a suitable chromatographic technique should be employed.

EXPERIMENTAL

Materials

As model contaminants, the following commercial products were chosen: non-ionic surfactant species were represented by Slovafof 905 (Sloveca, Slovak CONDEA Augusta, Nováky, Slovakia), the main component illustrated by the formula $\text{HO} \cdot (\text{CH}_2\text{CH}_2\text{O})_5 \cdot \text{C}_6\text{H}_4 \cdot (\text{CH}_2)_8\text{CH}_3$; mineral oil contaminants were represented by a Diesel oil, type NM4 (Chemopetrol, Litvínov, Czech Republic).

Carbon dioxide was of a purity 4.5 (Linde, Werksgruppe Tech. Gase, Düsseldorf, Germany).

Sorbents, i.e. Separon SGX C18, 60 μm (Tessek, Prague, Czech Republic), and Porasil A, 60 μm (Waters Associates, Framingham, USA), and a silane treated glass wool (Supelco, Bellefonte, PA, USA) were used.

As solvents methanol for HPLC (J. T. Baker, Deventer, The Netherlands) and analytical-grade carbon tetrachloride (P-Lab, Prague, Czech Republic) were used.

All other reagents used were of the highest purity available.

Apparatus

A spectrophotometer, model GBC 916 (GBC Scientific Equipment, Dandenong, Australia), was equipped with 10-mm quartz cells for UV measurements of methanolic surfactant solutions against pure methanol as reference. The absorbance at 276 nm yielded a straight-line calibration within the concentration range of 0.05 - 1.0 mg of Slovafof 905 per 5 mL of a solution. This procedure was also used for the analysis of water samples after preconcentration and transfer of the analyte to the medium of methanol.

An IR spectrophotometer, model FTIR Equinox 55 (Bruker Analytische Messtechnik, Karlsruhe, Germany), was equipped with 10 mm quartz cells for measurements in the region 3150 - 2750 cm^{-1} . The number of scans was 24 per one absorption spectrum measured for a carbon tetrachloride solution of a mineral oil against pure solvent as reference. The absorbance was evaluated at 2926 cm^{-1} for a calibration between 0.05 and 1.0 mg of mineral oil per a 5 mL eluate. The same procedure was used for water analysis after the preconcentration step and transfer of the analyte to carbon tetrachloride.

A commercial SFE apparatus, model SE-1 (SEKO-K, Brno, Czech Republic)¹⁴ was adapted for the supercritical fluid extraction of analytes retained on a sorbent Separon SGX C18. A stainless steel cartridge (inner volume of 5 mL) and a restrictor in the form of a quartz capillary (150 mm \times 25 μm i.d.) were used. In addition to that, the extractor was adapted as follows: a high pressure valve allowed a static extraction; the restrictor was provided with a heating attachment in order to prevent fouling of the tip; a sampling loop allowed a continuous modification of the supercritical phase.

Sample Preconcentration

The following procedure of solid-phase extraction was used. The sample of water to be analysed was passed by suction through a glass column (Fig. 1) of 10 mm inner diameter packed with a 15 mm layer of a sorbent Separon SGX C18. The end of the column was secured with a pack of glass wool. The constricted end of the column was connected to a water aspirator, the other end was immersed into the sample of water to be analysed. Always a volume of 1 litre of water sample in about 1 hour was passed through this column.

Elution of Retained Components

For SFE desorption of substances, retained on a sorbent, an extractor SE-1, adapted as described above, was used. The extraction medium used was carbon dioxide of purity grade 4.5 with a reduced amount of oil. The sorbent with

retained analytes was transferred to an extraction cartridge, which was then inserted into the extraction cell. The extraction was carried out at 100°C for 30 min at a pressure of 25 MPa for mineral oil contaminants or at a pressure of 40 MPa (with an addition of 5 % (v/v) of methanol) for surfactant species.

Retention of Analytes Following SFE

Use of Solvents

Transfer of the species from SFE into a suitable solvent was realized by introducing the end part of the restrictor into a 5 mL retention vial containing 3 mL of methanol for surfactants or the same volume of carbon tetrachloride for petroleum type contaminants. After SFE was complete, the volume of the solvent with analytes was made up to 5 mL and the retention vial was closed tight with a plastic cap.

Retention on Solid Sorbent

For analyte deposition onto a solid sorbent a glass column, shown in Fig. 4 (inner diameter of 5 mm, length of 50 mm), was designed. The column was filled with a 20 mm layer of a Porasil A (60 μm) silikagel adsorbent (Waters Associates, Milford, USA), provided with glass wool packing at both ends. The tip of the restrictor was introduced to the half-length of the sorbent layer. The column was then placed within two segmented parts of a cylindrical sheath (60 mm of length and 22 mm of outer diameter). This sheath was made of hard aluminium to fit the dimensions of the heated extractor block in order to ensure a good heat conductivity and thermostatic control of the sorbent column. The assembled device was then placed into the extractor and heating was adjusted to a temperature of 35°C. After the extraction was completed, the analytes were eluted from the column with 5 mL of the particular solvent.

RESULTS AND DISCUSSION

Sample Treatment for SFE

A commercial apparatus for SFE, such as model SE-1, cannot be used for liquid samples. It was designed primarily for the extraction of solid samples and a necessary adaptation would be expensive. Therefore, a prior preconcentration step of SPE was introduced before the actual extraction with supercritical carbon dioxide, which served as a mode of desorption.

According to information from literature, octadecylated silica gel (sorbent Separon SGX C18) was chosen as a sorbent; but it was necessary to verify if

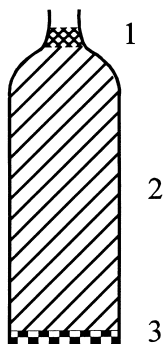


Figure 1. Glass column for retention of analytes from water samples with the use of SPE, 1 - Glass wool, 2 - Sorbent (Separon SGX C18), 3 - Porous sintered glass.

that particular sorbent was able to retain the two kinds of contaminants and if the sorption process was not irreversible.

Dimensions of a specially designed glass column shown in Fig. 1 permitted us to insert the column with retained analytes into the extraction compartment of the apparatus. However, supercritical carbon dioxide found paths of minimum resistance and bypassed the column to such extent that the recovery of extraction was low. A mode of quantitative transfer of the sorbent with retained analytes to the extraction cell was worked out.

Choice of the Test Substances and the Methods of Determination

Both previous experience and preliminary experiments indicated that the two types of contaminants, which at present cause frequently pollution of environment, can be represented by the following two products: a Diesel oil NM4 to represent mineral oil contaminants and a surfactant Slovafof 905 as a test substance for non-ionic surfactants.

As a finish for the determinations of the two types of contaminants, spectrophotometry was found to be sufficiently sensitive and suitable to provide information on a total contamination with these types of contaminants. Infrared spectroscopy was suitable to determine the content of contaminants within the region of valence vibrations of the C-H bonds. This region is also accessible for recording of the absorption spectra with the use of quartz cells. Both types of contaminants possess aromatic moieties, which allows the determination with the use of spectrophotometry in the ultraviolet region. On comparison of the absorption spectra of the two kinds of contaminants, as illustrated in

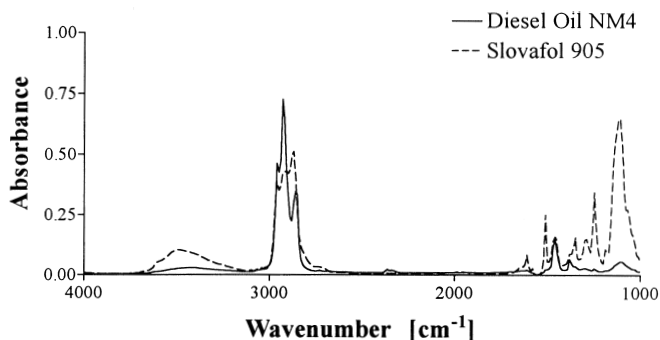


Figure 2. Absorption spectra of a diesel oil NM4 and Slovafof 905 in the infrared region.

Figs. 2 and 3, neither the ultraviolet nor the infrared region offered the possibility to find an absorption band at which the radiation would be absorbed only by one kind of the contaminants. A spectrophotometric finish can be realized, therefore, only after a prior separation.

Optimization of Supercritical Fluid Extraction

It was necessary to develop a procedure allowing a selective separation of only one component during the first step, to be then followed by the second step, to perform a quantitative extraction of the remaining component.

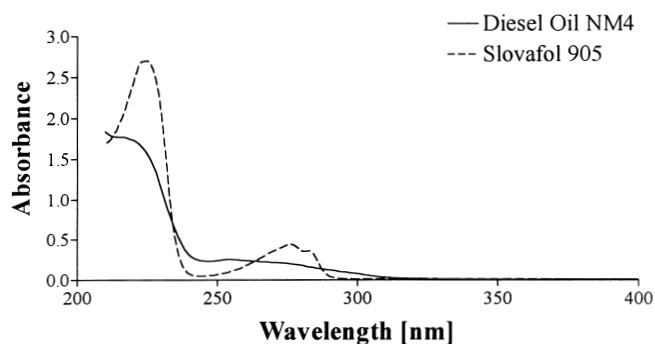


Figure 3. Absorption spectra of a diesel oil NM4 and Slovafof 905 in the ultraviolet region.

However, experimental conditions had to be found in order to verify, in practice, the assumption that less polar mineral oil contaminants should be eluted under milder arrangement of the extraction in comparison with non-ionic surfactants.

The following experiment exemplified this approach. First, approximately 0.1 mg of Diesel oil was introduced on a sorbent column in the extraction cell, which was then introduced into the extractor. The extraction was carried out for 30 min at a temperature of 100°C and a pressure of 25 MPa followed by deposition in carbon tetrachloride solvent to be analysed by a subsequent FTIR method. For a series of 10 experiments, an average degree of extraction of mineral oil components was 100.9%, with a standard deviation of 2.2%. A similar arrangement was used for the extraction of Slovafof 905, only methanol was used to retain the compounds extracted and the solutions obtained were subsequently analysed by UV spectrophotometry. An average degree of extraction was 1.48% with a standard deviation of 0.57%. From these results, it is evident that the extraction of mineral oil components was quantitative and, contrarily, the extraction of surfactants proceeded to a minimum extent.

Next, the conditions for a quantitative extraction of surfactant species had to be found. First, a series of 10 extractions was performed for a period of 30 min at a temperature of 100°C and a pressure of 40 MPa, with retention in methanol. An average degree of extraction of Slovafof 905 was 13.16% with a standard deviation of 0.17%. It was, thus, evident that under these conditions the extractions were rather incomplete. For the next series of 10 extractions an addition of 5% (v/v) of methanol was introduced to modify the extracting medium. An average result was thus increased to 101.3% with RSD 1.31%. An essential improvement leading to a quantitative extraction of surfactants was thus achieved by adding a small amount of methanol as modifier.

SFE Combined with Retention on Solid Sorbent

There were several reasons justifying a study of this arrangement. Firstly, a further separation of compounds retained on a column might be achieved by gradual elution. Secondly, the stability of the compounds retained on a solid sorbent is greater than that of solutions in organic solvents used for the retention.¹⁶ This mode might also be of some advantage if instrumentation for the analytical finish were not immediately ready for use. Various modes of combination of SFE with the deposition on solid sorbents are described in the literature,^{17,18} but not one of these arrangements was applicable for the type of extractor SE-1 used.

A glass column of special design (Fig. 4) was filled with a sorbent Porasil A, which was chosen as most suitable on consideration of the literature data.¹⁵

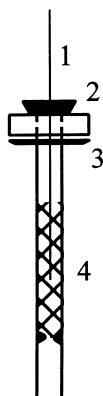


Figure 4. Glass column for retention on solid sorbent in the course of SFE, 1 - Restrictor, 2 - Septum, 3 - Plastic sealing, 4 - Sorbent (Porasil A).

However, it was necessary to verify effectiveness of elutions with the aid of solvents used for the subsequent spectrophotometry. So, an amount of 0.1 mg of Slovafof 905 was dosed on the sorbent column and then eluted with 5 mL of methanol. An average of 10 measurements was 99.5% recovery with RSD 1.22%. A similar experiment was performed with dosing of 0.1 mg of Diesel oil. The elution with 5 mL of carbon tetrachloride reached recovery of 97.9% with RSD 2.86%. These results confirmed feasibility of the proposed procedure.

A suitable fixing and positioning of the restrictor tip in the column of sorbent, as well as, the temperature of the column were further experimental factors to be examined. The path length of carbon dioxide carrying extractants should be sufficient to ensure an effective contact of analytes with the sorbent. The position of the restrictor within the middle of the column was found to be satisfactory.

Temperature also influenced the results of retention. At a low column temperature, the Joule-Thompson effect of expanding carbon dioxide caused icing up of the restrictor tip and, contrarily, a high temperature brought about a loss of more volatile components. A range between laboratory temperature and 50°C was investigated and a maximum recovery was found between 30°C and 40°C ($n = 5$, 97.3%, RSD 2.85, and 96.4%, RSD 2.98%, respectively). Therefore, a temperature of 35°C was chosen for further experiments.

The procedure was tested in series of 10 extractions: 0.1 mg of Diesel oil was extracted from a sorbent Separon SGX C18 for 30 min at a temperature of

100°C, pressure of 40 MPa and with the use of the solid sorbent for retention. Desorption with 5 mL of carbon tetrachloride gave an average result of 95.4% with RSD 2.3%. The same conditions were used for the extraction of 0.1 mg of Slovafof 905 but with a small addition of methanol as modifier and the elution using 5 mL of methanol. An average degree of extraction was 98.8% with RSD 1.8%.

These results indicated that the use of a solid sorbent for the retention represented a satisfactory alternative for laboratory practice.

Extractions of Model Samples of Water

For test experiments, 1 litre of a water sample was always taken with a content of about 0.1 mg of Diesel oil and 0.1 mg of Slovafof 905. The sample was passed through a column filled with a sorbent Separon SGX C18 and after a partial drying with air the sorbent was transferred quantitatively into the extraction cell. Supercritical fluid extraction was achieved in two steps. First, a mineral oil contaminant was selectively extracted for 30 min at 100°C and 25 MPa with the use of carbon tetrachloride for retention. Then the same sorbent was extracted for 30 min but at 100°C and 40 MPa with an addition of methanol as modifier and with the use of methanol for retention. The results listed in Table 1 indicate that this procedure can be used successfully for the determination of a total amount of mineral oil and surfactant contaminants.

Table 1

Assay of Model Samples of Water*

| Experiment No. | Diesel Oil Absorbance (2926 cm ⁻¹) | % Recovery | Slovafof 905 Absorbance (276 nm) | % Recovery |
|-------------------|--|------------|----------------------------------|------------|
| 1 | 0.064 | 94.15 | 0.049 | 91.07 |
| 2 | 0.072 | 105.92 | 0.047 | 87.35 |
| 3 | 0.068 | 100.03 | 0.047 | 87.35 |
| 4 | 0.065 | 95.62 | 0.049 | 91.07 |
| 5 | 0.067 | 98.56 | 0.048 | 89.21 |
| Average: | 0.067 | 98.86 | 0.048 | 89.20 |
| Std. Dev.: | | 4.58 | | 1.86 |

* Containing 0.117 mg of Diesel Oil and 0.104 mg of Slovafof 905 per litre.

The actual concentration of these substances in surface waters is usually quite low. For example, concentration of these contaminants should be in the range of tens of $\mu\text{g L}^{-1}$ according to standard regulations. Therefore, it might be necessary to increase the sample volume (to 2 - 3 litres) in some cases or, eventually, to use cells with a greater optical path length (20 or 50 mm). For a detailed analysis of contaminating components a suitable chromatographic technique should be used.

CONCLUSIONS

The results of the present study have shown that successful results can be obtained with a combination of preconcentration extraction with the use of a solid sorbent and the subsequent supercritical fluid extraction. In this manner it is possible to separate, selectively, particular types of the contaminating substances and then to determine them with the use of a sensitive spectroscopic method

As representative substances for the two types of frequent contaminants in waters, a Diesel oil was chosen for mineral oil contamination and a commercial product Slovafo1 905 for non-ionic surfactants. The two types of contaminants were then determined after SFE separation in carbon tetrachloride medium with the aid of FTIR and in methanolic solution with the aid of UV spectrophotometry, respectively. On consideration of the recovery achieved under optimized conditions with combination of two the extraction techniques, the limiting factor is given by the sensitivity of the relevant spectral method (reaching a numerical order of 0.05 mg of the component per 5 mL of the solvent). A total volume of water sample should thus match the sensitivity achieved with the spectroscopic finish.

The technique can provide sufficiently rapid and reliable information on the level of contamination of water in events of breakdown. Moreover, it can be applied and modified for a wide range of substances and various other problems.

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