

Booklet of theses

**KOMPLEX METHOD DEVELOPMENT FOR THE GAS  
CHROMATOGRAPHIC ANALYSIS OF HYDROCARBON  
CONTAMINATION OF WATER**

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## **Introduction**

In the past decades the worsening of environmental problems induced a more and more definite need in modern societies for the protection of the environment and the better understanding of the problem. The first step in dealing with an environmental damage caused by some contamination, is the qualitative and quantitative assessment of the contamination itself. The intensive and widespread use of hydrocarbon products leads to the increased danger of these compounds contaminating the environment. During improper handling, transport, use and disposal of these products different oils, fuels and other hydrocarbon products may leak into the soil and surface water. This contamination can damage the flora and fauna of these soils and waters. It can render the soil infertile or reaching deeper levels may endanger groundwater bodies. Oil contamination is especially dangerous for surface waters. It can spread quickly over a large area, decomposes slowly, toxic to several forms of life and while present hinders the salvation of oxygen in the water. This leads to a quick degradation of aquatic life in the affected area. A relatively small ( $\sim 0.1$  mg/ml) of gasoline is enough to give water unpleasant odour and render it unfit for drinking due to its toxicity. Therefore the analysis of hydrocarbon contamination in water and soil is an important, frequently applied branch of analytical chemistry.

An analytical task like the analysis of hydrocarbon contamination in water is composed of several work phases. The main phases are sampling, transportation, storage, sample preparation, analysis, evaluation, and report preparation. If one wants to increase the speed of the whole process one cannot concentrate on just one or two steps. If a bottleneck step is made more effective, another step can quickly become the new bottleneck. To have a considerable effect on the whole process it requires a complex method development that identifies the bottleneck and the soon-to-be-bottleneck steps and increase their effectivity. In the course of my PhD work I performed a complex development on the method for the analysis of hydrocarbons in water.

## Objectives

During my PhD work my goal was to develop a fast, effective, automated gas chromatographic method for the analysis of hydrocarbon contamination in water. A method that is capable of the analysis of hydrocarbons with boiling points between that of nonane (n-C<sub>9</sub>) and hexatriacontane (n-C<sub>36</sub>).

I divided the development into 3 phases: reducing the time of analysis by fast gas chromatography, replacing the evaporation step by large volume injection and automation of the extraction step. My goals can be summarized as follows:

- Development of a fast gas chromatographic method for the fast separation of hydrocarbons in the boiling point range defined by n-C<sub>9</sub> and n-C<sub>36</sub>;
- Development of a large volume injection method that is capable of injecting 50 µl of sample with good recovery throughout the above mentioned boiling point range;
- Validation of the large volume injection method;
- Development of an automated membrane assisted solvent extraction method for the extraction of hydrocarbon contamination from water;
- Development of the manual version of the membrane solvent extraction method;
- Validation of the manual and the automated membrane solvent extraction methods;
- Combination of the fast gas chromatographic, the large volume injection and the membrane assisted solvent extraction methods to a complex automated method for the analysis of hydrocarbon contamination of water.

## **Experimental**

### Standards and samples

For evaluation of the method performance a n-alkane standard mixture was used containing alkanes between C<sub>9</sub> and C<sub>36</sub> (C<sub>9</sub>, C<sub>10</sub>, C<sub>11</sub>, C<sub>12</sub>, C<sub>13</sub>, C<sub>14</sub>, C<sub>16</sub>, C<sub>18</sub>, C<sub>20</sub>, C<sub>22</sub>, C<sub>24</sub>, C<sub>28</sub>, C<sub>32</sub> and C<sub>36</sub>). The n-alkane standards were purchased from Sigma-Aldrich (Steinheim, Germany) and were of at least 99% purity. The gasoline was obtained at a local petrol station. The samples used in the validation were provided by the WESSLING Hungary Kft., and were prepared according to the MSZ20354:2003 standard.

### Fast gas chromatography

The fast gas chromatography method was developed on an Agilent 6890 gas chromatograph equipped with a flame ionization detector. The final method utilized an Agilent DB1 column with 10 m length, 0.1 mm internal diameter and 0.4 µm film thickness. The temperature of the injector was held at 325 °C, the applied injection type was pulsed splitless, with 1 µl injection volume, 1 min splitless time, 1 min pulse time and 828 kPa (120 psi) pulse pressure. The carrier gas was hydrogen at constant flow of 2 ml/min. The oven temperature was programmed the following way: 40 °C (1 min) 120 °C/min to 70 °C, 95 °C/min to 115 °C, 65 °C/min to 175 °C, 55 °C/min to 300 °C and 35 °C/min to 325 °C (3 min). The temperature of the detector was 325 °C, the detector operated at 200 Hz data collection speed.

### Large volume injection

The large volume injection method was developed on an Agilent 6890 gas chromatograph equipped with a flame ionization detector, an Agilent 10 m x 0.1 mm x 0.4 µm DB1 column, a Gerstel CIS 4 injector, a Peltier cooler and an Agilent 7683 automatic liquid sampler. The oven temperature program was identical with the one applied for the fast gas chromatographic measurements, only the initial time was varied. The injection parameters for the main methods are summarized in table 1. The carrier gas was hydrogen (5.0) at a constant flow of 1.2 ml/min. The parameters of the detector were the same as the ones in the fast gas chromatographic method.

**1. table – The parameters of the 3 key methods in the optimization of large volume injection**

Method name	Cold splitless injection	Solvent-split injection	Split-splitless injection
Injection volume	1 $\mu$ l	50 $\mu$ l	
Injection speed	300 $\mu$ l/min	150 $\mu$ l/min	
Vent pressure	-	0 Pa	
Vent speed	-	200 ml/min	
Vent time	-	0,51 s	0,44 s
Splitless time	1,5 min	2 min	6 min
Initial temperature	40 $^{\circ}$ C	10 $^{\circ}$ C	
Initial time	0,1 min	0,51 min	0,44 min
Heating speed	10 $^{\circ}$ C/s		
Final temperature	300 $^{\circ}$ C		
Final time	5 min		
GC oven initial time	1,5 min	2 min	6 min

### Membrane assisted solvent extraction (MASE)

The alkane standard solution used for the optimization contained the following normal alkanes in acetone: n-C<sub>9</sub>, n-C<sub>10</sub>, n-C<sub>12</sub>, n-C<sub>13</sub>, n-C<sub>14</sub>, n-C<sub>15</sub>, n-C<sub>16</sub>, n-C<sub>18</sub>, n-C<sub>20</sub>, n-C<sub>22</sub> and n-C<sub>24</sub>. The membranes and other devices for the membrane assisted solvent extraction were obtained from Gerstel. Before each application the membranes sonicated 2\*10 minutes in hexane in order to remove interferences and saturate the membranes with the solvent. For the automated MASE extraction 15 ml sample was transferred in a 20 ml headspace vial. The vial was equipped with a membrane bag attached to a metal funnel. After 700  $\mu$ l hexane was transferred into the membrane bag, the vial was closed with a metallic crimp cap and placed on the autosampler tray. After the sample was agitated for 2 hours at 40  $^{\circ}$ C by the autosampler 50  $\mu$ l of the extract was injected into the CIS injector. In the case of manual MASE the sample volume was also 15 ml but only 500  $\mu$ l hexane was filled into the membrane bag. The vial was then sonicated at room temperature for 50 minutes. 200  $\mu$ l of the extract was transferred into a 2 ml vial equipped with a microvolume insert.

The MASE measurements were performed on an Agilent 6890 gas chromatograph equipped with a flame ionisation detector, a CIS 4 injector with Peltier cooling, a 15 m x 0.25 mm x 0.1  $\mu$ m Agilent HP-1 column, and a CTC Pal automatic sampler. The injection speed was 2.5  $\mu$ l/min, the head pressure was 0 Pa and the vent speed was 200 ml/min. The temperature program of the injector was set as follows: 10  $^{\circ}$ C held for 0,4 minutes then heating with 10  $^{\circ}$ C/min to 60  $^{\circ}$ C held for 1 min, then heating with 10  $^{\circ}$ C/min to the final temperature of 300  $^{\circ}$ C held for 10 minutes.

The splitless time was 2.5 minutes. The temperature program of the oven was the following: 40 °C (for 2.5 min), 20 °C/perc to 250 °C, 35 °C/min to 300 °C (for 3 min). The carrier gas was hydrogen (5.0) at a constant flow of 2 ml/min.

#### Two dimensional gas chromatography

The two dimensional gas chromatographic measurements were carried out on an Agilent 7890 gas chromatograph equipped with a flame ionization detector and a CFT Flow Modulator. A 30 m x 0.25 mm x 0.25 µm Agilent J&W DB5-MS column served as the first dimension, and a 5 m x 0.25 mm x 0.15 µm HP-Innowax as the second dimension. The oven temperature program was the following: 40 °C held for 1 min, heating with 8 °C/min to 260 °C held for 20 min. The modulator parameters were the following: modulation time 1.5 s, flush time 0.1 s. The carrier gas was hydrogen (5.0) at a constant flow of 0.8 ml/min in the first dimension and at a constant flow of 20 ml/min in the second dimension.

## Summary and theses

### Fast gas chromatography

- I examined the possibilities of speeding up the gas chromatographic analysis of hydrocarbons in the boiling point range that of n-C<sub>9</sub> and n-C<sub>36</sub>.
- I developed a fast gas chromatographic method capable of separating the test mixture in 6.8 minutes.

### Large volume injection

- I developed a large volume injection method for that is capable of injecting 50 µl sample with good recovery throughout the n-C<sub>9</sub> – n-C<sub>36</sub> boiling point range. The method applies standard CIS injector with Peltier cooling. The effective recovery was made possible by the combination of split a splitless evaporation techniques.
- During method development I observed and characterized a type of discrimination affecting the large volume injection of high boiling compounds.
- The compliance of the method was proved through validation and its application to real samples.

### Membrane assisted solvent extraction (MASE)

- I developed an automated membrane assisted solvent extraction method for the analysis of hydrocarbon contamination in water.
- I also developed a simpler manual version of MASE that utilizes a simple ultrasonic bath for the extraction.
- Both methods were validated and tested with real samples.
- I demonstrated with the help of two dimensional gas chromatography that the MASE method does not discriminate to the typical compounds of diesel oil.
- Combining the three methods I presented a fast, automated, sensitive method for the analysis of hydrocarbon contamination of water.

## List of publications

### Articles

- Z. Szekeres, G. Volk, Zs. Eke, Development of split-splitless PTV large-volume injection for analytes covering a wide boiling point range, *Int. J. Env. Anal. Chem.* 89 (2009) 461-471.
- Z. Szekeres, Zs. Eke, T. Rikker, K. Torkos, Analysis of hydrocarbon contamination with membrane-assisted solvent extraction: Comparison of agitation and sonication methods, *J. Chromatogr. A*, 1216 (2009) 6964-6969.

### Posters

- Z. Szekeres, I. Csernyák, Zs. Eke, Determination of hydrocarbon contaminants in water using membrane-assisted solvent extraction coupled with large volume injection, 32<sup>nd</sup> ISCC, 2008
- Z. Szekeres, T. Rikker, G. Volk, Application of large volume injection to analytes covering a wide boiling point range, 7<sup>th</sup> Balaton Symposium, 2007