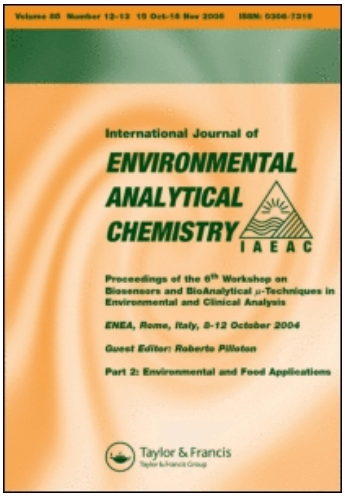

International Journal of Environmental Analytical Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713640455

Development of split-splitless PTV large-volume injection for analytes covering a wide boiling point range

Zoltán Szekeres[a]; Gábor Volk[b]; Zsuzsanna Eke[c]
[a] Joint Research and Training Laboratory on Separation Techniques, Eötvös Loránd University, H-1117, Pázmány Péter sétány 1/A, Budapest, Hungary [b] Wessling Hungary Ltd., H-1047, Fóti út 56, Budapest, Hungary [c] Eötvös Loránd University, H-1117, Pázmány Péter sétány 1/A, Budapest, Hungary

To cite this Article Szekeres, Zoltán , Volk, Gábor and Eke, Zsuzsanna(2009) 'Development of split-splitless PTV large-volume injection for analytes covering a wide boiling point range', International Journal of Environmental Analytical Chemistry, 89: 6, 461 — 471
To link to this Article: DOI: 10.1080/03067310902718896
URL: http://dx.doi.org/10.1080/03067310902718896

Intern. J. Environ. Anal. Chem.
Vol. 89, No. 6, 15 May 2009, 461–471

Taylor & Francis
Taylor & Francis Group

Development of split–splitless PTV large-volume injection for analytes covering a wide boiling point range

Zoltán Szekeres[a]*, Gábor Volk[b] and Zsuzsanna Eke[c]

[a]*Joint Research and Training Laboratory on Separation Techniques, Eötvös Loránd University, H-1117, Pázmány Péter sétány 1/A, Budapest, Hungary;* [b]*Wessling Hungary Ltd., H-1047, Fóti út 56. Budapest, Hungary;* [c]*Eötvös Loránd University, H-1117, Pázmány Péter sétány 1/A, Budapest, Hungary*

(*Received 14 August 2008; final version received 4 January 2009*)

A programmed-temperature vaporiser (PTV) – large-volume injection (LVI) method with a two-stage evaporation process was developed capable of effectively introducing analytes covering a wide boiling-point range (from that of *n*-nonane to that of *n*-tetracontane). The method uses speed-controlled sample introduction (50 μL) and a simple PTV setup with Peltier Cooling. Besides, an important cause of discrimination of high-boiling compounds in LVI was identified. The method was successfully applied to simplify the sample preparation in the extractable petroleum hydrocarbon analysis of water and soil samples. The method proved to be resistant to matrix contamination. Linearity was tested between 0.01 and 20 $\mu g\,mL^{-1}$. The correlation coefficients ranged from 0.996 to 0.999. The relative standard deviation calculated from five parallel runs was 2.73%. The major advantage of the method is its simplicity making it an attainable choice for smaller environmental laboratories.

Keywords: large-volume injection (LVI); programmed-temperature vaporiser (PTV); extractable petroleum hydrocarbon (EPH)

1. Introduction

It is a simple consequence of our oil-based economy that EPH analyses make up a considerable amount of GC analyses in the field of environmental analysis. The term EPH covers a large number of aliphatic, alicyclic and monoaromatic hydrocarbon molecules, in the boiling point range of that of C_9 and C_{40}. Because of the high number of samples to be analysed and the low concentrations to be detected, a large volume injection (LVI) – fast GC-coupled method has long been required in this field.

In the past two decades there has been a continuous interest in the capabilities and application of LVI in capillary gas chromatography, driven by the ever increasing demand for lower detection levels and faster analysis [1]. LVI can be used to lower the detection limits or to decrease overall analysis time by simplifying sample preparation methods. In addition to its higher speed, sample concentration through LVI generally produces more reproducible results than external solvent evaporation [2]. Programmed temperature vaporisation (PTV) was introduced by Vogt and co-workers in 1979 [3]. Nowadays, thanks to its effectiveness, simplicity and reliability, this is the most widespread LVI

*Corresponding author. Email: zoltan.szekeres@gmail.com

ISSN 0306–7319 print/ISSN 1029–0397 online

DOI: 10.1080/03067310902718896
http://www.informaworld.com

technique [1,4–6]. There are several injection techniques with PTV injectors, the most important is the PTV solvent-split (or solvent-vent) injection. It can separate the solvent from the higher-boiling sample components and vent it through the split valve in a continuous stream of carrier gas. The technique has been used effectively for the LVI of various types of samples including those with polar solvents (even water) [5]. Since its earliest application one of the major drawbacks of PTV solvent-vent injection was its loss of volatile components [7]. During solvent-split injection, these components are partly evaporated together with the solvent and lost through the split vent. Many techniques were developed to overcome this problem.

In 1988 a method called large volume splitless injection was proposed [8]. In this method the solvent is evaporated with the split valve closed, thus the volatile components that evaporate along with the solvent can be trapped in the swollen phase of the analytical column. In this case the flow through the liner is equal to the column flow making the evaporation very slow in comparison with the solvent-split injection.

The on-column large volume injection is the most effective LVI method for the analysis of volatile or thermally labile compounds [9]. By injecting the sample directly onto a pre-column the thermal shock applied to the components during conventional injection can be avoided since no high temperature is needed to transfer them from the injector. The evaporation of the solvent takes place in the pre-column, where the solvent effect can trap volatile analytes more effectively than in the liner. Using this technique even *n*-octane can be recovered from a hexane solution [10]. However, since it is highly sensitive to high-boiling impurities in the sample, it can be applied only to very clean matrices such as drinking water [11].

Liners packed with adsorbent such as Tenax were also effectively used to retain volatile compounds [12]. The drawback of this technique is that it does not really extend the range of the application, just shifts it towards the more volatile compounds. It cannot be applied to high-boiling analytes, since they would require too high a temperature and too long a time for desorption [7,13].

The recovery of volatiles in large volume injection can be enhanced by addition of a small amount of a higher boiling co-solvent. After the complete evaporation of the main solvent a fraction of the co-solvent remains in the injector maintaining the solvent effect. This enables efficient trapping of the most volatile compounds [14]. In our case, however, the peaks of the solvent (hexane) and the first analyte (nonane) are so close to each other (because of the broadening of the solvent peak) that a higher boiling solvent would threaten to cover the peak of the first analytes.

Solvent trapping is a very simple and convenient method for retaining volatile components. It does not require any additional material and the trapping effect stops once the evaporation is finished. Because solvent trapping could not be effectively applied in continuous or repetitive LVI, Mol *et al.* [15] developed the 'all at once' large volume injection [15]. The application of wide bore liners allowed the rapid introduction of samples up to 150 μL. After the rapid sample introduction the complete amount of the solvent is present during the evaporation process ensuring maximum effectiveness for solvent trapping. The results showed how powerful a tool solvent trapping can be if applied properly. With all at once injection 87% of *n*-octane could be recovered from hexane. The drawback of this technique is the application of wide bore liners, which are not compatible with some of today's PTV injectors and less convenient when coupled to narrow-bore columns.

In this article we present a method, which combines large volume split and splitless injection. It makes possible the use of continuous sample introduction and still effectively recover both the volatile and the high-boiling analytes in the range of C_9–C_{36}. An important feature of the method is that apart from a PTV injector that allows sub-ambient initial temperatures to be used it does not require any special instrumentation. We also present an investigation of the discrimination of high-boiling compounds in large volume PTV injection.

2. Experimental

2.1 *Chemicals*

For evaluation of the method performance a *n*-alkane standard mixture was used containing alkanes between C_9 and C_{36} ($C_9, C_{10}, C_{11}, C_{12}, C_{13}, C_{14}, C_{16}, C_{18}, C_{20}, C_{22}$, C_{24}, C_{28}, C_{32} and C_{36}) at concentrations of $1\,\mu g\,mL^{-1}$ each. The *n*-alkane standards were purchased from Sigma-Aldrich (Steinheim, Germany) and were of at least 99% purity. Hexane was from Merck (Darmstadt, Germany) and was of SupraSolv quality.

2.2 *Instrumentation*

The work was performed on an Agilent 6890N® gas chromatograph equipped with a flame ionisation detector (FID), an Agilent 7683 autosampler with straight, 100 mL syringe (Agilent 5183-2042). The injector was a Cooled Injection System 4® (CIS 4) type injector from Gerstel (Müllheim an der Ruhr, Germany) provided with Peltier cooling and glass-wool filled insert. The column was an Agilent DB-1 10 m × 0.1 μm i.d. column coated with cross-linked methyl silicone with a film thickness of 0.4 μm.

2.3 *GC conditions*

The initial temperature of the oven was 40°C (duration is specific for each method, see Table 1), increased to 70°C at $120°C\,min^{-1}$, to 115°C at $95°C\,min^{-1}$, to 175°C at $65°C\,min^{-1}$, to 300°C at $55°C\,min^{-1}$ and finally to 325°C at $35°C\,min^{-1}$ (for 3 min).

Table 1. Injector parameters for each method.

	Method 1	Method 2	Method 3
Method name	Cold splitless injection	Solvent-split injection	Split–splitless injection
Injection volume (μL)	1	50	
Injection speed ($\mu L\,min^{-1}$)	300	150	
Vent pressure (Pa)	–	0	
Vent flow ($mL\,min^{-1}$)	–	200	
Vent time (s)	–	0.51	0.44
Splitless time (min)	1.5	2	6
Injector initial temperature (°C)	40	10	
Injector initial time (min)	0.1	0.51	0.44
Injector heating rate (°C/s)		10	
Injector final temperature (°C)		300	
Injector final time (min)		5	

The temperature program was the same for all experiments, only the initial time was varied. Hydrogen was used as carrier gas with a constant flow of 1.2 mL min^{-1}. The injector program parameters are summarised in Table 1.

2.4 *Sample preparation*

The samples were prepared according to the EN ISO 9377-2 : 2001 standard procedure. Water samples: 1 L water sample was filled into a separation funnel. The pH of the sample was set to 1 by sulfuric acid solution. The sample was extracted twice with 10 mL hexane for 10 min at 300 cycles min^{-1}. The organic phases were combined and dried on dehydrated sodium sulfate. The dried hexane was filled in a 20 mL vial and concentrated to 1 mL under nitrogen stream at 40°C. Two gram silica was filled into a column and conditioned with 10 mL hexane. The 1 mL sample was loaded onto the column and eluted with 12 mL hexane. One millilitre of the extract was pipetted into a 2 mL GC vial. Soil samples: 5 g of soil was put into a 40 mL vial and shaken for 10 min with 10 mL acetone at 300 cycles min^{-1}. It was then sonicated twice for 25 min with 10 mL hexane. The extract was then treated like the water sample extracts.

3. Results and discussion

3.1 *Optimisation of the solvent-split injection*

For the solvent-split injection the inlet initial temperature was set to 10°C, the lowest possible with Peltier cooling, to ensure efficient cold trapping during the evaporation. The vent flow was set to 200 mL min^{-1} to reduce evaporation time. For the solvent trapping to take place it is essential to have an excess of solvent in the liner during the whole injection process. This requires an injection speed that is higher than that of the evaporation. The equation proposed by Gerstel® [16] gave an injection rate of 113 μL s^{-1}. To find the optimal value the injection rate was optimised. The vent time was also varied to find the optimal at every injection rate value. Since nonane is the compound most prone to evaporation the results were evaluated on the basis of the recovery of nonane. Figure 1 shows that the best recovery was obtained with the injection rate of 150 μL min^{-1}. It can be seen on the figure that shorter vent times resulted in better nonane recoveries. However, on the chromatograms that showed nonane recovery over 30% severe peak distortion (mostly leading and in more serious cases peak splitting) could be seen in the range of C_{10}–C_{16}. This peak splitting can generally be observed when compounds of moderate volatility evaporate and enter the column together with an excessive amount of solvent [15,17,18]. The experiment showed that nonane is very susceptible to overventing. Without solvent it disappears completely in a few seconds. Earlier experiments showed that if the valve closes only 1–2 s later than the optimal, severe losses of volatile compounds can be observed [19]. On the other hand, if the valve closes a few seconds earlier the excessive solvent leads to peak distortion. Consequently, finer optimisation is required to achieve the best results. With the injection speed set to 150 μL s^{-1} the vent time was varied between 0.50 and 0.55 min at intervals of 0.01 min. The optimal value was found to be 0.51 s (Method 2 in 2.3.1.), even with this value the recovery of nonane was only 29% (Table 2).

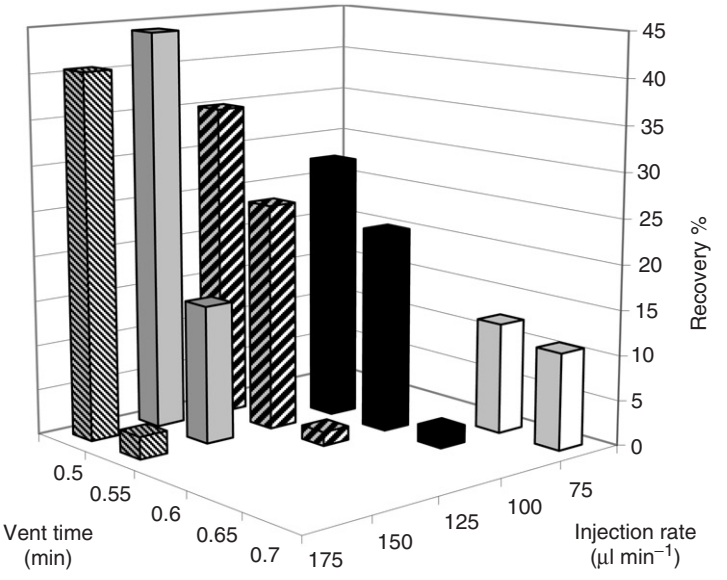

Figure 1. Optimisation of the split-vent injection. Recovery of nonane at different injection rate–vent time pairs.

Table 2. Recoveries with solvent-split evaporation.

Compound	Recovery (%)	RSD (%)
C_9	29	2.76
C_{10}	48	2.13
C_{11}	63	1.39
C_{12}	85	1.35
C_{13}	92	1.22
C_{14}	98	1.09
C_{16}	100	1.13
C_{18}	103	1.04
C_{20}	101	1.18
C_{22}	98	1.85
C_{24}	99	2.07
C_{28}	97	2.33
C_{32}	96	2.76
C_{36}	95	2.84

In another approach the vent flow was varied and (using calculated injection rates) the vent time was optimised for each value. The low flow rates increased the recovery of volatiles, but at the same time serious discrimination of the high-boiling compounds was observed. Figure 2 shows the peak areas of these compounds at different vent flows.

Such discrimination of high-boiling compounds at low injection rates has already been observed several times in the literature [20,21]. Longer splitless time or higher injection temperature did not ameliorate the recoveries, which suggested that the compounds are lost from the injector in some way. Since the effect was observed at low injection rates, flooding of the liner could not arise. At a vent flow of 200 mL min^{-1} low injection rates

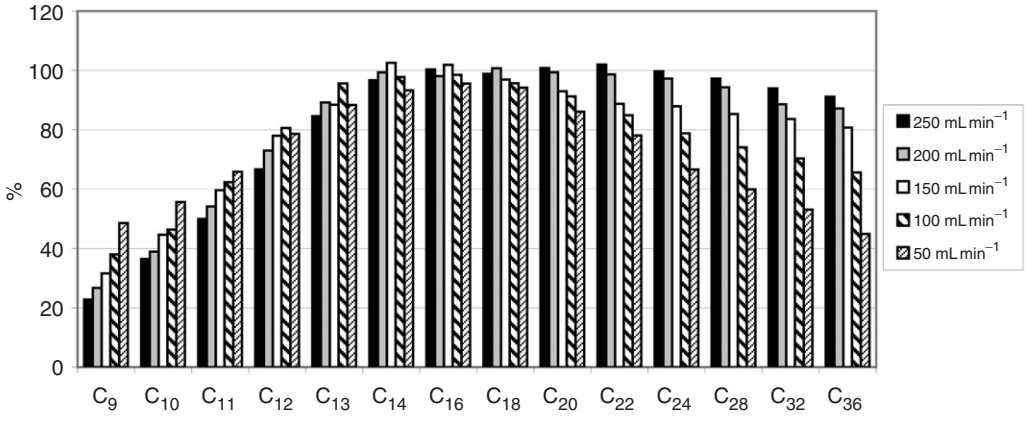

Figure 2. Recoveries at different vent flows. For the different vent flows calculated injection rates were used. These were 141, 113, 85, 56 and 28 mL min^{-1}, respectively.

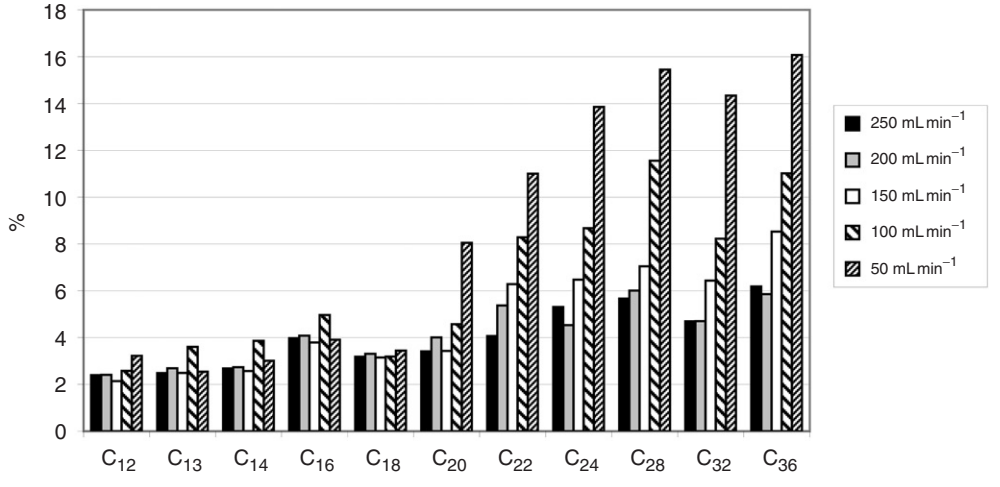

Figure 3. Analytes detected from injections of pure hexane after methods with different vent flows.

showed the same effect. That led us to the conclusion that the discrimination is caused by the rapid evaporation of the solvent.

At low injection rates the solvent leaves the needle as droplets, which cling to and spread over the needle tip before becoming large enough to drop [20]. During this time high-boiling compounds, which are (usually) the least soluble, can to some extent dry-in on the needle tip. This amount is then drawn out with the needle at the end of the injection and lost to the analysis. To verify this theory 50 µL of pure solvent was injected with Method 2 (2.3.1.) after those methods showing discrimination without washing the needle. The results showed that precipitation onto the needle tip is largely responsible for this type of discrimination (Figure 3). Thus, when working with high-boiling analytes optimisation of the injection speed is of capital importance. Evaluation of the injection parameters does not work properly in these cases because it does not take into consideration the deposition of analytes on the needle.

Table 3. Split–splitless vent time pairs with the achieved nonane recovery.

Split vent (min)	Splitless vent (min)	Nonane recovery (%)
0.48	2	43
0.47	3	51
0.46	3	65
0.45	4	72
0.44	4	76
0.43	5	79
0.42	6	81

3.2 *The split–splitless evaporation*

The experiments with shorter solvent elimination time showed that solvent trapping is very effective up to the last few seconds. Most of the lost volatile analytes are evaporated with the last few microlitres of the solvent. If just these last few microlitres could be transferred to the column without further splitting, it would considerably increase the recovery of the volatile compounds. We introduced a second (evaporation) step after the first, incomplete evaporation. In this second step, the remaining sample should be evaporated and transferred onto the column in a manner that avoids peak distortion due to excessive solvent recondensation. In large volume splitless injection the solvent is evaporated with the split valves closed. The volatiles that evaporate along with the solvent are trapped in the swollen phase of the analytical column. The two techniques can be coupled: the bulk of the solvent can be evaporated through the split valve and the last, few microlitres in a splitless manner. This way it is possible to recover most of the volatile compounds without negatively affecting the recoveries of the higher boiling compounds.

3.2.1 *Optimisation of the splitless evaporation step*

For the splitless evaporation step two new parameters have to be optimised. These are the temperature and the duration of the second venting step. In addition, the vent time has to be re-optimised to leave enough but not too much solvent in the liner.

To avoid peak distortion the evaporation temperature must be kept under the boiling point of the solvent. At this point the split valves are already closed, and to maintain column flow, there is an elevated pressure in the system the boiling point of the solvent is therefore higher than at atmospheric pressure. This effect is more significant when working with narrow bore columns, which require higher head pressures. The pressure-corrected boiling point can be calculated using the Antoine equation [22]. It showed that at the 308 kPa head pressure in our method the boiling point of hexane is 109°C. In order to find the value at which the evaporation is the fastest possible without any peak distortion the temperature was optimised. Measurements were taken between 110°C and 70°C at intervals of 10°C; and of those, 90°C proved to be optimal. At higher temperatures the evaporation was too fast which resulted in bad peak shapes.

The split and the splitless vent times are not independent of each other, thus cannot be optimised separately. The shorter the split vent time the more the solvent remains in the liner and the longer should the splitless vent be to remove it. Therefore, the split and the splitless vent times were both varied. Table 3 shows the split vent times with the

relevant splitless vent times and the obtained nonane recovery. The 0.44 and 4 min were chosen as the optimal pair (Method 3 in 2.3.3.).

The results show that excessive solvent recondensation in the column does not subsequently lead to peak distortion. Since in our case the column is kept at 40°C during the whole evaporation process, all the solvent that evaporates after the closing of the split vent (several microlitres) recondenses in the first section of the analytical column. The chromatograms taken with this method show no peak distortion (in spite of the large amount of recondensed solvent in the column). Peak distortion can be detected usually when the excessive amount of solvent pass into the column with the analytes in a very short time. When the solvent and the components reach the column separately, as in our case, this detrimental effect is avoided.

3.2.2 *Description of the evaporation process*

The heating program of the injector contains three plateaus and two ramps (Figure 4). The first step is the solvent-split evaporation. During this step the injector is at 10°C, at this temperature the bulk of the solvent is evaporated via the split vent. Before completion of the evaporation the split vent closes, the injector is heated up to 90°C and the venting continues through the column. The elevation of the temperature is necessary to ensure fast evaporation. During this step the evaporation of the volatile components is no longer a problem because they will be trapped in the swollen phase of the analytical column (kept at 40°C). After completion of the evaporation of the solvent the injector is heated up to final temperature (300°C) and all the analytes are transferred to the column. The chromatogram obtained with the optimised method is shown in Figure 5. The recoveries can be seen in Table 4. With this technique 76% of nonane could be recovered from hexane solution, while the recoveries of the high-boiling *n*-alkanes up to C_{36} are all above 92% (Figure 6).

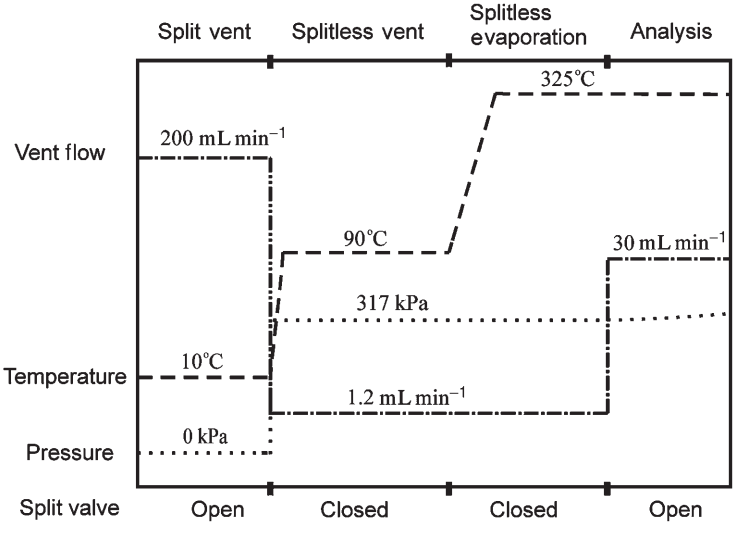

Figure 4. Evaporation diagram of the split–splitless evaporation method.

3.2.3 *Analysis of real samples*

The previous results show that using our method the large volume injection does not change the hydrocarbon profile of the sample. Therefore, it is applicable to EPH samples where the discrimination-free analysis is particularly important. To test the effectiveness of the split–splitless evaporation water and soil extracts were prepared and analysed with our method. A chromatogram of a water sample is shown in Figure 7.

To calibrate the method and check linearity standard solutions with concentrations of 0.01, 0.1, 1.0, 4.0, 7.0, 10.0 and 20.0 $\mu g\,mL^{-1}$ were injected. The method proved to be linear in the range of 0.01 and 20 $\mu g\,mL^{-1}$. Correlation coefficients ranged from 0.996 to 0.999.

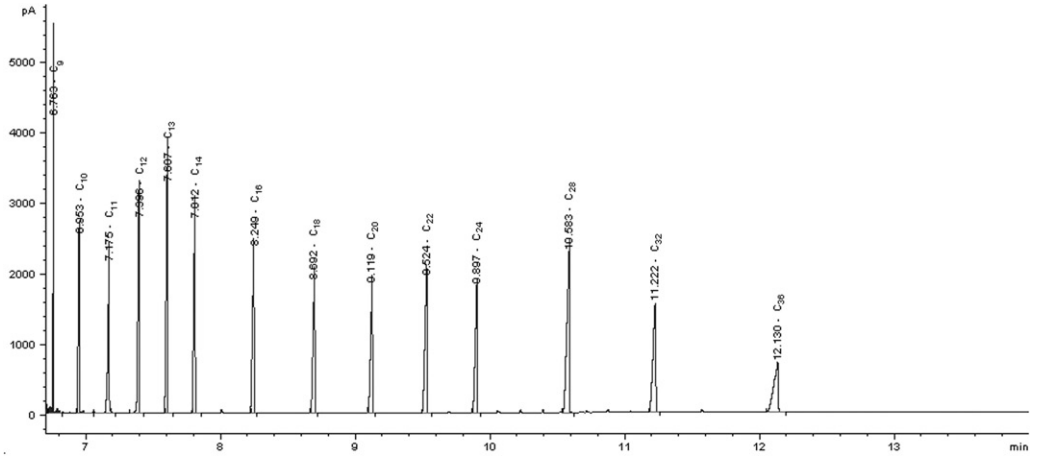

Figure 5. Chromatogram of the standard mixture with the split–splitless evaporation method.

Table 4. Recoveries with the optimised split–splitless evaporation method.

Compound	Recovery (%)	RSD (%)
C_9	76	0.87
C_{10}	87	1.06
C_{11}	95	0.85
C_{12}	99	1.08
C_{13}	101	1.07
C_{14}	99	1.05
C_{16}	103	0.82
C_{18}	98	0.96
C_{20}	101	1.27
C_{22}	100	2.16
C_{24}	99	1.94
C_{28}	97	2.57
C_{32}	95	2.91
C_{36}	92	2.96

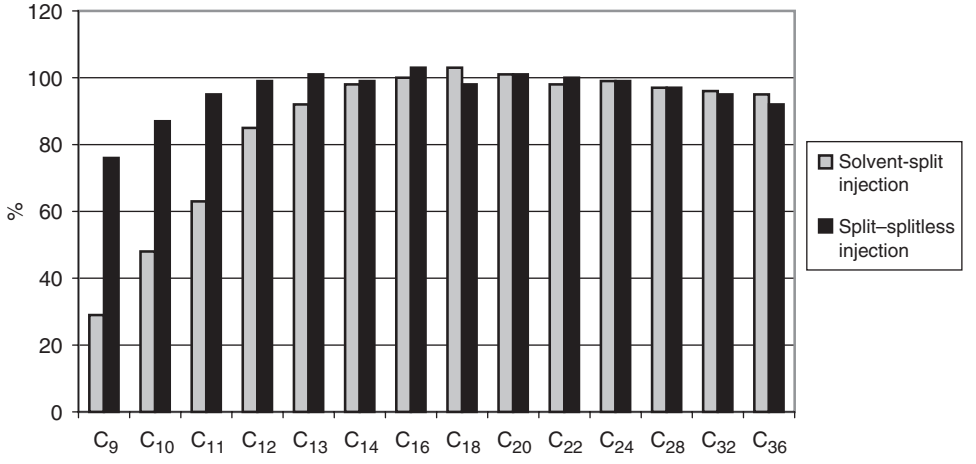

Figure 6. Comparison of the solvent-split and the new split–splitless evaporation methods.

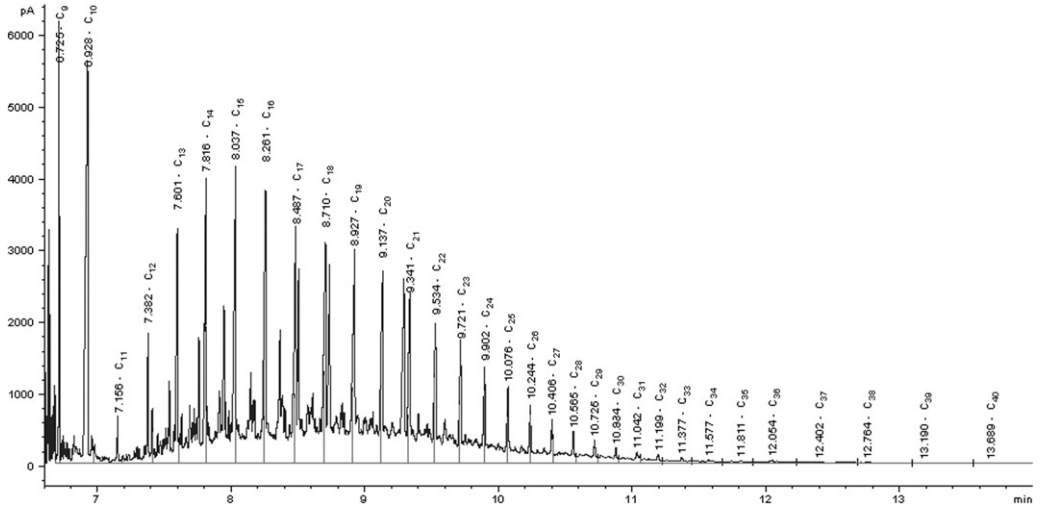

Figure 7. Chromatogram of a water sample with split–splitless evaporation method.

The method proved to be resistant to matrix contamination. Fifty samples containing high concentrations of hydrocarbons (over 50,000 $\mu g\,mL^{-1}$ EPH value) were injected in a sequence with QC runs after every 10 samples. All the QC results were satisfactory, their relative standard deviation (RSD) was 2.27%. The RSD of the samples was calculated from five parallel runs and found to be 2.73%.

4. Conclusions

Split–splitless evaporation can effectively retain volatile components down to nonane without negatively affecting the recoveries of the high-boiling compounds. It provides good recoveries and precision for mixtures containing C_9–C_{36}. Continuous sample

introduction allows the injection of large sample volumes (50 μL) into the PTV liner, while the application of a glass-wool filled liner makes the method fairly resistant to impurities. With this method it becomes possible to apply large volume injection in the EPH analysis, reaching lower detection limits and avoiding time-consuming sample preparation steps. The frequently observed discrimination of high-boiling compounds in LVI (at inappropriate vent flow – injection rate pairs) was also evaluated. Precipitation onto the needle tip was found to be the major cause of the losses of these compounds.

Acknowledgements

This work was made possible by financial assistance from the WESSLING International Research and Educational Center and the Kromat Ltd.

References

[1] J. Teske and W. Engewald, Trends in Anal. Chem. **21**, 584 (2002).
[2] J. Villen, T. Herraiz, G. Reglero, and M. Herraiz, J. High Res. Chromatogr. **12**, 633 (1989).
[3] W. Vogt, K. Jacob, and H.W. Obwexer, J. Chromatogr. **174**, 437 (1979).
[4] R. Bailey, J. Environ. Monit. **7**, 1054 (2005).
[5] W. Engewald, J. Teske, and J. Efer, J. Chromatogr. A **856**, 259 (1999).
[6] E. Hoh and K. Mastovska, J. Chromatogr. A **1186**, 2 (2008).
[7] H.G.J. Mol, H.-G. Janssen, C.A. Cramers, and U.A.Th. Brinkman, Trends in Anal. Chem. **15**, 206 (1996).
[8] K. Grob and Z. Li, J. High Res. Chromatogr. **11**, 626 (1988).
[9] K. Grob and M. Biedermann, J. Chromatogr. A **750**, 11 (1996).
[10] M. Adachour, E.M. Kristenson, R.J.J. Vreuls, and U.A.Th. Brinkman, Chromatographia **53**, 237 (2001).
[11] J. Zrostlíková, J. Hajšlová, M. Godula, and K. Maštovská, J. Chromatogr. A **937**, 73 (2001).
[12] M. Herraiz, G. Reglero, and T. Herraiz, J. High Res. Chromatogr. **12**, 442 (1989).
[13] H.G.J. Mol, P.J.M. Hendriks, H.-G. Janssen, and C.A. Cramers, J. High Res. Chromatogr. **18**, 125 (1995).
[14] M. Termonia, B. Lacombiez, and F. Munari, J. High Res. Chromatogr. **11**, 890 (1988).
[15] H.G.J. Mol, H.-G. Janssen, C.A. Cramers, and U.A.Th. Brinkman, J. High Res. Chromatogr. **18**, 19 (1995).
[16] Inlets for capillary gas chromatography, Gerstel < www.gerstel.com >.
[17] P.G. Van Ysacker, H.M. Snijders, H.-G.M. Janssen, and C.A. Cramers, J. High Res. Chromatogr. **21**, 491 (1998).
[18] H.-J. Stan and M. Linkerhägner, J. Chromatogr. A **727**, 275 (1996).
[19] C. Bosboom, H.G. Janssen, H.G.J. Mol, and C.A. Cramers, J. Chromatogr. A **724**, 384 (1996).
[20] P. Tollbäck, J. Björklund, and C. Östman, J. Chromatogr. A **991**, 241 (2003).
[21] M. Mandalakis and Ö. Gustafsson, J. Chromatogr. A **996**, 163 (2003).
[22] S. de Koning, M. Kurano, H.-G. Janssen, and U.A.Th. Brinkman, J. Chromatogr. A **1023**, 165 (2004).