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Short communication

Large-volume injection in capillary gas chromatography using a programmed-temperature vaporizing injector in the on-column or solvent-vent injection mode

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Abstract

The use of the programmed-temperature vaporizing (PTV) injector as a versatile interface for large-volume injection in capillary GC is proposed. By using a special on-column insert, in addition to large-volume solvent-vent injection, also large-volume on-column injection can be performed with the PTV injector. For this, a set-up consisting of a retention gap, a retaining precolumn and an early solvent vapour exit is installed between the on-column insert and the analytical column. The performance of this set-up for large-volume injection was evaluated and found to be similar to that of large-volume injection using a conventional on-column injector. The proposed instrument hence allows PTV and on-column large-volume sampling to be performed using only one injector. This greatly reduces instrument costs for large-volume sampling equipment. Guidelines are given for method development for large-volume sampling.

Keywords: Injection methods; Programmed-temperature vaporizer; Large-volume injection; Alkanes

1. Introduction

Recently, there has been increased interest in the introduction of large sample volumes in capillary gas chromatography (GC). Several injection techniques have been reported that allow the introduction of large volumes (e.g. [1–5]). A good review of these techniques and of the fundamentals of large-volume injection in capillary GC was given by Mol et al. [6].

The most important techniques for the introduction of large sample volumes in capillary GC are partially concurrent solvent evaporation (PCSE) using an on-column interface [2], fully concurrent solvent evaporation (FCSE) using a loop-type interface [7] and solvent-vent injection using a programmed-temperature vaporizing (PTV) injector [4,8,9]. PTV solvent-vent injection can be carried out either in a rate-controlled manner or in a rapid "all at once" fashion [4]. Rate-controlled introduction allows sample volumes to exceed the maximum capacity of the liner, by applying an introduction rate adjusted to the evaporation rate [10]. In the all at once injection technique, liners with larger inner

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diameters are used, which allows larger sample volumes to be introduced rapidly.

Each technique for large-volume sampling has its own advantages and disadvantages [6]. On-column injection has the widest application range, in terms of both volatility and thermostability of the analytes. If the time the solvent release system is open is carefully optimized, components with boiling points only slightly above that of the solvent can be recovered quantitatively. The technique, however, is generally less suited for dirty samples, as involatile sample constituents easily contaminate the column inlet. This results in a poor long-term stability. FCSE injection using a loop-type interface is restricted to components eluting at relatively high temperatures. Typically, the technique is not suited for analytes more volatile than n-C_{18}. Volatile components are lost together with the solvent, as there is no liquid film to retain the analytes. Analogous to FCSE, the user-friendly PTV injection technique is less suited when analysing volatile components, because only components with volatilities significantly below that of the solvent are trapped in the cold liner, unless liners packed with a selective adsorption material or two-dimensional GC set-ups are used [10,11]. Large-volume PTV injection is rugged and suited for the analysis of 'dirty' samples. On the other hand, however, it is less suited for the analysis of thermo-labile components owing to possible degradation of these solutes in the liner during the splitless transfer to the column.

The choice of a large-volume injection technique to be used for a given sample depends mainly on the composition of the sample and the type of analytes to be determined. For highly volatile components and/or thermally unstable solutes, the on-column technique is most suited. For other applications, the loop-type interface hardly offers any advantages over PTV-based techniques. Therefore, for such samples PTV sampling should be the method of choice. On comparing PTV and on-column large-volume sampling, it is evident that on-column sampling has a wider application range with regard to the analysis of volatile and thermally unstable components. PTV injection is, however, often preferable because of its ease of use and simplicity. Method development for large-volume sampling should therefore ideally start with the investigation of the applicability of PTV sampling. If unsuccessful, one should resort to the on-column injection technique. In practice, this means that both a PTV and an on-column injector have to be available in the laboratory.

In this paper, the use of one interface, allowing on-column and PTV-based large-volume injection techniques to be performed in one instrument, is proposed and evaluated. By installing a special on-column insert in the PTV injector, the injector can be converted into an on-column sampling device. Both on-column and PTV-based large-volume sampling techniques can now be performed using only one injection device. To switch from one method to the other only the liner has to be exchanged. The performance of the proposed technique, PTV on-column injection, is compared with the use of the standard on-column injection technique and the PTV-based rate-controlled and all at once injection techniques. Important aspects in this comparison are the recoveries obtained for 100-μl injections of n-alkane standard mixtures and for 100-μl injections of test samples containing polar and thermally unstable components.

2. Experimental

2.1. Instrumentation

The instrumental set-up for large-volume injection using the on-column and the PTV–on-column interface is depicted schematically in Fig. 1. Two different GC systems were used. One consisted of a gas chromatograph (Model 8180; Carlo Erba, Milan, Italy) provided with a flame ionization detector and an on-column injector. This system was used for the (standard) on-column large-volume sampling experiments. The other system consisted of a gas chromatograph (Model 5890; Hewlett-Packard, Avondale, PA, USA) equipped with a flame ionization detector. In this system a CIS-3 PTV injector (Gerstel,

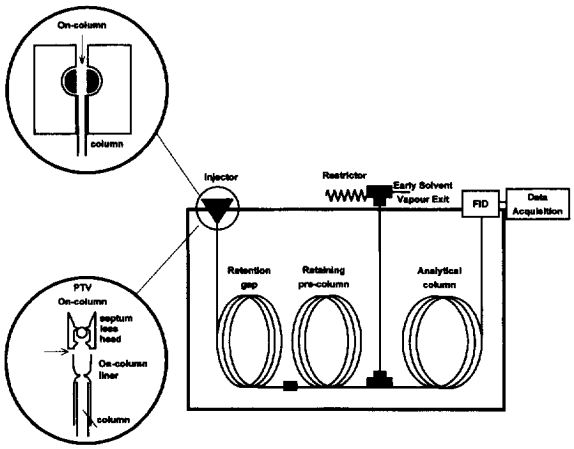

Fig. 1. Schematic diagram of the GC system used for large-volume sampling using (PTV) on-column injection. The inset show schematic drawings of the standard on-column injector and the PTV injector in the on-column mode.

Mülheim a/d Ruhr, Germany) equipped with a special on-column insert (Gerstel) was installed. Large-volume samples (100 μl) were injected using a 1-ml rate-programmable syringe (Digi-sampler; Gerstel). The sample was transferred into the on-column injector via a 30 cm $\times$ 0.32 mm I.D. fused-silica capillary, which was connected to the syringe with a union (Valco, Houston, TX, USA). When using PTV for on-column injection, a syringe needle (50 mm) was connected to the end of the fused-silica capillary to facilitate injection through the septumless head of the PTV injector. The injection speed was 2 ml/min in all cases. The chromatographic (pre)columns used in the two instruments were the same. In the (PTV) on-column set-up, one end of the 10 m $\times$ 0.53 mm I.D. polymethylsiloxane deactivated retention gap (Chrompack, Middelburg, Netherlands) was attached to the injector. The other end of the retention gap was connected to the retaining precolumn (3 m $\times$ 0.32 mm I.D., coated with 0.5-μm CP-Sil 5 CB; Chrompack) using a glass press-fit (Chrompack). Between the retaining precolumn and the analytical column (22 m $\times$ 0.32 mm I.D., 0.5 μm CP-Sil 5 CB; Chrompack) an early solvent-vapour exit was installed via a glass Y-press fit (Chrompack). This Y-press fit was connected to a metal T-piece (Gerstel) using a 35 cm $\times$ 0.32 mm I.D. fused-silica capillary. The early solvent vapour exit consisted of a 15 cm $\times$ 0.32 mm I.D. fused-silica capillary. During injection and subsequent solvent evaporation, this exit could be opened using a low-volume on–off valve. A small leak flow was applied to prevent back-diffusion of solvent vapour from the exit line into the chromatographic pathway. The leak restrictor was a 30 cm $\times$ 0.05 mm I.D. fused-silica capillary.

The initial temperature for the GC oven was 50°C. The time needed for elimination of the solvent was determined by means of a tea-kettle lamp placed at the outlet of the solvent vapour exit as described by Grob [1]. After solvent elimination, the solvent vapour exit was closed and the temperature programme was started. For the analysis of the *n*-alkane standard mixture the temperature programme was initially 50°C, increased at 20°C/min to 325°C (held for 5 min). For the analysis of the polarity/stability test mixture, the temperature programme was initially 50°C (held for 1 min), increased at 15°C/min to 290°C (held for 5 min). When applying PTV on-column injection, the initial temperature of the injector was 50°C. After solvent elimination, the PTV was heated to the final GC oven temperature at 2°C/s. Helium was used as the carrier gas at a pressure of 140 kPa. Data collection was done using an Omega integration system (Perkin-Elmer, Norwalk, CT, USA).

2.2. Materials and reagents

For the evaluation of the system performance, two test mixtures were used. An *n*-alkane standard mixture was made up in hexane. This mixture contained alkanes from C_8 to C_{36} at concentrations of 0.5 μg/ml. The other test mixture contained 27 compounds of various polarity, volatility and thermal stability (names are given in the figures and Table 2). This mixture was made up in ethyl acetate. For large-volume injections the sample was diluted in hexane.

3. Results and Discussion

3.1. Application of the various techniques to the analysis of volatiles

In earlier work, we evaluated the implications of the liner diameter on the choice of whether to apply PTV large-volume sampling in the all at once mode or in a rate-controlled manner [4]. Based on these results, guidelines were given for the selection of the PTV liner I.D. best suited for a given application, depending on the sample volume, the volatility of the analytes and also on their thermo-stability. Larger I.D. liners proved to be advantageous because of their higher sample capacity, allowing sample volumes up to ca. 150 μl to be injected rapidly, preventing losses of volatiles down to nonane. In the (standard) on-column and PTV on-column technique for large volume sampling, the analytes are retained in the retention gap and retaining precolumn, while the solvent evaporates through the early solvent vapour exit (ESVE). For quantitative recovery of volatiles, the moment of closing the exit is critical. Under the experimental conditions used solvent elimination required 2.7 min. Closing the exit only 1–2 s later resulted in losses of the volatile components eluting immediately after the solvent peak. When the exit is closed a few seconds before solvent elimination reaches completion, 80% recovery is found for *n*-octane. For this component the moment of closure is very critical. Decane is still quantitatively retained in the retention gap and/or the retaining precolumn up to 10–15 s after completion of solvent elimination. As was to be expected, the results obtained with the conventional on-column injector and the PTV injector in the on-column mode were very similar.

In Table 1 the results for 100-μl on-column injections (both standard on-column and PTV on-column) of the *n*-alkane standard mixture are shown, and experimental data for PTV solvent-vent injections are also given for comparison [4]. With the latter technique, two injection modes are distinguished, all at once injection and rate-controlled injection. With rate-controlled injection, losses of volatile alkanes are most severe, despite the use of sub-ambient initial PTV temperatures. For the all at once injection, the recoveries resembled those obtained for on-column injection. From Table 1 it can be seen that it was possible to retain 87% of octane when applying the PTV all at once injection technique. However, this is only possible if closure of the solvent split exit is carefully timed. Variation of only a few seconds leads to significant losses of this component.

With both the standard on-column approach and the PTV on-column method of large-volume sampling, almost quantitative recovery is easily obtained for all compounds except octane. As both techniques use the same set-up, their application is equally difficult. The experimental set-ups were found to be not very rugged. The five press-fit connectors were a potential source of error as leakage was sometimes observed. Leakage affects the flow-rate through the system and hence the solvent evaporation time. The same problem was encountered when part of the system, e.g., the retention gap, (parts of the) early solvent-vapour exit or even a press-fit had to be replaced. In practice, this means that each time the retention gap or a press-fit is replaced, the time the solvent release system is kept open should be re-optimized. In contrast, the set-up for PTV solvent-vent injection involves only one connection, that of the analytical column to the injector. For maintenance, the liner is very easy to replace and in general there is no need to repeat optimization after liner replacement.

3.2. Application of the various techniques to thermo-labile components

An important advantage of the use of on-column techniques for large-volume injection over the use of PTV solvent-venting techniques is that with on-column injection the analytes are vaporized in an, ideally, very inert environment, a well deactivated retention gap. This minimizes possible degradation of thermo-labile analytes. When using PTV injectors in the solvent-vent mode, the thermal stress applied to the analytes is generally more severe. This puts limitations on the application of PTV solvent-vent injection to

Table 1
Recoveries obtained after 100-μl injections of an *n*-alkane mixture in hexane using different large-volume injection techniques

Parameter	Large-volume injection technique			
	On-column	PTV on-column	PTV solvent vent[a]	
			Rate-controlled	All at once
PTV liner I.D. (mm)	–	–[b]	1.2	3.4
PTV temperature (°C)	–	50	−30	0
Vent time (min)	2.65	2.55	–[c]	2.5
Oven temperature (°C)	50	50	40	40
Compound	Recovery (%)[d]			
Octane	85	81	0	87
Nonane	n.m.[e]	n.m.	11	97
Decane	96	97	15	97
Dodecane	98	101	47	99
Tetradecane	100	100	93	103
Hexadecane	100	101	97	101
Octadecane	98	101	102	100
Eicosane	101	103	101	103
Docosane	101	102	n.m.	n.m.
Tetracosane	100	103	n.m.	n.m.
Octacosane	105	109	n.m.	n.m.
Dotriacontane	98	107	n.m.	n.m.
Hexatriacontane	97	106	n.m.	n.m.

[a] Data from Ref. [4].
[b] Special on-column insert.
[c] Rate-controlled injection, 25 μl/min; additional solvent vent time after injection, 45 s.
[d] Recovery relative to 1-μl on-column injection; areas are normalized to C_{14}.
[e] n.m. = Not measured.

thermo-labile analytes. In a previous study, the inertness of several packing materials for PTV solvent-vent injection of thermo-labile components was evaluated [9]. This was done using a test mixture containing 27 compounds differing widely in polarity, volatility and thermal stability. Ideally, the packing should be highly inert and thermo-stable. The packed liner should not retain high-boiling analytes too strongly in order to minimize the thermal stress applied to these compounds upon splitless transfer to the column. Also, the packed liner should retain a large volume of liquid sample in order to allow rapid introduction of large sample volumes without overloading the liner with liquid.

Fig. 2 shows a chromatogram of the 27-component test mixture for a 1-μl direct on-column injection using the Carlo Erba on-column injector. In this experiment the retention gap and retaining precolumn were not yet installed. Good peak shapes were obtained for all solutes except *n*-octanol, which showed some adsorption on active sites in the chromatographic column. For large-volume sampling the mixture was diluted such that the amounts of components injected in a 100-μl injection were equal to those introduced in a 1-μl standard on-column injection. Fig. 3 shows the analysis of the test mixture using the PTV on-column large-volume sampling mode. This chromatogram clearly illustrates the possibility of performing on-column large-volume injections using a PTV injector in the on-column

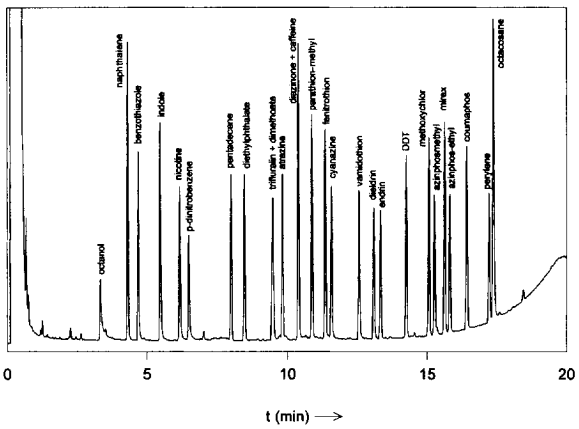

Fig. 2. Gas chromatogram of 1-μl direct on-column injection of a polarity/stability test mixture containing 27 analytes (concentrations 5–10 μg/ml). Temperature programme: initially 50°C (held for 1 min), increased at 15°C/min to 290°C.

mode. When comparing the chromatograms of the 1-μl on-column injection of the concentrated sample and that of the 100-μl PTV on-column experiment, it can be seen that the peak shapes in the large-volume sampling experiment are clearly inferior to those in the 1-μl injection. The poor peak shapes for the highly adsorptive components such as octanol, *p*-dinitrobenzene and vamidothion indicate that the system containing

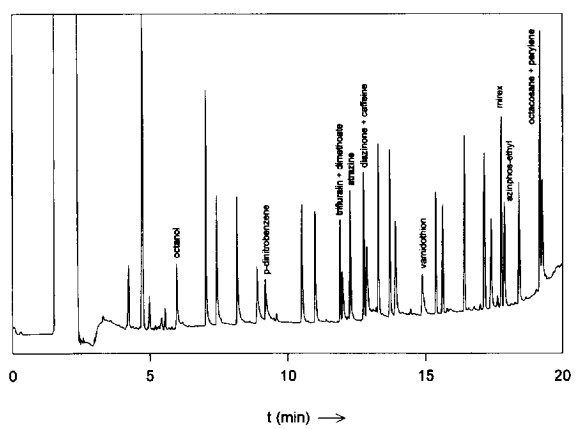

Fig. 3. Gas chromatogram of 100-μl injection of the 27-component polarity/stability test mixture using PTV on-column injection (concentrations 50–100 ng/ml). PTV temperature programme: initially 50°C (held for 1 min), increased at 2°C/s to 290°C (held for 5 min). GC temperature programme: 50°C (held for 1 min), increased at 15°C/min to 290°C.

the retention gap, retaining precolumn and the press-fits is more likely to cause activity problems than is a single chromatographic column. Experiments with 1-μl injections in the system equipped with the large-volume sampling facilities (retention gap, retaining precolumn, etc.) installed showed a much higher activity of the system, when compared with 1-μl on-column injections directly on to the analytical column. Apart from the press-fits, the retention gap is also expected to show some activity after prolonged usage. Peak shapes obtained with the standard PTV solvent-vent large-volume sampling technique were significantly better [9]. This is not surprising as in these systems no retention gaps and press-fits are used.

A comparison of the recoveries of the components from the 27-compound test mixture using the two on-column large-volume sampling techniques and the PTV solvent-vent technique is given in Table 2. With both on-column techniques the recoveries of "troublesome" analytes such as *p*-dinitrobenzene, dimethoate, vamidothion and azinphos-methyl are clearly better than with the PTV solvent-vent technique using packed inserts. The average recovery is above 90%. With PTV solvent-vent injection using the Dexsil-packed liner, the average recovery is slightly lower. Using the Tenax-packed liner the volatile components are easily retained, even at 30°C, but analytes less volatile than dieldrin can not be desorbed unless impractically long splitless times are used.

3. Conclusions

The selection of the most appropriate injection technique for large-volume sample introduction depends on the properties of the components of interest and also those of the matrix. A large overlap exists between the application areas of PTV solvent-vent injection and on-column injection. As PTV solvent-vent injection is much more rugged and user-friendly, method development in large-volume injection should ideally start with the investigation of the applicability of this simple PTV technique. If not successful, e.g., in

Table 2
Comparison of performances of several large-volume injection techniques

Parameter	Large-volume injection technique							
	PTV solvent vent[a]				On-column		PTV on-column	
Packing	Dexsil		Tenax		–		–	
Sample volume (μl)	60		100		100		100	
Concentration (ng/ml)	80–160		50–100		50–100		50–100	
PTV temperature (°C)	0		30		50		50	
Vent time (min)	2.0		0.7		2.65		2.55	
Compound	Rec.[b]	R.S.D.[c]	Rec.[b]	R.S.D.[c]	Rec.[b]	R.S.D.[c]	Rec.[b]	R.S.D.[c]
Octanol	108	6.4	116	2.5	99	4.6	95	4.6
Naphthalene	85	11	98	0.1	103	2.0	89	2.0
Benzothiazole	90	2.1	103	0.6	102	1.9	95	1.9
Indole	90	2.6	99	0.2	93	2.1	98	2.1
Nicotine	84	1.8	80	1.4	86	5.8	98	11
p-Dinitrobenzene	56	2.3	65	0.7	80	1.2	104	7.8
Pentadecane	93	2.4	100	–[d]	100	–[d]	100	–[d]
Diethyl phthalate	97	1.0	105	0.5	98	2.3	94	7.0
Trifluralin	92	1.1	91	0.4	94[e]	2.3	86[e]	5.9
Dimethoate	91	2.5	76	1.3	94[e]	2.3	86[e]	5.9
Atrazine	92	0.9	97	1.6	90	3.1	78	2.1
Diazinone	98	0.7	101	0.5	98[e]	1.5	94[e]	7.4
Caffeine	98	1.2	99	0.8	98[e]	1.5	94[e]	7.4
Parathion-methyl	91	1.4	82	1.0	93	2.7	92	12.1
Fenitrothion	92	0.8	93	3.1	99	3.1	8.7	5.7
Cyanazine	87	3.2	67	1.6	112	4.3	98	6.8
Vamidothion	34	14	34	2.3	65	3.5	71	16.9
Dieldrin	100	–[d]	98	1.5	101	2.4	88	8.9
Endrin	94	1.6	62	3.8	100	2.6	87	7.6
p,p-DDT	82	2.9	7	8.4	104	4.3	88	6.0
Methoxychlor	83	3.9	6	7.5	104	3.8	87	7.7
Azinphos-methyl	70	3.5	7	8.6	98	3.8	82	8.6
Mirex	100	0.8	35	7.7	103[e]	3.5	85[e]	7.4
Azinphos-ethyl	92	1.8	11	7.1	103[e]	3.5	85[e]	7.4
Coumaphos	92	2.1	11	11	95	3.4	85	7.9
Octacosane	100	1.2	99	2.0	104[e]	5.1	97[e]	8.1
Perylene	93	2.2	6		104[e]	5.1	97[e]	8.1

[a] Data from Ref. [9].
[b] Recovery (%) relative to 1-μl on-column injection (without retention gap/vapour exit).
[c] Relative standard deviation (%), $n = 3$.
[d] Used as internal standard.
[e] Average of sum of two co-eluting peaks.

the case of very volatile or labile analytes, one has to resort to on-column techniques. If this proves to be necessary, the PTV injector can easily be transformed into an on-column injector by using a special on-column insert. With this set-up similar resuls can be obtained as with the standard on-column interface. The integration of both methods into one injection system offers

great flexibility in method development and also reduces instrument costs.

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