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AT-column, a novel concentrating technique for large-volume injections in gas chromatography

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Abstract

Nowadays, large-volume injection is widely used for the GC determination of trace analytes, specifically to improve detectability. The most popular injectors for large-volume injections are the programmable temperature vaporisation (PTV) injector and the cold on-column (COC) injector, where each device has its own advantages and limitations. The novel AT-column concentrating technique combines features of two other injection techniques, loop-type large-volume and vapour overflow. AT-column injection is based on solvent evaporation in an empty liner with solvent vapour discharge via the split line. Little or no optimisation is required. The only relevant parameter is the injection temperature which can easily be calculated using the equation of Antoine. As an application, AT-column injection is combined with GC–MS for the trace-level determination of labile analytes and with GC–flame ionisation detection for the analysis of high molecular weight polymer additives. In summary, AT-column is an injection technique that combines the inertness of the COC, and the flexibility and robustness of the PTV large-volume technique.
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1. Introduction

In recent years, many studies were reported in which large-volume injection (LVI) methods were efficiently used for the GC determination of trace-level analytes. The major advantage of LVI techniques is that a much better analyte detectability can be obtained. Instead of the maximum volume of about 2 μl that can be injected when using a conventional technique such as splitless injection, with LVI injection volumes of 50–100 μl can easily be used [1,2]. Alternatively, if the improved detectability is not, or only partially required, sample preparation can be simplified by omitting time-consuming solvent evaporation steps which, in addition, often cause analyte losses. Typical LVI injectors are the programmable temperature vaporiser (PTV) [3,4] and the cold on-column (COC) injector [4–7]. In the PTV technique, the injector contains a liner packed with a sorbent to retain the large volume of solvent in the liner. When a PTV-type large-volume injection is performed, the injector temperature is set 10–40 °C below the boiling point of the solvent. The large volume is rapidly injected into the injector in the split mode, thereby providing a high carrier gas flow rate. The solvent is evaporated and the solvent vapour is eliminated through the split line by the high flow of carrier gas, while the analytes are retained on the packing of the liner. After evaporation of the solvent, the injector is switched to the splitless mode and the temperature is programmed to volatilise the analytes, which are then transferred to the capillary column. A disadvantage of PTV large-volume injection is that quite a few labile compounds are prone to decomposition due to catalytic effects of the packing material [8,9]. Moreover, heavy compounds are so strongly retained on the packing that desorption cannot be effected anymore. With the large-volume COC technique, a long pre-column is used to separate the sample solvent

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and the analytes of interest. A solvent vapour exit (SVE) is positioned between the pre-column and the capillary GC column. The large volume is injected onto the pre-column where it is evaporated. Then, the solvent vapour is vented to waste via the SVE. After evaporation of the solvent the SVE is closed and the analytes are transferred to the capillary column. The large-volume COC technique needs a pre-column and the injection speed of the autosampler should be precisely controlled to prevent flooding of the system [10,11]. Hence, optimisation can be tedious. Investigations to make GC injection techniques for LVI easier, more flexible and robust are a hot topic in current GC research. A recent example is the "concurrent solvent recondensation LVI splitless injection (CSR-LV)" technique of Magni and Porzano [12].

In order to eliminate the drawbacks of the injection techniques briefly introduced in the previous paragraph, a novel injection technique has been developed, AT-column LVI. With this technique, a PTV-type injector is used, but now with an empty liner combining the features of two other injection techniques, loop-type large-volume [13–18] and vapour-overflow [19–21]. As a consequence, no decomposition of labile compounds occurs, and there are no losses due to too strong adsorption either. Solvent evaporation occurs in the liner and the target compounds are concentrated at the inlet of the capillary GC column under relatively low-temperature conditions, as with the COC technique. Consequently, there is no need for a long pre-column, and no precise control of the injection speed is required. In the present article the principle, optimisation and application of AT-column LVI will be discussed. AT-column LVI should not be confused with the at-column technique described by Hagman and Roerade [22] in the early 1990s. This technique, where 'at' is written in lower case, was developed for injecting sample volumes not exceeding 2.5 μl into narrow-bore columns.

2. Experimental

2.1. Instrumentation

For the AT-column experiments two gas chromatographic systems were used. The first part of the work was performed on an HP 5890 GC (Agilent Technologies, Wilmington, DE, USA) equipped with an OPTIC 2 programmable injector (ATAS GL International, Veldhoven, The Netherlands) and a flame ionisation detection (FID) system. This system was used to set up the injection parameters based on *n*-alkane standard solutions; the injections were performed manually. The second part of the work was performed on an HP 6890 GC system (Agilent Technologies) equipped with an OPTIC 3-S programmable injector (ATAS GL International) and an HP 5973 mass-selective detector (Agilent Technologies). This system was used to test the system for 'activity' and assess the robustness of the method when injecting labile compounds. The injector liners used for hot splitless, packed PTV LV and on-column injections were from ATAS GL. The injections were performed using a Focus sample introduction system (ATAS GL International). In both systems, the capillary GC column was a DB-5MS 30 m × 250 μm i.d. column, with a film thickness of 0.50 μm (Agilent Technologies). The pre-column was a 60 cm × 530 μm i.d. de-activated fused-silica capillary (Agilent Technologies) which was connected to the capillary GC column by a press-fit connector (Techrom, Purmerend, The Netherlands). Helium 5.0 (Hoekloos, Schiedam, The Netherlands) was used as carrier gas in all experiments.

2.2. Chemicals

An S1280 *n*-alkane standard in heptane (C_{10}–C_{44} even carbon numbers at 50 ng/μl, C_{26} at 75 ng/μl and C_{42} missing) was purchased from AccuStandard (New Haven, CT, USA). Dichlorvos, bendiocarb, carbaryl, methiocarb, endrin, 4,4′-DDT, iprodion and *O*-ethyl *O*-(4-nitrophenyl)ester phenyl phosphonothioic acid (EPN) were from Riedel-de Haën (Seelze, Germany) and were of at least 98% purity. Eicosane with a purity of ≥97% was purchased from Fluka (Buchs, Switzerland). The solvents to prepare dilutions and/or mixtures were from various sources and were all of p.a. quality.

3. Results and discussion

3.1. Principle and design of the AT-column injector

Next to the PTV and on-column methods that are now widely used for large-volume sampling, several other methods have been developed for GC LVI. Two techniques worth mentioning are the loop-type large-volume method and the vapour-overflow technique. The AT-column LVI method combines features of both the loop-type and the vapour overflow method. To explain the mechanism of the AT-column injector it is, therefore, appropriate to take a closer look at these two earlier LVI methods.

In the loop-type LVI technique, an LC-type injection valve ('loop-type valve') is installed on top of the GC. A transfer capillary runs from the valve through the oven wall and is connected to the capillary column using a press-fit connector. For proper operation the temperature setting of the GC oven is crucial: it has to be slightly above the pressure-corrected boiling point of the solvent. Upon injection, the sample, that was temporarily stored in the loop of the injection valve, is transferred through the transfer capillary into the GC oven. The driving force for this transport is the carrier gas flow. Carrier gas pushes the contents of the loop into the transfer capillary. When the plug of sample enters the section of the transfer capillary that penetrates the GC oven wall, it enters a zone with a positive temperature gradient. At some point in the gradient the front of the solvent plug reaches a temperature where the liquid starts to evaporate. The vapour

pressure created in that way pushes the liquid back into the colder zone and an equilibrium situation is reached where the pressure created by the evaporating solvent balances the carrier gas pressure. The solvent plug continues to evaporate from the front until all the solvent has evaporated. Solvent vapour formed upon evaporation is discharged via an early SVE. Loop-type injection was the first method that was developed for LVI in GC. It gained some popularity, but is now largely replaced by on-column and PTV methods because of three distinct disadvantages: (i) losses of volatile analytes, (ii) uncontrolled 'shooting' of liquid into the capillary column as a result of boiling-delay, and (iii) carry-over due to liquid lagging behind in the transfer capillary between valve and column.

The new AT-column injection technique closely resembles loop-type injection, but eliminates the disadvantages summarised above. As with loop-type injection it is again essential to introduce the sample into a zone where a temperature gradient exists. This is now the liner of the AT-column injector. When the injector is kept at a temperature below the solvent boiling point while the GC oven temperature is above this value, a positive temperature gradient is created. A schematic of the injector-column configuration is shown in Fig. 1. The liner now basically replaces the transfer capillary of the loop-type interface. A distinct improvement is that the volume of the liner, 120 μl, is large enough to accommodate the entire sample. At the end of the injection, the liner is heated, thereby eliminating carry-over. From the cool liner, the liquid flows into a 60 cm × 0.53 mm i.d. de-activated fused-silica capillary pre-column. This de-activated capillary is press-fit connected to the outlet of the liner, at one end, and to the capillary GC column at the other end. There is no vapour exit between the capillary pre-column and the GC capillary. At some point in the first few centimetres of this capillary, the solvent reaches the boiling temperature. The vapour pressure created upon evaporation pushes the excess of liquid that entered the fused-silica capillary back towards the colder liner. The liquid that has entered the capillary evaporates and new liquid can only flow into it once the pressure created inside the capillary has dropped below the carrier gas pressure set on the system. Again, a steady state is created where the flow of liquid solvent into the column equals the (mass) flow of solvent vapour leaving the system via the GC column. This process is repeated until the very last drops of solvent have flown into the capillary. As a result, all sample constituents will be concentrated at the top of the de-activated fused silica capillary. Next, the injector and oven temperature are programmed to their respective final values and the GC separation is begun.

A crucial feature in the design of the AT-column liner is the approximately 1 mm diameter glass bead present in the bottom section. This glass bead functions as a restrictor for liquid flow. It prevents large volumes of liquid sample from entering the de-activated fused silica capillary at the start of the injection process when the pressure in the de-activated capillary does not yet balance the carrier gas pressure. The use of a short length of a small diameter capillary, e.g. 0.2 mm i.d., would probably also provide the required flow resistance. However, for practical reasons we prefer the glass bead approach. An important drawback of the loop-type injector, the 'shooting' of liquid into the column due to boiling-delay, is nicely eliminated by this restriction. As

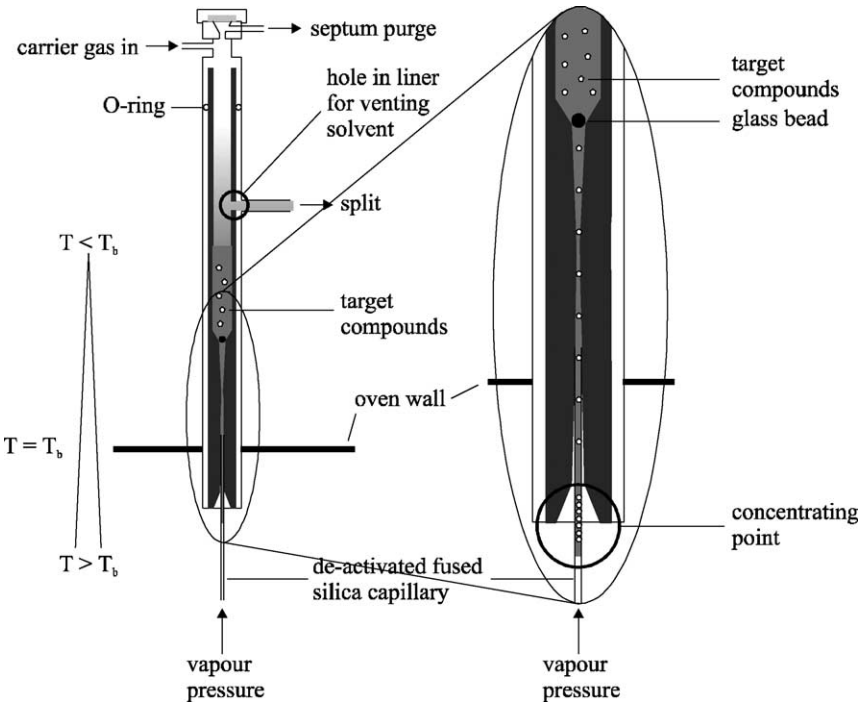

Fig. 1. Schematic of the AT-column injector configuration.

mentioned previously, carry-over caused by the liquid film adhering to the wall of the transfer capillary or the sample loop is absent because the only zone that is in contact with the liquid sample, the injector liner, is heated to a high temperature after each injection. Finally the other disadvantage of loop-type LVI, the loss of volatile analytes, can be circumvented when using AT-column LVI. With standard loop-type injection, solvent evaporation only takes place from the 'hot side' of the solvent zone. Analyte molecules that escape from the liquid enter a zone where the temperature is even higher, and are readily lost. This situation is further aggravated by the low flow resistance: it is only a short distance to the nearest exit, the SVE. The AT-column injection exploits the vapour-overflow mechanism. Solvent evaporation mainly occurs from the 'cold' side of the solvent zone. Solvent vapour formed in the injector liner is discharged via an exit at the top of the injector. To effect this, a liner with a 2 mm diameter gas exit in the top section has to be used. Because of the large flow resistance of the GC column, only a marginal fraction of the solvent vapour is discharged from the system via the column.

Due to the shape of the AT-column liner, contact of analytes with the metal surface of the injector body is excluded. The solvent elimination process in the AT-column injector is rather different from that in a packed liner. Firstly, the surface from which the solvent evaporates is much smaller. Secondly, the solvent vapour leaves the AT-column injector by diffusion, which is a rather slow and inefficient process compared to that occurring in packed-bed liners where the carrier gas flows through the bed and dynamically purges the solvent vapour from the liner. As a consequence, with the AT-column injector, the initial injector temperature has to be substantially higher. Typically, a liner temperature close to the pressure-corrected solvent boiling point plus a high purge flow have to be applied to obtain acceptable solvent vent times. Although, at a first glance, these are unfavourable settings with regard to loss of volatiles, in practice good recoveries were obtained because of the small solvent surface area from which these analytes can escape and the strong solvent effect in the bulk liquid phase present in the injector. As explained before, the GC initial temperature has to be above the solvent boiling point to create a sufficiently high solvent vapour pressure to prevent flooding of the capillary column. Too high an initial GC temperature should be avoided, because this will adversely affect the focusing effect for low-boiling compounds.

Optimisation of the AT-column LVI method is straightforward. Basically, only three parameters have to be considered: injector temperature, purge flow and maximum sample volume. The maximum sample volume to be injected at-once is determined by the volume of the liner, which is typically 120 μl. Larger sample volumes can be handled when doing speed-controlled or repetitive injections. The purge flow is not very critical because the evaporation process is fully self-adjusting. A purge flow between 100 and 200 ml/min will give good results. The only parameter that has to be carefully selected is the liner temperature. Due to the fact that there is an elevated pressure in the system, the solvent boiling point is higher than at atmospheric pressure, as described by the equation of Clausius–Clapeyron. The pressure-corrected boiling point can be calculated using this equation or, preferably, the empirical Antoine equation:

$$\log P_{\mathrm{mmHg}} = A_{\mathrm{mmHg}} - \frac{B}{T_{^\circ\mathrm{C}} + C} \quad (1)$$

Here, A, B and C are the solvent-dependent empirical Antoine coefficients. The pressure, P, is in mmHg and the temperature, T, in °C. By substituting the proper Antoine coefficients for the solvent to be injected and the carrier gas pressure, the corrected boiling point can be calculated. To obtain corrected boiling points close to the atmospheric boiling point and, consequently, to be able to keep the GC initial temperature as low as possible, the purge pressure should be set as low as possible. Table 1 gives the Antoine coefficients as well as the corrected boiling points of some common solvents at an injector carrier gas pressure of 125 kPa (absolute pressure).

3.2. Temperature optimisation

3.2.1. Initial injector temperature

To keep the solvent boiling point inside the injector as low as possible, the pressure in the injector during solvent venting ('purge pressure') was set to 22 kPa. Due to the flow resistance of the long split line, this was the lowest pressure at which the carrier-gas system could still maintain the split flow at the desired value of 140 ml/min. The sample used for the optimisation was a hydrocarbon standard containing C_{10}–C_{44} in *n*-hexane. The corrected boiling point of *n*-hexane at 22 kPa injector purge pressure (122 kPa absolute pressure) is 75 °C. To ensure that the solvent vapour pressure in the capillary column is high enough, the GC initial temperature was set to 100 °C. After solvent evaporation the GC was ramped to 350 °C (10 min hold) at 15 °C/min; during the analysis, the injector pressure was kept constant at 100 kPa with a split flow of 35 ml/min. The injection volume was 100 μl and the injector initial temperature was varied from 66 to 78 °C in steps of 2 °C. The venting flow was 140 ml/min for all injections and the capillary column was

Table 1
Corrected boiling point of common solvents as calculated by Antoine equation

Solvent	*A*	*B*	*C*	Corrected boiling point (°C)[a]
Pentane	6.87632	1075.78	233.205	43
Hexane	6.89748	1181.85	225.500	76
Dichloromethane	7.08030	1138.91	231.460	46
Heptane	6.89385	1264.37	216.636	106
Acetonitrile	7.07350	1279.20	224.010	88
Isooctane	6.81189	1257.84	220.735	107
Methyl acetate	6.31695	815.09	179.411	63

[a] Injector carrier gas pressure: 25 kPa.

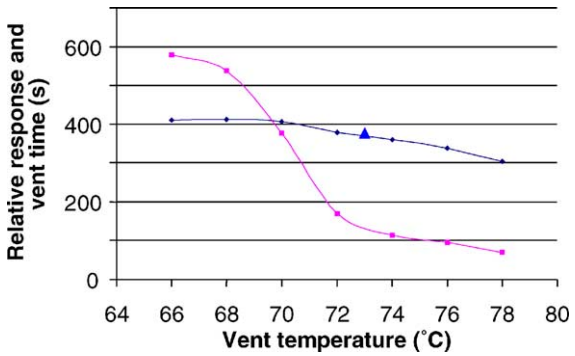

Fig. 2. Influence of injector venting temperature on (◆) the C_{20} peak area and (■) the solvent venting time. The symbol (▲) indicates situation where recovery loss is 10% (see text).

a 30 m × 0.25 mm i.d. HP5-MS with a film thickness of 0.5 μm. A somewhat thicker stationary phase film was chosen to improve focusing at the relatively high initial oven temperature. Fig. 2 shows typical results for the C_{20} peak. This compound was selected because it will be focused sufficiently at an initial oven temperature of 100 °C. Moreover, it will not easily be lost during solvent evaporation in the injector liner. Fig. 2 clearly shows that the selection of the liner temperature is not very critical. There is no real minimum temperature, except that evaporation times can become unacceptably long. Higher temperatures constitute a risk of explosion-like evaporation of the solvent in the liner. Typically, the initial temperature can be set slightly above the boiling point of the solvent. It is also clear from the figure that the recovery rapidly decreases at higher temperatures. If recovery losses of up to 10% are considered acceptable, this results in a venting temperature of 72–73 °C. To generalise, the optimal initial injector temperature is 2–3 °C below the corrected boiling point of the solvent.

3.2.2. Initial GC temperature

The experiments on the optimisation of the initial injector temperature showed that an initial GC temperature of 100 °C can be used for semi-volatile compounds like C_{20}. In order to obtain stronger focusing for lower-boiling compounds, the initial GC temperature has to be as low as possible, but, evidently, too low temperatures where flooding of the column can occur, should be avoided. The initial GC temperature was optimised in 5 °C steps from 100 down to 70 °C. The initial injector temperature was set at the optimised value of 73 °C. All other parameter values were the same as before. Fig. 3 shows that at an initial GC temperature of 70 °C the column becomes flooded with solvent, which results in collapsing of the peaks. On the other hand, there is essentially no difference between the peak shapes recorded at 75, 80 and 85 °C. Based on these results, it was decided to take 80 °C as the optimum initial oven temperature. To generalise, the initial oven temperature should be about 5 °C above the corrected boiling point of the solvent, equal to 7–8 °C above the initial injector temperature. Fig. 4 shows

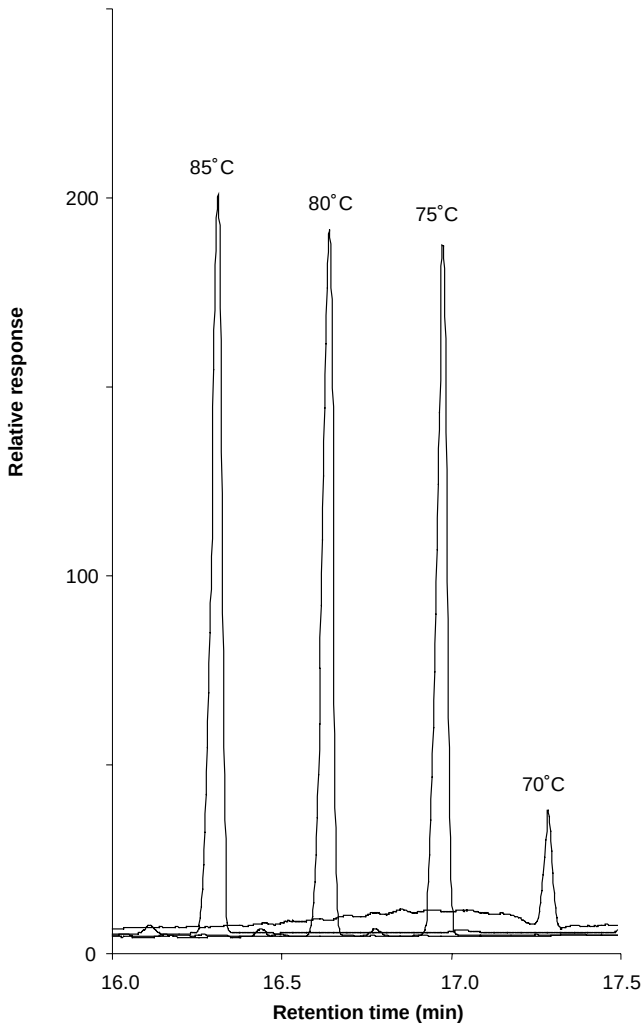

Fig. 3. Influence of initial oven temperature (indicated for each peak in °C) on peak shape of C_{20}.

a GC–FID chromatogram of a 100 μl AT-column injection of the alkane mixture in hexane performed at the optimised initial temperature settings. Due to the constant-pressure approach of the analysis and the relatively thick film, the later eluting peaks are rather broad. Nevertheless, their relative recoveries are close to 100%, as can be read from the legend to the figure.

3.3. Application range

As is true for all LVI methods, the current method also has a finite application range. Very volatile analytes will be lost, while there will be also a limit on the higher molecular weight side. The results presented in Fig. 4 (and its legend) show that the recovery for C_{14} (and lower boiling compounds) is less than 90% compared with C_{20}. In order to establish the actual application range of the AT-column injection technique, *n*-alkane solutions were prepared in several frequently used GC solvents, viz., hexane, pentane, heptane, dichloromethane, acetonitrile, isooctane and

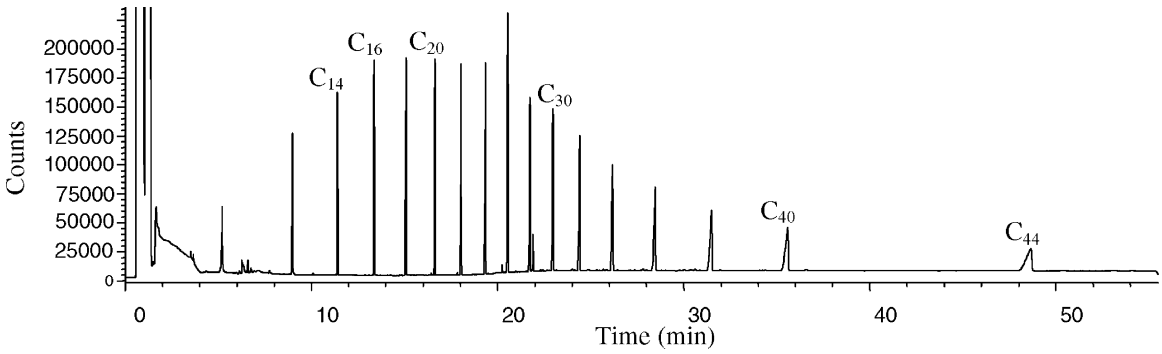

Fig. 4. GC–FID chromatogram of a 100 μl AT-column injection of an *n*-alkane mixture in *n*-hexane, using optimised injector and oven temperatures (73 and 80 °C, respectively). For selected alkanes, the relative recoveries (compared with C_{20}) were: C_{14}, 84%; C_{16}, 93%; C_{30}, 102%; C_{40}, 97%; C_{44}, 97%.

Table 2
Recoveries for selected compounds injected in four different solvents

Solvent	Initial injection temperature (°C)	Initial GC temperature (°C)	Relative recovery
Pentane	39	47	C_{10} 0.89 C_{12} 0.98 C_{44} 0.96
Dichloromethane	42	50	C_{14} 0.59 C_{16} 0.90 C_{44} 0.97
Methyl acetate	60	68	C_{14} 0.87 C_{16} 0.96 C_{44} 0.93
Isooctane	103	111	C_{20} 0.83* C_{22} 0.91* C_{44} 0.95*

For further conditions, see text and Fig. 5.
* Recovery compared to C_{30}; others to C_{20}.

methyl acetate. The injection parameters were set according to the rules derived above. Fig. 5 shows a selected set of chromatograms recorded at the predicted optimal temperatures. Quantitative recovery data are given in Table 2 for a selected number of analytes. Table 3 lists the first eluting compound for which 90% recovery was obtained for each of the solvents tested. In this table, also the difference in atmospheric boiling points between the compound and the solvent are given.

Table 3
Difference in atmospheric boiling point between solvent and first *n*-alkane yielding 90% recovery

Solvent (atmospheric boiling point, °C)	First 90%-recovery compound (atmospheric boiling point, °C)	Difference in atmospheric boiling point (°C)
Pentane (36)	C_{10} (216)	180
Hexane (69)	C_{14} (253)	184
Dichloromethane (39)	C_{16} (287)	248
Heptane (98)	C_{16} (287)	189
Acetonitrile (81)	C_{20}[a] (342)	261
Isooctane (126)	C_{24}[a] (391)	265
Methyl acetate (57)	C_{14} (253)	196

[a] Recovery compared to C_{30}; others to C_{20}.

One important conclusion that can be drawn from the chromatograms in Fig. 5 is that the application range extends up to at least C_{44} (the highest molecular weight alkane tested), independent of the solvent used. This maximum is determined only by the final temperature of the PTV and the GC column. On the lower side the solvent clearly affects the performance of the method. Table 3 shows that there is a minimum boiling point difference between the solvent and the first eluting 90% compound of 180–195 °C for apolar organic solvents, which increases to 260 °C for more polar organic solvents. The poorer recovery seen for the more polar solvents is caused by the reduced solubilisation of the non-polar analytes in these solvents in the injector liner.

3.4. Analytical performance data

If the carrier gas is monitored for the presence of solvent vapour during solvent venting, no optimisation of the vent time is needed. This means that the optimised settings can also be used for sample volumes other than 100 μl. For a study on the analytical performance, the injection parameters were set as optimised in the previous sections; the *n*-alkane solution was prepared in *n*-pentane. Table 4 shows the relevant analytical performance data for the linearity of the peak area response as a function of the injection volume and the repeatability for a selected number of *n*-alkanes. The results for both parameters can be called satisfactory. Except

Table 4
Analytical performance data for AT-column–GC–FID of *n*-alkanes

n-Alkane	Area $= f(v_{inj}) + C$	Correlation coefficient[a] (r^2)	R.S.D.[b] (%)
C_{10}	$0.064v_{inj} + 0.556$	0.992	14
C_{12}	$0.075v_{inj} + 0.459$	0.993	6.5
C_{20}	$0.117v_{inj} + 0.087$	0.999	4.0
C_{26}	$0.180v_{inj} + 0.073$	0.999	4.0
C_{30}	$0.120v_{inj} - 0.068$	0.999	5.0
C_{40}	$0.113v_{inj} - 0.220$	0.999	5.0
C_{44}	$0.119v_{inj} - 0.801$	0.998	6.5

[a] Based on injections of 10, 25, 50, 75 and 100 μl.
[b] $n = 8$ (100 μl injections).

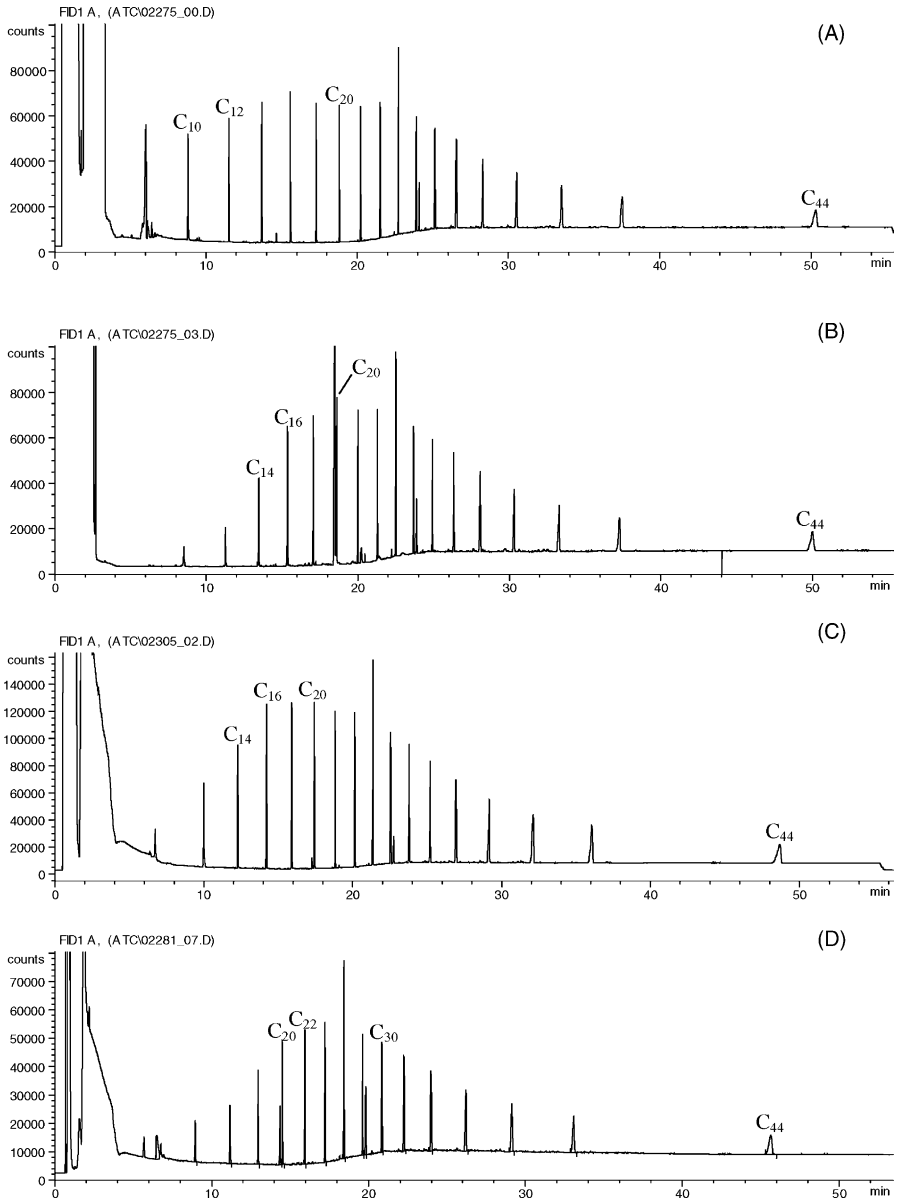

Fig. 5. Selected set of 100 μl AT-column–GC–FID chromatograms at predicted optimal initial temperatures for a selection of solvents: (A) pentane, (B) dichloromethane, (C) methyl acetate and (D) isooctane. Recoveries vs. C_{20} (or C^*_{30}) for selected compounds are given in Table 2.

for C_{10} and C_{12} all r^2 values were above 0.998, while the R.S.D. values were, typically, 4–5%.

3.5. Applications

3.5.1. Labile pesticides

Because of the design of the AT-column injector it is expected that there will be less degradation of labile analytes than with the conventional PTV large-volume technique. To test the degradation behaviour of analytes in AT-column LVI, a 0.1 ng/μl solution in pentane was prepared which contained dichlorvos, bendiocarb, carbaryl, methiocarb, endrin, 4,4′-DDT, iprodion, EPN [*O*-ethyl *O*-(4-nitrophenyl)ester phenyl phosphonothioic acid] and eicosane (used as internal standard). With this solution 100 μl injections were performed using both AT-column LVI and conventional PTV LVI with a liner packed with a Chromosorb-based material. A 100-fold more concentrated solution of the same mixture was used to perform hot splitless and COC injections to create reference chromatograms. All four types of injection were carried out on the same OPTIC 3 programmable injector. Fig. 6 shows full-scan GC–MS chromatograms for the four injection techniques. The GC traces of the hot splitless injection and the PTV LVI analysis show severe analyte degradation as is manifest from the, sometimes complete, loss of the test compounds and the occurrence of several new peaks resulting from the degradation. In marked contrast, both the AT-column and the COC chromatograms show only the peaks of the injected compounds. This indicates that the inertness of the AT-column technique is similar to that of

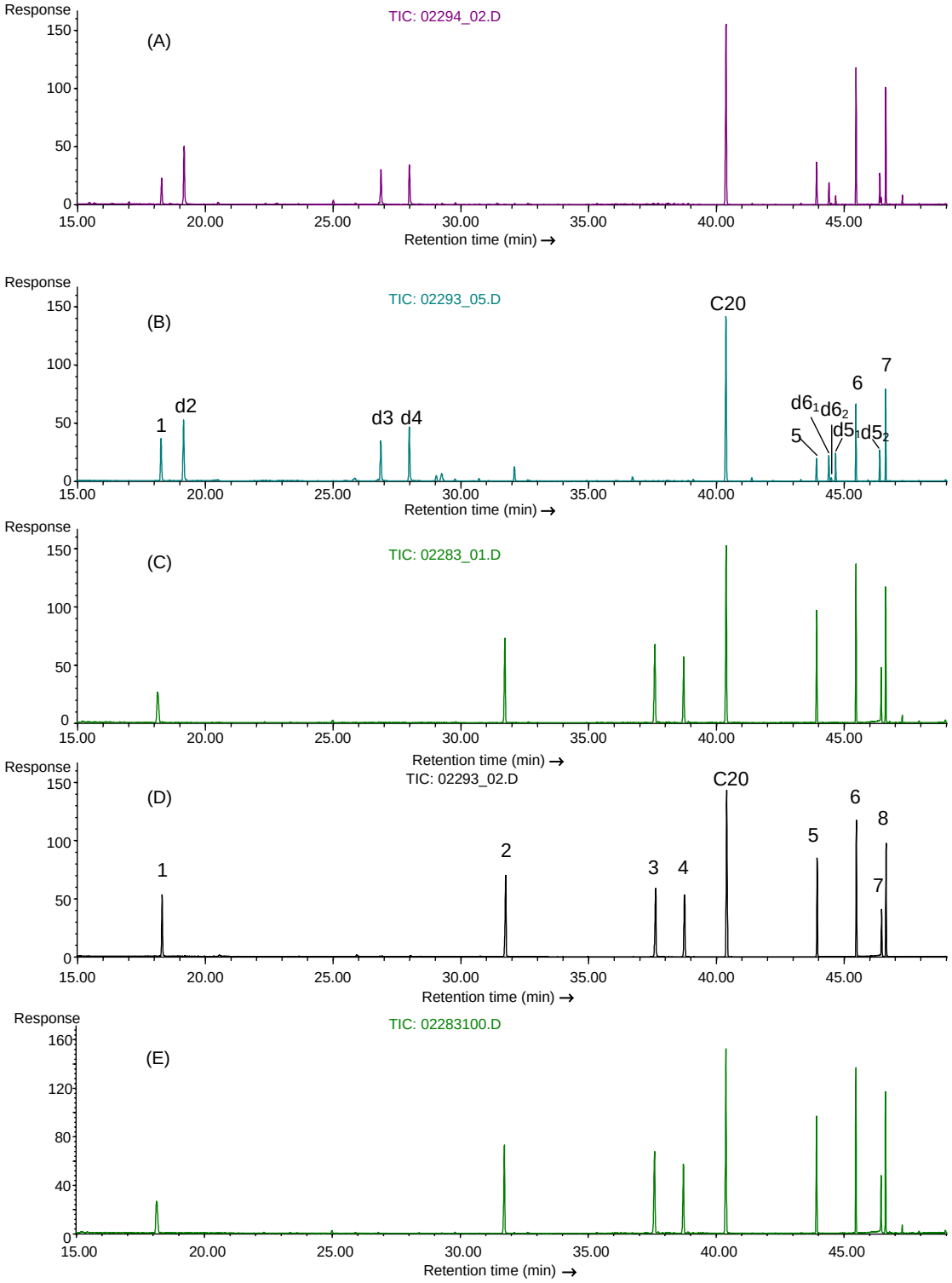

Fig. 6. Full-scan chromatograms of hot splitless (A), packed PTV LVI (B), AT-column (C), on-column (D) injection, and run 100 (E); 1: dichlorvos, 2: bendiocarb, 3: carbaryl, 4: methiocarb, 5: endrin, 6: 4,4′-DDT, 7: iprodion, 8: EPN and C_{20}: eicosane. The designation 'd' indicates degradation products: d2, unknown; d3, 1-naphthalenol; d4, unknown; $d5_1$, endrin aldehyde; $d5_2$, endrin ketone; $d6_1$, DDMU; $d6_2$, DDD; injector: 39 °C → 4 °C/min → 300 °C, 140 ml/min vent flow, 1 ml/min constant column flow; GC oven: 47 °C (2 min) → 4 °C/min → 200 °C → 10 °C/min → 300 °C (10 min).

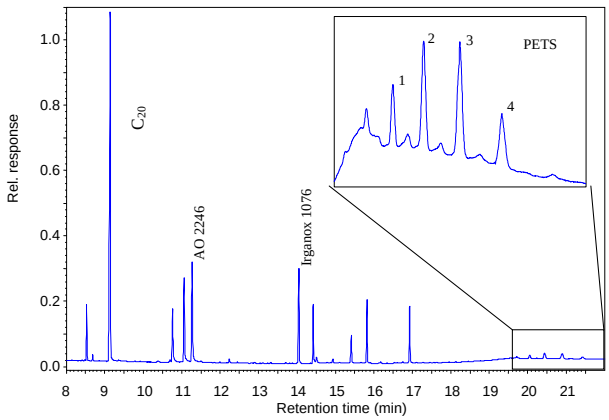

Fig. 7. AT-column–GC–FID analysis of 500 μl of a solution of 100 ppb polymer additives. GC oven programming at 20 °C/min to 300 °C and next at 35 °C/min to 400 °C. Capillary column: DB5-HT, 15 m × 0.32 mm i.d. Film thickness, 0.1 μm. Pre-column: J&W deactivated prosteal capillary of 2 m × 0.53 mm i.d.

the COC method. These techniques are clearly superior to hot splitless and conventional PTV LVI injections.

Finally, the ruggedness of the AT-column approach was tested by a series of 100 injections of 100 μl of the labile analytes' test sample. Comparison of the first (Fig. 6C) and the last chromatogram (Fig. 6E) convincingly illustrates that there is (almost) no difference in the peak heights and the absence of degradation.

3.5.2. Sorption problems

The GC analysis of high-molecular-weight compounds often causes problems, primarily due to losses during the transfer of sample from the injector to the column, with one main cause being the adsorption of the target analytes on the wall of the liner or, if present, the surface of the packing material. Hence, R.S.D. values for such analytes are often very high. AT-column LVI should be an approach to improve such analyses, because the analytes are now transferred to the GC column dissolved in the last droplets of the injection solvent flowing from the injector into the column, which reduces the risk of liner adsorption to a minimum. Fig. 7 shows an AT-column–GC–FID analysis of 500 μl of a sample consisting of polymer additives dissolved in dichloromethane (100 ng/ml), with the *n*-alkane C_{20} as internal standard. The polymer additives have molecular weights ranging to well over 900. This represents the upper limit of molecular weights amenable to gas chromatography [23]. Table 5 shows R.S.D. and recovery data. The latter were calculated by comparison with a 1 μl on-column injection. Because of the very large sample volume, the injection had to be performed at a controlled rate. An injection speed of 500 μl/min was used. During injection and solvent elimination, the injector conditions were 43 °C and 25 kPa with a 150 ml/min vent flow; the GC oven was held at 56 °C. After solvent elimination, the injector was heated to 475 °C at 1 °C/s, where the pressure was programmed from 62 to 241 kPa. The data of Table 5 clearly show that, while the recoveries are satisfactory with values of 82–105% for all but one additive, the repeatabilities are good, with R.S.D.s ranging from 2 to 7% ($n = 5$).

Table 5
Repeatability and recovery data for AT-column–GC–FID additive analysis

Peak	AO 2246	Irganox 1076	PETS			
			1	2	3	4
R.S.D. (%)[a]	33.5	22.0	7.0	3.5	65.5	5.5
Recovery (%)	105	68	82	84	88	100

[a] $n = 5$.

4. Conclusions

AT-column large-volume injection is a promising alternative to existing large-volume injection techniques. The AT-column technique combines the user-friendliness, flexibility and robustness of PTV injections with the high inertness of on-column sample introduction. The tolerance for contaminated samples is at least comparable to that of the on-column LVI technique. The use of the Antoine equation for the selection of the initial injection temperatures makes optimisation straightforward. AT-column LVI can be used with a wide range of solvents and its analytical performance data are fully satisfactory. Interesting areas of application are the analysis of samples that contain thermally labile analytes or high-molecular-weight compounds.

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