Journal of Chromatography, 625 (1992) 237–245
Elsevier Science Publishers B.V., Amsterdam

CHROM. 24 504

Drying step for introduction of water-free desorption solvent into a gas chromatograph after on-line liquid chromatographic trace enrichment of aqueous samples

Jolan J. Vreuls, Rudy T. Ghijsen, Gerhardus J. de Jong* and Udo A. Th. Brinkman

Department of Analytical Chemistry, Free University, De Boelelaan 1083, 1081 HV Amsterdam (Netherlands)

(Received May 15th, 1992)

ABSTRACT

Two procedures are described which effect the rigorous removal of water from the liquid chromatographic (LC) precolumn during the on-line LC trace enrichment–capillary gas chromatography (GC) of aqueous samples, thereby preventing the deterioration of the performance of the retention gap and, thus, the loss of analytes. After LC preconcentration of an aqueous sample on a polymer-packed precolumn, the ethyl acetate used for desorption is led to the GC system either via a small cartridge containing a drying agent (anhydrous sodium sulphate or silica) or after removal of residual water from the precolumn by means of a 30-min nitrogen purge. Regeneration of the drying agents by electric heating permits re-use of the cartridges for about 20 runs. For both procedures, experiments with a series of *s*-triazine herbicides and several volatile test compounds showed that analyte losses are negligible, even at the sub-ppb level and the repeatability is satisfactory.

INTRODUCTION

In recent papers we have discussed a system for column liquid chromatography (LC) coupled on-line with gas chromatography (GC) that can be used for the LC-type preconcentration of aqueous samples [1] and for trapping compounds eluting from either a reversed-phase LC [2] or an immunoselective preconcentration system [3]. After (re)concentration of the compounds on a short LC precolumn, they are introduced into the GC system using ethyl acetate as desorption solvent. Direct introduction of traces of water which are still present in the LC precolumn into the gas chromatograph is prevented by optimizing the time to fill the LC precolumn and capillary tubing with ethyl acetate and push the water to waste, the so-called delay time. Although the method has been used successfully, problems sometimes arose with compounds that elute at high temperatures, *i.e.* above about 200°C, in GC. The origin of these problem has been described in detail by Grob [4]. A short discussion is as follows.

The deactivation layer in silylated retention gaps is hydrolysed by water present in the ethyl acetate. This results in an active surface of the retention gap. In subsequent runs at low temperatures such a retention gap will be deactivated by the few per cent of water that are dissolved in the ethyl acetate. Consequently, compounds that pass through the retention gap under these conditions have a normal peak shape in GC. However, once the water has been removed as a result of the steadily increasing temperature in the GC programme, compounds then still present in the retention gap can interact with the surface. As a result, peaks will be distorted or no

Correspondence to: Professor U. A. Th. Brinkman, Department of Analytical Chemistry, Free University, De Boelelaan 1083, 1081 HV Amsterdam, Netherlands.

* Present address: Analytical Development Department, Solvay-Duphar BV, P.O. Box 900, 1380 DA Weesp, Netherlands.

0021-9673/92/$05.00

peak will show up at all. In other words, the weak point of such an LC–GC system is that up to 3% of water can dissolve in the ethyl acetate. The introduction of 50–75 μl of ethyl acetate used as desorption solvent into the retention gap has the consequence that several microlitres of water also enter, which has the deleterious effect already described.

Self-evidently, solving the above problem is highly desirable in order to extend the application range and improve the robustness of on-line (reversed-phase) LC–GC. A practical solution should preferably require no major hardware changes. In addition, it should not cause contamination nor lead to loss of compounds, and regeneration of the system should be automatable. One option is removal of the water via a postcolumn reaction. However, the reaction conditions generally will not be favourable, requiring the presence of chemicals or a catalyst, a high temperature and/or a long reaction time. The reaction of water with triethyl orthoformate or 2,2-dimethoxypropane is a typical example [5]. Another solution is the use of Nafion tubing (DuPont), which allows the selective removal of water through the pores in the tube [6]. Apart from the fact that loss of small polar compounds can be a problem (reported for drying of gaseous samples [7]), in our case incorporating the tubing in the existing LC–GC set-up cannot easily be achieved. Actually, adapting drying procedures which are routinely used in liquid–liquid and solid-phase extraction, such as the addition of anhydrous sodium sulphate or drying a column by sucking air through it, provides much simpler solutions to remove water rigorously from an organic desorption solvent. Such procedures do not cause analyte losses, even at very low concentration levels [8,9].

In this work, two approaches were examined. One alternative is to incorporate a cartridge containing a drying agent (sodium sulphate or silica) into the existing LC–GC apparatus in order that drying of the desorption solvent can be carried out on-line with trace enrichment and desorption. Water present in the desorption solvent binds to the agent when passing it. Regeneration of the drying agent is done by heating the cartridge in combination with a helium purge. The other approach is to remove the water present in the LC-type precolumn by a nitrogen purge before the analyte desorption [10,11]. The main aspect studied was the recovery of compounds after trace enrichment and on-line drying.

EXPERIMENTAL

Reagents

Nitrogen used as a drying gas was of 5.0 grade from Hoekloos (Schiedam, Netherlands). The drying agents silica and anhydrous sodium sulphate were obtained from J.T. Baker (Deventer, Netherlands). Ethyl acetate (J.T. Baker) was freshly distilled before use and HPLC-grade water was prepared by purifying demineralized water in a Milli-Q filtration system (Millipore, Bedford, MD, USA). Two aqueous test mixtures were used: (i) a solution of twelve *s*-triazines (97–99% purity; Dr. Ehrenstorfer, Augsburg, Germany) and (ii) a solution containing nitrobenzene, *m*-cresol, phenanthrene, tributyl phosphate, atrazine and cyanazine.

System for on-line trace enrichment, drying and desorption

The scheme of the LC trace enrichment–GC set-up is shown in Fig. 1. Aqueous standards were enriched using a Gilson (Villiers-le-Bel, France) Model 302 pump, a valve switching unit (Kontron, Zürich, Switzerland) and a laboratory-made 10 mm × 2 mm I.D. preconcentration column (LC precolumn) packed with 10 μm PLRP-S styrene–divinylbenzene copolymer (Polymer Labs., Church Stretton, UK). The valve switching unit consisted of a solvent-delivery valve and four six-port valves. Desorption with ethyl acetate into the GC system was carried out with a Phoenix 20 syringe pump (Carlo Erba, Milan, Italy) through a 20 cm × 0.075 mm I.D. fused-silica capillary permanently mounted in the on-column injector of the gas chromatograph. All steps in the procedure, *i.e.*, changing the solvents during trace enrichment by switching the solvent-delivery valve, flushing the capillaries between solvent exchanging, trace enrichment, optional drying with nitrogen, desorption, transfer into the retention gap, starting data acquisition and optional heating of the drying cartridge, were executed by adequate programming of the four six-port valves and the auxiliary outputs of the time programmer of the valve switching unit.

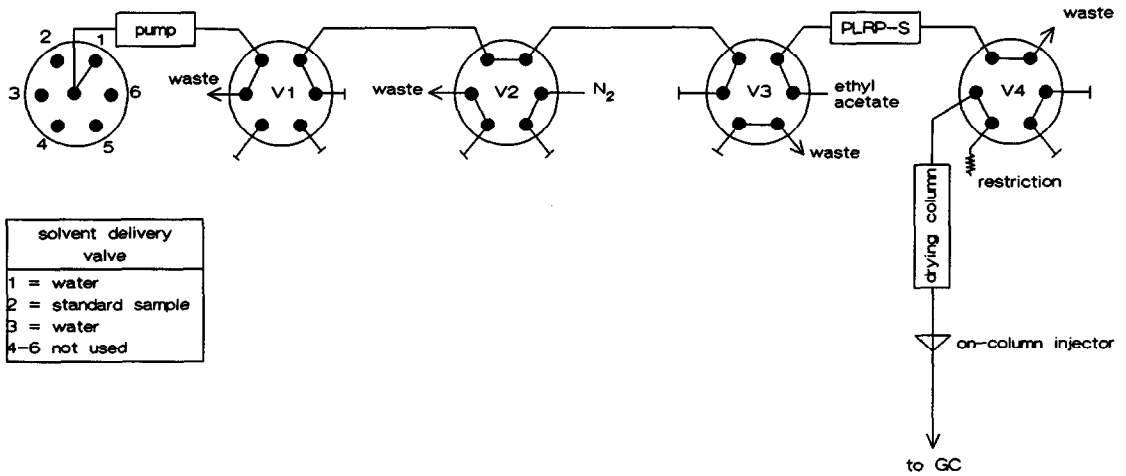

Fig. 1. Scheme of the system used for on-line LC trace enrichment on a PLRP-S column, clean-up, drying and desorption into the GC system, consisting of a solvent-delivery valve and four six-port valves (V1–V4). Drying was carried out using either a drying agent packed in a cartridge positioned between valve V4 and the on-column injector or a nitrogen purge of the PLRP-S column introduced via valve V2.

GC system

A Carlo Erba Mega gas chromatograph equipped with an on-column injector, a flame ionization detector and a Nelson data storage system (Perkin Elmer, Gouda, Netherlands) was used. The 7.5 m × 0.32 mm I.D. diphenyltetramethyldisilazane-deactivated retention gap, (DPTMDS; B. Schilling, Zürich, Switzerland), was used for the introduction of 50–75 μl of ethyl acetate under partially concurrent solvent evaporation conditions [12]. It was connected to the 15 m × 0.25 mm I.D. GC column (DB 1701, d_f 0.25 μm) via a glass press-fit connector. Helium was used as the carrier gas at an inlet pressure of 90 kPa. After elution of the solvent peak a temperature programme from 84 to 285°C at different ramps was used.

Procedure

Table I lists the two time schedules that were used to run the fully automated system, *viz.* steps I and II or steps I and III.

Steps I and II. The PLRP-S precolumn is subsequently flushed with 2.5 ml of HPLC-grade water to remove ethyl acetate from the previous run, with 10 ml of the aqueous sample (trace enrichment) and again with 2.5 ml of HPLC-grade water (to provide further clean-up in real analyses) at 5 ml/min by switching of valves V1 and V3. Next, desorption with ethyl acetate is started at a flow-rate of 25 μl/min by switching valve V3 again. During this step water is removed from the precolumn and capillary tubing and pushed to waste by ethyl acetate. When ethyl acetate reaches valve V4, *i.e.*, after 1.25 min, it is introduced into the system through the 10 mm × 2 mm I.D. cartridge filled with the drying agent by switching this particular valve. When the cartridge is filled with ethyl acetate, which takes 0.67 min with the 10 mm × 2 mm I.D. cartridge used in this study, the data acquisition and GC programme are started, and ethyl acetate is introduced into the retention gap for 2.00 min at a flow-rate of 25 μl/min. After completion of the transfer, valve V4 is switched and ethyl acetate, still present in the cartridge and capillaries, is pushed out by the helium back-pressure in the on-column injector.

Prior to the next run, the sodium sulphate- or silica-containing cartridge is dried for 30 min at 150 and 180°C, respectively. Drying is promoted by the small helium purge through the cartridge. During the whole procedure, the PLRP-S precolumn is continuously flushed with ethyl acetate. The next run is started after the end of the GC programme in order that the introduction of the desorption solvent takes place when the oven has cooled down.

Steps I and III. When a nitrogen purge is used as a drying step after loading and flushing of the

TABLE I

TIME SCHEDULES FOR AUTOMATED LC TRACE ENRICHMENT–CAPILLARY GC OF AQUEOUS SAMPLES WITH AN IN-LINE DRYING STEP

Conditions: loading of sample at 5 ml/min; desorption with ethyl acetate at 25 μl/min; GC–FID as reported in the text; in-line drying with drying agent in a cartridge or with a nitrogen purge of 40 ml/min.

Step	Time (min)	S[a]	V1[b]	V2[b]	V3[b]	V4[b]	Comments
I. Preconcentration	0.00	Water	A	A	A	A	Flush capillaries with water
	0.50		B		B		Flush PLRP-S column (2.5 ml)
	1.00	Sample	A				Flush capillaries with sample
	1.50		B				Load sample (10 ml)
	3.50	Water	A				Flush capillaries with water
	4.00		B				Clean-up step (2.5 ml); pump switched off at end
II. Drying	4.50		A		A		Start desorption (displacing water from PLRP-S column)
	5.75					B	Introduction into cartridge (filling with ethyl acetate)
	6.42						Actual transfer; start GC programme and data acquisition
	8.42					A	Stop transfer; further cleaning of PLRP-S column until next run
	10.00						Drying agent heated for 30 min to 150 or 180°C during GC programme
	45.00						System ready for next run
III. Nitrogen purge	4.50		A	B			Drying with nitrogen
	34.50			A	A		Start desorption
	35.70					B	Switch just before actual introduction into GC system; filling of transfer line
	35.80						Start GC programme and data acquisition
	37.80					A	Further cleaning of PLRP-S column
	45.00						System ready for next run

[a] S = Solvent pumped by Gilson pump selected by solvent-delivery valve.
[b] V1–V4 = Positions of six-port valves (position A refers to position in Fig. 1).

PLRP-S precolumn (for details, see above), the precolumn is purged for 30 min at ambient temperature (40 ml/min of gas). Next, desorption is started. When the precolumn has just been filled with ethyl acetate, the introduction valve V4 is switched and kept in that position for 2.1 min (0.1 min to fill the transfer line; 2.0 min to transfer the analytes into the retention gap). While the GC separation proceeds, first the PLRP-S precolumn is flushed with ethyl acetate. Then the next run can be started after 45 min, as preconcentration and drying of the LC precolumn can be carried out at the same time as the GC separation of the previous sample.

RESULTS AND DISCUSSION

Trace enrichment

In the LC trace enrichment of aqueous samples coupled on-line with GC analysis there are several main parameters. First, the PLRP-S precolumn, which is not discarded after a single analysis but is repeatedly re-used, should be cleaned after each run by flushing with ethyl acetate (at least *ca.* 150 μl) and, next be reconditioned with water (2.5 ml). Second, breakthrough of analytes on the precolumn should be avoided while on the other hand a sufficient amount of these analytes should be trapped to allow the desired overall sensitivity to be obtained. If the limit of detection is set at 10–30 ppt (w/w), at least *ca.* 10 ml of an *s*-triazine-containing sample has to be loaded to permit detection by means of GC with flame ionization detection (FID). Fortunately, the breakthrough volumes of the s-triazines on a 10 mm × 2 mm I.D. polymer-packed column are of the order of 30–100 ml [13], that is, no loss of analytes will occur during this step.

As regards desorption of analytes from the precolumn, earlier work has convincingly shown that

50–75 μl of ethyl acetate suffice for their quantitative transfer to the retention gap [2,3]. During transfer, the speed of introduction into the retention gap should be higher than the evaporation rate of the solvent to ensure solvent trapping of volatile compounds [14]. For the present GC system, the evaporation rate of ethyl acetate was found to be 12 μl/min. As the retention gap should have such a length that the solvent film created on its wall does not reach the stationary phase of the analytical GC column, the amount of solvent that is introduced into the retention gap in the liquid state, *i.e.*, $(25-12)$ μl/min × 2.0 min = 26 μl, should be multiplied by the so-called flooded zone, which is about 20 cm/μl for ethyl acetate in a DPTMDS-deactivated retention gap [15]. In other words, the retention gap should have a length of at least 5 m. In all our experiments we used a 7.5 m × 0.32 mm I.D. retention gap.

Drying procedure

In this study, the main aspect of interest was to prevent any water from reaching the retention gap, *i.e.*, to prevent any deterioration of the retention gap performance. The presence of a trace amount of water in the desorption solvent can easily be detected by leading it into 100 μl of *n*-hexane rather than into the retention gap after the optimum delay time, the *n*-hexane turns opaque if water is present. Two alternatives were studied in order to remove water rigorously from the ethyl acetate, *viz.*, the on-line insertion of a small cartridge filled with anhydrous sodium sulphate or silica, or drying by purging with nitrogen.

When a sorbent-packed drying column was used, the ethyl acetate was found to contain no water at all. However, whereas with the silica column the *n*-hexane turned opaque already after the second analysis, with the sodium sulphate there was no breakthrough of water even after ten consecutive runs. Obviously, with the present configuration, 15 μl of water can be removed by the latter sorbent as against only 1–2 μl with silica. In order to improve the practicality of the system, the drying module was modified to include an electrical heating unit. If heating of the cartridge for 30 min at 150–180°C was combined with a small helium purge, the hexane receiving solvent did not turn opaque even after 25 runs (the largest number tested at this stage), irrespective of whether sodium sulphate or silica was used as the sorbent.

One note of warning should be added here. Under actual operating conditions (see the next section), it was occasionally observed that the sodium sulphate particles partially disintegrated, with the fines so formed being swept through the outlet screen of the cartridge and into the GC part of the system. The disintegration is probably the result of water present within the particles becoming overheated. As this never occurred with a sodium sulphate packing that had been used for less than 25 runs, in all final experiments a fresh cartridge was installed after each 20 runs.

As regards drying of the PLRP-S precolumn by means of a nitrogen purge, recent experience with the drying of alkyl-bonded silica- and polymer-bonded membrane extraction discs has shown that purging should be continued for at least 20 and 10 min, respectively, at ambient temperature [16]. In this work it was found that a nitrogen purge of 30 min, at a flow rate of 40 ml/min, obtained by applying a pressure of 3 bar, sufficed to remove water completely from the precolumn. Because the use of a nitrogen purge as drying step has been considered in some detail elsewhere [16], in the final part of this work most attention was devoted to the LC trace enrichment–drying sorbent–GC–FID set-up.

On-line drying for LC trace enrichment–GC

Drying over a sorbent. Preliminary experiments revealed that using sodium sulphate or silica as drying agent without any further clean-up caused severe contamination and a high background in GC–FID. As an example, Fig. 2a shows a chromatogram obtained using a freshly packed sodium sulphate cartridge. In this instance, 75 μl of ethyl acetate containing 7.5 ng of each of twelve *s*-triazines were injected directly on to the drying cartridge; these analytes elute between 21 and 27 min. For comparison, Fig. b shows the chromatogram obtained when using sodium sulphate purified for 4 h by Soxhlet extraction with ethyl acetate. A similarly dramatically improved result was observed, for both sodium sulphate and silica, after flushing the packed cartridge overnight with 10 μl/min of ethyl acetate.

Inserting the sorbent cartridge did not cause a noticeable loss of analytes with either sodium sul-

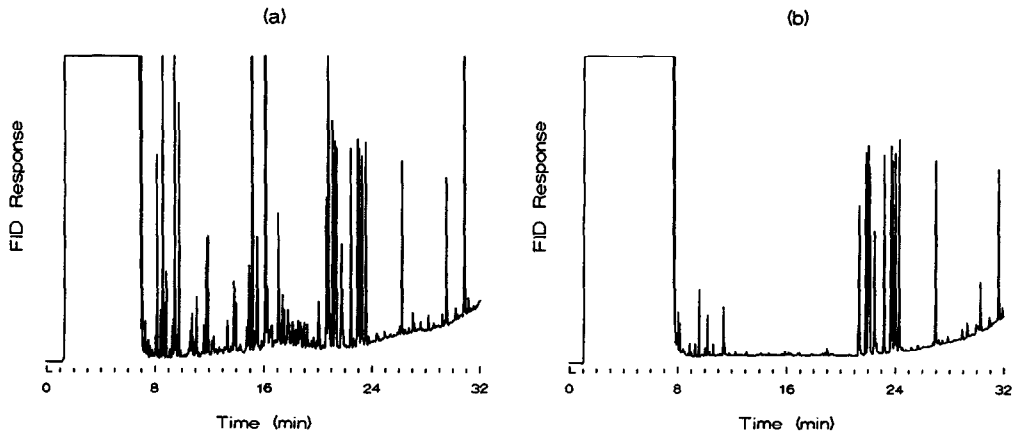

Fig. 2. GC–FIC trace obtained after introduction of 75 μl of *s*-triazine standard (7.5 ng per compound) through a cartridge filled with anhydrous sodium sulphate either (a) used as received or (b) purified for 4 h by Soxhlet extraction with ethyl acetate. GC temperature programme: 84°C until complete solvent elution, then increased to 285°C at 6°C/min; for other conditions, see Experimental. The twelve *s*-triazine herbicides elute between 21 and 27 min.

phate or silica. This is illustrated in Fig. 3, in which part of the chromatogram obtained after the injection of 75 μl of the *s*-triazine standard on to a sodium sulphate cartridge is compared with the corresponding part of the chromatogram of a 75-fold concentrated 1-μl on-column injection. All twelve analyte peaks had the same area to within 3% in Fig. 3a and b. The tails on the peaks in both chromatograms due to atraton and secbumeton are caused by active sites in the retention gap. The slightly different elution times in Fig. 3a and b are the result of slightly different linear velocities.

Using the complete system, with the cartridge packed with either sodium sulphate or silica, on-line LC–GC–FID was carried out for 10-ml samples containing 27 ppt–2 ppb of the test solutes. Results of two such runs are shown in Fig. 4. Above the 0.1 ppb level (the 0.2 ppb level is given as an example in Fig. 4), all twelve analytes showed up well, indicating that real trace-level analysis is possible. At the

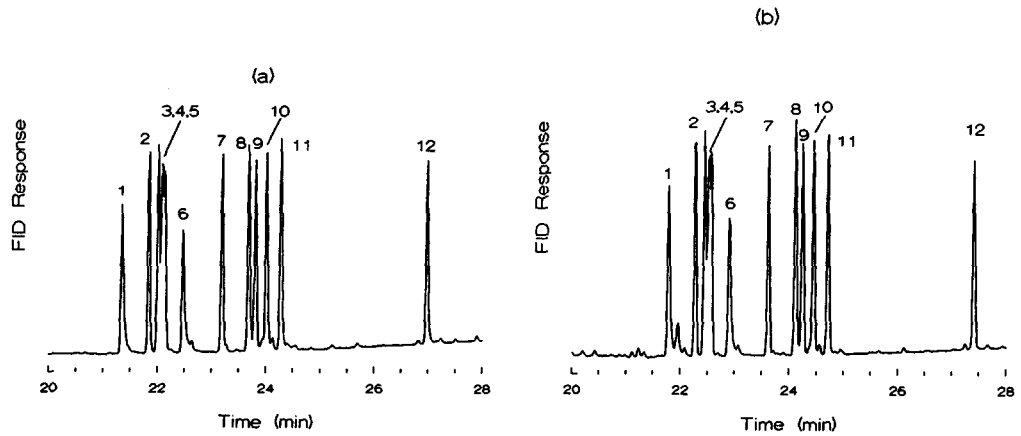

Fig. 3. Part of GC–FID trace obtained after introduction of (a) 75 μl of *s*-triazine standard (7.5 ng per compound) through a Soxhlet-extracted sodium sulphate column and (b) 1 μl of 75-fold concentrated *s*-triazine standard. Same conditions as in Fig. 2. Peak assignment: 1 = atraton; 2 = trietazine; 3 = simazine; 4 = atrazine; 5 = propazine; 6 = secbumeton; 7 = sebutylazine; 8 = prometryn; 9 = simetryn; 10 = terbutryn; 11 = dipropetryn; 12 = cyanazine.

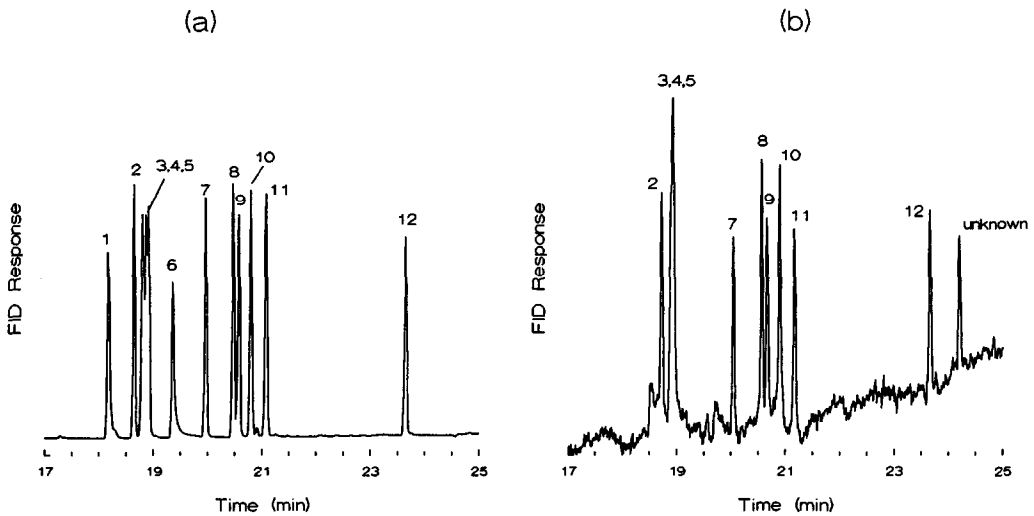

Fig. 4. Part of GC–FID trace obtained after preconcentration of 10 ml of an aqueous standard containing twelve *s*-triazines at a concentration of (a) 0.2 ng/ml or (b) 27 pg/ml. Desorption with ethyl acetate through a cartridge containing 45 mg of sodium sulphate; total volume introduced into the GC system, 50 μl. GC temperature programme: 84°C until complete solvent elution, then increased to 285 °C at 8°C/min. Peak assignment as in Fig. 3.

TABLE II

AVERAGE RECOVERY OF *s*-TRIAZINES AT THREE CONCENTRATION LEVELS (n = 4) USING LC TACE ENRICHMENT–CAPILLARY GC OF 10 ml OF STANDARD WATER SAMPLES WITH IN-LINE DRYING OVER A SORBENT BED

Conditions: loading of sample at 5 ml/min; desorption with 50 μl of ethyl acetate at 25 μl/min; GC–FID as in Fig. 4; in-line drying with sodium sulphate or silica.

Compound	Recovery (%)					
	Sodium sulphate			Silica		
	2 ppb[a]	0.2 ppb[b]	27 ppt[c]	2 ppb[a]	0.2 ppb[b]	27 ppt[c]
Trietazine	103	98	91	109	108	89
Simazine	90	112	95	93	106	98
Atrazine	109	93	91	105	105	94
Propazine	105	93	91	110	93	94
Sebutylazine	103	93	93	111	103	97
Prometryn	105	99	96	103	104	98
Simetryn	109	95	97	105	97	101
Terbutryn	106	91	90	102	99	90
Dipropetryn	104	99	98	102	103	100
Cyanazine	104	95	94	106	107	95

[a] Relative standard deviation (R.S.D.) range, 0.4–3.9%.
[b] R.S.D. range, 0.2–6.2%.
[c] R.S.D. range, 4.3–21.1%.

extremely low level of 30 ppt, ten of the twelve *s*-triazines could still be easily recognized, although peaks 3, 4 and 5 were not resolved at all (Fig. 4b). As expected, at this sub-ppb level, atraton and secbumeton are attacked to such an extent by the active sites in the retention gap that they have completely disappeared from the chromatogram. Actually, when a new DPTMDS-deactivated retention gap was installed these analytes were lost even when using conventional 1-μl on-column injections containing the same amount of analyte (270 pg).

Some relevant data on the analytical performance of the on-line LC trace enrichment–sorbent drying–GC–FID system are given in Table II. For obvious reasons, no data are given for atraton and secbumeton. With both drying agents tested, the FID response was linear over the range 27 ppt–2 ppb with regression coefficients between 0.991 and 0.999 for all ten analytes. Analyte recoveries were quantitative (89–112%) compared with 1-μl on-column injections. The repeatability was good above the 0.2 ppb level (0.2–6.2%) and acceptable at the 27 ppt level (4.3–21%). The limits of detection with 10-ml aqueous standards typically were between 10 and 20 ppt (*cf.*, Fig. 4).

Purging with nitrogen. With the present set-up, using a nitrogen purge instead of drying over a sorbent bed presents no technical problems. The nitrogen supply can be connected to valve V2, and a pressure of 3 bar suffices to obtain a gas flow-rate of 40 ml/min. Because of the large volume of gas used, care should be taken to use extremely pure nitrogen, such as, *e.g.* 5.0 grade, or to install suitable filters in the supply line. We preferred the former option.

The main risk with nitrogen purging is the loss of volatile analytes of interest. Therefore, in this instance the test mixture contained, in addition to two triazines, compounds such as nitrobenzene and *m*-cresol. However, even though some of these compounds elute just after the solvent peak [1], they were quantitatively recovered at the 0.1–0.4 ppb level, as is evident from the data in Table III. For the two *s*-triazines tested, the repeatability (2.4 and 2.6%) was the same as observed with drying over a sorbent bed at the 0.2 ppb spiking level (2.3 and 2.6%; individual data not shown).

TABLE III

AVERAGE RECOVERIES OF SIX ANALYTES USING LC TRACE ENRICHMENT–CAPILLARY GC OF 10 ml OF STANDARD WATER SAMPLES WITH IN-LINE DRYING BY MEANS OF A NITROGEN PURGE

Conditions: loading of sample at 5 ml/min; desorption with 50 μl of ethyl acetate at 25 μl/min; GC–FID as in Fig. 4; 30-min nitrogen purge at 40 ml/min.

Compound	Concentration (ppb)	Recovery (%)	R.S.D. (%)
Nitrobenzene	0.41	93	2.4
m-Cresol	0.25	88	3.3
Phenanthrene	0.12	96	0.5
Tributyl phosphate	0.14	91	3.6
Atrazine	0.10	95	2.6
Cyanazine	0.12	97	2.4

CONCLUSIONS

The main problem in on-line LC trace enrichment–capillary GC of aqueous samples is deterioration of the performance of the retention gap caused by the introduction of traces of water dissolved in the ethyl acetate used for the desorption of the analytes of interest from the LC precolumn into the GC system. This work has shown that this problem can be solved either by the on-line insertion of a small column containing a drying agent between the LC trace enrichment module and the on-column injector or by purging the trace enrichment column with nitrogen. With a series of *s*-triazine herbicides and some rather volatile analytes as test compounds, it was demonstrated that no noticeable losses occur even at the sub-ppb level.

With the present LC trace enrichment–capillary GC system, at least *ca.* 20 analyses can be performed without exchanging the drying cartridge, provided that the drying agent is regenerated after each run by electric heating at 150–180°C. Drying by means of a nitrogen purge is even easier to perform. The *ca.* 30-min purge time cannot be considered a real disadvantage, as drying can be carried out during the GC analysis of the previous sample. In order to reduce the drying time (if necessary), polymer-loaded membrane extraction discs can be used as an alternative to a polymer-packed precolumn [16]. Current research is aimed at using the present system for the fully automated analysis of drinking and surface water samples and at testing more vola-

tile desorption solvents to extend the volatility range of the analytes.

ACKNOWLEDGEMENT

The authors thank DSM, Geleen, Netherlands, for financial support.

REFERENCES

1 J. J. Vreuls, W. J. G. M. Cuppen, G. J. de Jong and U. A. Th. Brinkman, *J. High Resolut. Chromatogr.*, 13 (1990) 157.
2 J. J. Vreuls, V. P. Goudriaan, U. A. Th. Brinkman and G. J. de Jong, *J. High Resolut. Chromatogr.*, 14 (1991) 475.
3 A. Farjam, J. J. Vreuls, W. J. G. M. Cuppen, G. J. de Jong and U. A. Th. Brinkman, *Anal. Chem.*, 63 (1991) 2481.
4 K. Grob, in W. Bertsch, W. G. Jennings and P. Sandra (Editors), *On-line Coupled LC-GC*, Hüthig, Heidelberg, 1991, pp. 200–205.
5 J. Chen and J. S. Fritz, *Anal. Chem.*, 63 (1991) 2016.
6 R. W. Coutant and G. W. Keighley, *Anal. Chem.*, 60 (1988) 2536.
7 W. F. Burns, D. T. Tingey, R. C. Evans and E. H. Bates, *J. Chromatogr.*, 269 (1983) 1.
8 J. M. Vinuesa, J. C. M. Cortes, C. I. Cañas and G. F. Pérez, *J. Chromatogr.*, 472 (1989) 365.
9 J. C. Moltó, Y. Picó, G. Font and J. Mañes, *J. Chromatogr.*, 555 (1991) 137.
10 A. T. Boo and J. Krohn, *J. Chromatogr.*, 301 (1984) 335.
11 E. Noroozian, F. A. Maris, M. W. F. Nielen, R. W. Frei, G. J. de Jong and U. A. Th. Brinkman, *J. High Resolut. Chromatogr. Chromatogr. Commun.*, 10 (1987) 17.
12 F. Munari, A. Trisciani, G. Mapelli, S. Trestianu, K. Grob, Jr. and J. M. Colin, *J. High Resolut. Chromatogr. Chromatogr. Commun.*, 8 (1985) 601.
13 J. Slobodnik, E. R. Brouwer, R. B. Geerdink, W. H. Mulder, H. Lingeman and U. A. Th. Brinkman, *Int. J. Environ. Anal. Chem.*, in press.
14 K. Grob, Jr., *J. Chromatogr.*, 253 (1982) 17.
15 K. Grob, in W. Bertsch, W. G. Jennings and P. Sandra (Editors), *On-line Coupled LC-GC*, Hüthig, Heidelberg, 1991, p. 209-210
16 P. J. M. Kwakman, J. J. Vreuls, R. T. Ghijsen and U. A. Th. Brinkman, *Chromatographia*, 34 (1992) 41.