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Simple and versatile injection system for capillary gas chromatographic columns
Performance evaluation of a system including mass spectrometric and light-pipe Fourier-transform infrared detection

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Abstract

A cryogenic concentrator, a pre-trap, and ancillary systems were developed to facilitate the introduction of large volumes of either gaseous or liquid samples to a capillary GC column. This large-volume injection system, referred to as LVIS, is used in conjunction with the conventional split/splitless injector of a gas chromatograph. The performance of the split/splitless injector is essentially unchanged by the installation of the cryogenic concentrator; thus, the gas chromatograph can be operated as usual. Reproducibility, accuracy, and inertness were demonstrated while performing injections of a hydrocarbon mixture (n-C_7–C_{22}) and the Grob-programmed test mixture. Liquid samples, up to 100 μl, were conveniently handled by the system. Applicability to gas-phase analyses was demonstrated by sampling perfume components in the headspace of a granular detergent and by sampling pyrolysis products of Kraton 1107. When the LVIS was used with a gas chromatograph equipped with mass-selective (MSD) and light-pipe Fourier-transform infrared (FT-IR) [IRD] spectrometers, it was possible to achieve identification limits by IRD approaching 1 ppb v/v when analyzing one liter of headspace, and ca. 100 ppb when analyzing 100 μl of a liquid sample. Identification limits with the MSD were lower.

Keywords: Injection methods; Large-volume injection

1. Introduction

Commercially available GC instrumentation, equipped with a split/splitless injector and multiple detectors, provides unparalleled capabilities for the identification and quantification of minute amounts of volatile organic compounds. However, the power of the instrumentation would be enhanced by the ability to introduce larger liquid samples to the column, e.g., >1–2 μl. This is particularly true when using detectors capable of providing structural information, since some, e.g., light-pipe FT-IR, may require 10–20 ng to produce an interpretable and/or searchable spectrum. In addition, the utility of the instrumentation would be increased if it could handle matrices other than liquids.

Because most of the samples analyzed by GC today are dissolved in a liquid phase, a great deal of

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effort has been devoted to the introduction of large volumes of liquid solutions to capillary columns. Fundamentally, the introduction of a large volume of solution requires elimination of most of the solvent prior to starting the chromatography. Two solvent-elimination approaches have been developed: one uses a column, i.e., a retention gap, as a means of forming a thin film of liquid to control the evaporation, while the other approach uses a device external to the column, often packed with inert material, to accomplish the same task.

The use of a retention gap [1,2] allows the introduction of ca. 100 μl of liquid solution and offers a practical approach to interfacing liquid and gas chromatography [3–5]. However, the use of a retention gap is limited to 'clean' samples since even moderate amounts of non-volatile material in solution would severely compromise subsequent analyses. If contamination occurs, the only alternative is to replace the retention gap.

Higher versatility and ruggedness compared to a retention gap is achieved by the use of devices external to the column, e.g., programmed-temperature vaporizers (PTV) [6,7]. Packing a PTV with a suitable sorbent would further increase the ability to retain analytes while minimizing loses due to packing activity [8]. With suitable packings, a PTV could be used to perform headspace analyses [9], and its capabilities could be further enhanced by devices offering cryogenic cooling capabilities [10]. Importantly, if contamination occurs, replacement of the liner or packing is easily performed with minimal down-time or inconvenience.

In spite of these developments there remains a need for an injection system capable of handling large sample volumes and different matrices. Although there is a high degree of commercial activity aimed at providing sample-introduction modules designed to perform a specific function, e.g., purge-and-trap analyses, those modules lack the versatility needed to handle a variety of matrices. For example, a purge-and-trap system would be optimized to facilitate the transfer of volatile organics from a liquid phase to the gas phase; therefore, transferring high boilers, introducing a large volume of a liquid sample, or performing pyrolysis experiments with such a system would not be possible or would require extensive modification of the equipment. The most notable exceptions are the modular systems described as the 'short path thermal desorption system' [11,12] and the 'thermal desorption cold trap system' [13].

The 'short path thermal desorption system', the 'thermal desorption cold trap system', as well as other systems [14–16], use cryogenic cooling to concentrate volatile materials at the head of a fused-silica capillary column while introducing samples, previously collected in a suitable medium, by thermal desorption. Particularly critical to the successful operation of those systems are the collection and volatilization of analytes, and the quantitative transfer of those analytes to the head of the column for reconcentration. Some systems allow concentration of analytes selectively and independently of the column; thus, the column and detectors can be effectively isolated from the sampling system, thereby preventing column contamination and unwanted changes in detector output [16]. When performed off-line, with a demountable sampling module, e.g., a pre-trap [15,16], solvent elimination, trapping, volatilization, and transfer to the head of the column can be performed optimally. For example, solvent elimination from ca. 1-ml samples allowed ppt-analyses, with an FID, while quantitatively recovering compounds as light as n-C_{10} [16]. In addition, the pre-trap could be used to sample headspace, or collect thermal desorption or pyrolysis products, or conveniently perform mass-balance studies when using radiolabeled materials [15].

A system, i.e., LVIS or large-volume injection system, consisting of a cryogenic concentrator, a pre-trap and heater-cartridge, and ancillary equipment, was developed to be used in conjunction with the conventional inlet of a gas chromatograph. It was designed to approach the performance of an inlet system we developed to introduce large volumes of gaseous, liquid, or solid samples to capillary columns [16]. Importantly, the LVIS was designed to be easily constructed and installed with minimal changes to the existing equipment. In this communication we report on the construction of the LVIS, and on the capabilities of a chromatographic system that includes the LVIS, FID, and mass- and FT-IR spectrometers, to identify and quantify volatile organic

compounds present in gaseous, liquid and solid samples.

2. Experimental

2.1. Standards and solvents

Hydrocarbon standards (n-C_7–C_{22}) were obtained from Alltech Associates (Deerfield, IL, USA), and a stock solution containing ca. 540 ng of each compound per μl was prepared in pentane. A Grob-programmed test mixture [17], containing ca. 280 to 530 ng per compound per μl, was obtained from Supelco (Bellefonte, PA, USA). It was used after an extended storage period. Kraton D1107P was obtained from Shell (Oak Brook, IL, USA) and stock solutions were prepared in methylene chloride. Burdick & Jackson (B&J GC^2) capillary GC/GC–MS-grade solvents were obtained from Baxter Diagnostics (McGaw Park, IL, USA). Dilute solutions for large-volume injections were made in pentane.

2.2. Equipment

Measurements were made with a Hewlett-Packard (HP) Model 5890 Series II GC, equipped with flame ionization (FID), HP 5971 mass-selective (MSD), and HP 5965B infrared (IRD) detectors. MSD and IRD signals were processed by the Chemstation software, and the FID output was processed by a Perkin-Elmer Nelson system (Turbochrom-3 software). A piece of deactivated fused-silica capillary tubing (1 m×0.32 mm I.D., Restek, Bellefonte, PA, USA) was used as a transfer line between the inlet and the column. A methyl silicone (RTX-1, Restek), 60 m×0.32 mm I.D., 1 μm film thickness, served as the analytical column. A Merlin microseal septum (Merlin, Half Moon Bay, CA, USA) was used instead of the conventional septum of the split/splitless injector. An inverted-cup liner was used for all injections. A Mitsubishi FX0-14MR-ES/FX-10P system controller (Cole-Parmer, Niles, IL, USA) was used for the automation of the operations required by the LVIS. Pyrolysis experiments were performed with a CDS Ribbon Pyroprobe (CDS Analytical, Oxford, PA, USA).

2.3. Construction of the large-volume injection system (LVIS)

The LVIS consists of two modules and ancillary controllers. The two modules are the cryogenic concentrator (D) and the pre-trap and heater cartridge (E), shown in Fig. 1. The cryogenic concentrator is built around a specially designed tee made with glass-lined tubing (Scientific Glass Engineering (SGE), Austin, TX, USA), shown in Fig. 2A. The special tee is modified by attaching a heater, i.e., by wrapping a coil of glass-coated Nichrome-60 wire, 4 ft (6.8Ω resistance/ft; Pelican Wire, Naples, FL, USA), and an iron–constantan thermocouple (OMEGA Engineering, Stamford, CT, USA). The parallel arms of the modified tee were connected, via 1/16″ O.D., 0.03″ I.D. (one inch is 2.54 cm) ss-tubing, to solenoid-actuated valves (Clippard Instrument Laboratory, Cincinnati, OH, USA) located outside the GC oven. Two additional solenoid-actuated valves were installed on the split vent and

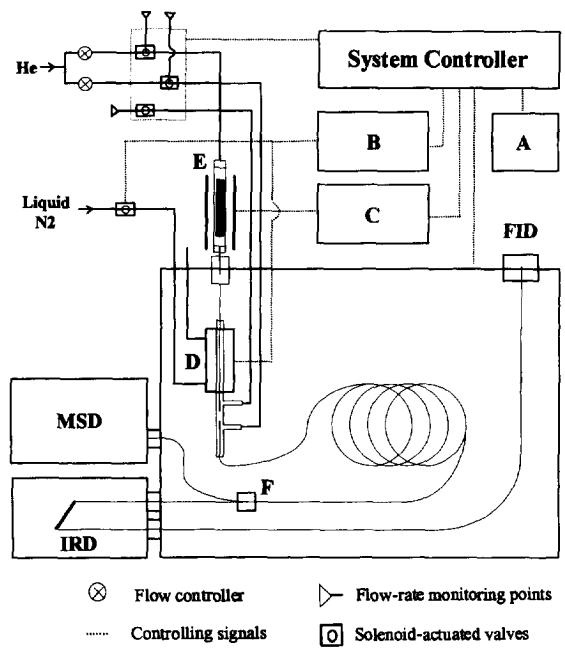

Fig. 1. Schematic diagram of the large-volume injection system. A=Sequence programmer; B=cold-trap temperature controller; C=cartridge temperature controller; D=cryogenic concentrator; E=pre-trap and heater cartridge; F=effluent splitter.

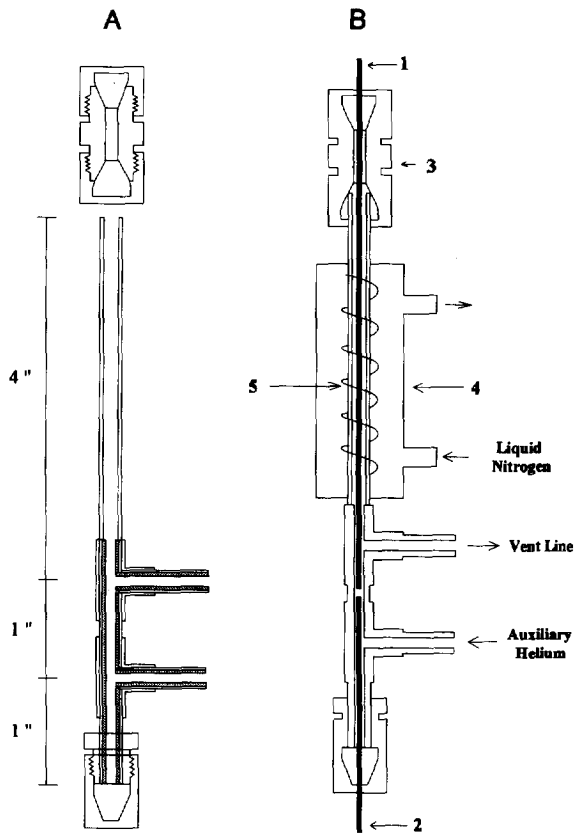

Fig. 2. Schematic of tee and finished cryogenic concentrator. (A) Specially constructed, glass-lined tee from SGE. (B) Finished cryogenic concentrator: 1=transfer line from inlet; 2=analytical column; 3=1/16″ Swagelok ss-union; 4=liquid-nitrogen jacket; 5=heater.

septum purge outlets of the chromatograph. Together, the valves are used to control the sample flow from the pre-trap, to the cryogenic concentrator, to the GC column. The modified tee is housed in a jacket made from two brass male (Swagelok 1/4″ tube to 1/4″ pipe) fittings soldered back-to-back, and drilled to accept 1/4″ copper lines for liquid nitrogen introduction and removal, as shown schematically in Fig. 2B. The finished cryogenic concentrator was mounted in the GC oven, and was connected to the GC inlet and analytical column as shown in Fig. 1. One end of the transfer line was connected to the inlet base and the other was connected to the cryogenic concentrator. The end of the transfer line and the head of the column were positioned at the mid point of the segment joining the two short parallel arms of the special tee, their distance adjusted to ca. 3 mm, and the transfer line and column sealed in place with graphite-vespel ferrules.

A pre-trap was used to collect either gaseous or liquid samples and functions as a demountable, temperature-programmed sorption–desorption module. Details of construction of the pre-trap and heater cartridge were described in a previous communication [15]. Briefly, the pre-trap was made from a 1-ml syringe barrel with a threaded glass tip (1/4″-28, Spectrum, Houston, TX, USA) packed with deactivated glass wool (ca. 30–50 mg) and Tenax TA (ca. 120–150 mg). A special 23 ga. (0.025″ O.D.) staked flange needle was specially ordered from Spectrum to fit the Merlin microseal. The special needle and a PTFE seal were attached to the syringe barrel by means of a machined vespel nut [15].

A general-purpose temperature controller (OMEGA 6100) and a microcomputer thermometer (OMEGA DP701) were used to perform the cooling and heating operations of the cryogenic concentrator. All operations, starting with the transfer of sample from the pre-trap to the GC system, and ending with the initiation of data collection, were controlled by the Mitsubishi system controller.

2.4. Conditions and procedures

2.4.1. Gas chromatography

Inlet temperature, 250°C; oven temperature, 50°C for 2 min, then programmed to 280°C at 6°C/min, followed by an isothermal period of 5 min. Nominal column flow-rate was set at 3.22 ml/min, and the column was operated at constant flow. The column effluent was split ca. 1:10 between the MSD and IRD using an SGE glass-lined splitter.

2.4.2. Mass-selective detection

Transfer line 280°C, giving an ion source temperature of ca. 185°C, electron energy 70 eV. Mass range m/z 20–300 (2.5 scan/s) for the first 20 min, and m/z 30–350 (2.2 scans/s) after 20 min.

2.4.3. Infra-red detection–flame ionization detection

IRD transfer lines 250°C, light-pipe cell 250°C, source power 21.0 W. IR spectra, from 750 to 4000 cm^{-1}, were obtained at a resolution of 8 cm^{-1} and

were acquired at 1.5 scans/s. The effluent from the IRD was introduced to the FID via a transfer line. The FID temperature was set at 280°C.

2.4.4. Solvent removal from a liquid sample

To perform 50-μl injections, the sample was carefully aspirated into the glass-wool portion of the pre-trap to avoid wetting the Tenax packing. When using pentane, excess solvent was removed by flowing ca. 300 ml of helium (at 20 ml/min) through the pre-trap needle. To perform 100-μl injections the sample was introduced in two portions. After introducing the first 50-μl portion, excess solvent was removed with 100 ml of helium. After introducing the second portion, excess solvent was removed with 300 ml of helium.

2.4.5. Headspace sampling

A headspace sample of the granular detergent was obtained using a 200-ml glass container. The container had three necks: one was used for sample introduction and the remaining two served as helium-purge inlet and outlet. The outlet terminates in a fractional tube (1/16″) to fractional tube stub (1/8″) Swagelok fitting, attached to the glass with a high-temperature, machineable epoxy. The use of the Swagelok fitting allows a gas-tight connection between the container outlet and the pre-trap needle. A 5-g sample was weighed into the container and the air in the container was flushed with helium. The sample was sealed and stirred overnight to equilibrate. After connecting the pre-trap to the glass container, a helium flow (20 ml/min) was used to transfer the headspace sample. The volume of headspace sample was determined by time and the helium flow-rate.

2.4.6. Pyrolysis gas chromatography

The pyroprobe was inserted in a glass housing designed to minimize dead volume and facilitate the transfer of pyrolysis products to the pre-trap via a Swagelok connector. The housing was heated to 200°C with a cartridge similar in design to that used for the pre-trap. Kraton solutions were deposited in the center of the ribbon pyroprobe using a 10-μl syringe. After sealing the pyroprobe to the housing, the solvent was fully evaporated and removed by a helium stream flowing through the housing at 20 ml/min. Upon removal, the pre-trap was attached and pyrolysis performed at 700°C under a helium atmosphere (1000°C/s, and a 20-s heating period). A 100-ml volume of helium (20 ml/min×5 min) was used to transfer the pyrolysis products to the pre-trap.

2.4.7. Desorption and sample introduction to column

After transferring a sample to a pre-trap, the pre-trap was placed in a heating cartridge and the needle inserted in the GC injection port. The column headpressure was set to zero, the inlet set to splitless, and the solenoid valves actuated to close the purge and split vent valves and allow helium flow through the cryogenic concentrator. After the cryoconcentrator reaches an internal temperature of −135°C, a helium line is attached to the back of the pre-trap, and the pre-trap is thermally desorbed for 8 min at 180°C, while flowing helium at 15 ml/min through it. Non-condensable materials are vented and prevented to enter the column by the vent and auxiliary helium lines built into the concentrator (Fig. 1 and Fig. 2). After the transfer, the solenoid valves were switched, the system pressurized, and the cryogenic concentrator heated to 200°C at 15°C/s to transfer compounds to the analytical column. The start of the heating was synchronized with the signal used to start the chromatography.

3. Results and discussion

The ability to identify compounds in complex GC chromatograms is enhanced by the efficient introduction of large samples to a capillary column, and by the interface of the capillary column to spectrometers capable of producing structural information. In this regard, the interface of 0.32 mm I.D. columns to a spectrometer, e.g., MS or IR, is particularly suitable and poses little problem with present-day instrumentation. However, identification would be facilitated by monitoring the column effluent with multiple, orthogonal detectors as a means to obtain additional structural or confirmatory evidence needed to substantiate the assignment of identity. Simultaneous monitoring with multiple spectrometers and/or detectors (e.g., a GC–MS–FT-IR), as opposed to having dedicated systems inter-

faced to a single spectrometer or detector (e.g., a GC–MS and a GC–FT-IR), is particularly advantageous when attempting to identify small components of a very complicated sample. This is true because nominally identical columns, installed in different dedicated systems, frequently show slight differences in selectivity and/or activity which could produce slight peak shifts, peak reversals, or even complete disappearance of small peaks, thereby introducing uncertainty in the identification. The uncertainty may be reduced by installing the same column in the different systems; however, inlet and interface activity still may be factors. Also, re-installing columns requires down-time and introduces the possibility of contaminating the system.

While commercial equipment allows the interface of capillary GC columns to MS and IR spectrometers, the introduction of sample is limited by the use of the split/splitless injector commonly used with that equipment. Therefore, the LVIS was designed to allow the introduction of large sample volumes, either gaseous or liquid, to a capillary column while using the conventional injector as an entry port. Importantly, either sample type would be handled identically by the LVIS, thereby minimizing the need to change the instrumentation. Solid samples are handled by thermal desorption or pyrolysis, as needed. The ability to inject compounds encompassing a wide range of functionality and volatility was evaluated using the Grob-programmed test mixture and a hydrocarbon mixture containing n-C_7 to n-C_{22}. The choice of test mixtures was dictated by two factors: the availability of a well-defined test mixture for column activity, i.e., the Grob mix, and the need to identify and quantify compounds as small as C_7 but not heavier than C_{22} in headspace.

3.1. Benchmark performance

As a design criterion, we wanted to preserve the performance of the chromatographic system so that the installation of the cryogenic concentrator would be transparent to the user when performing conventional split/splitless injections. The near-identical FID chromatograms, generated before (Fig. 3A) and after installation of the concentrator (Fig. 3B), illustrate the efficiency and inertness of the system. The mass introduced by the injection of 1 μl of a Grob mix, split 1:6, or ca. 45–85 ng per compound, is sufficient to obtain excellent mass and IR spectra of the compounds in the mix.

Results in Table 1 include relative compositions obtained by performing split or splitless injections, with (B) or without the cryogenic concentrator installed (A). Low recoveries of n-C_7, n-C_8 and 2,3-butanediol were observed in some cases. For splitless injection, the low results may be due to integration errors: the high initial column temperature prevents effective reconcentration; thus, early-eluting peaks are broadened and difficult to integrate. In general, slight discrimination was observed for both split and splitless injection, e.g., areas of n-$C_7 <$ 95%, n-$C_{22} >$93%. The slight discrimination may be a result of the relatively large volume of solvent injected when using a solvent flush, e.g., 2 μl total volume, as reported for backpressure-regulated systems by Hinshaw [18]. The poorer reproducibility observed for the split injection of high-molecular-mass materials ($>n$-C_{18}) with the cryogenic concentrator installed suggests poor transfer during the short reconcentration time involved in split injection. Because the effect is not observed with splitless injection, we postulated it would have no consequence when performing gas-phase analyses or when introducing a large volume of liquid with the LVIS.

3.2. Large-volume injection of liquids

Large volumes, e.g., 50–100 μl, of liquid samples were introduced to the capillary column by means of a pre-trap. The pre-trap was used to vent most of the solvent and prevent the introduction of non-volatile materials to the capillary column. In addition, the use of a pre-trap offers advantages regarding ease of packing, freedom from cross-contamination, and the ability to smell trapped materials compared to dedicated systems, e.g., purge and trap, programmed-temperature vaporizer.

The ability to deliver large volumes of solutions to a capillary column, and the inertness of the combined pre-trap/cryogenic concentrator, i.e., LVIS system, are illustrated by the chromatograms shown in Fig. 4, obtained while injecting equal masses of a Grob mix contained in 1- and 100-μl volumes. While virtually identical peak shapes were obtained for most compounds, there are some differences in the

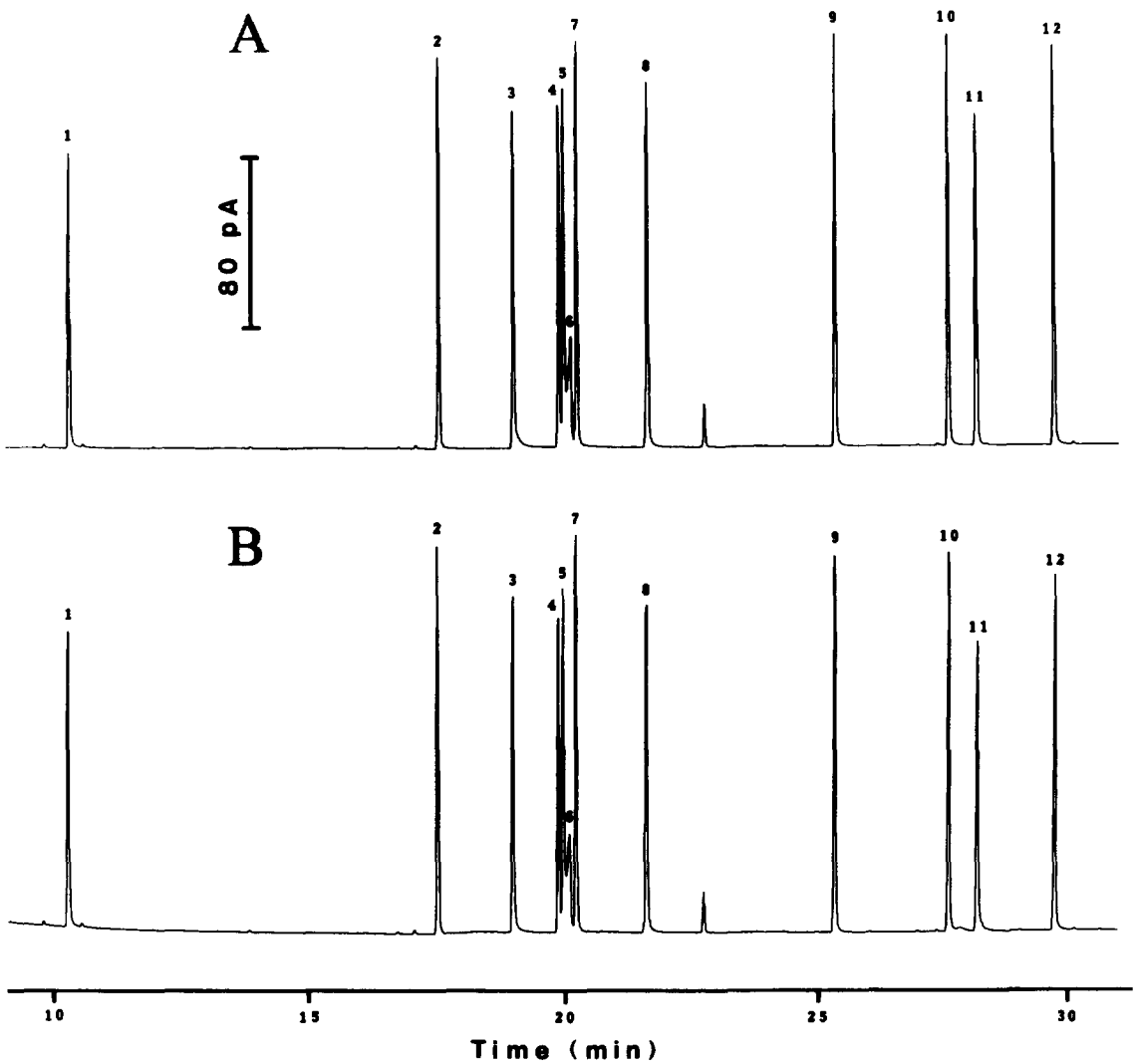

Fig. 3. FID chromatograms of a Grob mix obtained before equipment modification (A) and after installation of the cryogenic concentrator (B). Sample split 1:6. Peaks: 1=2,3-butanediol; 2=*n*-decane; 3=1-octanol; 4=nonanal; 5=2,6-dimethylphenol; 6=2-ethylhexanoic acid; 7=*n*-undecane; 8=2,6-dimethylaniline; 9=C_{10} methyl ester; 10=C_{11} methyl ester; 11=dicyclohexylamine; 12=C_{12} methyl ester. For mass injected see Table 1, range ca. 45–85 ng.

chromatograms. For example, the more volatile materials (2,3-butanediol and *n*-decane, peaks 1 and 2, respectively) show improved peak shapes resulting from better reconcentration with the LVIS (Fig. 4B) injection compared to splitless injection (Fig. 4A). However, peaks corresponding to nonanal (peak 4, Fig. 4B) and 2,6-dimethylaniline (peak 8, Fig. 4B) were reduced in height.

These results are best understood by looking at the quantitative results shown in Table 2. The data show that the LVIS produces comparable results to conventional splitless injections when analyzing 50- and 100-μl volumes of pentane solutions of hydrocarbons. For example, quantitative (>90%) and reproducible recoveries (<5% R.S.D.) were observed for compounds ranging in volatility from C_9 to C_{22} when injecting a sample containing ca. 500 ng per compound. The exceptions are lower recoveries and

Table 1
FID areas obtained by conventional syringe injection (solvent flush), with unmodified GC (A) and cryogenic concentrator installed (B)

Hydrocarbon test mixture	Nominal (%)	Splitless injection (mass: 100%=ca. 540 ng)				Split 1:6 injection (mass: 100%=ca. 90 ng)			
		A (n=4)		B (n=4)		A (n=8)		B (n=13)	
		Ave. (%)	R.S.D.	Ave. (%)	R.S.D.	Ave. (%)	R.S.D.	Ave. (%)	R.S.D.
Heptane C_7	95.5	79.2	4.1	74.9	16.8	94.2	1.6	93.9	4.5
Octane C_8	95.5	87.7	2.2	90.1	5.0	97.2	1.3	98.2	2.0
Nonane C_9	95.5	94.3	1.1	94.7	3.2	99.0	1.1	100.0	1.9
Decane C_{10}	95.5	95.9	0.7	96.4	1.1	98.9	0.7	100.6	1.3
Undecane C_{11}	100	97.7	0.4	98.0	0.7	98.9	0.4	100.5	1.1
Dodecane C_{12}	100	100.0	0.0	100.0	0.0	100.0	0.0	100.0	0.0
Tridecane C_{13}	100	98.6	0.8	99.6	0.6	98.1	0.6	97.0	1.9
Tetradecane C_{14}	100	101.7	1.4	102.4	0.8	100.8	1.0	99.5	2.2
Pentadecane C_{15}	94.6	95.5	2.0	95.7	1.7	93.8	1.5	93.3	3.4
Hexadecane C_{16}	93.1	101.3	2.1	101.0	0.6	99.9	1.5	98.8	4.7
Heptadecane C_{17}	94.4	101.7	2.3	100.8	1.1	101.6	1.3	99.6	5.9
Octadecane C_{18}	93.1	105.0	1.9	103.4	1.5	106.6	2.7	105.8	7.5
Nonadecane C_{19}	93.3	101.8	2.3	100.0	2.0	104.4	3.5	104.4	9.2
Eicosane C_{20}	93.1	105.7	2.9	104.1	2.1	109.1	3.9	111.0	11.6
Heneicosane C_{21}	93.3	100.6	3.1	99.5	2.3	104.4	4.0	107.9	13.5
Docosane C_{22}	93.1	101.2	3.3	100.7	2.3	105.5	4.6	114.1	18.1
Grob mix	Mass (ng/μl)	Splitless injection (mass: 100%=ca. 280–530 ng)				Split 1:6 injection[a] (mass: 100%=ca. 45–85 ng)			
		A (n=4)		B (n=4)		A (n=4)		B (n=4)	
		Ave. (%)	R.S.D.	Ave. (%)	R.S.D.	Ave. (%)	R.S.D.	Ave. (%)	R.S.D.
2,3-Butanediol	530	65.3	1.1	63.0	2.0	69.9	1.4	74.9	2.0
Decane	280	89.2	1.4	89.1	1.6	88.4	1.4	93.8	1.9
1-Octanol	360	82.4	0.3	85.3	0.7	84.5	0.8	86.4	1.8
Nonanal	400	75.9	0.8	74.7	1.0	74.9	1.1	73.8	3.5
2,6-Dimethylphenol	320	87.0	0.9	84.2	0.2	90.3	0.6	92.7	2.4
2-Ethylhexanoic acid +undecane	380+290	138.5	0.5	142.5	1.3	144.6	1.3	147.1	2.0
2,6-Dimethylaniline	320	81.8	0.3	79.0	2.3	90.0	0.5	85.6	3.6
C_{10} acid methyl ester	420	98.1	0.6	99.7	0.5	98.8	0.3	98.2	0.8
C_{11} acid methyl ester	420	100.0	0.0	100.0	0.0	100.0	0.0	100.0	0.0
Dicyclohexylamine	310	82.5	1.3	80.3	1.5	89.7	1.5	85.2	2.1
C_{12} acid methyl ester	410	99.8	0.2	96.5	0.3	99.4	0.6	96.9	0.6

[a] Chromatograms shown in Fig. 3.

higher R.S.D. with the LVIS for n-C_7 and n-C_8 (ca. 50%, R.S.D. 10–15% and ca. 75%, R.S.D. 5–7%, respectively). The lower recoveries are a consequence of the limited capacity of a pre-trap packed with Tenax TA to retain the more volatile compounds, and the need to remove excess solvent with a helium flush. These results are in agreement with results reported in a previous communication [16].

Because the injection of hydrocarbons did not reveal unexpected problems, we conclude that low recoveries observed with nonanal and dimethylaniline must be due to sample decomposition or interactions with surfaces during injection. Note that desorption of components from the pre-trap, at the chosen flow-rate (15 ml/min), requires 8 min at 180°C. This temperature is significantly lower than

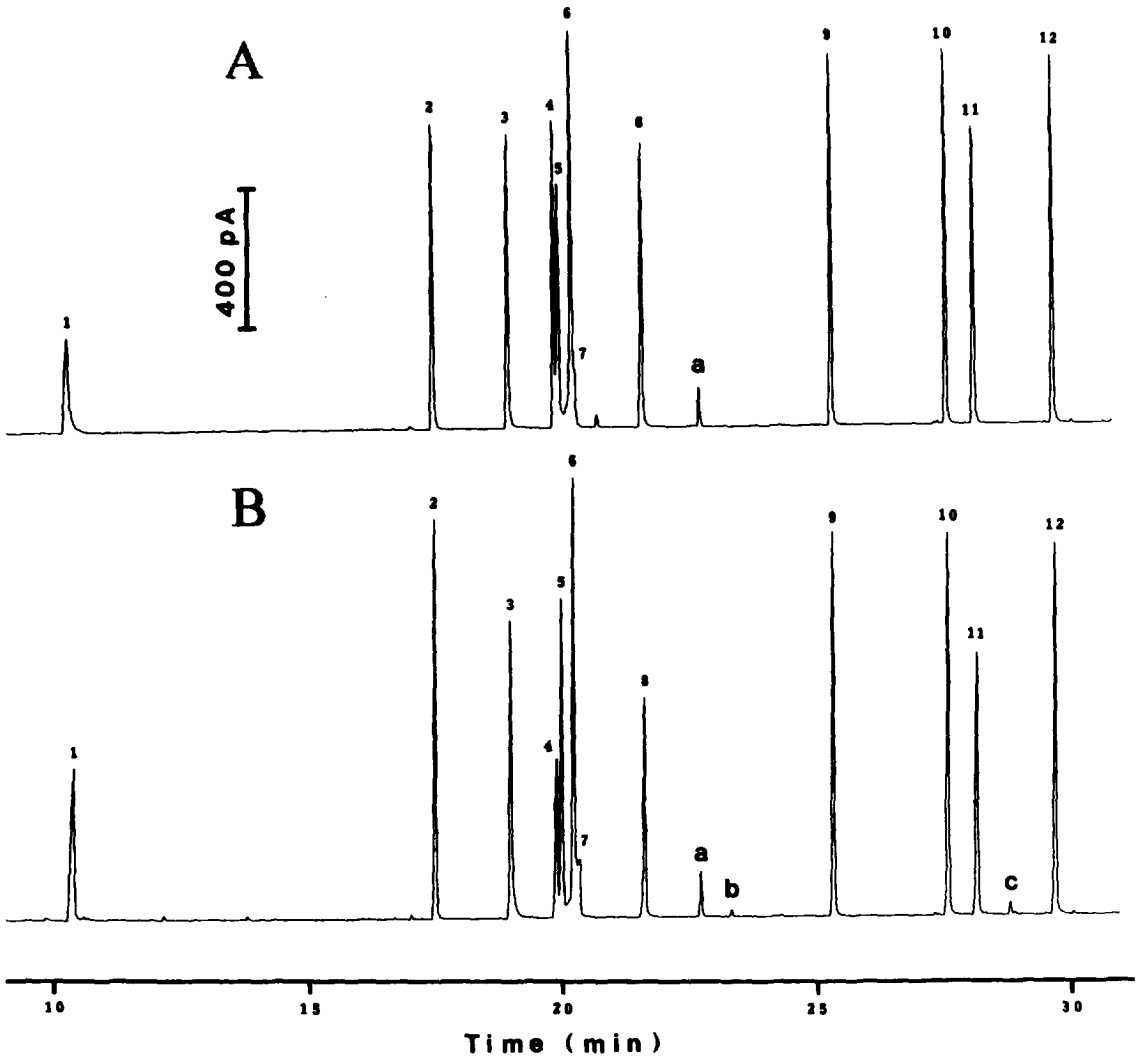

Fig. 4. FID chromatograms of a conventional 1-μl splitless injection without cryogenic reconcentration (A) and a 100-μl injection with LVIS (B). Peaks: 1=2,3-butanediol; 2=*n*-decane; 3=1-octanol; 4=nonanal; 5=2,6-dimethylphenol; 6=*n*-undecane; 7=2-ethylhexanoic acid; 8=2,6-dimethylaniline; 9=C_{10} methyl ester; 10=C_{11} methyl ester; 11=dicyclohexylamine; 12=C_{12} methyl ester. For masses see Table 2, range ca. 280–530 ng.

that typically used with conventional inlets and should contribute to minimizing sample degradation or reactions. However, in spite of the lower temperature, at the high mass (280–530 ng) we observed lower recoveries for nonanal and dimethylaniline when the injection volume was 100 μl (44.8% vs. 74.7% and 57.8% vs. 79%, respectively, for 100 μl vs. 1 μl, as shown in Fig. 4 and Table 2). This observation suggests decomposition and/or reaction involving the pre-trap and/or the cryogenic concentrator. However, the lower recoveries were not observed when injecting the high mass standard in a lower volume (50 μl) or when injecting a lower mass (28–53 ng) in the larger volume.

In an attempt to ascertain the reason(s) for the losses, we looked for possible reaction products. The chromatogram obtained with the LVIS, Fig. 4B, shows the presence of two new peaks, labeled 'b' and 'c', in addition to peak 'a', previously observed in Fig. 3 and also present in Fig. 4A. Peak 'a' was

Table 2
FID areas obtained by conventional splitless injection (solvent flush), and by the use of the LVIS (cryogenic concentrator installed for all runs)

Hydrocarbons test mixture (mass: 100%=ca. 540 ng)	Nominal (%)	Splitless injection		1 μl w/Pre-trap		50 μl w/Pre-trap		100 μl w/Pre-trap	
		Ave. (%) (n=4)	R.S.D.	Ave. (%) (n=3)	R.S.D.	Ave. (%) (n=3)	R.S.D.	Ave. (%) (n=3)	R.S.D.
Heptane C_7	95.5	74.9	16.8	55.1	14.5	48.9	10.9	54.2	0.8
Octane C_8	95.5	90.1	5.0	77.8	6.8	73.3	6.5	87.9	5.4
Nonane C_9	95.5	94.7	3.2	93.1	3.4	91.2	2.6	97.3	3.9
Decane C_{10}	95.5	96.4	1.1	99.8	1.3	98.6	2.2	101.1	3.2
Undecane C_{11}	100	98.0	0.7	101.0	0.2	100.5	1.7	101.8	1.6
Dodecane C_{12}	100	100.0	0.0	100.0	0.0	100.0	0.0	100.0	0.0
Tridecane C_{13}	100	99.6	0.6	93.3	0.5	94.8	2.3	94.9	1.0
Tetradecane C_{14}	100	102.4	0.8	96.8	1.1	98.5	2.5	99.3	0.6
Pentadecane C_{15}	94.6	95.7	1.7	90.9	1.6	92.4	2.5	93.7	0.7
Hexadecane C_{16}	93.1	101.0	0.6	94.4	2.2	97.3	3.4	95.6	0.6
Heptadecane C_{17}	94.4	100.8	1.1	93.1	2.4	96.7	3.0	94.5	0.5
Octadecane C_{18}	93.1	103.4	1.5	96.1	2.3	99.3	1.8	97.2	0.9
Nonadecane C_{19}	93.3	100.0	2.0	94.8	2.0	96.2	0.9	94.7	1.1
Eicosane C_{20}	93.1	104.1	2.1	100.9	2.5	100.4	2.8	100.1	1.3
Heneicosane C_{21}	93.3	99.5	2.3	98.5	2.9	97.0	4.2	96.0	1.3
Docosane C_{22}	93.1	100.7	2.3	101.5	3.2	99.8	5.8	97.6	1.2

Grob mix		Splitless injection[a] (mass: 100%=ca. 280–530 ng)		w/Pre-trap 280–530 ng in 50 μl		280–530 ng in 100 μl[a]		28–53 ng in 100 μl	
Contents	Mass (ng/μl)	Ave. (%) (n=4)	R.S.D.	Ave. (%) (n=4)	R.S.D.	Ave. (%) (n=3)	R.S.D.	Ave. (%) (n=4)	R.S.D.
2,3-Butanediol	530	63.0	2.0	66.4	2.3	66.9	0.6	31.4	9.8
Decane	280	89.1	1.6	93.2	1.7	93.2	1.7	91.8	6.6
1-Octanol	360	85.3	0.7	89.9	0.5	89.7	0.5	83.0	5.3
Nonanal	400	74.7	1.0	65.9	3.5	44.8	6.7	83.6	3.0
2,6-Dimethylphenol	320	84.2	0.2	89.1	0.6	88.3	0.3	100.6	4.3
2-Ethylhexanoic acid +undecane	380+290	142.5	1.3	150.8	1.0	149.6	0.8	102.6	4.0
2,6-Dimethylaniline	320	79.0	2.3	77.1	3.7	57.8	3.8	85.0	4.4
C_{10} acid methyl ester	420	99.7	0.5	100.2	0.3	99.3	0.5	99.7	2.5
C_{11} acid methyl ester	420	100.0	0.0	100.0	0.0	100.0	0.0	100.0	0.0
Dicyclohexylamine	310	80.3	1.5	80.3	2.1	75.1	4.0	82.0	2.3
C_{12} acid methyl ester	410	96.5	0.3	98.0	0.3	99.3	0.3	113.9	5.3

[a] Chromatograms shown in Fig. 4.

tentatively identified by MSD and IRD as a chloromethyl ester [m/z 164(12), 166(4), 136(100), 138(31), 127(39), 121(22), 123(9), 100(28), 70(69), 57(59); IR bands: 2969, 2943, 2878, 1772, 1457, 1260, 1193, 1108, 1031 cm^{-1}] and is present as a contaminant in the Grob mixture. Peaks 'b' and 'c' were tentatively identified as cyclohexyl isothiocyanate [m/z 141(95), 83(65), 67(30), 55(100), IR bands 2946, 2870, 2047, 1455, 1361, 1319 cm^{-1}] and a compound similar to butylated hydroxy toluene (BHT) [Kovats index 1466 vs. 1509 for BHT, m/z 220(25), 205(100), 180(18), 165(25), 57(29)]. With the possible exception of the chloromethyl ester, those compounds are contaminants external to the solution and do not result from reaction of components in the Grob mix. No evidence was found for a Schiff base in this chromatogram. The observed m/z 164 of the ester corresponds to a molecular formula $C_7H_{13}O_2Cl$, indicative of a chloromethyl ester of hexanoic acid. However, the Kovats index

(ca. 1200) suggests that the compound has a higher molecular mass than M_r 164. Two key fragments, m/z 164 and 136, can be rationalized by the McLafferty rearrangement of the chloromethyl ester of 2-ethylhexanoic acid, i.e., M_r 192, loss of 28 and 56 by cleavage one bond removed from the carbonyl carbon. Therefore, we conclude that the ester is produced in solution by a reaction involving the 2-ethylhexanoic acid and a reactive species resulting from methylene chloride decomposition.

As mentioned above, a diluted sample of the Grob mix, containing ca. 28–53 ng per compound, was also analyzed using a 100-μl injection. At the low mass, we recovered only ca. 50% of the 2,3-butanediol compared to the higher mass. This recovery is likely the result of glass-wool activity in the pre-trap and is not surprising since the difficulty of properly deactivating glass wool has been reported [11]. Even with 50% recovery, there is still sufficient mass to obtain interpretable mass and IR spectra, resulting in an identification limit of lower than 0.2 ppm in the injected solution, e.g., 10–20 ng reaching the IRD out of 53 ng in the 100-μl sample. The other quantitative difference in Table 2 is due to the change in retention time of 2-ethylhexanoic acid. As expected, at the lower mass the ethylhexanoic peak shifted towards shorter retention, and the relative abundances in the table reflect the different integration caused by the shift.

3.3. Analysis of headspace

The inertness of the LVIS and the ability to directly sample the headspace with the pre-trap needle make this system useful for both identification and quantification. Importantly, we found that components of perfumes used in granular detergents provide an excellent sample for calibration and testing of headspace analyzers. The detergent has sufficient mass for repetitive analyses and the relative composition does not change when sampling as little as 100 ml or as much as 800 ml of headspace. Over this range, mass recovered increased linearly with the headspace volume sampled. In addition, the odor of materials released from the pre-trap resembled the sample odor, suggesting that the analysis would reflect the composition of the odor-significant compounds in the sample.

A chromatogram of 300 ml of headspace over a 5-g sample of a granular detergent is shown in Fig. 5. The MSD and IRD signals were obtained by splitting the output of the column ca. 1:10 between the MS and IR spectrometers to better match the sensitivities and retention times of peaks detected by the two instruments. The correspondence of retention times (ca. 0.01–0.02 min), and preservation of band shapes allow the unequivocal identification of small peaks or even partially resolved compounds within a peak (e.g., front of peak at 22.90 min). Quantification with the FID is also highly reliable because most of the sample mass will reach the FID and slight changes in the split ratio due to temperature programming will produce negligible changes in mass reaching it. The quantitative reliability provided by this splitting arrangement is specially important since the FID is the detector we use to establish the mass of unknown compounds in the sample.

An example of the ability to identify small components of a complex mixture is provided by the small peak labeled 'a' in Fig. 5. The mass in this peak, corresponding to ca. 10–15 ng on-column, provided searchable spectra by MSD and IRD as shown in Fig. 6. Note the abundance of spectral features in Fig. 6 [e.g., m/z 154(16), 136(69), 121(54), 111(16), 110(17), 109(19), 108(21), 95(100), 93(49), and IR bands at 2961.7, 2887.0, 1756.7, 1462.7, 1368.1, 1236.8, 1190.1, 1055.4, and 1020.7 cm^{-1}], suggesting the ability to interpret in addition to compare spectral features. A mass of 15 ng of this compound in 300 ml corresponds to a concentration of ca. 8 ppb. In general, it is possible to achieve identification limits by IR approaching ca. 1 ppb v/v when analyzing 1000 ml of headspace. Even with a 1:10 split, identification limits by MSD were slightly lower than those achieved with the IRD.

3.4. Analysis of pyrolysis products

The use of the LVIS–GC–IR–MS instrumentation to perform both qualitative and quantitative analysis of headspace can be extended to analyze volatile products generated by thermal desorption or pyrolysis of a sample. This use is illustrated by the off-line pyrolysis of Kraton 1107, a styrene–isoprene block copolymer. Pyrolysis produced a simple and

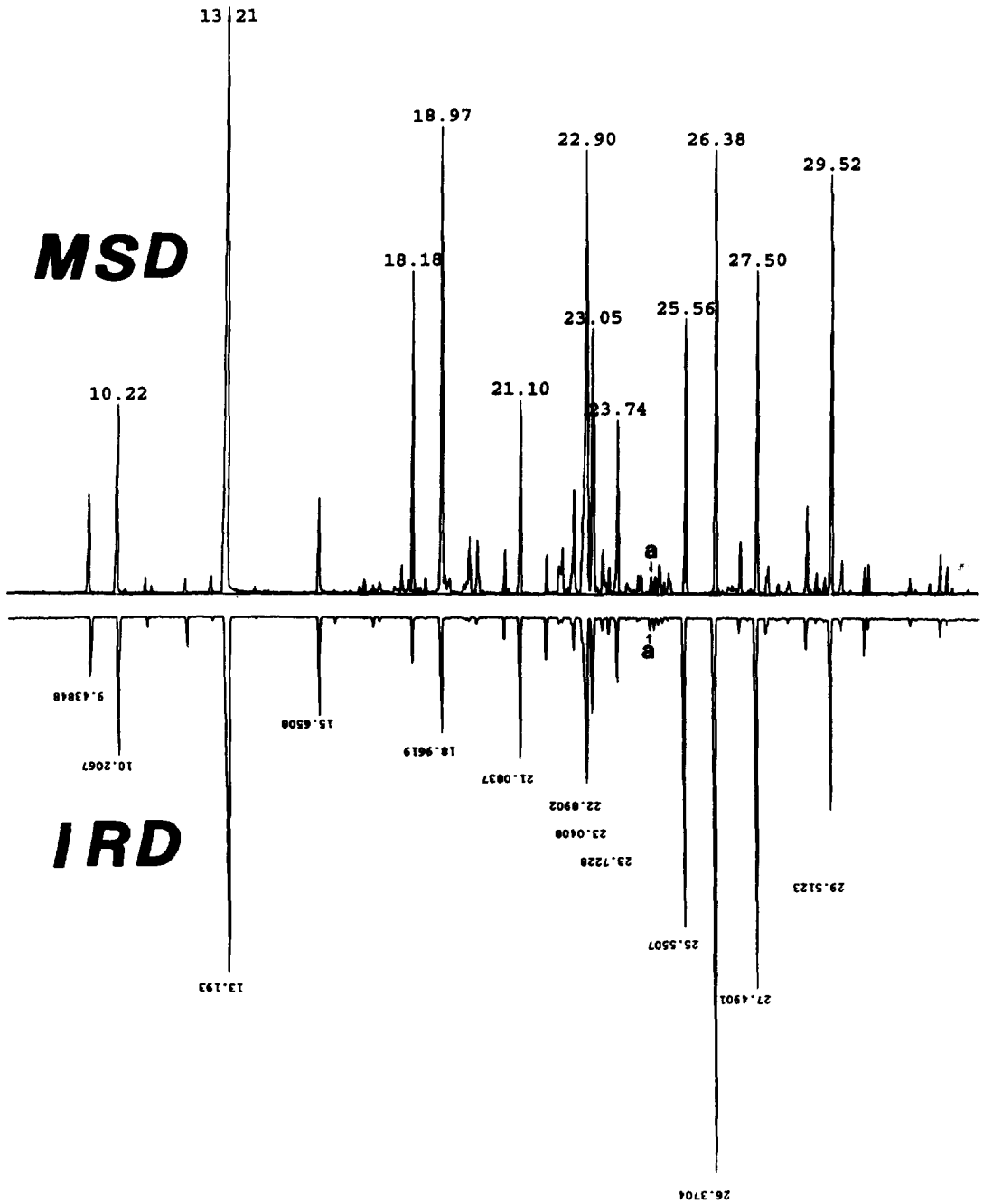

Fig. 5. MSD and IRD chromatograms of a 300-ml headspace sample of a granular detergent.

well-defined fragmentation pattern, showing four major peaks accounting for >95% of the total mass recovered. For this reason, Kraton 1107 was proposed as a standard for the characterization of pyrolyzers and as a means to improve interlaboratory reproducibility by Levy and Walker [19]. In their paper, the four major compounds were identified as isoprene, styrene, 1,4-dimethyl-4-vinyl-1-cyclohex-

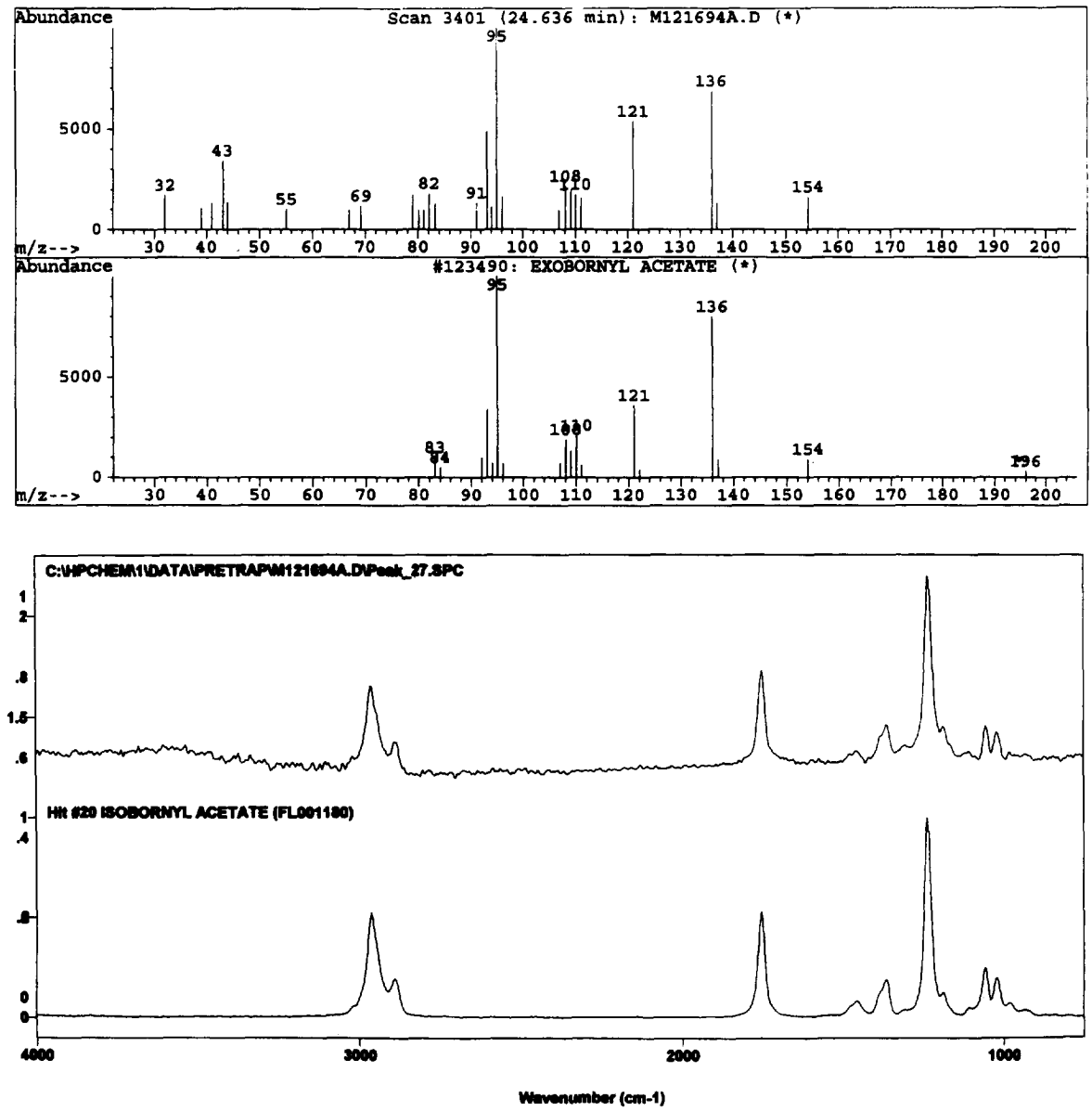

Fig. 6. Results of MS and IR searches on peak 'a', shown in Fig. 5.

ene (DMVCH), and dipentene (racemic limonene). The assignment of identity reported by Scanlan and Houriet differs in that DMVCH is identified as a limonene isomer [20]. We confirmed the identity of the peak labeled dipentene by Levy and Walker as limonene by comparison of its mass and IR spectra and Kovats index (1035) with existing libraries and literature. Also, the IR spectra of the pyrolysis product and limonene (Robertet Flavor/Fragrance IRD library, 2004 spectra) were virtually superimposable (3082.5, 2972.0, 2925.8, 1643.0, 1448.9, 1380.1, 1151.9, 892.1, 796.9 cm^{-1}).

While the abundance of the largest fragments in the mass spectrum of the compound labeled DMVCH differs from limonene by ca. 10% or less, i.e., limonene *m/z* 136 (30), 121 (28), 107(25),

94(30), 93(81), 79(34), 68(100), 67(68), vs. DMVCH *m/z* 136 (22), 121 (34), 107(31), 94(29), 93(69), 79(30), 68(100), 67(61), its IR spectrum (3087.8, 2967.9, 2925.1, 1637.5, 1448.2, 1377.9, 1000.3, 912.4, 799.4 cm^{-1}) shows some important differences. In particular, the 1000.3 and 912.4 cm^{-1} bands suggest the existence of a vinyl group in the molecule. Thus, the assignment as DMVCH is congruent with the IR evidence. The Kovats index, 965, is also congruent: a regression of tabulated Kovats indices vs. boiling points of monocyclic and bicyclic terpene hydrocarbons produced a linear fit [Kovats index=261+4.35·BP (°C), R^2=0.96, n=10], and a predicted BP=162°C, at atmospheric pressure, for a compound with Kovats index=965. The boiling point of 1,4-dimethyl-4-vinyl-1-cyclohexene is 160.5–161.5°C at 741 mmHg (ca. 99 kPa) [21].

Interestingly, both recovery and relative composition of the four compounds were mass-dependent as shown in Table 3. For example, the isoprene/dipentene ratio and the total yield of pyrolysis products increase as the sample mass increases, e.g., from 1.62 to 2.14, and from 33% to 44%, for masses of 0.5 μg and 10 μg, respectively. These results suggest catalytic activity on the Pt-ribbon pyroprobe: if catalytic activity is confined to few layers in close proximity to the Pt-surface, when a small mass is pyrolyzed, the fraction undergoing catalytic decomposition is larger compared to the total mass. Thus, to obtain mass-independent results, it would be necessary to use a sample size larger than 5 μg. The isoprene/dipentene ratio is in good agreement with the value reported (1.78) for pyrolysis at 650°C [19].

Note that although reproducibility (R.S.D.) is typically better than 4%, it improves as mass increases, e.g., is 1% or better for masses >5 μg. The improvement is not due to larger masses reaching the FID since in all cases there is more than enough mass for high-precision measurements. Just as in the case of relative composition and yield, reproducibility may depend on catalytic activity of the pyrolyzer. Other factors affecting reproducibility have been discussed previously [22]. The design of instrumentation to overcome problems encountered with pyrolysis will be the subject of another communication. The high reproducibility also suggests the ability to quantitatively trap materials as light as isoprene, BP=34°C at 760 mmHg (ca. 101 kPa), under our experimental conditions.

4. Conclusions

The LVIS offers a convenient and versatile means of introducing large volumes of either gaseous or liquid samples to a GC capillary column. The system can be constructed from simple components and its installation and usage require minimal changes to existing hardware. Importantly, the installation of the cryogenic concentrator does not significantly change the performance of the existing split/splitless injector; thus, the GC system can be operated as usual.

The LVIS was used to perform large-volume injections of liquid solutions (ca. 50–100 μl), gas-phase analyses of granular detergents (100–800 ml headspace), and solid-phase analyses (off-line pyrolysis GC). The ability to introduce large vol-

Table 3
Pyrolysis of Kraton 1107 at 700°C (relative composition and recovery as a function of sample mass)

Compound	0.5 μg		1 μg		5 μg		10 μg	
	Composition (%)	R.S.D. (%)	Composition (%)	R.S.D. (%)	Composition (%)	R.S.D. (%)	Composition (%)	R.S.D. (%)
Isoprene	41.2	4.1	43.1	0.6	45.3	0.4	47.0	0.4
Styrene	27.6	3.8	27.3	2.7	26.8	0.4	25.8	0.7
DMVCH	5.7	1.3	5.7	0.5	5.3	0.4	5.1	0.6
Dipentene	25.4	2.8	23.9	3.7	22.5	0.4	22.0	1.0
Isoprene/dipentene	1.62		1.81		2.01		2.14	
Recovery (%)[a]	33		37		42		44	

[a] As measured by FID. R.S.D.s established with n=3.

umes of liquid or gaseous samples enhanced the identification power of the MSD–FT-IR instrumentation by increasing the mass of analytes reaching the detectors. Identification limits in the low ppb for gaseous samples, and 100 ppb for solutions in pentane were reached by light-pipe IR, while identification limits by mass spectrometry were lower.

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