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Journal of Chromatography A, 985 (2003) 67–78
JOURNAL OF CHROMATOGRAPHY A
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New high-performance cryofocalizer injector for in-tube solid-phase microextraction and headspace capillary gas chromatographic applications

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Abstract

The construction of a high-efficiency but cheap injector for volatile and very volatile compounds is shown. The device focuses the compounds in a fused-silica (FS) transfer capillary with the aid of liquid nitrogen. A 6.2 mm O.D. glass tube liner (ca. 25 cm ×1.5 mm I.D.) is inserted in the heated (~200 °C) injector of the gas chromatograph in place of the standard glass liner, and extends further externally through a liquid nitrogen container made with styrofoam-like material. Inside this glass tube, the FS transfer line passing through the oven door is connected like a pre-column to the analytical high-resolution GC column. It can move fast between the heated and the cooled zone (↔, ΔL=13 cm), and when this movement starts, cryofocused analytes are injected ''at once'' resulting in symmetrical and sharp injection bands with ''zero'' carryover. The performance of this device is demonstrated by its application to in-tube solid-phase microextraction and to spice volatiles analysis.

Keywords: Injection methods; Headspace analysis; Extraction methods; Cryofocusing; Volatile organic compounds

1. Introduction

To avoid band broadening, gas chromatography (GC) injection processes should introduce samples into the gas chromatographic flow-path as a short injection plug and in a brief lapse of time. This certainly requires practice [1,2], combined with suitable instrumentation, sometimes fitted with special accessories.

One of these are the cryofocusing devices [3], technical systems devoted to focus sample bands (otherwise strongly broadened by the injection process) through the use of cryogens such as liquefied gases, solid carbon dioxide, Peltier elements, etc. Readers could find several interesting examples of cryofocusing apparatus scattered within the literature [4–8], but they probably could retain the impression, as a whole, that cryofocusers might be either too difficult to operate without automation, or otherwise expensive if automation is warranted. A cryofocus device made with a beaker filled with liquid nitrogen in which a fused-silica precolumn is immersed, is the simplest mean to focus effectively even very volatile organic compounds (VOCs) but apart from that, too much reproducibility might not be expected by this crude arrangement.

Appearance can be deceptive, however, because it is the intention of this brief work to show how a high performing (i.e., precise, accurate) cryofocusing sys-

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PII: S0021-9673(02)01698-9

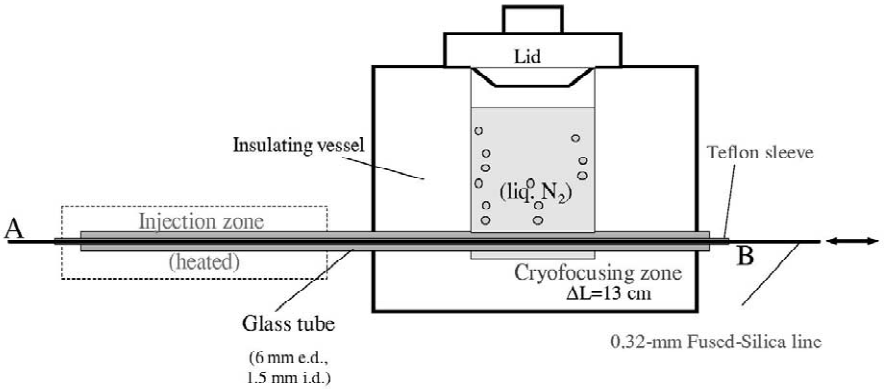

Fig. 1. Cryofocusing assembly. The 0.32 mm I.D. FS transfer line was easily moved releasing an elastic mechanical force by hands (double arrow). This movement transferred almost instantaneously the injection zone from the cold (−196 °C) to the hot zone (about 200 °C).

tem may be easily assembled with very inexpensive materials and mounted successfully onto usual GC instrumentation. The proposed device has been found particularly useful for capillary extraction applications and to determine VOCs in various gas streams.

2. Materials and methods

2.1. Cryofocus construction

A 50 cm long piece of deactivated 0.32 mm I.D.

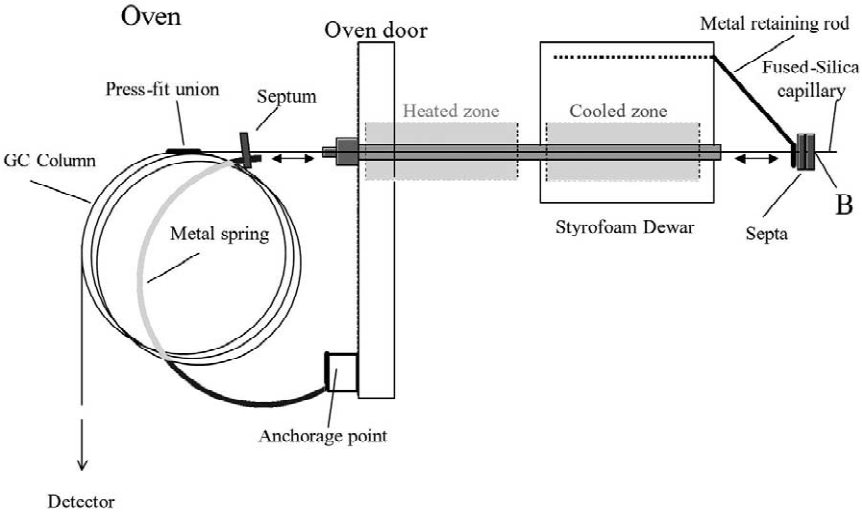

Fig. 2. Draft showing the cryofocuser put in place of the standard injector liner, between GC oven and carrier/sample inlet. The fused-silica transfer line is hooked (through the couple of silicone septa on the right) to the metal retaining rod, which is opposing to the tension made with the metal spring put inside the oven; this way the transfer line is kept in the focusing position for the focusing time (VOCs may be driven in the carrier flow by several means: syringe injections, injections by diffusion tubes and valve, capillary extractors). Unhooking the septa, the transfer line is pulled fast on the left by a distance (~ 13 cm) optimized to flash-vaporize analytes without carryover. Note that the cryofocusing system may be disassembled with ease, restoring in brief time the original Perkin-Elmer injector.

fused-silica (FS) was conceived to be manually moved within a PTFE tube sleeve (~0.6 mm I.D., ~1.2 mm O.D.) which is contained concentrically in a glass tube of 21 cm×1.5 mm I.D.×~6.2 mm O.D.; the glass tube is threaded leak-tight through the lateral walls of an insulated container made with a styrofoam-like material. The FS moved forward or backward (Fig. 1) just by applying or releasing an elastic force (Fig. 2). This movement determined the reinjection of focused volatiles.

2.2. Cryogenic container

The insulated container (a kind of ''Dewar'', externally with a parallelepiped shape) was costless, made from pieces of polyolefinic ''styrofoam-like'' bricks (from packaging materials) stuck together with room temperature-vulcanizing silicone rubber. Its outer volume was 19.5 cm×13.5 cm×10 cm), whereas internally it contained ~400 ml of liquid nitrogen. Lateral and bottom walls were 4 cm thick, enough to give good insulating power: a full charge of liquid nitrogen might last more than 1.5 h. Two holes were made (cork-borer) near the bottom of the internal chamber; through them a glass tube (21 cm×~6.2 mm O.D.×1.5 mm I.D.) was inserted (see Section 2.1 and Fig. 1). The external glass diameter fitted the holes rather tightly, so that liquid nitrogen could not spill out. An upper lid completed the insulation.

2.3. Diffusion tubes and spice containers

Some ''diffusion tubes'' [9] for *n*-hexane were laboratory-made from 10 cm×1/16 inch O.D.×0.3 mm I.D. PTFE tubes any of which was filled with pure solvent, capped with thin glass stoppers and then encased in a glass tube made by two mated glass parts (with a comprehensive length of ~15 cm×3 mm O.D.×1.6 mm I.D.) joined by sliding externally on them a 1 cm PTFE tube sleeve (1 inch=2.54 cm). Press-fit ends were embedded at the ends of any diffusion tube [10] in order to allow its easy finger-tight coupling with 0.32 mm FS capillaries.

This same conceptual design was retained to prepare in the laboratory some dried-spice containers, the only difference being a larger glass tube (8 mm O.D.×5 mm I.D.). The item identified as ''VOC emitter'' in Fig. 3 may give an idea of such versatile containers (having embedded press-fits [10]). Crushed spice leaves (about 200–300 mg) were easily charged inside these versatile containers with a funnel, after disassembling the two mating glass parts and inserting a small plug of glass wool into any tapered extremity. By reconnecting the parts with the PTFE sleeve a kind of versatile diffusion tube for spice volatiles was obtained, which was able to release characteristic VOCs whenever some flow of carrier flowed through it. When full of sample, but not in use, the tubes were capped with press-fits or polyolefin caps.

2.4. GC system and analytical methods

GC analyses on samples of various origin (see

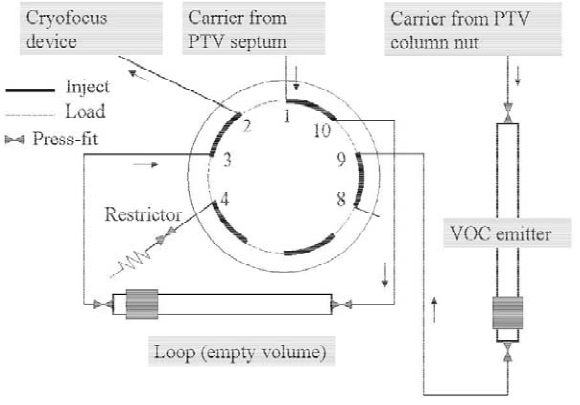

Fig. 3. Schematic draft of the sampling device: a 10-port Valco rotating valve (C10WP), kept physically screwed on the sliding door of the gas chromatograph, with FS connecting lines and a couple of diffusion tubes, one of which is empty, used just as a loop, and the other full of the sample, emitting volatile vapors. The shown set-up (only used ports are numbered) gave good sampling precision after some flow equilibration. Load: gas carrier taken from the PTV column nut enters the VOC emitter where it takes up VOCs from the matrix; then it flushes and stabilizes vapor concentration into the loop made with an empty tube similar to that used to contain the sample, kept between ports number 10 and 3. During a brief period of concentration stabilization, the ''sample'' flow is discharged through an optional restrictor (port 4), which may have the function to reduce the gas flow through the emitter tube, increasing VOC concentration in the loop. Inject: Carrier, taken from the septum nut of the PTV, flushes towards the cryofocalizer the VOC vapors contained in the loop. Port 8 could be left open, or plugged to avoid depletion of the emitter tube.

above) were carried out with or without cryofocusing activation by means of a Perkin-Elmer 8500 gas chromatograph provided with a flame ionization detection (FID) system, a couple of 1/8 inch packed column injectors and a capillary column programmed temperature vaporizer (PTV) injector which, however, remained unheated all the time. This last was selected as the suitable source of hydrogen carrier gas, sometimes helium, regulated by pressure (Fig. 3). Analytical columns (dimensions are indicated in the specific examples) were home-made by static coatings of a PS255 polydimethylsiloxane gum onto Duran borosilicate glass supports, according to valuable recipes [11]. Chromatograms were acquired at a sampling-rate of 25 Hz by means of ''Borwin'' software, version 1.5, from Jasco (Como, Italy). Integrations were made with Borwin, calculation and data reduction were partly performed with Microsoft Excel.

2.5. GC injection modes

Several injection modalities were adopted to furnish the cryofocuser with trace amounts of VOCs from various sources, with the aim to determine cryofocalizer performance:

Injection by ''capillary extractors'' [12–16];

Syringe injections: spice volatiles were taken from the headspaces of screw-capped glass vials by piercing septum liners, the syringe was then directly coupled to the cryofocuser by a press-fit connection and analytes' vapors delivered by hand within a few seconds;

Injection of VOC vapors using diffusion tubes (Section 2.3).

The above injection modalities were initially performed taking the carrier source externally from the (unused) PTV. This was obtained piercing the PTV septum with a 0.25 or 0.32 mm I.D. FS

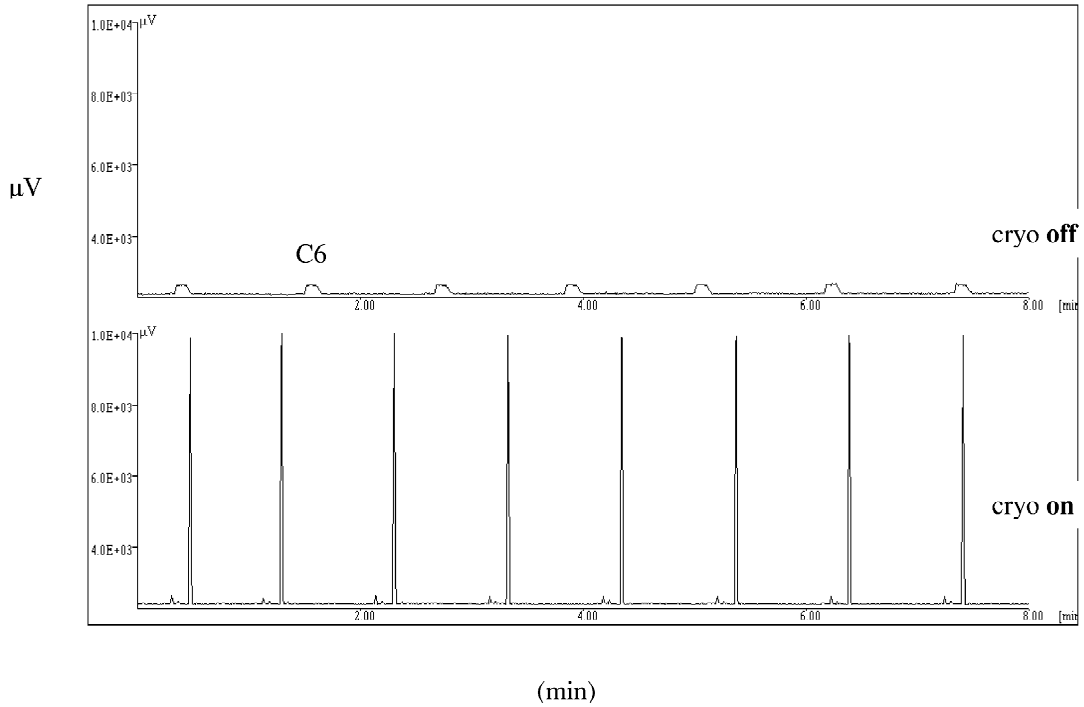

Fig. 4. Series of replicate injections of *n*-hexane vapor delivered with a C6 diffusion tube (''VOC emitter'' of Fig. 3, Section 2.3). Lower run was performed with cryofocus activation. Column was 3 m×0.16 mm I.D., 0.5 μm PS255 (polydimethylsiloxane), with hydrogen carrier at 10 p.s.i.g. and FID (200 °C) (1 p.s.i.g.=6894.76 Pa above atmospheric pressure). Oven: 35 °C, isothermal. Injection sequence for each injection step (cryofocused run): 12 s of sample delivering, then valve rotation and ''at once'' transfer capillary activation (cold zone=liquid nitrogen; hot zone=200 °C).

capillary and using this external FS line as an out-of-the-oven pressure-regulated carrier source, easily connectable by press-fits. Successively it was found more convenient to adopt a 10-port rotating injection valve (C10WP, from Valco, Schenkon, Switzerland), used to comfortably mount a loop carrying the glass diffusion tubes or the spice-containers described in Section 2.3. Moreover, using this very versatile valve (Fig. 3) there was the possibility to strongly increase the reproducibility of sampling and to avoid carrier leakage and analyte depletion during passive-time operations.

Samples' diluting medium was usually the carrier gas (diffusion tubes), sometimes air (syringe injections). Specific examples with additional sampling details are indicated in the Discussion section (see below).

3. Results and discussion

3.1. General concepts and cryofocuser assemblage

The cryofocusing approach discussed here might be adapted to other GC models having horizontal split/splitless injectors or PTVs, since it consists in the easy and quite reversible modification of a standard injector port for 1/8 inch packed columns. ''Reversible'' means here that the original Perkin-Elmer injector might be reassembled within a few minutes.

The cryofocuser idea was inspired to the author by literature reading [17], and consisted in the assemblage of a FS transfer capillary system that might be easily and very quickly moved within an adjustable distance (about 13 cm) between the cryofocus zone

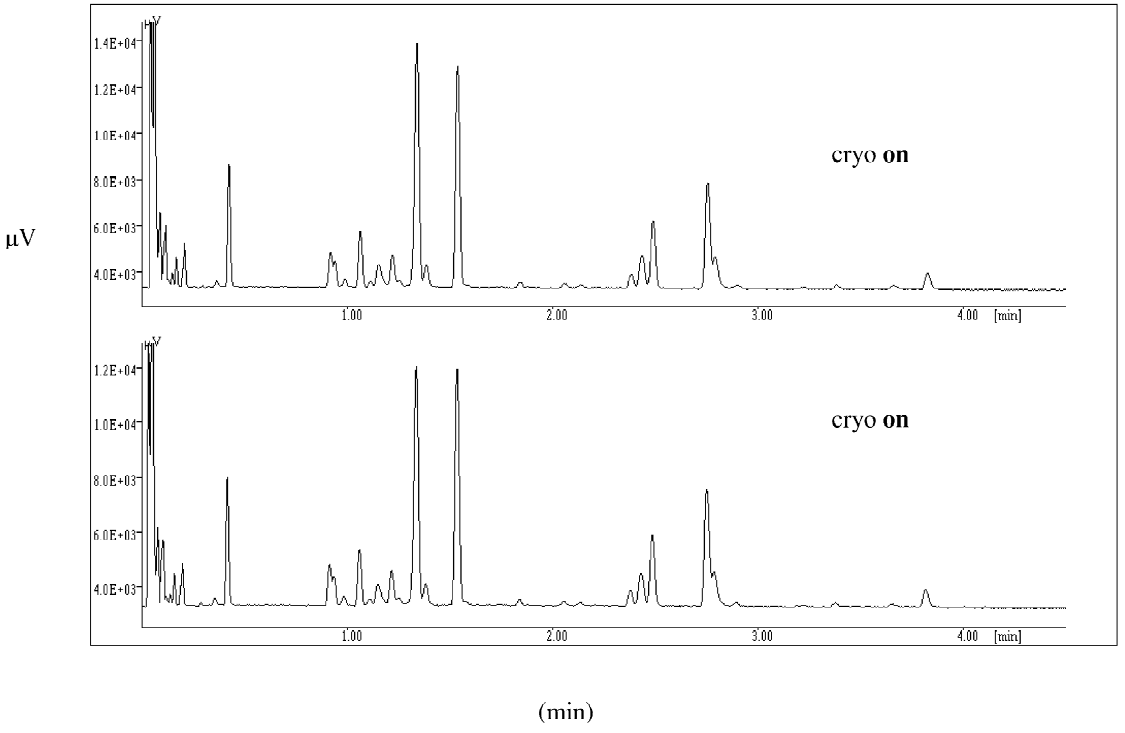

Fig. 5. Duplicate HRGC analyses of 5 ml headspace from dried oregano leaves for table use (syringe injection; injection valve bypassed) with and without cryofocused injection. Column was 3 m×0.16 mm I.D., 0.5 μm PS255 (polydimethylsiloxane), with hydrogen carrier at 15 p.s.i.g and FID (200 °C). Oven: 40 °C for 0.2 min, then programmed at 30 °C/min till 170 °C.

and the hot zone, that are adjacent and overlooking each other. It should be presumed, in fact, that band spreading due to the reinjection of focused bands is linked to the fastness of this movement which was inherently fast (within a few tenths of a second); no attempt was undertaken to modify its fastness since this could affect injection repeatability.

Fig. 1 reports the cryofocuser with its major parts: deactivated FS transfer capillary, ''Dewar'', glass tube, PTFE tube. The portion of the glass tube extending externally from the insulated container (only 4 cm of glass tube are truly immersed in liquid nitrogen) was fitted into the GC injection port, in place of the original Perkin-Elmer glass liner. The PTFE sleeve had an important function: being rather heat resistant and hydrophobic, it allowed free sliding between itself and the uncoated but deactivated FS transfer capillary, even at liquid nitrogen temperatures, in spite of the presence of some ice crystals coming from atmosphere humidity condensing on cold parts. During transfer capillary assembling, the FS capillary was threaded from outside through the PTFE+glass concentric tubes, crossed the oven door and was joined with a press-fit union to the analytical column inside the oven.

During normal operation, a part of the FS transfer line was at high temperature (200–250 °C normally) whereas the adjacent part was cryogenically cooled at −196 °C by liquid nitrogen. ''B'' of Fig. 1 is a virtual reference point to imagine the reinjection process. Cryofocused VOCs were reinjected (flash-vaporized) as soon as B was shifted toward the hot zone by the distance ΔL. This distance was important, since carryover happened whenever ΔL was too short. Carryover effects, however, were easily prevented with ΔL optimization.

A rapid ΔL shift was realized with user intervention, releasing a moderate elastic force which acted on the transfer capillary. In practice (Fig. 2) a couple of GC septa were threaded through the FS transfer capillary to act as a FS rest-point toward a stainless steel retaining rod, ~30 cm total length×1 mm diameter, supported by the ''Dewar'' wall. This rod was allowed to exercise its pulling action on the

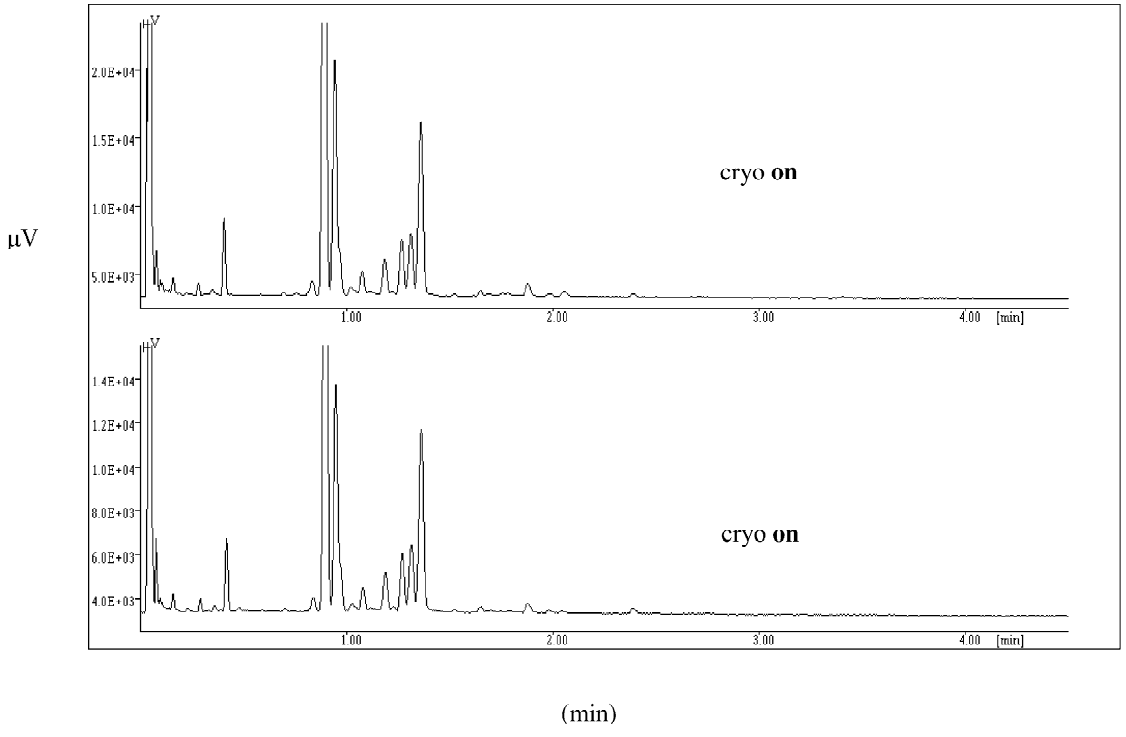

Fig. 6. Duplicate HRGC analyses of 5 ml headspace from dried rosemary leaves for household use. Cryofocused injection. GC conditions: see Fig. 5 caption.

transfer FS capillary during the ''focusing time'' required to preconcentrate analyte from the gas phase; whenever the FS transfer capillary was anchored on the retaining rod, it was subjected to a moderate elastic force opposite to that exerted towards the oven by another piece of metal rod put under mechanical tension inside the oven. A third GC septum, threaded to the end of this in-oven brace rod, cushioned the FS transfer capillary near the union with the analytical column from the (mild) mechanical stress which originated during fast ΔL movements.

The assembled cryofocuser was able to function as soon as liquid nitrogen was added into its styrofoam container, plus a few minutes to allow focus zone to reach its working temperature.

The thermal mass of the 0.32 FS transfer capillary was negligible. Moreover, concentric tubes had matched diameters to reduce air clearances in order to give enhanced kinetic of heat exchange. The reinjection time (a fraction of a second) could be operatively judged from chromatograms of cryofocused runs (see below). While injection repeatability was good, the problem of ice-plug [18,19] which usually goes along with cryofocusing devices, was encountered with certain ''critical'' samples, namely those injections performed by sampling (with syringe) air as vapor sample medium. These samples required pre-treatment with anhydrous sodium sulfate.

3.2. FS transfer capillary selection

Practical experience has shown that the 0.32 mm I.D. FS capillary was the best, since with I.D.=0.25 mm the chance of ice-plug with critical samples (e.g. headspace from neat spices for household use) is rather high, whereas with 0.53 mm I.D. the problem was some breakthrough of very volatile analytes caused by aerosol formation and/or reduced cooling efficiency. Moreover, free movement of the transfer

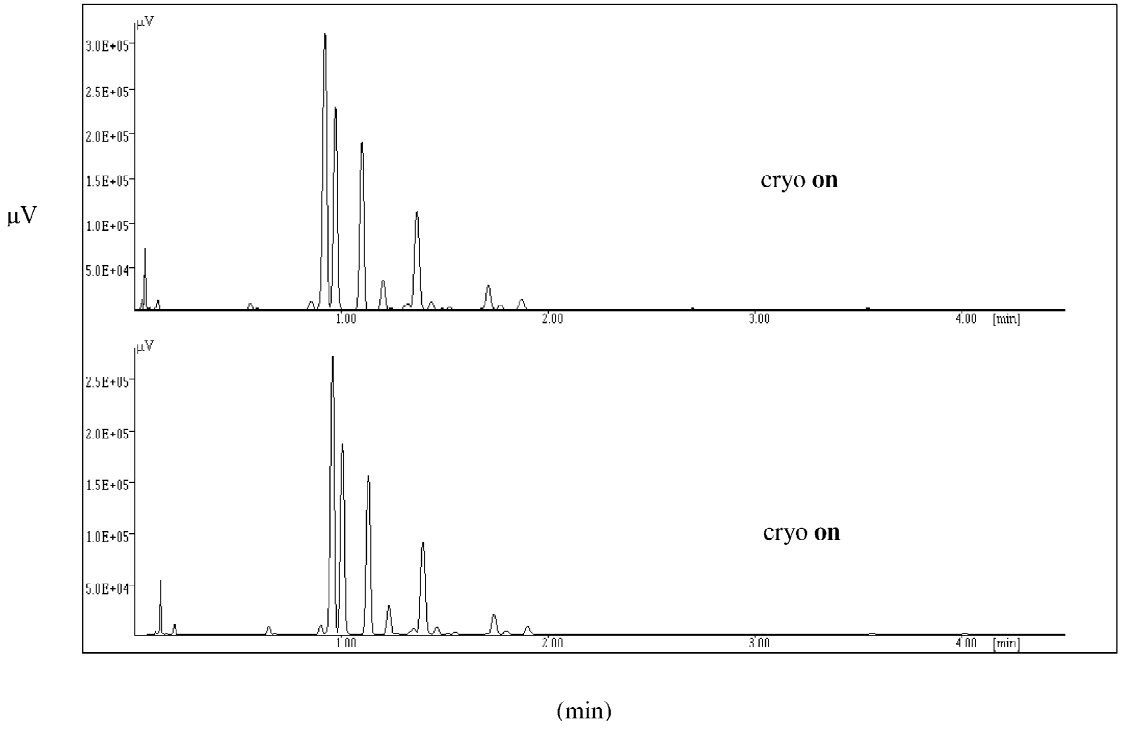

Fig. 7. Duplicate HRGC analyses of 5 ml headspace from dried sage leaves for household use. Cryofocused injection. Column: 3 m×0.16 mm I.D., 0.5 μm PS255 (polydimethylsiloxane), with helium carrier at 10 p.s.i.g and FID (200 °C). Oven: 35 °C, isothermal runs.

capillary within the thin PTFE sleeve was somehow hindered with the 0.53 mm I.D. capillary.

When a substantial risk of ice-plugs was suspected with solid samples, they were reanalyzed after an intimate mixing with anhydrous sodium sulfate and this pre-treatment was resolutive.

Reported below are some applications, selected here to show the repeatability as well as the accuracy (absence of carryover) of the proposed cryofocuser.

3.3. Selected examples

3.3.1. Organic vapors from diffusion tubes

Fig. 4 shows the repeatability of vapor phase diffusion tube injection of *n*-hexane (*n*-pentane was also tried, both alone and together with *n*-hexane, with equally good results) with and without cryofocuser activation after 12 s of focusing time. In practice, the C6 diffusion tube was mounted by means of the 10-port sampling valve shown in Fig. 3, which allowed also several injection configurations (for example, using simultaneously two different VOC emitter tubes, configuration not shown). At the end of the focusing period, the valve was rotated to stop sample delivery to the focusing transfer line, pure carrier was supplied to this line and simultaneously flash vaporization was started by ΔL displacement of transfer capillary. Injection repeatability by area counts was less than 1% on a RSD base ($n=7$), and both major component and minute details due to impurities were reproducible.

3.3.2. Spice volatiles

Qualitative repeatability of cryofocused injection can also be observed in Figs. 5–7, which report couples of replicate analyses (with cryofocus) of household spice volatiles, oregano, rosemary, and sage, respectively. The spices volatiles were delivered by syringe sampling the headspaces above the spice leaves kept in closed vials. Also studied was the set-up shown in Fig. 3 (spices kept into the VOC emitters; see Section 2.3 for some details of VOC emitter preparation) giving encouraging results. The fingerprint of the replicate chromatograms was

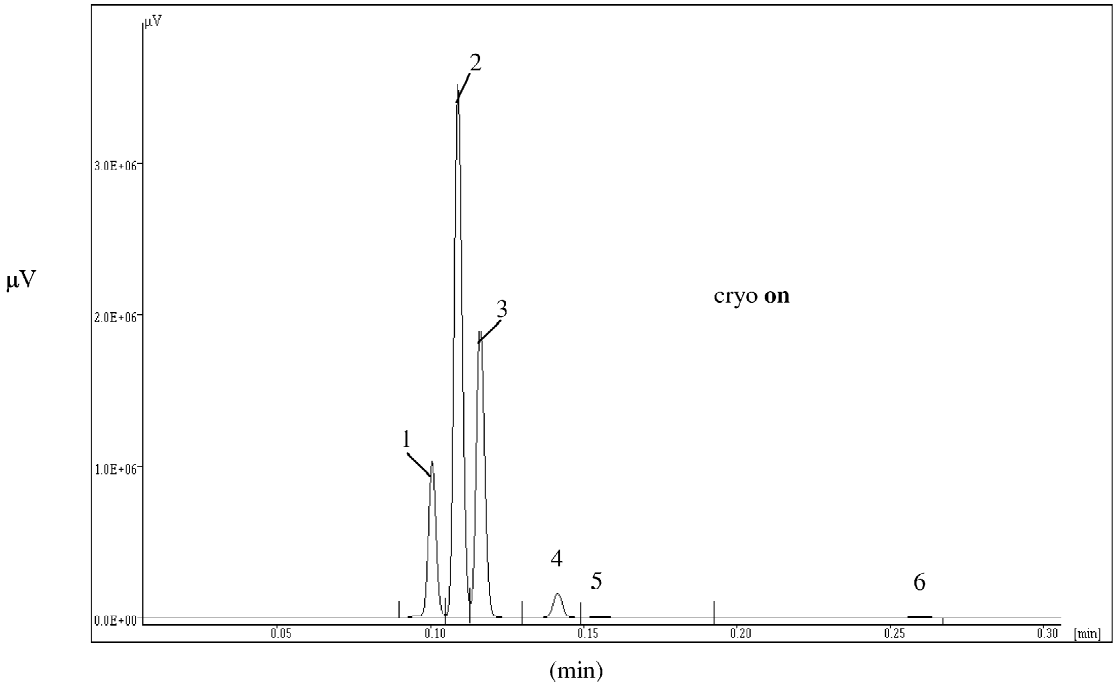

Fig. 8. Fast-GC analysis of headspace vapor from a cigarette lighter gas (syringe injection, with cryofocusing). Column: 3 m×0.16 mm I.D., 0.5 μm PS255; hydrogen carrier at 7 p.s.i.g and FID (200 °C). Oven: 35 °C, isothermal runs. Peak numbers (Table 1) refer to a few paraffins and isoparaffins from *n*-propane to *iso*-pentane.

Table 1
t_R Repeatability of cryofocused injections of very volatile compounds

	Peak number					
	1	2	3	4	5	6[a]
Average t_R (min)	0.0988	0.1068	0.1144	0.1386	0.1522	0.2555
% RSD (n=5)	0.45	0.42	0.78	1.1	1.1	0.28

[a] n=3.

very similar, suggesting the cryofocuser performance was quite suitable.

3.3.3. Cigarette lighter gas

Cigarette lighter gas was used to ascertain quantitative repeatability of retention time even with cryofocused injection of very VOCs. Five replicates were carried out. Each chromatogram (Fig. 8) showed at least six resolved peaks. Table 1 reports their t_R repeatability, which resulted in ≤1.1% RSD.

3.3.4. Chlorinated solvents

The cryofocuser proposed here was particularly suitable to be used in combination with ''capillary

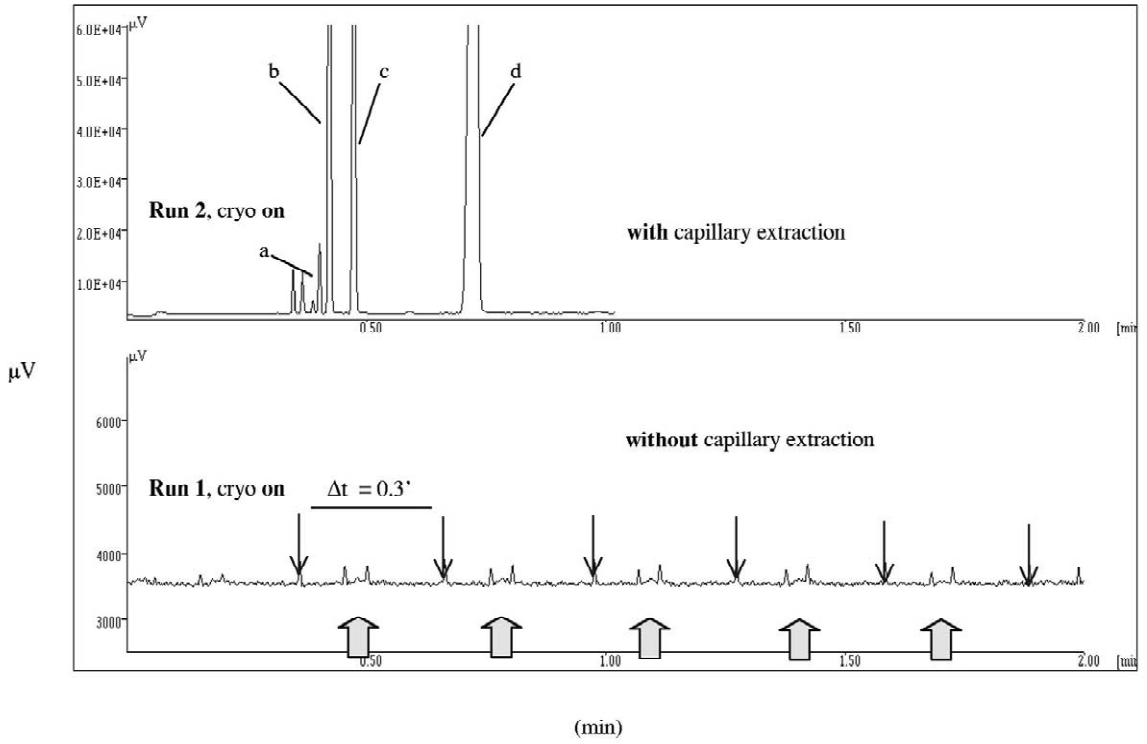

Fig. 9. (Run 2) Cryofocused HRGC analysis of a diluted aqueous solution of chlorinated solvents (0.44 ppm each) by capillary extraction–HRGC. Peak letters refer to chloroform (a), 1,1,1-trichloroethane (b), trichloroethylene (c), and tetrachloroethylene (d). Detection was by FID. (Run 1) Multiple ''blank'' injections without sample extractor in place (every analysis lasted 0.3 min: 0.1 min of focusing-time, plus 0.2 min of run-time). Thin arrows indicate movements of FS transfer capillary towards the operator to prepare the next injection. Thick arrows indicate some trace impurities present in the carrier, repeatedly detected by FID at every injection step. Such impurities would have gone undetected without the use of cryofocusing, contributing only to enhance FID baseline level and noise. Repeatability of the cryofocusing system is evident.

Table 2
Detection limits (DL, 2σ) for some chlorinated solvents obtained by fast squeezed capillary extraction on a 1 ml sample, with and without salting but with cryofocusing

	Chloroform	1,1,1-Trichloroethane	Trichloroethylene	Tetrachloroethylene
DL (2σ), ppb (v/v)	8.4	0.75	1.0	0.50
DL (2σ) with NaCl salting	1.6	0.3	0.3	0.4

extractors'' [12–16]. Actually, it was conceived for that use. Fig. 9 reports the cryofocused analysis of a diluted aqueous sample of four chlorinated solvents (chloroform, 1,1,1-trichloroethane, trichloroethylene, and tetrachloroethylene, each at 0.44 ppm v/v) extracted from the aqueous sample by means of the in-tube solid-phase microextraction (SPME)–high-resolution GC (HRGC) approach [13–16]. A volume of 1 ml of sample was extracted/preconcentrated into a rather long extractor (76 cm×0.251 mm I.D., 0.3 μm polydimethylsiloxane), within a few seconds, by the so-called ''squeezed extraction'' [13,16]. No salting was applied. Fig. 9 reports also the baseline profile obtained by focusing carrier impurities for 0.1 min, then moving the transfer capillary into the hot zone for 0.2 min and finally resetting its position. In practice several run cycles are shown, each of 0.3 min. As can be noted, the cryofocus use allowed rather low detection limits with the capillary extraction technique even without salting and with rugged FID (Table 2); the approach is worthwhile, considering that (a) detection here was by FID [electron-capture detection (ECD) would increase the sensitivities of several orders of magnitude, reaching easily low ppt], and (b) using a cryofocuser, capillary extraction sensitivity might be increased very much by just increasing extractor size [13,16].

The coupling of ''HRGC–ECD+cryofocused

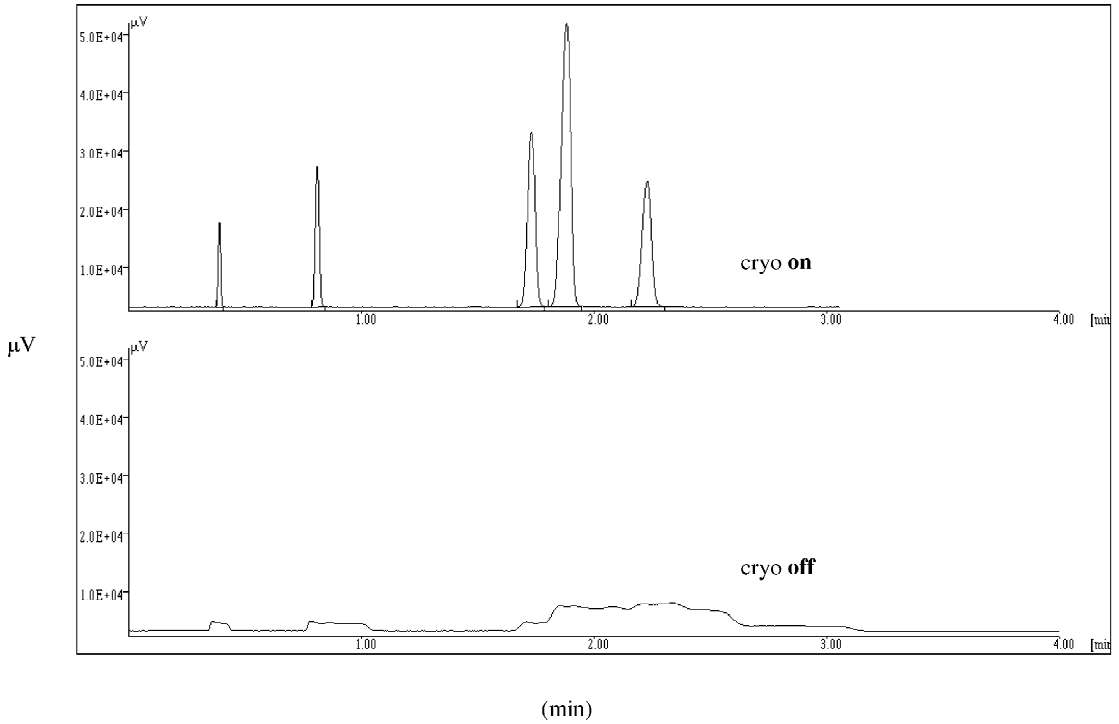

Fig. 10. Capillary extraction analyses of an aqueous sample of BTEX [146 ppb (v/v) per component]. The lower run did not use the cryofocuser.

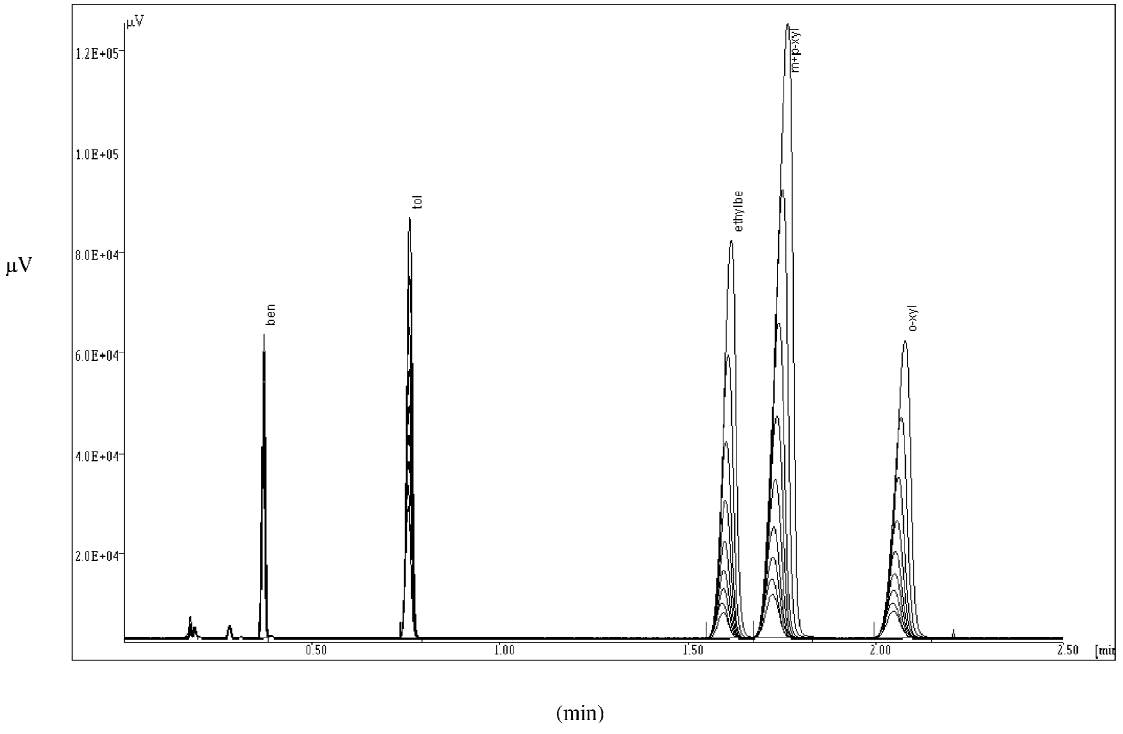

Fig. 11. Repetitive in-tube SPME extractions of the same sample: 1 ml of BTEX aqueous solution at 146 ppb (v/v) per component. Analytes are depleted proportionally to their partition coefficients K_d. This allows the easy calculation of partition coefficients [15,17]. Extraction method: fast squeezed method [13] performed at ambient temperature. Time required for each extraction: 60–70 s. Detection: FID. GC oven temperature: ambient. Focusing time: 3 min. Analytical column is the same as reported in Fig. 8.

capillary extraction'' is, on the chart, a high throughput (extraction can be performed within a few seconds) sensitive approach to the analysis of alogenated compound in clean water matrices, complementary to sister techniques like SPME or stir-bar sorptive extraction (SBSE).

3.3.5. Benzene, toluene, ethylbenzene and xylenes (BTEX) from a water sample

Another example of the advantageous use of the present cryofocusing device with capillary extraction (see also Section 3.3.4) is reported in Fig. 10, concerning capillary extraction of BTEX at 146 ppb in water. Here the comparison between the unfocused analysis and the focused one is impressive. In fact, in comparison with the analytical column, the capillary extractor was rather long (76 cm×0.21 mm I.D., 0.3 μm polydimethylsiloxane) selected this way to show the convenience of cryofocusing when capillary extraction sensitivity must be increased. The remarkable precision and accuracy of the coupling of cryofocusing with capillary extraction is clear also from the BTEX depletion experiments (Ref. [15], and this symposium volume), useful to measure distribution constants by capillary extraction (Fig. 11). Here the BTEX compounds (146 ppb initial concentration, 1 ml sample) are progressively extracted at equilibrium from the same sample aliquot using a capillary extractor of 70 cm×0.474 mm I.D. internally coated with 0.48 μl of polydimethylsiloxane phase. After each extraction, the extractor is mounted as a pre-column and BTEX analytes desorbed at room temperature for 3 min, with cryofocusing on, and then reinjected as explained above.

4. Conclusions

A useful and functional cryofocusing system was

easily made in the laboratory from simple and extremely cheap materials. Details in this paper should allow interested users to construct their own high-performance cryofocusing injector for general use. The cryofocuser gave repeatable and accurate injections which helped GC separations of VOCs coming from solid or gaseous matrices and also trace analysis by capillary extraction [13] of organic compounds in aqueous matrices. Cryofocusing design is such that the original hot injector could be reassembled as it was originally, within a few minutes.

The high reproducibility of the system (though being manually operated) depends, firstly, on the high temperature stability of the heated/cooled zones (a boiling liquid nitrogen cold zone, and a thermostated hot zone) and secondly from the negligible thermal mass per unit length of FS. Another clear advantage is the fast reinjection time (<1 s). The proposed cryofocuser is also accurate, because after an easy optimization of just two parameters (ΔL distance, focusing-time) carryovers do not happen.

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