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COLD SAMPLE INJECTION WITH EITHER THE SPLIT OR SPLITLESS MODE OF TEMPERATURE-PROGRAMMED SAMPLE TRANSFER

DESIGN AND TESTING OF A NEW, ELECTRICALLY HEATED CONSTRUCTION FOR UNIVERSAL APPLICATION OF DIFFERENT MODES OF SAMPLING

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SUMMARY

A new and simple device is described for "cold" injection with subsequent temperature-programmed sample transfer. The liquid sample is introduced into the cold, low-volume, easy to exchange and easy to clean glass insert, or alternatively by direct insertion of a special syringe needle into the column itself after only minor technical changes. The insert is electrically heated by a cartridge using the standard facilities of modern gas chromatographic instrumentation. With the cold injection, the split or the splitless mode can be adopted, and such an injection system can therefore be considered to possess nearly universal capabilities. Improved precision and accuracy in quantitative analysis can be achieved with different types of samples.

INTRODUCTION

Gas chromatographic (GC) systems have to be operated at elevated temperatures in order to produce high enough partial pressures in the mobile phase even when low-volatility components of the mixtures are to be analysed. Only then can such components migrate through the column with reasonable retentions. The introduction of various types of samples into the chromatographic system, *i.e.*, either into special sampling devices or on to the column itself of the chromatographic system, involves special problems, depending on the average volatility of the mixture, the range of component volatilities and the temperatures that must be maintained in the entire system[1].

With the new "cold" sampling systems, cold (temperature programmed, TP)[1–3] and cold (on-column)[4–6] injection, the liquid sample enters the system at temperatures which are not higher than the column itself, or even lower. The complete vaporization of the liquid sample is not initiated before the temperature of the injector or of the column inlet is elevated by slow or fast temperature programming. There may also be reasons for cooling the injector or the column inlet even below ambient temperature if samples must be introduced that contain major components or solvents of very high

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volatility (low boiling points). Too high sampling temperatures cause difficulties with the fast and complete transfer into the column and decrease the resolution, as well as the precision and accuracy of quantitative analyses. These difficulties are: selective vaporization from the needle of the syringe, which is the most commonly used device for varying the volume of sample introduced, and too sudden or even explosive vaporization of the sample, which is associated with pressure increases, changes of splitting and column flows, sample losses by back ejection, aerosol formation, etc. These sources of errors affect the performance of quantitative analysis particularly when split-mode sampling techniques are used.

With the splitless types of "cold" sampling techniques, selective vaporization from the needle is completely avoided and no discrimination and very low standard deviations are obtained even with the components of mixtures that vary widely in volatility.

It was of interest to establish whether split sampling can also be optimized by cold injection and programmed smooth vaporization, and especially whether the absolute peak areas (*i.e.*, the actual column loads) correspond to the adjusted sample volume and splitting ratio. The proper operation of split sampling would be of great practical value because the variation of the column load by the splitting ratio, in addition to the possibility of syringe volume adjustment, may be very useful for certain types of practical samples of the less diluted type, such as those arising in production and quality control, for example, in the chemical industry. Moreover, split sampling has the advantage of fast sample transfer by split flow from the vaporization chamber into the column, a feature which is of importance for the achievement of optimum separation efficiency, *e.g.*, resolution especially in the isothermal mode of column operation, where band focusing to compensate for too slow a sample transfer within the column inlet does not occur, because the column temperatures applied are higher.

OBJECTIVES

At the Fourth Hindelang Symposium on Capillary Chromatography we described the designs of various types of cold (TP) injectors[1] and also presented preliminary experimental test data. In a separate paper also intended for presentation at the Fifth International Symposium on Capillary Chromatography at Riva del Garda[7], we report on experiments on the comparison of a commercial version of cold (TP) injection operated in either the splitless or the split mode with a commercial cold on-column injector. In this paper we describe a new device designed to avoid certain technical difficulties of the cold (temperature-programmed vaporizer, PTV) DANI injector (see Fig. 1). The new device can be used for three principally different modes of sampling, the splitless, the split and the on-column modes, allowing the injector temperature to be decreased before the introduction of the sample and subsequently elevated by a ballistic programme for vaporization of the sample and its transfer into the column. In the splitless and split modes of cold (TP) injection the capillary column projects into the vaporization insert by only a few millimetres. If the same device is to be used for the cold on-column technique, arrangements have to be made which allow either the introduction of a suitably long syringe needle of small outer diameter into the capillary column inlet, or for the column to be pushed upwards towards the septum to

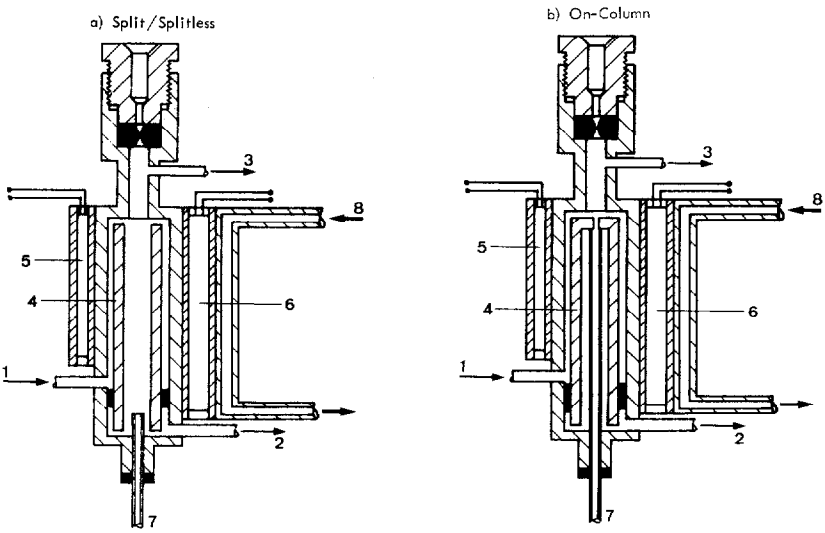

Fig. 1. Universal temperature-programmable cold injector for splitless, split and on-column modes of operation. 1 = Carrier gas; 2 = split outlet; 3 = septum purge; 4 = glass insert; 5 = resistance thermometer (PT 100); 6 = heater cartridge; 7 = capillary column; 8 = air cooling.

permit the application of shorter syringe needles. With this version of the cold on-column injection additional heating of the sample introduced into the column itself is also possible, which may be of advantage if the sample contains compounds of very low volatility.

Especially when using the commercial cold (PTV)–DANI injector in the split mode we observed a negative influence of technical imperfections, for example generated by poor sealing of the insert and imperfect separation of the column flow line from the split flow line. The discrimination, the standard deviations and the total column load were not proportional to the sampling volume and the splitting ratio. When an appropriate sealing is used with, *e.g.*, Vespel as sealing material, discrimination of the high-volatility (low-boiling) compounds usually occurs, whereas with less perfect sealing a reverse or even no discrimination of the low-volatility components is obtained. Configurations of the flow system may emerge or exist in which both counteracting effects of discrimination compensate each other, thus giving the appearance of a discrimination-free status of the system. However, in such cases the early and late peaks are recorded with increased standard deviation of the relative areas, whereas the peaks of medium retention are recorded with the usual, lower standard deviation.

INSTRUMENTAL

In our first paper[1] on cold (TP) injection we presented three different constructions: sample lift (A), air cooling and heating (B) and air cooling and electrical heating (C). Version (B), based on alternating cool or hot air flows to produce temperature changes in the insert, was very similar to the independently designed DANI construction[2]. Version (C) was favoured primarily because it can be heated quickly

by the electrical resistance of a stainless-steel mantling tube, but it also suffers severely from the above-mentioned sealing problems. Moreover, the temperature control is elaborate and requires special devices. Therefore, we designed a new version of an injector heated electrically by cartridge and air cooled, which is characterized by the following features: a low-volume, easy to change vaporization insert which is thin walled for fast heat transfer; low heat capacity of the entire device for quick ballistic heating and cooling; additional cooling by air flow is not generally necessary, but air flow cooling is provided; heating of the device is possible by using the injector heating facilities which are commonly available in modern GC instrumentation; the cold (TP) version can be operated in the splitless and split modes; the column inlet is also accessible by a suitable small outer diameter syringe needle; therefore, the column inlet can be pushed up to the top of the vaporization insert (cold on-column mode); the introduction of the syringe needle is carried out either through a screw-tightened seal, a septum or a suitable microvalve, and can also be done automatically, except in the cold on-column mode; high air consumption, especially for heating, is avoided.

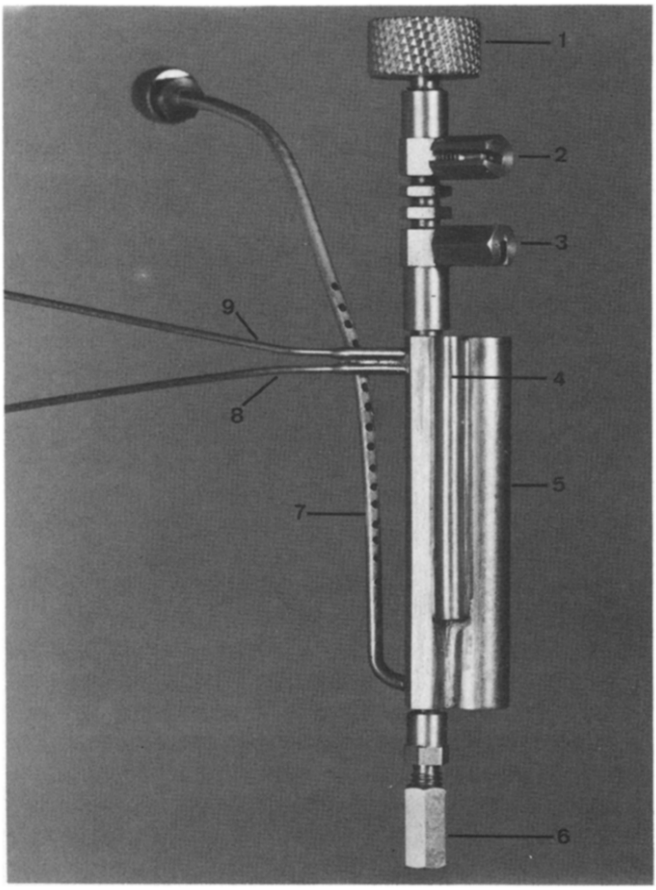

Fig. 2. Photograph of cold (TP) injector device with special arrangements for solvent backflushing. 1 = Slit for syringe needle introduction; 2 = exit for septum flush; 3 = carrier gas inlet; 4 = sleeve for PT 100 thermometer; 5 = sleeve for heater cartridge; 6 = column connection; 7 = air cooling; 8 = split outlet; 9 = carrier gas inlet for solvent backflush mode.

A photograph of the new universal construction is shown in Fig. 2. The heater cartridge and the platinum resistance thermometer cartridge were removed for taking the photograph.

EXPERIMENTAL

Measurements were made with the usual test mixtures, containing alkanes with a wide range of carbon numbers (volatilities), diluted to different concentrations with *n*-heptane as the solvent. The device was operated in all three modes: cold (splitless) (Fig. 1a), cold (split) (Fig. 1a) and cold on-column (Fig. 1b).

Operated in these three different modes, the desired low standard deviations of absolute and relative peak areas and a negligibly low discrimination of either high- or low-volatility components were obtained (see Table I).

When the new device was operated in the splitless and the on-column modes, the same data on precision and accuracy were obtained as with the cold (PTV) DANI injector or the common cold on-column injectors. Using the split mode we obtained results similar to those in the splitless modes, *i.e.*, no discrimination. With the DANI design operated in the split mode, low standard deviations of relative peak areas and negligible discrimination were achieved under conditions at which the column loads did not correspond to the splitting ratio, although the absolute peak areas were reproducible with very low standard deviations (see ref. 7, Table 1, p. 347). After perfect sealing of the insert, the absolute peak areas corresponded to the splitting ratio, but now discrimination was observed[8].

Further measurements must be made to investigate other sampling parameters: insert temperature at sample introduction; rate of heating and end temperature in the sampling device; volatility of solvent; maximum sampling volume; and splitting ratio.

Gas chromatograms of the polyaromatic hydrocarbons of coal tar obtained by cold (TP) injection illustrate that compounds of very low volatility (coronene) can also be vaporized from the new device without difficulty. Similar chromatograms were obtained with the splitless mode with a sample diluted (1:50) in toluene and benzene (Fig. 3) and the split mode applied to a concentrated solution (Fig. 4). No difference in performance between the splitless and the on-column mode was observed.

CONCLUSION

The described sampling device allows the flexible application of different sampling modes required for different sample types. Regarding the standard deviations of absolute and relative peak areas and the discrimination, no problems arose in the sampling of diluted mixtures of compounds with a wide range of volatilities if the splitless cold (TP) or the cold on-column modes were applied. When split sampling was applied to the same but less diluted test sample, data of similarly good precision and accuracy could also be obtained. The cold injection techniques using the common 10-μl syringes also guarantee highly improved reproducibility of absolute single peak areas (1–2% relative) and the total peak area (which corresponds to the actual column load), even with sampling volumes as low as 0.5 μl. This feature is of impor-

TABLE I

DISCRIMINATION TESTS USING THE NEW COLD (TP) INJECTOR DESIGN OPERATED IN ON-COLUMN, SPLITLESS AND SPLIT MODES

Relative and absolute peak areas, including standard deviations of repeatability. No. of measurements in each mode: 5.

Parameter	*Mode*		
	A	*B*	*C*
Sample	0.5 μl C_{10}–C_{32} in C_7; 0.002% each component	0.5 μl C_{10}–C_{32} in C_7; 0.002% each component	0.5 μl C_{10}–C_{32} in C_7; 0.1% each component. Splitting ratio: 1:30
Column	30 m SE-52, d_f 0.1 μm	30 m SE-52	30 m SE-52
Temperatures	25–320°C at 15°C/min; Inj.: 25–200°C	25–320°C at 15°C/min; Inj.: 50–250°C	25–320°C at 15°C/min; Inj.: 35–200°C
Carrier gas	0.5 bar H_2	0.5 bar H_2	0.5 bar H_2
Instrument	Siemens Sichromat 2	Siemens Sichromat 2	Siemens Sichromat 2

Mode	*Relatieve peak areas*	C_{10}	C_{12}	C_{14}	C_{16}	C_{18}	C_{20}	C_{22}	C_{24}	C_{36}	C_{28}	C_{30}	C_{32}	*Sum of absolute peak areas*
On-column (A)	Peak area (%)	8.13	8.31	8.32	8.28	8.34	8.40	8.51	8.26	8.26	8.39	8.43	8.45	Sum: $8.2 \cdot 10^6$
	S.D. (%)	1.25	0.78	1.05	0.43	0.50	0.49	0.70	0.39	0.45	0.66	0.31	0.69	S.D.: 1.98%
														Corr.*: $412 \cdot 10^6$
Splitless (B)	Peak area (%)	7.88	8.27	8.28	8.35	8.30	8.26	8.59	8.33	8.37	8.46	8.47	8.46	Sum: $7.8 \cdot 10^6$
	S.D. (%)	1.52	0.72	0.69	0.41	0.41	0.57	0.13	0.42	0.93	0.08	0.46	0.40	S.D.: 3.11%
														Corr.*: $394 \cdot 10^6$
Split (C)	Peak area (%)	8.40	8.51	8.26	8.24	8.20	8.14	8.42	8.15	8.20	8.40	8.51	8.57	Sum: $14.6 \cdot 10^6$
	S.D.(%)	1.07	1.04	0.86	0.94	0.69	0.65	0.85	0.47	0.78	0.65	0.63	0.88	S.D.: 1.49%
														Corr.*: $439 \cdot 10^6$

* For splitting or dilution, respectively. For the test procedure in the splitless and on-column mode the sample that was used for the determination of the absolute peak areas with split sampling was diluted 1:50. Therefore the correction of the sum of the peak areas, as listed in the table, was done by multiplication with the dilution factor (50) in cases A and B, whereas in case C (split mode) the sum of the areas were multiplied by the splitting ratio (30) only.

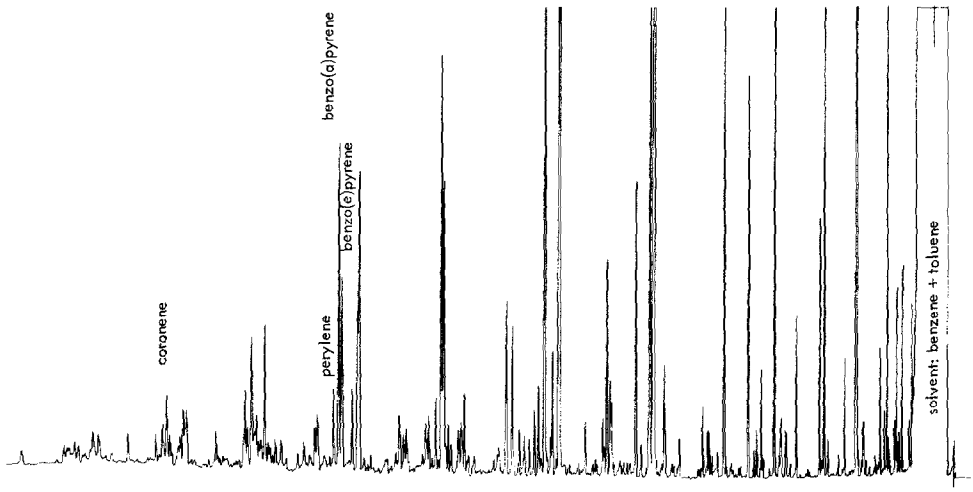

Fig. 3. Cold (TP) injection in splitless mode: sampling of components of very low volatility [polyaromatic hydrocarbons of coal tar (highly diluted) in benzene]. Sample: 0.4 μl of coal tar. Column: 20-m methylpolysiloxane OV-1 on fused silica. Column temperatures: 1 min isothermal at 25°C, ballistic heating from 25 to 80°C, then from 80 to 320°C at 8°C/min; injector, 35–280°C, ballistic heating. Carrier gas: 0.4 bar hydrogen. Analysis time: 35 min.

tance with regard to less elaborate calibration measurements for highly diluted samples, as usually encountered in trace analysis. The new device can be considered to be nearly universal with regard to different types of samples and different objectives of analyses.

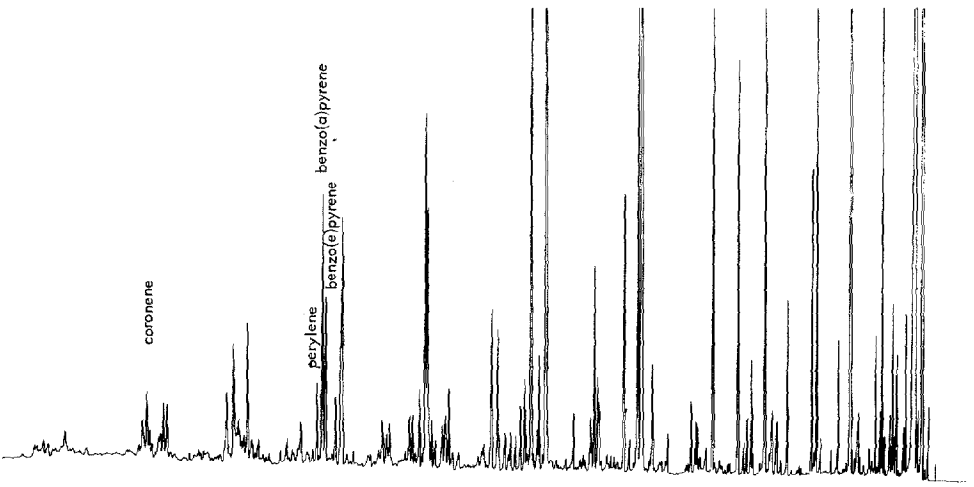

Fig. 4. Cold (TP) injection in split mode: sampling of components of very low volatility [polyaromatic hydrocarbons of coal tar (less diluted) in toluene]. Sample: 0.2 μl of coal tar diluted in toluene. Column: 20-m methylpolysiloxane OV-1 on fused silica. Column temperatures: from 25 to 80°C with ballistic heating, from 80 to 320°C at 8°C/min; injector, 25–280°C, ballistic heating. Carrier gas: 0.4 bar hydrogen. Analysis time: 35 min.

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