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Application of programmed-temperature split/splitless injection to the trace analysis of aliphatic hydrocarbons by gas chromatography☆

M. Miñones Vázquez, M.E. Vázquez Blanco, S. Muniategui Lorenzo*, P. López Mahía, E. Fernández Fernández, D. Prada Rodríguez

Department of Analytical Chemistry, Faculty of Sciences, University of A Coruña, Campus A Zapateira s/n, 15071 A Coruña, Spain

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Abstract

The dependence of the programmed-temperature solvent split sampling technique using a PSS (programmed-split/splitless) injection mode on different variables affecting the introduction of large sample volumes for a mixture of alkanes in capillary GC was evaluated. Apart from the studies found in the literature on different factors such as speed of injection, presence of adsorbent in the liner, internal diameter of the liner, initial and final injector temperature, split flow-rate and initial split time, affecting the chromatographic signal of different compounds, others were studied whose influence has not been considered until now. They include length of the microsyringe needle, adsorbent distribution in the liner, injection volume on analyte discrimination, speed of injector heating, time which the column stays at the initial temperature and time that the injector stays at the final temperature. Once finalised, the study of the PSS injection mode was compared with the conventional mode of gas chromatography splitless injection, and found that the proposed method increases sensitivity in GC trace analysis. Finally, the application of both injection modes in the determination of aliphatic hydrocarbons was tested in an atmospheric particulate sample.

Keywords: Programmed-temperature split/splitless injection; Injection methods; Instrumentation; Air analysis; Programmed-temperature vaporiser; Environmental analysis; Hydrocarbons

1. Introduction

Analysis of aliphatic hydrocarbons from environmental matrices is difficult because they are frequently found at trace levels. Careful optimisation is required to minimise losses of volatile hydrocarbons and to decrease discrimination of some compounds over others. The major source of sampling discrimination is produced by selective vaporisation from the syringe needle when it is placed in a hot injector. Excessive temperatures in the injector give rise to decomposition of labile sample constituents [1]. Introduction of sample into cold injectors, as in techniques that include cold on-column injection and

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*Corresponding author. Tel.: +34-981-167-000; fax: +34-981-167-065.

E-mail address: smuniat@udc.es (S. Muniategui Lorenzo).

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programmed temperature injection [2–4], improves this situation.

On-column injection is the simplest and most reliable of these techniques. However, there are drawbacks to using this technique, the most important being contamination of the column inlet with non-volatile sample materials [5,6]. With programmed temperature sample introduction the negative effect of column contamination can be greatly avoided because non-volatile products are retained in a vaporising chamber without reaching the analytical column [5].

In 1964, Abel [7] proposed temperature-programmed sample introduction of C_8–C_{20} fatty acid methyl esters (FAMEs). In 1979 Vogt and co-workers [8,9] constructed a temperature programmable injector and applied it for the introduction of large sample volumes (up to 250 μl) of aliphatic hydrocarbons (C_{18}–C_{32}), in order to reduce detection limits to extreme levels. They assayed different volumes of sample, containing the same amounts of compounds. They also tested others factors as heating rate and type of solvent. In 1981 Poy et al. [1] demonstrated with pesticides, polycyclic aromatic hydrocarbons (PAHs) and aliphatic hydrocarbons (C_{10}–C_{40}), that temperature-programmed sample introduction offers many advantages in comparison with hot injection techniques. They showed that cold split or splitless injection reduced the discrimination of high-boiling-point components.

The use of liners packed with an adsorbent has been reported to be an efficient mean to minimise losses of volatiles [10]. A group of researchers [11–13] studied the influence of various packing materials (e.g., VolaspherA-2, Chromosorb W, glass wool and Tenax) for mixtures of alkanes (C_9–C_{19}), ethyl esters, alcohols and carboxylic acids, in order to minimise the losses of volatile compounds during solvent elimination. They also studied the splitting ratio, different end temperatures in the sampling device and type of solvent. Mol et al. [14] evaluated several types of materials for two test mixtures, as alternatives for glass wool packed liners and they found that PTFE wool and Dexsil were much more inert than glass wool.

Herraiz et al. [15] studied the influence of the sample amount, the injected volume (which affect to the retention power in the injector) and the nature of the solvent on the accuracy and precision with a synthetic mixture of alkanes (C_{11}–C_{20}), ethyl esters, alcohols and carboxylic acids. They found that 1 μl of Freon 11 provided the best accuracy and precision. In 1994 Medina et al. [16] evaluated the influence of some parameters as type of packing material, solvent elimination temperature, nature of the solvent and solute vaporisation temperature in the analysis of C_{14}–C_{22} FAMEs. The use of toluene as solvent, silanised glass-wool as packing material, and 45°C as the solvent elimination temperature during a splitting time of 60 s allows the determination of these compounds without discrimination.

Staniewski and Rijs [17] studied others parameters such as sample volume entering the injector without flooding it, liner design and temperature, speed of sample introduction and purge gas flow-rate by means of a theoretical model and with synthetic standard mixtures that contained alkanes and components of different polarity and volatility. The solvent elimination rate can be increased at increased purge gas flow-rates and a reduced pressure in the liner. Enlargement of the gas–liquid contact area improves the process of saturation of the purge gas by solvent vapour, which is beneficial in the solvent elimination process. Villén and co-workers [18–20] studied several parameters, such as maximum injected volume in the liner, solvent elimination flow, initial programmed-temperature vaporiser (PTV) temperature, nature of solvent and length and type of adsorbent by means of mathematical optimisation procedures with synthetic standard mixtures. The optimum conditions found are as follows: 25 μl, 80°C, methanol and Tenax length of 0.5 cm.

Mol et al. [21] evaluated and compared temperature programmable injectors with different liner diameters for solvent split injection of large volumes. PTV liners with internal diameters of 1.2, 2.3 and 3.4 mm were tested for mixtures of alkanes, and found that larger I.D. liners are advantageous because of their higher solvent capacity.

In this paper, a detailed study on the different factors affecting the chromatographic signal of various alkanes (C_{14}–C_{36} range) injected by programmed temperature injection is presented. The influence of some of the factors studied in this work has not been considered until now. These parameters include microsyringe needle length, adsorbent dis-

tribution in the liner, injection volume on analyte discrimination, speed of injector heating, the time the column stays at initial temperature and the time the injector stays at its final temperature. We also compared quantitative data obtained by programmed-split/splitless (PSS) and splitless injection modes. PSS is an injection method similar to the PTV; however, with the former, two temperature rates can be set in the same injection program, whereas with PTV, only one is possible. The range of molecular masses studied in this work is wide. Studies found in the literature focus on more limited ranges, because favourable conditions to the more volatile compounds often discriminate the compounds with higher molecular mass and vice versa.

2. Experimental

2.1. Instrumentation

A Perkin-Elmer (Norwalk, CT, USA) Autosystem gas chromatograph with a Turbochrom 4 software integrator, equipped with a flame ionisation detection (FID) system at 320°C, and a PSS injector was used.

Sample introduction was performed by means of an autosampler.

2.2. Test mixtures

A synthetic test mixture, consisting of aliphatic hydrocarbons, C_{14} to C_{36} from Alltech (Deerfield, IL, USA), C_{16} from Analyticals Carlo Erba (Milan, Italy) was used. Pristane and phytane were purchased from Larodan (Malmö, Sweden), and acetone and hexane from Romil (Cambridge, UK). Standard solutions (200 μg/ml) were prepared with hexane as solvent. In all experiments, a standard working solution with a concentration of 5 μg/ml was used.

In the series of measurements, each injection was repeated five times for statistical analysis.

2.3. Sample pretreatment

Real atmospheric particulate samples were Soxhlet extracted with hexane–acetone (1:1). The extract was evaporated and the residue redissolved in 1 ml of hexane, which was loaded onto a silica and alumina glass column. Aliphatic hydrocarbons were eluted with 2 ml of hexane. This fraction was concentrated and the residue redissolved in 1 ml of hexane prior to analysis by gas chromatography (GC)–FID.

2.4. Operating conditions

Helium was used as the carrier gas at an inlet pressure of 18 p.s.i. (1 p.s.i.=6894.76 Pa). For the GC separation a 30 m×0.25 mm, 0.25 μm fused-silica capillary column, coated with 5% diphenylmethylsiloxane Sugelabor (Madrid, Spain) was used.

The GC oven temperature programme for programmed temperature injection was kept at an initial temperature of 40°C for several times (0, 0.2, 0.8, 1.5, 2.45 and 3 min), then increased at 6°C/min to 300°C (held for 20 min, isothermal). In the case of splitless injection, the oven temperature programme was the same but with an initial temperature of 60°C and the initial isothermal time was 1 min.

The PSS injector was operated as a cold injector (with the solvent split mode) or a classical hot injector in the splitless mode.

A 10 μl Model 801 or a 50 μl Model 805 Hamilton (Reno, NV, USA) microsyringe with a needle length of 5 cm, and a 5- or 50-μl Perkin-Elmer XPress microsyringe with a needle length of 7 cm were used.

Two PSS quartz liners of 1 and 2 mm I.D. (Table 1) were used, both with a length of 8.6 mm. The vaporisation liner was used without packing or packed with a plug of silanised glass wool from Supelco (Bellefonte, PA, USA).

The samples were injected at low temperature while the split vent was opened for several initial split times (0.1, 0.2, 0.3, 0.5 and 0.75 min) and with different split flow-rates (5, 35, 40, 50 and 100 ml/min). After a certain time, the split vent was closed and the injector temperature was raised from 50 to 300°C at varying rates (6°C/min, 200°C/min and a combination). The combination ramp consisted of an initial heating rate of 6°C/min from 50 to 53°C and then, the temperature was increased from 53 to 300°C at a rate of 200°C/min. The final temperature was kept constant for different times (1, 3, 5, 7, 11 and 15 min). The injection took 1 s, a speed the

Table 1
Liners capacity according to their I.D.

Internal diameter (mm)	Maximum admitted amount of adsorbent (mg)	Maximum admitted volume (μl)	ΣAreas (mV s)
1	4	10	631
2	25	50	3345

Perkin-Elmer manual called ''normal'' for sample introduction, and five sample volumes were tried (5, 10, 15, 25 and 50 μl).

The splitless injection mode parameters were also optimised in order to compare this conventional method with the PSS one. The variables analysed included microsyringe needle length (5 or 7 cm), speed of injection (normal, slow or fast), injector temperature (300 or 310°C), split flow-rate (5 or 50 ml/min), split time (0.25 or 1.25 min), injection volume (0.5 or 1.5 μl) and adsorbent (presence or not) (see Table 2 for detection limits).

3. Results and discussion

Solvent evaporation creates a volume of vapour that tends to be underestimated and creates a strong pressure pulse that may expel sample vapours from the liner. Expulsion may be by an incorrect positioning of the vapour cloud. To place the site of evaporation near the bottom of the liner requires a long syringe needle [22]. Two different microsyringe needle lengths were used in this study, 5 and 7 cm. When the shorter one was employed with C_{24} to C_{36}, a significant decrease was observed in the signal and in precision. Chromatographic experiments were better when the 7 cm needle was used, because the sample liquid is released in the centre of the glass wool packing (Table 3).

The choice of PSS liner and packing is important. Other studies found in the literature analysed very volatile compounds, therefore, a special adsorbent like Tenax was needed [11,14,16]. In our work, this parameter was not studied; because a wide range of analytes (C_{14}–C_{36}) with very different volatilities was being used, such a critical adsorbent was not needed. In this regard, glass wool was chosen as adsorbent in the liner.

The behaviour of the PSS injection mode was studied when the liner was without adsorbent or

Table 2
Detection limits (ng/ml) for the two injection modes tested

Compound	Splitless	PSS
C_{14}	20	1.8
C_{15}	20	1.8
C_{16}	20	1.7
C_{17}	20	1.7
Pristane	30	1.9
C_{18}	20	1.8
Phytane	20	1.9
C_{19}	30	1.8
C_{20}	30	1.8
C_{21}	30	1.9
C_{22}	30	1.8
C_{24}	40	1.8
C_{27}	60	1.9
C_{28}	70	1.9
C_{32}	120	1.9
C_{36}	120	2.1

Table 3
Influence of needle microsyringe length (area in mV s)

Compound	7 cm needle	5 cm needle
C_{14}	260.79 (0.93)	254.89 (2.62)
C_{15}	259.99 (1.17)	259.49 (2.28)
C_{16}	263.91 (1.08)	262.85 (2.06)
C_{17}	270.86 (1.16)	268.63 (1.70)
Pristane	271.68 (0.93)	269.29 (1.75)
C_{18}	276.25 (1.26)	273.52 (1.27)
Phytane	271.61 (1.16)	269.39 (1.44)
C_{19}	279.76 (1.37)	276.64 (1.05)
C_{20}	275.74 (1.29)	272.41 (0.95)
C_{21}	270.63 (1.06)	265.85 (0.95)
C_{22}	278.95 (1.15)	274.42 (1.29)
C_{24}	276.17 (1.22)	271.17 (2.30)
C_{27}	275.35 (1.09)	267.76 (3.43)
C_{28}	276.72 (1.05)	269.58 (4.99)
C_{32}	267.77 (1.12)	254.58 (5.98)
C_{36}	260.34 (1.01)	246.31 (6.29)

Values in parentheses are ±1 standard deviation of the mean value of replicate injections; $n=5$.

packed with a plug of silanised glass wool, and found that the results were better with the packed liner. The degree of saturation increases when the gas–solvent contact area in the liner is enlarged. Packing the liner with glass wool appears to be an efficient means of increasing the contact area. Therefore, any modification, which results in an increased gas–solvent contact area, will be beneficial for the analysis [17,23,20].

An important parameter needed to take into account is the distribution of the packing material in the liner. No references that included this factor were found in the literature.

Three different distributions were tested:

(i) Distribution A: glass-wool was tightly packed at the bottom and loosely at the top.

(ii) Distribution B: glass-wool was homogeneously packed along the liner.

(iii) Distribution C: glass-wool was tightly packed at the top and loosely at the bottom.

As seen in Table 4, the highest-molecular-mass compounds were discriminated when the irregular distribution was used (A, C). A higher and more equal signal was observed for all the compounds when the packing was homogeneously placed.

Most of the programme temperature injectors are equipped with narrow liners, typically of 1 mm internal diameter, which can retain small amounts of solvent [21]. Therefore, in this work, two different sizes of liners were studied in order to increase the injected volume.

Table 1 shows the main differences between the liners analysed (1 and 2 mm I.D.). Their size presented limitations as to the amount of adsorbent and sample volume injected. When the 2 mm I.D. liner were used, a larger volume could be injected than with the 1 mm I.D. liner.

Liner volume is another significant variable to consider; too little volume limits sample size and increases the possibility of discrimination and sample loss [24]. The maximum volume of liquid that can be injected at once into the PSS system depends on the dimensions of the liner and the properties of the packing material and it is limited by the solvent elimination rate [17]. It was determined by trial and error, increasing volumes of liquid were injected. When the maximum volume was exceeded, liquid was pushed into the column, flooding its inlet. This caused band broadening in space, distorting all peaks.

No peak distortion was observed when introducing 50 μl volumes into a liner of 2 mm I.D. (Table 5). When volumes of 10 μl or less were injected, a discrimination of the more volatile compounds was observed. In 1979 Vogt et al. [9] studied the influence of sample volume (1 and 20 μl) on the linearity of the response, finding a correlation coeffi-

Table 4
Influence of distribution of the adsorbent in the liner (area in mV s)

Compound	Distribution A	Distribution B	Distribution C
C_{14}	261.63	239.37	245.75
C_{15}	250.76	244.96	250.48
C_{16}	250.21	252.05	256.11
C_{17}	244.60	249.04	253.55
Pristane	233.79	238.46	242.41
C_{18}	240.32	247.97	252.25
Phytane	254.64	263.95	267.77
C_{19}	244.90	255.36	259.35
C_{20}	239.46	253.53	256.58
C_{21}	234.78	253.12	255.89
C_{22}	230.91	254.54	254.57
C_{24}	222.88	256.40	248.77
C_{27}	208.19	253.41	229.34
C_{28}	207.56	253.41	228.11
C_{32}	188.98	254.10	205.23
C_{36}	178.11	253.73	183.19

Table 5
Influence of injection volume (expressed as area/injection volume in mV s/μl)

Compound	5 μl	10–15 μl	25 μl	50 μl
C_{14}	2.46	3.41	3.54	3.54
C_{15}	3.59	3.89	3.94	3.89
C_{16}	3.92	4.07	4.15	4.10
C_{17}	3.85	3.97	4.09	4.07
Pristane	3.61	3.76	3.88	3.87
C_{18}	3.79	3.94	4.07	4.09
Phytane	4.06	4.22	4.38	4.41
C_{19}	3.91	4.06	4.21	4.27
C_{20}	3.86	3.99	4.17	4.25
C_{21}	3.78	3.99	4.13	4.26
C_{22}	3.83	4.00	4.19	4.29
C_{24}	3.81	3.99	4.21	4.36
C_{27}	3.76	3.91	4.14	4.33
C_{28}	3.83	3.98	4.22	4.43
C_{32}	3.75	3.90	4.12	4.40
C_{36}	3.82	3.91	4.10	4.31

Table 6
Influence of speed of injector heating (area in mV s)

Compound	6°C/min	200°C/min	Combination
C_{14}	234.69	219.37	215.51
C_{15}	234.09	239.96	240.37
C_{16}	226.90	252.05	241.29
C_{17}	212.34	249.04	233.12
Pristane	205.46	238.49	222.63
C_{18}	203.40	247.97	230.17
Phytane	217.99	263.95	243.97
C_{19}	201.69	255.36	235.34
C_{20}	192.68	253.53	232.10
C_{21}	186.68	253.12	231.38
C_{22}	180.94	254.54	230.60
C_{24}	163.91	256.50	229.29
C_{27}	166.87	253.41	223.67
C_{28}	156.88	258.10	226.55
C_{32}	145.79	254.10	221.43
C_{36}	127.00	253.73	225.91

cient of 0.9999. This corresponds to a range of aliphatic hydrocarbons that begins with C_{18}, because of its medium volatility, no discrimination was found between compounds. As a range of compounds that starts with C_{14} (a hydrocarbon with high volatility) is being used, the discrimination becomes an important parameter to analyse.

The changes in the speed of injector heating will affect the response of the compounds. When the 6°C/min ramp was used, a big discrimination in the signal of the higher-molecular-mass analytes was produced, but there was an improvement in the signal of the C_{14} (with respect to the 200°C/min ramp). The best and more homogeneous signal was obtained when the 200°C/min ramp was used, but no great differences were observed between these and the combination ramp (Table 6)

With regard to the split flow-rate, 40 ml/min was chosen because it yielded the most uniform signal (Table 7). With 50 and 100 ml/min there was a slight discrimination of the higher-molecular-mass compounds.

The initial split time is the time during the split valve is opened. When the split valve remained open for long periods of time, there was a discrimination of the more volatile analytes (Table 8). The best split time was when the valve was open for times between 0.1 and 0.3 min.

It was observed that when the time that the column stands at the initial temperature was 0 min, a low signal was obtained, mainly for the less volatile compounds. This signal was improved by increasing the time of the initial temperature of the column (0.8 min) (Table 9).

When the time that the injector stands at its final temperature was 1 min, an extremely low signal was

Table 7
Influence of split flow-rate (area in mV s)

Compound	5 ml/min	35–40 ml/min	50 ml/min	100 ml/min
C_{14}	232.43	237.16	240.06	226.28
C_{15}	236.18	243.32	243.78	235.62
C_{16}	242.85	249.81	247.62	240.78
C_{17}	241.78	247.32	243.23	237.02
Pristane	241.82	246.70	242.72	236.94
C_{18}	247.79	251.45	236.83	230.29
Phytane	253.16	256.95	251.66	244.80
C_{19}	252.08	253.99	248.30	241.41
C_{20}	252.67	252.35	245.75	239.10
C_{21}	254.46	252.92	246.56	239.40
C_{22}	256.52	253.41	245.99	238.47
C_{24}	260.11	254.69	247.05	239.08
C_{27}	258.50	250.62	243.27	235.01
C_{28}	263.61	254.93	247.49	238.39
C_{32}	261.09	250.24	242.65	234.71
C_{36}	262.74	251.29	244.02	237.40

Table 8
Influence of initial split time (area in mV s)

Compound	0.1–0.3 min	0.5 min	0.75 min
C_{14}	215.60	157.55	117.83
C_{15}	231.91	238.69	177.19
C_{16}	245.76	244.60	231.07
C_{17}	243.12	245.37	242.47
Pristane	232.77	234.93	232.28
C_{18}	242.46	244.48	243.36
Phytane	257.67	259.62	258.34
C_{19}	250.08	251.41	248.93
C_{20}	248.87	249.11	245.08
C_{21}	249.76	248.68	243.04
C_{22}	250.33	247.35	240.84
C_{24}	252.06	246.60	237.53
C_{27}	248.56	239.35	229.83
C_{28}	253.00	242.50	232.88
C_{32}	248.75	234.98	227.15
C_{36}	249.74	232.59	228.94

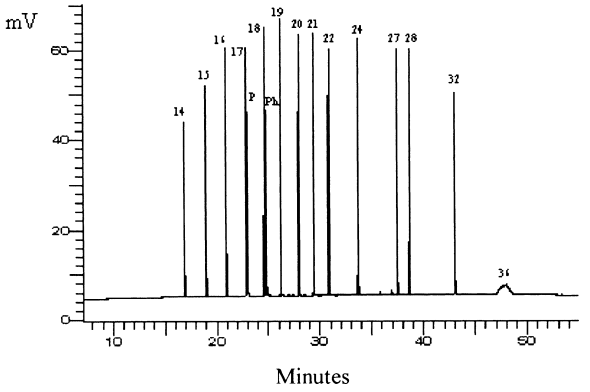


Fig. 1. Chromatogram of a synthetic mixture when the injector stays at the final temperature during 1 min.

obtained for the C_{36} compound (Fig. 1), and there was band broadening in space, distorting the peak. There were not differences in the results if times between 3 and 15 min were applied (Table 10).

It is worth noting that although the last two variables analysed greatly influence the optimisation of the programmed-temperature technique, no study was found on these in the literature search.

The PSS injection mode was optimised by the study of the variables mentioned, and subsequently, it was compared with the optimised splitless injection mode. The optimum values found for splitless injection were microsyringe needle length of 7 cm, normal speed of injection, injector temperature of 300°C, split flow-rate of 5 ml/min, split time 0.25 min, injection volume of 0.5 μl and no adsorbent in the liner of 1 mm I.D.

Once the optimum values of the variables analysed were established, the synthetic mixture containing the range of hydrocarbons was injected by the two

Table 9
Influence of time the column stays at its initial temperature (area in mV s)

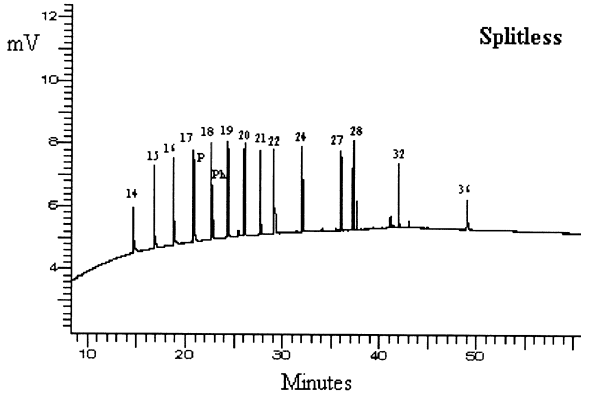
Compound	0 min	0.2 min	0.8 min	1.5–3 min
C_{14}	234.90	234.76	245.92	241.18
C_{15}	240.56	240.84	252.01	247.34
C_{16}	244.70	245.49	256.84	251.82
C_{17}	240.73	242.16	253.77	248.37
Pristane	242.69	244.05	254.87	249.87
C_{18}	250.52	252.11	263.87	258.38
Phytane	247.36	249.07	260.53	255.30
C_{19}	252.97	254.94	267.01	261.45
C_{20}	249.48	251.60	263.50	258.14
C_{21}	250.84	253.06	263.32	258.70
C_{22}	253.71	258.34	266.94	262.41
C_{24}	252.30	259.73	265.35	261.61
C_{27}	250.67	260.95	264.02	261.88
C_{28}	251.95	263.25	265.74	264.01
C_{32}	251.52	262.69	265.96	265.57
C_{36}	242.39	252.71	256.70	257.04

Table 10
Influence of time the injector stays at its final temperature (area in mV s)

Compound	1 min	3–15 min
C_{14}	239.06	240.47
C_{15}	246.18	246.73
C_{16}	252.29	251.81
C_{17}	259.75	258.26
Pristane	251.46	250.00
C_{18}	260.31	258.14
Phytane	257.14	255.05
C_{19}	263.88	261.24
C_{20}	260.94	257.92
C_{21}	261.50	258.57
C_{22}	264.94	262.31
C_{24}	264.54	262.24
C_{27}	264.79	262.86
C_{28}	267.28	265.20
C_{32}	268.51	266.40
C_{36}	190.32	267.75

injection methods studied. A greater signal was produced when the sample was injected by means of PSS injection mode, avoiding the discrimination of the higher-molecular-mass compounds (Fig. 2).

Linearity range for splitless injection was 0.05–200 μg/ml, and 3.5 ng/ml–6 μg/ml for PSS injection. In the case of the more volatile hydrocarbons, the detection limits were 10 times higher in the splitless than in the PSS injection, and 60 times higher in the less volatile analytes (Table 2), varying between 0.02 and 0.12 ng/ml for splitless and 1.7 and 2.1 ng/ml for PSS injection. The relative standard deviations (RSDs) for the splitless were between 1.5 and 2.5% and for the PSS injection, between 0.4 and 1.2%. Therefore, the PSS injection mode was chosen for the determination of aliphatic hydrocarbons in atmospheric particulate samples.



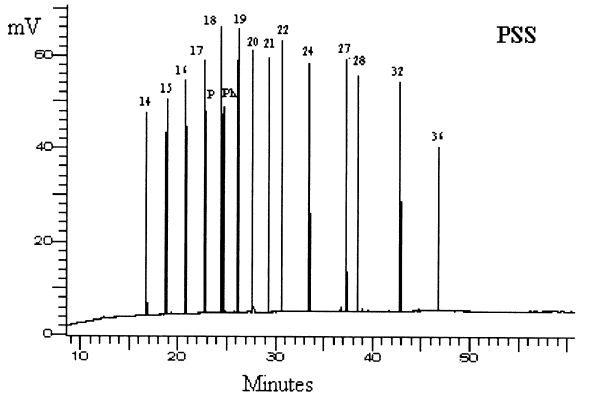
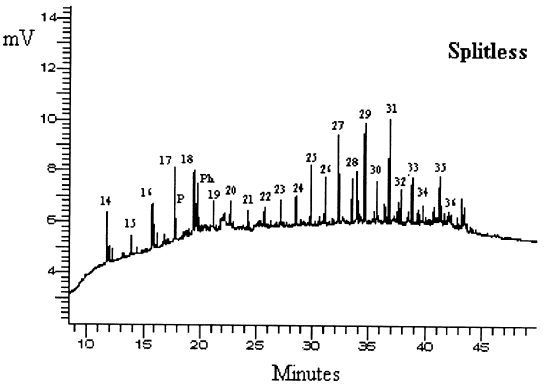


Fig. 2. Chromatograms of a synthetic mixture of 5 μg/ml injected by the two injection methods.



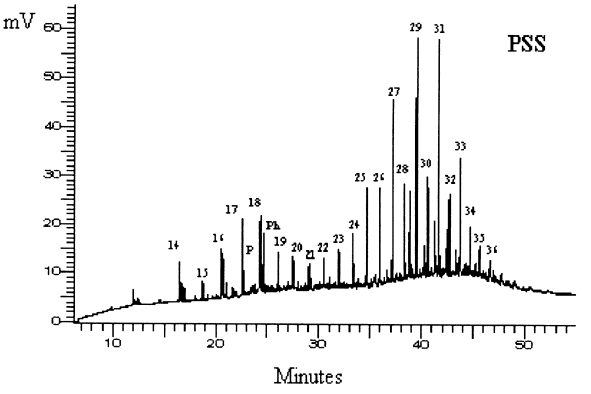


Fig. 3. Chromatograms of an extracted sample injected by the two injection methods.

Then, an extracted atmospheric particulate sample was injected by the two injection methods (Fig. 3). When the PSS mode was used the best results were obtained. With this injection method a greater signal is obtained, making it easier to integrate compounds that appears at low concentrations.

4. Conclusions

Using a PSS injection mode, the selected conditions increase sensitivity in the trace analysis of a

wide range of aliphatic hydrocarbons and provide the best performance of the analysis. The PSS technique consist in injecting 50 μl of sample by discharging a microsyringe with a 7 cm needle quickly (1 s) into a liner of 2 mm I.D. homogeneously packed with glass wool. During injection the split vent was open for an initial split time below 0.3 min in order to vent the solvent with a split flow-rate of 40 ml/min. Then, the split vent was closed and the injector was heated at a high rate and remains at its final temperature for 11 min. The split valve was closed 2.45 min after the start of the chromatographic analysis. The column is maintained at its initial temperature during this step (0.8 min) and then the temperature programme is continued.

Comparing the two injection techniques (splitless and PSS), PSS solvent split is clearly superior, being an attractive alternative to splitless injection. The reasons are that with the PSS injection method, there are not problems due to selective vaporisation in a hot microsyringe needle, and it causes far less discrimination of high boiling and adsorptive compounds than conventional splitless injection.

The use of PSS injection in the solvent split mode provides the best detection limit and precision for mixtures containing C_{14}–C_{36} alkanes in comparison with data obtained by classical splitless mode. The proposed gas chromatographic sampling technique increases the sensitivity in trace analysis, and good recoveries and satisfactory RSD values can be obtained when it is used in the analysis of atmospheric particulate samples.

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