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EVALUATION OF A PROGRAMMED TEMPERATURE VAPORIZER FOR QUANTITATIVE ANALYSIS BY SPLIT INJECTION

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SUMMARY

The influence of several parameters affecting sampling with cold temperature-programmed injection were studied. The parameters were types and lengths of packings used in the glass insert, end temperatures in the sampling device, solvents and splitting ratio. The accuracy and precision of the sampling was measured for a test mixture of *n*-alkanes using a programmed temperature vaporizer in the split mode.

INTRODUCTION

In order to achieve desirable accuracy and precision in a quantitative analysis, first it is necessary to consider the type of sample to be analyzed such as its dilution, the number of components and their volatilities, concentrations and thermal stabilities. It is also essential to consider all the possibilities and restrictions of the sampling techniques that are now available. The most reliable procedure for any given analysis can then be chosen.

Irreversible adsorption on the column or lack of linearity or stability of the detector can bring about systematic errors when quantitative analysis is carried out, but the main source of error occurs during sample introduction. In spite of recent studies on sample introduction into capillary columns, it is unlikely that an universal injection system will be ideal for all types of separations. Consequently, it is of great importance carefully to optimize all of the experimental parameters of the sample introduction system to be used.

In general, cold sample introduction is preferred especially when quantitative analyses of high precision and accuracy are to be made[1]. The cold-on-column injection procedure[2,3] gives excellent quantitative data provided that the experimental parameters have been carefully optimized. The programmed temperature vaporizer (PTV)[4,5] allows a cold injection either in the split or in splitless mode. Several studies

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TABLE I

PRECISION AND ACCURACY OF RELATIVE PEAK AREAS FOR A DISCRIMINATION TEST MIXTURE DURING PTV-INJECTION ONTO A GLASS INSERT CONTAINING VARIOUS PACKINGS

M = Average value (from five measurements) of relative (normalized) peak area; C.V. = coefficient of variation of relative peak area.

Compound	*Concentration (%, w/w)*		*Packing material*									
			None	*Glass beads*		*Volaspher*		*Chromosorb W*		*Glass wool*		
				1 cm	*2 cm*	*1 cm*	*2 cm*	*1 cm*	*2 cm*	*1 cm*	*2 cm*	*3 cm*
C_9	9.97	*M*	12.38	7.92	7.12	6.89	7.21	5.23	8.17	7.95	8.74	10.61
		C.V. (%)	10.98	6.81	9.65	5.55	3.44	12.37	2.40	4.16	7.61	2.90
C_{10}	9.97	*M*	10.29	8.69	7.49	9.14	8.83	7.03	8.55	8.43	9.18	7.30
		C.V. (%)	10.74	2.58	5.82	1.26	2.68	9.48	1.36	4.27	7.44	6.03
C_{11}	10.03	*M*	9.47	10.50	9.26	9.32	9.39	8.32	9.06	8.74	9.93	10.29
		C.V. (%)	9.75	2.90	8.36	1.02	0.98	4.15	0.73	3.71	2.96	1.49
C_{12}	9.97	*M*	9.74	10.47	9.23	9.28	9.45	9.08	9.23	9.39	10.12	10.14
		C.V. (%)	2.10	2.88	8.84	0.70	1.39	3.32	1.81	2.99	1.78	0.75
C_{13}	10.03	*M*	9.55	10.42	9.67	9.43	9.79	9.72	9.32	9.84	11.23	9.35
		C.V. (%)	1.72	2.75	8.34	0.23	3.14	3.15	3.49	2.15	6.89	1.27
C_{14}	9.97	*M*	9.20	10.86	11.14	10.09	10.52	11.62	10.20	10.85	11.65	10.37
		C.V. (%)	4.65	5.92	5.54	3.88	4.00	3.02	0.71	1.07	6.45	2.50
C_{15}	9.97	*M*	9.27	11.12	12.02	10.81	10.91	11.94	10.64	11.26	12.32	10.16
		C.V. (%)	7.19	11.85	3.54	1.39	1.31	2.88	0.97	1.80	4.18	2.75
C_{16}	10.03	*M*	9.34	10.42	10.58	9.55	9.57	10.23	9.39	9.98	9.71	10.55
		C.V. (%)	7.11	8.02	3.64	1.20	1.15	3.36	1.24	1.47	2.02	4.50
C_{18}	10.10	*M*	10.11	10.17	11.77	11.54	11.21	12.17	11.61	10.91	8.27	10.32
		C.V. (%)	10.25	9.25	11.50	0.56	2.08	3.45	1.51	1.90	6.21	0.75
C_{19}	9.97	*M*	10.64	9.22	11.60	13.06	12.32	14.20	13.25	11.80	7.09	10.90
		C.V. (%)	14.41	13.28	18.71	1.06	3.94	4.23	2.08	3.32	14.13	2.06

have shown that the PTV-splitless technique yields good quantitative data[4,6,7]. Furthermore, Poy *et al.*[8,9] have obtained good results using PTV-injection in the split mode. However, it was reported that use of the latter technique can bring about some discrimination favouring volatile constituents if poor sealing of the vaporization insert or imperfect separation of the column flow line from the split flow line results in undefined splitting conditions[7]. To overcome this problem, Schomburg *et al.*[1,10,11] proposed the so-called "cooled needle technique" for split as well as splitless sampling by cold injection onto capillary columns.

In spite of the papers that have been published on the evaluation and optimization of the PTV, further investigations are necessary. In this work we have studied the effect of sampling parameters such as the end temperature in the sampling device, volatility of the solvent and splitting ratios on the performance of PTV injection in the split mode. Since previous experiments on vaporizing injectors carried out in our laboratory[13] as well as by others[2,12] showed that the packing material of the glass insert caused several problems, it was also evaluated in this work.

EXPERIMENTAL

A Perkin-Elmer PTV cold injector coupled to a Perkin-Elmer 8320 gas chromatograph with the required software to integrate peak areas was used. This commercial PTV design provides a proper sealing of the injector at the bottom and does not produce changes in pressure within the injector chamber; a defined splitting ratio is thereby obtained.

The following instrumental conditions were used: column, 50 m × 0.2 mm I.D. fused-silica capillary coated with a 0.2-μm layer of cross-linked Carbowax 20M; temperature programme, column, 60°C for 3 min then raised at 10°C/min to 220°C, PTV, from 40°C to 250, 300, 350 or 400°C raised at 14°C/s; detector, flame ionization at 300°C; carrier gas (helium) flow-rate injector, 150 ml/min; splitting ratio, 1:100, 1:140 or 1:200; vaporization glass tubes: 90 mm × 1 mm I.D. × 2 mm O.D.

In all cases the amounts sampled were identical (1600 ng of each compound) and injections were made by discharging the syringe quickly after needle insertion. A 10-μl standard Hamilton Model 701N syringe having a needle length of 5 cm was used.

A mixture containing C_9–C_{19} *n*-alkanes in *n*-pentane, *n*-hexane or *n*-heptane was used. The weight percentages of the *n*-alkanes are given in Table I.

In each series of measurements, each injection was repeated five times for statistical reasons. The PTV injector was operated only in the split mode. The vaporization insert was used without packing as well as packed with different materials provided in plugs of several lengths: deactivated glass wool (length of the plug 1, 2 and 3 cm); glass beads (100–120 mesh) (lengths 1 and 2 cm); Volaspher A-2 (100–120 mesh) (lengths 1 and 2 cm), a siliceous synthetic support for gas chromatography from Merck; and Chromosorb W HP (80–100 mesh) (lengths 1 and 2 cm). For all of the measurements, the position of the plug with respect to the syringe needle at injection was not varied.

After setting up the most suitable packing material, four different end temperatures (250, 300, 350 and 400°C) in the sampling device were tested. The influence of the boiling point of the solvent to be used for dilution was also considered by

substituting *n*-pentane or *n*-heptane for *n*-hexane. Finally, three different splitting ratios were studied.

RESULTS AND DISCUSSION

Table I shows the mean values and the coefficients of variation of the relative peak areas obtained for each compound with each of the packing materials tried. For each packing material, the Cochran test[14] was used to investigate the hypothesis of equal variances. The packings whose variances were not homogeneous were not used for further study. For example, the glass insert without packing was excluded because it gave high variances for C_9, C_{10}, C_{11}, C_{18} and C_{19}. The use of a glass insert packed with 1 cm of glass beads was also excluded as it gave poor quantitation for C_{15}, C_{16}, C_{18} and C_{19}. A glass liner packed with 2 and 3 cm of deactivated glass wool, 1 cm of Chromosorb W and a 1-cm plug of deactivated glass wool were also not studied further.

Thus Volaspher A-2 (1 and 2 cm) and Chromosorb W (2 cm) were the only packings from which data with homogeneous variances were obtained. Subsequently, the analysis of variance showed insignificant differences for these three packings and all of them were suitable for the analysis in this work. We selected Volaspher A-2 because the length of the packing did not seem to affect the sample introduction. This property is advantageous for obtaining reproducible results when the packing material is changed for cleaning purposes. A 2-cm plug of Volaspher A-2 was selected for further study since its use provided the lowest values of the coefficients of variation of the absolute peak areas. Comparative data for the best three packings are shown in Table II.

Four different end temperatures in the sampling device were studied. Table III shows the average value of the relative peak areas as well as its coefficient of variation. Table IV gives the coefficients of variation of the absolute peak areas obtained from the test mixture used. Cochran's test demonstrated in this case that homogeneous

TABLE II

COEFFICIENTS OF VARIATION OF ABSOLUTE PEAK AREAS USING A PTV WITH DIFFERENT PACKINGS MATERIALS

Compound	*Packing material*		
	Volaspher, 1 cm	*Volaspher, 2 cm*	*Chromosorb W, 2 cm*
C_9	13.42	6.54	18.62
C_{10}	14.54	4.89	17.48
C_{11}	14.84	5.98	17.60
C_{12}	15.08	7.30	17.58
C_{13}	15.03	4.64	20.75
C_{14}	15.42	4.43	17.79
C_{15}	15.09	6.68	17.60
C_{16}	15.62	6.87	17.49
C_{18}	13.57	7.90	16.51
C_{19}	15.61	9.68	16.67

TABLE III

ACCURACY AND PRECISION OF RELATIVE PEAK AREAS IN DISCRIMINATION TESTS USING A PTV AT DIFFERENT END TEMPERATURES

M and C.V. as in Table I.

Compound		*End temperature (°C) in the sampling device*			
		250	*300*	*350*	*400*
C_9	*M*	8.56	9.06	8.82	7.21
	C.V. (%)	7.21	2.24	2.47	3.28
C_{10}	*M*	9.45	9.71	9.53	8.83
	C.V. (%)	2.19	1.16	0.98	2.12
C_{11}	*M*	9.62	9.80	9.75	9.39
	C.V. (%)	0.93	0.92	0.79	2.14
C_{12}	*M*	9.68	9.88	9.84	9.45
	C.V. (%)	0.72	0.48	0.88	1.98
C_{13}	*M*	9.89	10.04	10.05	9.79
	C.V. (%)	0.01	0.44	0.80	1.44
C_{14}	*M*	10.09	10.19	10.22	10.52
	C.V. (%)	0.91	0.62	1.26	0.63
C_{15}	*M*	10.48	10.50	10.51	10.91
	C.V. (%)	0.96	0.79	1.60	1.79
C_{16}	*M*	9.01	8.97	9.04	9.57
	C.V. (%)	1.12	1.04	1.05	2.17
C_{18}	*M*	10.49	9.98	10.17	11.21
	C.V. (%)	3.16	0.80	1.91	2.30
C_{19}	*M*	11.93	11.18	11.29	12.32
	C.V. (%)	4.40	1.36	1.98	2.30

TABLE IV

COEFFICIENTS OF VARIATION OF ABSOLUTE PEAK AREAS IN DISCRIMINATION TESTS USING A PTV AT DIFFERENT END TEMPERATURES

Compound	*End temperature (°C) in the sampling device*			
	250	*300*	*350*	*400*
C_9	13.47	4.11	5.44	1.95
C_{10}	13.98	4.10	3.98	1.04
C_{11}	14.20	5.00	3.06	5.37
C_{12}	14.44	5.26	2.80	0.43
C_{13}	7.72	4.86	3.02	0.90
C_{14}	14.23	5.02	3.75	2.11
C_{15}	14.96	4.83	2.26	2.73
C_{16}	14.75	5.57	1.90	4.21
C_{18}	16.45	5.49	4.47	4.38
C_{19}	17.33	5.93	4.42	4.38

TABLE V

INFLUENCE OF THE SOLVENT TYPE ON THE ACCURACY AND PRECISION OF QUANTITATIVE DATA OBTAINED IN PTV-SPLIT INJECTION

M and C.V. as in Table I.

Compound	*n-Pentane*			*n-Hexane*			*n-Heptane*		
	M	*C.V. (Absolute areas) (%)*	*C.V. (Relative areas) (%)*	*M*	*C.V. (Absolute areas) (%)*	*C.V. (Relative areas) (%)*	*M*	*C.V. (Absolute areas) (%)*	*C.V. (Relative areas) (%)*
C_9	8.82	5.44	2.47	9.10	4.33	1.69	9.46	8.59	7.21
C_{10}	9.53	3.98	0.98	8.58	6.01	4.12	8.77	4.11	1.45
C_{11}	9.75	3.06	0.79	8.95	4.03	2.19	8.44	4.01	1.13
C_{12}	9.84	2.80	0.88	9.09	3.74	1.82	8.72	3.78	0.66
C_{13}	10.05	3.02	0.80	9.26	3.48	0.96	9.15	3.05	0.54
C_{14}	10.22	2.75	1.26	9.38	3.21	0.70	9.52	2.90	0.67
C_{15}	10.51	2.26	1.66	9.61	2.68	0.74	9.72	2.66	1.02
C_{16}	9.04	1.90	1.05	8.58	4.55	0.77	8.66	2.69	1.52
C_{18}	10.17	4.47	1.91	11.06	2.31	1.03	11.10	2.58	1.31
C_{19}	11.29	4.42	1.98	13.03	2.27	0.99	13.08	2.45	1.55

TABLE VI

EFFECT OF THE SPLITTING RATIO ON THE ACCURACY AND PRECISION OF QUANTITATIVE DATA USING A PTV

M and C.V. as in Table I.

Compound	*Splitting ratio 1:100*			*Splitting ratio 1:140*			*Splitting ratio 1:200*		
	M	*C.V. (Absolute areas) (%)*	*C.V. (Relative areas) (%)*	*M*	*C.V. (Absolute areas) (%)*	*C.V. (Relative areas) (%)*	*M*	*C.V.(Absolute areas) (%)*	*C.V. (Relative areas) (%)*
C_9	8.09	7.74	6.55	8.82	5.44	2.47	8.65	1.11	2.03
C_{10}	8.79	5.97	4.09	9.53	3.98	0.98	9.07	1.45	0.88
C_{11}	9.26	5.85	0.51	9.75	3.06	0.79	9.10	0.82	0.87
C_{12}	9.41	4.94	1.76	9.84	2.80	0.88	9.15	1.64	1.00
C_{13}	9.62	4.84	1.65	10.05	3.02	0.80	9.25	1.22	0.70
C_{14}	9.81	4.68	1.58	10.22	2.75	1.26	9.47	1.66	1.53
C_{15}	9.98	4.67	1.28	10.51	2.26	1.66	9.54	1.50	0.97
C_{16}	8.84	4.77	1.81	9.04	1.90	1.05	8.34	1.44	0.57
C_{18}	11.36	4.35	0.79	10.17	4.47	1.91	10.68	1.76	0.97
C_{19}	13.14	4.63	0.77	11.29	4.42	1.98	12.02	1.85	1.19

variances are obtained only if the end temperature in the sampling device is either 300 or 350°C. Since the coefficients of variation of the absolute peak areas are lower if the end temperature is 350°C, we selected it for further experiments.

The effect of the solvent type upon the accuracy and precision of quantitative data is summarized in Table V. *n*-Pentane provided the best coefficients of variation of the relative peak areas as well as of the absolute peak areas. On the other hand, Cochran's test revealed that the most volatile solvent was the most suitable.

In regard to the splitting ratio (Table VI), the statistical study of the relative peak areas showed poor performance with a splitting ratio of 1:100 and also that homogeneous variances were obtained with a splitting ratio of either 1:140 or 1:200. Moreover, the last ratios gave no significant differences in performance.

CONCLUSIONS

Using a PTV, packings with Volaspher A-2 provided the best accuracy and precision of absolute and relative peak areas for a test mixture containing C_9–C_{19} *n*-alkanes. Therefore this packing material gave the most complete vaporization and homogenization of the injected sample. It has a further advantage with regard to practical work, *i.e.*, in removing involatile residues by changing the glass insert. The length of the Volaspher A-2 plug in the glass insert seems to have little influence on the performance of the cold temperature-programmed injection. Moreover, the compactness of the plug can easily be reproduced, while in this respect other materials (like glass wool) could cause particular problems.

In regard to the end temperature in the sampling device, solvent type and splitting ratio, the best results were obtained when the temperature in the sampling device was set close to 350°C, a solvent of not too high volatility was used and the analysis performed with a splitting ratio between 1:140 and 1:200.

This work suggests that for quantitative measurements using cold temperature-programmed injection, critical parameters such as the packing material, solvent volatility, etc., should be optimized for the particular mixture to be analyzed.

In comparison with earlier experiments on vaporizing injectors[13], we conclude that PTV injection in the split mode seems to provide better performance than classical split injection for the particular conditions (type of test mixture, amount sampled, injector temperature, carrier gas, splitting ratio, glass insert packing, etc.) that were used. On the other hand, further measurements with test mixtures containing higher polarity compounds should be made to evaluate the performance of the PTV for wider applicability. These studies are currently underway and will be discussed in a forthcoming paper.

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