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Note

Programmable temperature vaporizer applications in an high-resolution gas chromatographic method for the quantitation of impurities in illicit heroin

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The problem of comparison of various heroin batches in forensic toxicology is of great importance. The delicacy of this task, the results of which are often used as evidence of illicit narcotic dealing, requires an extreme precision and accuracy of quantitative data. In the heroin mixtures available on the street, the "marker" used for comparison is the concentration of impurities or, better, the ratios between these substances. In fact, these products, *i.e.*, 6-monoacetylmorphine, acetylcodeine, papaverine, narcotine, are present, in all heroin mixtures in minor or major concentrations; some of these are unchanged in time and their concentration ratios are therefore independent of subsequent dilutions or adulterations. Only 6-monoacetylmorphine changes in concentration with time, because of the low stability of the acetyl group in the 6-position; acetylcodeine, on the contrary, is more stable, so that traces of codeine are seldom present in the mixtures. Papaverine and narcotine concentrations are the most stable of the impurities.

Gas–liquid, high-performance liquid, and most often high-resolution gas chromatography (HRGC) on capillary columns have been employed to separate these substances and good results were obtained, especially with temperature-programmed methods[1–15]. In HRGC, the traditional "split", and the "split–splitless" inlet in a single injection block, offer some advantages but some limitations also: insufficient accuracy of quantitative data; discrimination of high-molecular-weight compounds; poor linearity of the detector response, especially at low concentrations. These disadvantages can be obviated with the "on-column" capillary inlet; however this system has other inconveniences, and it is complementary and not substitutive of the "split–splitless" inlet. Ideally, an inlet for capillary columns should provide the following: improved accuracy and precision over conventional split–splitless injection; reduced discrimination of high-molecular-weight compounds; the possibility of injecting thermally sensitive samples. Our experience has demonstrated that all these aims can be achieved by employing a programmable temperature vaporizer inlet (PTV).

The PTV inlet is essentially a split–splitless capillary inlet which is temperature programmable. It eliminates the discrimination problems when analysing compounds with a large range of boiling points, with a consequent high linearity and reproducibility. The sample can be introduced from the syringe needle into the inlet

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under cold conditions, eliminating the major cause of sample discrimination and also reducing chances for sample thermolysis. After introduction, the sample is rapidly vaporized, because of the rapidity of heating of the inlet: its temperature is programmable from 50 to 400°C; the PTV inlet is heated to 200°C within 10 s, evenly across the entire inlet. The time to 90% temperature increase is about 30 s. The heating system of the injector body is programmed using an air flow; the vaporizer is a quartz liner; the splitting ratio is set as desired and programmable with an automatic valve (in split or in split–splitless mode). Rapid cooling of the injector is a further benefit of this injection system. Furthermore it is possible to obtain a pre-separation of solvent from the solute by selecting the "solvent purge" mode; here, the solvent is vented during cold injection. Once the purge is complete, the split valve is closed and the sample, remaining in the inner liner, is vaporized into the column by temperature programming in the inlet, reducing the peak profile distortion.

We applied this inlet system from some months in our studies on heroin mixtures, planning experimentally all parameters for simultaneous separation of narcotics from manufacturing and/or original products, varying the inlet and the oven programmable temperature and computing the standard deviation and coefficient of variation of for some analyses of illicit heroin samples.

EXPERIMENTAL

Equipment

A Perkin-Elmer series 8500 PTV gas chromatograph for capillary columns with a data handling facility was used. Injector: PTV capillary inlet, 45–370°C; split flow on (50 ml/min) from 1.0 min to the end of analysis. Detector: flame ionization, at 350°C. Oven: 240°C for 1.0 min; 10°C/min to 300°C; 300°C for 3.0 min. Column: DB-1 fused-silica capillary, 30 m × 0.253 mm I.D., 0.25-μm film. Carrier: hydrogen at 20 p.s.i.

Materials

Heroin, 6-monoacetylmorphine, acetylcodeine, papaverine, and narcotine were part of the reference collection of our Forensic Toxicology Laboratory. Dieldrin was obtained from Fluka (Buchs, Switzerland). All reagents, analytical grade, were obtained from E. Merck (Darmstadt, F.R.G.).

Method

The calibration graphs were constructed from alcoholic solutions of standard pure substances at known concentrations selected to correspond to those of the same substances in illicit heroin street samples. The concentration ranges were: heroin, 0.600–9.600; 6-monoacetylmorphine, 0.0625–1.000; acetylcodeine, 0.065–1.040; papaverine and narcotine, 0.125–2.000 mg/ml. Each graph was based on five concentrations. The internal standard was dieldrin, in alcoholic solution at 0.250 mg/ml.

An aliquot of each calibration solution was injected into the column. Ten determinations at different times were carried out for each concentration of each calibration solution group. The average value ($\pm$S.D.) of the ratios substance:internal standard for each calibration point was used to study the linearity of the response, the reproducibility and the precision of the quantitative data.

A linear relationship between the substance amount and the ratio substance/internal standard was observed for each calibration point. An excellent reproducibility

was obtained for each substance at each concentration: the coefficient of variation (C.V.) was in all cases very low (Table I).

On the basis of these calibration graphs, twenty illicit heroin samples, seized in the Florence area, were examined. The samples were chosen from a large number of mixtures, picking out those in which the quantitative composition as regards the heroin percentage might range from a very low to the highest concentration, with all impurities present, at various concentrations.

An 10-mg amount of each sample was homogenized and dissolved in 1.0 ml of ethanol; 1.0 ml of the internal standard solution was added and the contents of heroin, 6-monoacetylmorphine, acetylcodeine, papaverine and narcotine were calculated by reference to the calibration graphs with "data handling" according to the "internal standard method". Each heroin sample solution was examined ten times, and the average of all results, expressed as a percentage of the sample weight, was employed to calculate the standard deviation and the coefficient of variation. Fig. 1 shows a typical chromatogram obtained from an illicit heroin sample.

RESULTS AND DISCUSSION

Table II shows the composition of the twenty heroin samples chosen for the present study. The aim of the study was the evaluation of the performance of the GC capillary column method with the programmable temperature inlet. In fact the PTV

TABLE I

CALIBRATION DATA FOR EACH SUBSTANCE TESTED AT FIVE DIFFERENT CONCENTRATIONS

$n = 10$.

Substance	*Standard solutions: calibration*						*Regression equation*
Heroin	Concentrations (mg/ml)	0.600	1.200	2.400	4.880	9.600	$y = 0.59x - 0.255$
	Ratios average	0.125	0.327	1.226	2.632	5.359	($r^2 = 0.999$)
	S.D.	0.051	0.030	0.045	0.110	0.042	
	C.V. (%)	1.05	1.24	2.48	2.19	0.68	
Monoacetylmorphine	Concentrations (mg/ml)	0.0625	0.125	0.250	0.500	1.000	$y = 0.99x - 0.021$
	Ratios average	0.050	0.108	0.224	0.452	0.983	($r^2 = 0.999$)
	S.D.	0.005	0.015	0.021	0.030	0.025	
	C.V. (%)	1.85	1.28	0.80	0.79	1.83	
Acetylcodeine	Concentrations (mg/ml)	0.065	0.130	0.260	0.520	1.040	$y = 1.08x - 0.007$
	Ratios average	0.064	0.134	0.270	0.555	1.098	($r^2 = 0.999$)
	S.D.	0.002	0.001	0.003	0.003	0.004	
	C.V. (%)	2.46	1.27	1.30	0.98	1.25	
Papaverine	Concentrations (mg/ml)	0.125	0.250	0.500	1.000	2.000	$y = 0.72x - 0.034$
	Ratios average	0.070	0.151	0.319	0.665	1.420	($r^2 = 0.999$)
	S.D.	0.001	0.002	0.006	0.005	0.032	
	C.V. (%)	1.24	0.95	2.02	0.79	2.58	
Narcotine	Concentrations (mg/ml)	0.125	0.250	0.500	1.000	2.000	$y = 0.30x - 0.018$
	Ratios average	0.028	0.061	0.127	0.263	0.588	($r^2 = 0.999$)
	S.D.	0.001	0.001	0.006	0.012	0.018	
	C.V. (%)	1.55	1.80	2.80	1.55	3.85	

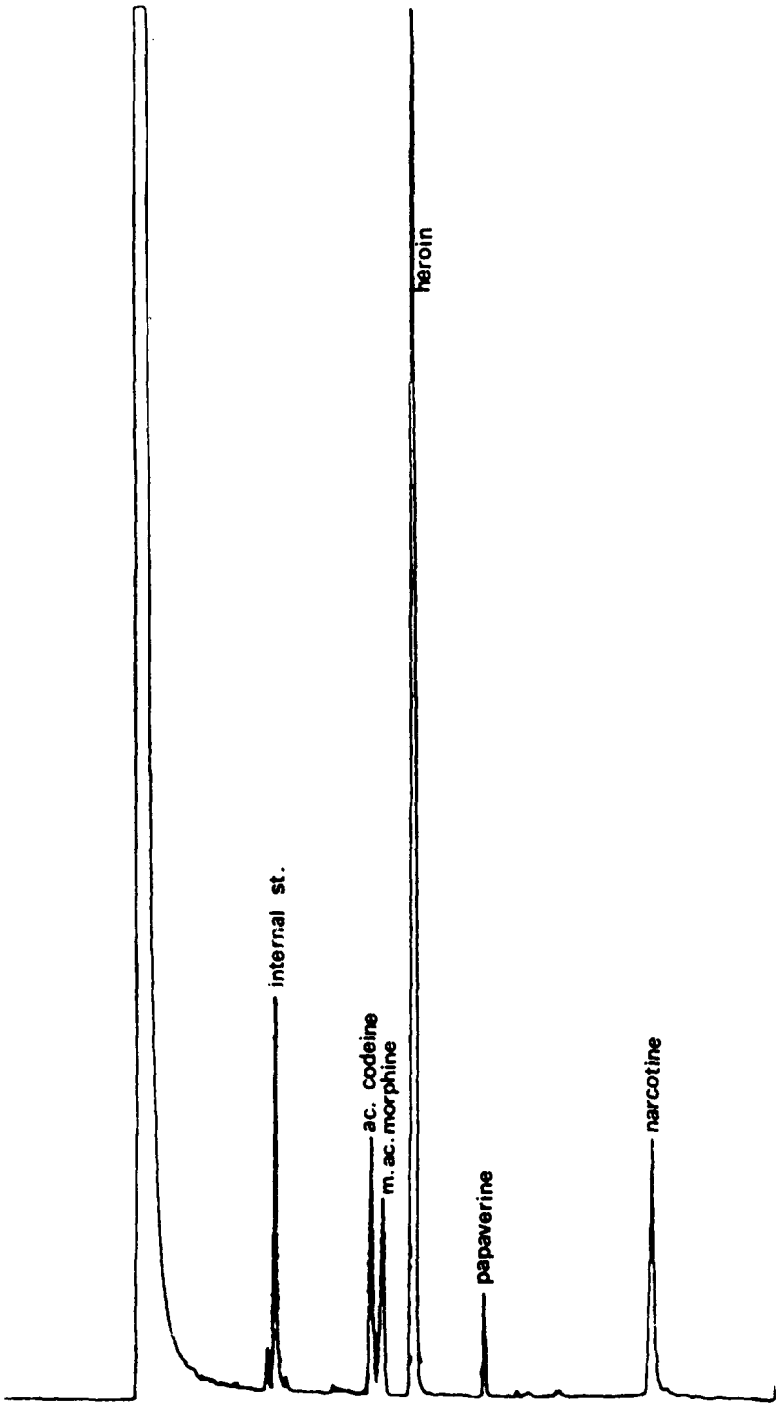

Fig. 1. Typical chromatogram obtained from an illicit heroin sample.

TABLE II

RESULTS OBTAINED FOR TWENTY STREET HEROIN SAMPLES: STATISTICAL STUDY

M = Mean; n = 10.

Sample		*Heroin*	*Monoacetylmorphine*	*Acetylcodeine*	*Papaverine*	*Narcotine*
1	M	57.092	0.027	0.924		13.307
	S.D.	0.704	0.001	0.002		0.030
	C.V. (%)	1.23	2.83	2.51		1.63
2	M	65.758	4.828	3.871	0.633	1.601
	S.D.	0.226	0.024	0.003	0.002	0.001
	C.V. (%)	0.34	2.78	0.89	1.42	2.74
3	M	69.240	0.603	1.193		12.167
	S.D.	0.217	0.003	0.001		0.002
	C.V. (%)	0.31	2.54	1.41		1.43
4	M	43.881	5.392	3.042	2.040	13.498
	S.D.	0.164	0.031	0.006	0.002	0.013
	C.V. (%)	0.38	2.38	1.95	2.01	2.66
5	M	5.942	2.542	0.497	0.632	9.863
	S.D.	0.104	0.001	0.005	0.001	0.002
	C.V. (%)	1.76	0.46	1.07	2.13	1.04
6	M	10.941	5.422	0.827	0.872	6.214
	S.D.	0.730	0.003	0.001	0.0008	0.001
	C.V. (%)	0.67	0.70	1.02	1.79	0.75
7	M	55.653	1.426	4.325	0.658	12.256
	S.D.	0.606	0.001	0.007	0.0005	0.013
	C.V. (%)	1.09	1.25	2.07	1.83	1.34
8	M	77.537	1.296	4.128	0.853	13.523
	S.D.	1.030	0.004	0.004	0.0008	0.012
	C.V. (%)	1.33	1.49	0.98	1.74	2.99
9	M	17.461	0.421	0.854	0.481	2.854
	S.D.	0.372	0.0005	0.0008	0.0007	0.0005
	C.V. (%)	2.13	2.41	0.93	2.89	0.80
10	M	34.061	0.965	2.115	1.943	11.715
	S.D.	0.311	0.004	0.001	0.001	0.006
	C.V. (%)	0.91	2.35	0.87	1.27	2.11
11	M	31.311	0.721	0.652		13.844
	S.D.	0.472	0.003	0.004		0.039
	C.V. (%)	1.51	2.33	2.35		3.35
12	M	23.373	1.459	1.295	0.658	3.112
	S.D.	0.264	0.003	0.001	0.001	0.001
	C.V. (%)	1.13	2.70	1.16	2.13	1.47
13	M	21.327	1.325	1.215	0.621	2.589
	S.D.	0.222	0.002	0.002	0.0007	0.002
	C.V. (%)	1.04	2.42	1.90	2.36	1.43
14	M	20.914	1.208	1.214	0.685	2.745
	S.D.	0.116	0.008	0.000	0.0004	0.001
	C.V. (%)	0.56	3.29	0.00	1.50	1.67
15	M	31.160	0.658	0.621		18.845
	S.D.	0.355	0.003	0.001		0.024
	C.V. (%)	1.14	2.08	3.11		3.09
16	M	58.620	10.845	7.528	6.948	25.383
	S.D.	0.691	0.055	0.008	0.002	0.085
	C.V. (%)	1.18	2.46	1.05	1.06	0.49
17	M	70.535	1.022	4.820	1.009	12.480
	S.D.	0.411	0.004	0.003	0.0005	0.015
	C.V. (%)	0.58	1.64	0.91	1.16	3.89

TABLE II (*continued*)

Sample		*Heroin*	*Monoacetylmorphine*	*Acetylcodeine*	*Papaverine*	*Narcotine*
18	M	45.653	0.711	2.854	0.481	10.835
	S.D.	0.308	0.003	0.003	0.0007	0.008
	C.V. (%)	0.68	1.52	1.36	2.83	2.18
19	M	59.438	0.398	1.320		3.911
	S.D.	0.514	0.001	0.009		0.002
	C.V. (%)	0.87	3.41	2.65		3.63
20	M	45.810	0.720	2.600	0.750	8.323
	S.D.	0.385	0.001	0.001	0.005	0.011
	C.V. (%)	0.84	2.54	0.59	1.38	2.85

quickly and simply resolves the problems of quantitative analysis: the low standard deviation and the very low coefficient of variation (always less than 4.0 and some times = 0) for each component shows the high reproducibility of the method, even when very low or high concentrations of substances were determined. This is of great importance because in street heroin samples the contents of heroin and its impurities are very variable. Furthermore, in forensic toxicology, only high reproducibility and accuracy of the quantitative data permit the comparison of samples in most cases it will be possible to ascertain whether two or more samples are different and, in many cases, to determine with reasonable certainty whether two or more samples have a common origin. The PTV inlet in combination with HRGC provided sufficient accuracy and reproducibility in quantitation for street heroin mixtures, at any concentration of heroin and all impurities that occur in the black market samples. This is very important in Forensic Toxicology where the exact chemical profile of the samples forms the basis for comparative analysis. It also makes it possible to distinguish the places of the origin of the heroin samples and their distribution routes.

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