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SIMULTANEOUS DETERMINATION OF NARCOTICS, ADULTERANTS AND DILUENTS IN STREET SAMPLES BY MEANS OF GAS CHROMATOGRAPHY WITH CAPILLARY COLUMNS

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SUMMARY

The various substances present in street samples of narcotics were detected in a single analysis by means of silylation and high-resolution gas chromatography. This technique allows the detection of narcotics (cocaine, heroin, etc.), of most common adulterants (procaine, lidocaine, etc.) and of organic diluents (sugars, mannitol, etc.) at the same time.

INTRODUCTION

Street samples of narcotics (cocaine, heroin, etc.) frequently contain adulterants (procaine, lidocaine, etc.) and diluents (sugars, mannitol, etc.) the proportions of which may progressively increase during transfer from the first seller to the ultimate consumer. The identification of narcotics, adulterants and diluents is of great importance, as it allows comparisons among the various street samples to be made and makes it possible to establish their provenance, at least in some cases[1].

The techniques routinely used in many laboratories for the identification of all the substances present in a single street sample include thin-layer chromatography[2], gas chromatography[3–5] and high-performance liquid chromatography[6,7], but they are unsatisfactory for several reasons. Even if it is possible to separate, identify and measure the various nitrogenous substances, both narcotics and adulterants, by means of these techniques, it is not possible to detect the diluents (sugars, etc.) at the same time.

The aim of this study was to detect, in a single analysis, the narcotics, adulterants and diluents, in order to be able to provide reliable data for legal purposes. The method adopted was gas chromatography with capillary columns[8,9], which has two advantages: high sensitivity, which allows detection of minimal amounts of substances, and a high resolving power, which allows the separation of substances not separable by other techniques. The compounds of interest in the samples were first converted into silyl derivatives. This method allows not only the identification but

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also the measurement of all the components present in street samples. Over twenty substances were detected.

EXPERIMENTAL

Preparation of sample

As it is well known that a street sample of heroin (prepared by acetylation of morphine) contains small amounts of other alkaloids of opium, such as codeine, thebaine, papaverine, narcotine, acetylcodeine and monoacetylmorphine, all of these substances were mixed with the narcotics (cocaine and heroin) and with the most common adulterants (ephedrine, phenmetrazine, caffeine, diphenhydramine, lidocaine, procaine, methaqualone, quinine and strychnine) and diluents (fructose, glucose, lactose, sucrose and mannitol). A small amount of dieldrin was added to the mixture as an internal standard. To a small sample (10–50 mg) of the dry mixture, 1.0 ml of (hexamethyldisilazane–trimethylchlorosilane–pyridine (3:1:9) (Supelco) was added. The tubes were tightly stoppered and placed in a heating block at 60°C for 15 min. After cooling, 4.0 ml of dichloromethane were added. After vigorous shaking,

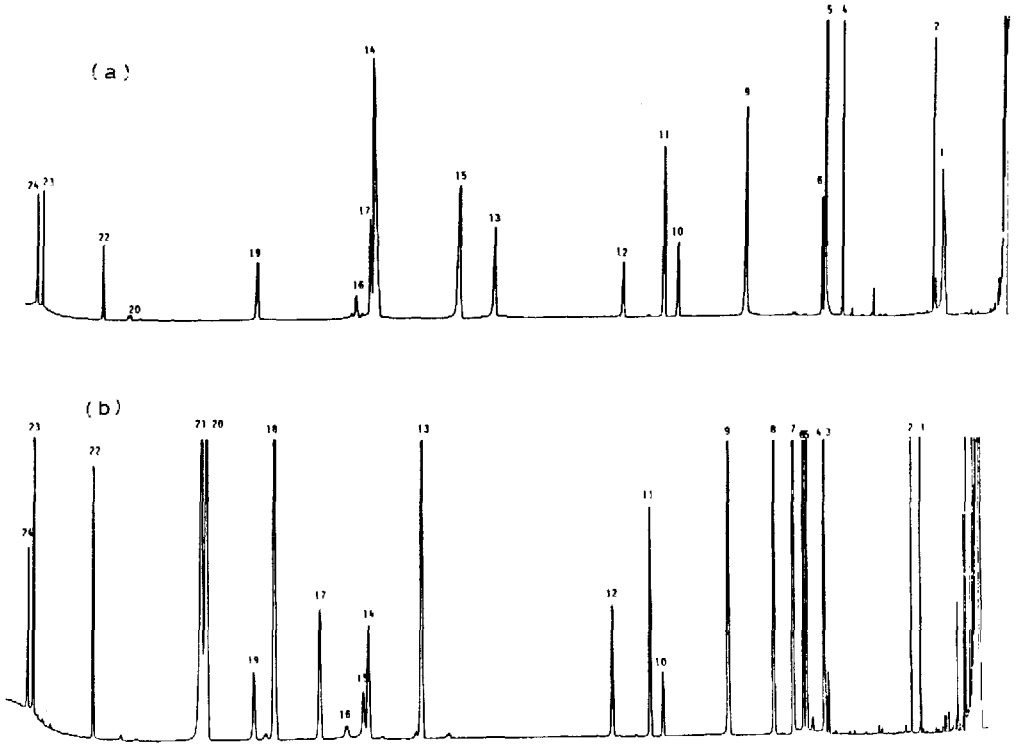

Fig. 1. Chromatograms of a mixture of narcotics, adulterants and diluents. (a) Before silylation: 1 = ephedrine; 2 = phenmetrazine; 4 = caffeine; 5 = diphenhydramine; 6 = lidocaine; 9 = procaine; 10 = dieldrin (reference peak); 11 = methaqualone; 12 = cocaine; 13 = codeine; 14 = acetylcodeine; 15 = morphine; 16 = thebaine; 17 = monoacetylmorphine; 19 = heroin; 20 = quinine; 22 = papaverine; 23 = strychnine; 24 = narcotine. (b) After silylation: peaks as in (a), plus 3 = fructose 7 = glucose; 8 = mannitol; 18 = lactose; 21 = sucrose.

TABLE I
RETENTION TIMES OF MIXTURE BEFORE SILYLATION
RP is reference peak.

Compound	*Retention time (min)*	*Relative retention time**	*Elution temperature (°C)*
Ephedrine	5.15	0.201	153
Phenmetrazine	6	0.234	161.5
Caffeine	12.9	0.504	175.9
Diphenhydramine	14.3	0.559	177.1
Lidocaine	14.6	0.570	177.4
Procaine	20.4	0.797	183.2
Dieldrin (RP)	25.6	1.000	188.2
Methaqualone	26.15	1.021	188.8
Cocaine	29.75	1.162	192.4
Codeine	39.95	1.501	202.6
Acetylcodeine	49.25	1.924	211.4
Morphine	42.7	1.668	205.3
Thebaine	50.45	1.986	213
Monoacetylmorphine	49.55	1.941	211.7
Heroin	58.15	2.270	220.3
Quinine	68.1	2.66	262.5
Papaverine	70.3	2.746	264.7
Strychnine	74.95	2.928	311.2
Narcotine	75.45	2.947	316.2

* Relative to dieldrin = 1.000.

TABLE II
RETENTION TIMES OF MIXTURE AFTER SILYLATION
RP is reference peak.

Compound	*Retention time (min)*	*Relative retention time**	*Elution temperature (°C)*
Ephedrine	5.35	0.211	158
Phenmetrazine	6.1	0.240	165
Fructose	12.55	0.494	175.8
Caffeine	12.85	0.504	176
Diphenhydramine	14.25	0.561	177.4
Lidocaine	14.5	0.571	177.6
Glucose	15.3	0.602	178.3
Mannitol	16.8	0.661	179.8
Procaine	20.3	0.799	183.4
Dieldrin (RP)	25.4	1.000	188.4
Methaqualone	26.7	1.051	189.3
Cocaine	29.45	1.159	192.4
Codeine	44.5	1.752	207.4
Acetylcodeine	48.7	1.917	211.6
Morphine	49.1	1.933	212
Thebaine	50.45	1.986	213.4
Monoacetylmorphine	52.5	2.067	215.5
Lactose	56.1	2.209	218.9
Heroin	57.65	2.270	220.6
Quinine	61.4	2.417	224.4
Sucrose	61.8	2.433	224.8
Papaverine	70.2	2.764	263.7
Strychnine	74.9	2.949	312
Narcotine	75.35	2.967	316.3

* Relative to dieldrin = 1.000.

aliquots of 1 μl were injected into a Carlo Erba Model 4160 capillary column gas chromatograph equipped with a flame-ionization detector. The same procedure was followed for the analysis of street samples.

Gas chromatographic analysis

Glass capillary columns (25 m) were used, with SE-54 (film thickness 0.4–0.45 μm) as the stationary phase. Split injection was used. The temperature was programmed from 100 to 170°C at 10°C/min, from 170 to 230°C at 1°C/min and from 230 to 320°C at 10°C/min, with an isothermal hold at 320°C for 5 min. The temperature of the detector and injector was 320°C. The flow-rate of the carrier gas (hydrogen) was 0.4 kg/cm^2.

RESULTS

Fig. 1 shows chromatograms of a mixture consisting of narcotics (cocaine and heroin), other opium alkaloids (codeine, thebaine, papaverine, narcotine, acetylcodeine and monoacetylmorphine), adulterants (ephedrine, phenmetrazine, caffeine, diphenhydramine, lidocaine, procaine, methaqualone, quinine and strychnine) and diluents (fructose, glucose, lactose, sucrose and mannitol). As shown in Fig. 1a, the diluents were not eluted from the column unless the sample was first silylated procedure. Using silyl derivatives (Fig. 1b), all the substances under investigation could be detected. The retention times (t_R), the retention times relative to dieldrin (RRT) and the elution temperatures of the individual substances before and after silylation are reported in Tables I and II, respectively.

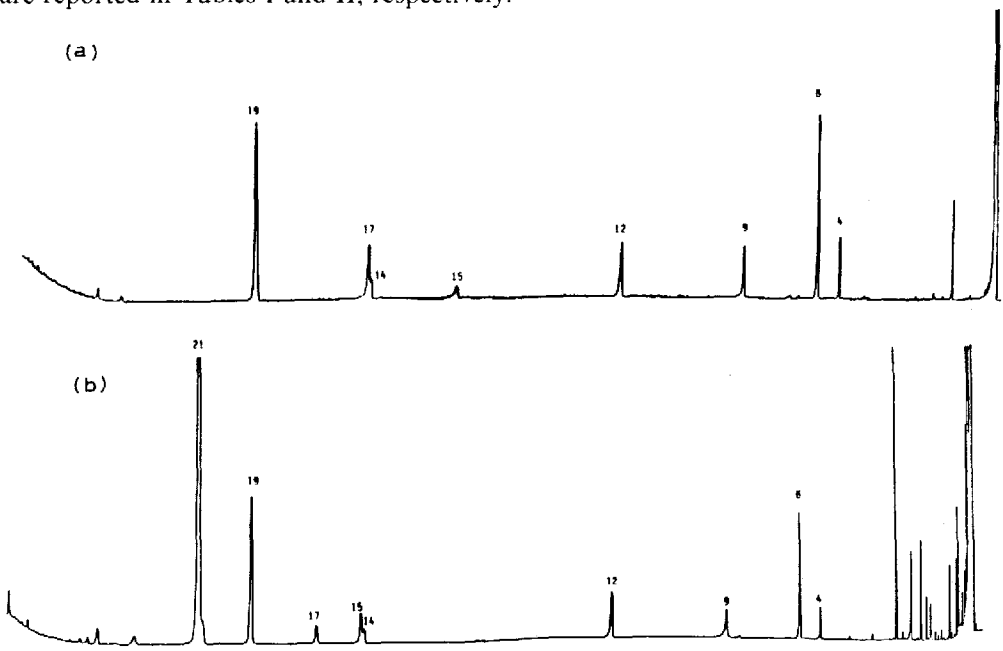

Fig. 2. Chromatograms of a street sample of narcotics. (a) Before silylation; 4 = caffeine; 6 = lidocaine; 9 = procaine; 12 = cocaine; 14 = acetylcodeine; 15 = morphine; 17 = monoacetylmorphine; 19 = heroin. (b) After silylation: peaks as in (a), plus 21 = sucrose.

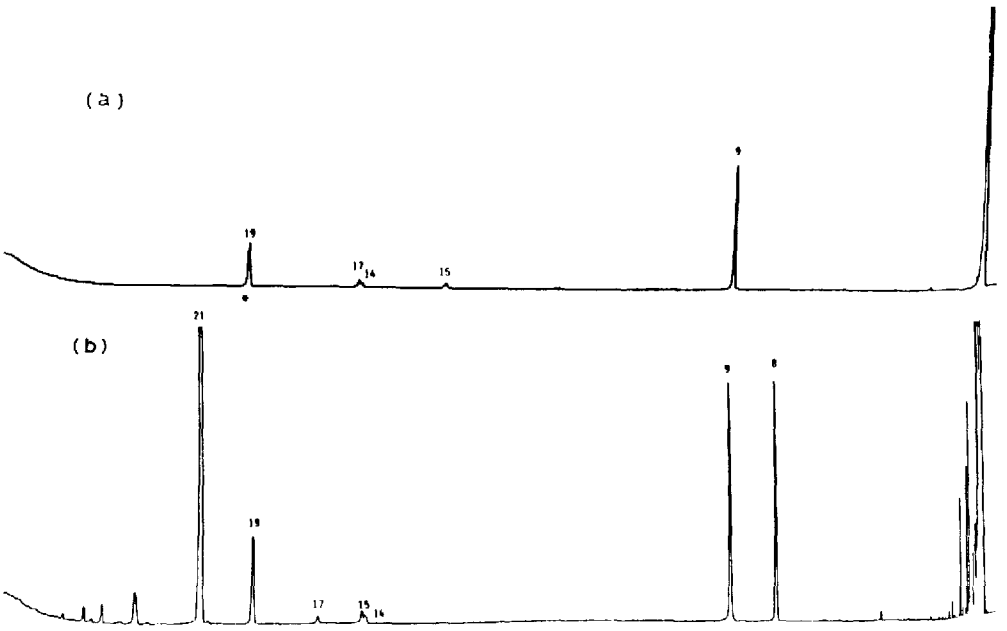

Fig. 3. Chromatogram of a street sample of narcotics. (a) Before silylation: 9 = procaine; 14 = acetylcodeine; 15 = morphine; 17 = monoacetylmorphine; 19 = heroin. (b) After silylation: peaks as in (a), plus 8 = mannitol; 21 = sucrose.

Fig. 2 shows chromatograms of a street sample (a) before and (b) after silylation. Sucrose is detectable when the silylated derivatives were prepared.

Fig. 3 shows chromatograms of another street sample (a) before and (b) after silylation. Sucrose and mannitol are detectable when the silylated derivatives were prepared.

The results indicate that the technique used allows the detection of all the substances (narcotics, adulterants, and diluents) present in a street sample in a single analysis.

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