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THERMAL ANALYTICAL TECHNIQUES APPLIED TO THE NARCOTIC FIELD: COCAINE ANALYSIS

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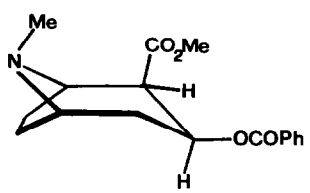
ABSTRACT

The cocaine sold in the illegal market is normally a mixture of cocaine with different kinds of cuts. For legal purposes, it is compulsory to know the exact quantity of cocaine present in each sequestered sample, while at the same time it is important to know the type of cuts used. The analytical methods commonly used are not very reliable and take a long time. In this paper, the use of thermoanalytical techniques is suggested for the direct analysis of cocaine and cuts without any preliminary sample treatment, thus avoiding artifacts due to the sample pretreatment or to the analytical operative conditions. The proposed method is time saving and reliable with a maximum analytical error of the order of about 4%, while the mean error is of the order of about 2%.

INTRODUCTION

Cocaine is the 3-benzoiloxy-8-methyl ester of 8-azabicyclic octane-2-carboxylic acid and its structure is



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Cocaine is almost insoluble in water and so the drug is commonly used as its hydrochloride. The raw cocaine hydrochloride is obtained in the form of blocks, "rock cocaine". Further refinements give pure cocaine hydrochloride in the form of flakes, "flake cocaine".

Cocaine is sold on the illegal market not pure, but cut with different substances. At production level, the cutting substance is dissolved together with the cocaine and then the solution is treated so that the typical blocks are reobtained. At the level of small dealers, the cut and the cocaine, both powdered, are mixed directly.

The cuts can be divided into three categories: (1) active cuts, substances showing some psychoactive properties similar to those of cocaine; (2) anaesthetic cuts, substances acting as local anaesthetics simulating a typical collateral effect of the cocaine; and (3) inert cuts, substances serving only to increase the mass.

The active cuts, not very common, are usually amphetamines and, very seldom, yohimbine or PCP.

The most-used anaesthetic cuts are drugs such as carbocaine, lidocaine, novocaine, tetracaine and tropocaine. These drugs, practically innocuous if taken by nasal ingestion, can be very dangerous when injected intravenously.

Among the inert cuts, the most widely used is mannite. Mannite has an appearence very similar to that of cocaine, does not give any collateral effect, does not irritate the mucous membranes, is not poisonous and is not detected by the majority of the tests. Other inert cuts commonly used are glucose and lactose.

Inorganic cuts such as calcium carbonate or talc are sometimes also used; these are very dangerous if intravenously injected because they can produce embolisms.

Finally, caffeine is another cut which is used increasingly.

Of the cocaine sold in the illegal market, about 65% is a mixture of cocaine and inert cuts, about 25% is a mixture of cocaine and anaesthetic cuts, while the remaining 10% are mixtures of cocaine with other substances such as caffeine, in the majority of cases, or amphetamines, PCP, etc. Sometimes samples sold as cocaine do not contain cocaine, but only local anaesthetics.

For legal purposes, it is compulsory to know the exact quantity of cocaine present in each sequestered sample, while, at the same time, it is important to know the type of cuts used.

Cocaine analysis is carried out by many different techniques such as spectrophotometry, IR spectroscopy, thin layer chromatography, gas chromatography, HPLC, mass spectroscopy and immunological methods.

Spectrophotometric methods [1–5] can be used directly by means of the peaks at 233, 275 or 281 nm when the cocaine is dissolved in 0.1 N sulphuric acid or by the peaks at 230, 274 or 281 nm when the free base is dissolved in

ethanol. Collateral reactions using lithium aluminium hydride and the Marquis or the Liebermann reactions can also be used. Nevertheless, all these methods show low sensitivity and are not specific.

Infrared spectroscopy is used for the analysis of cocaine using the peaks at 1106, 1275, 1700 and 1728 cm^{-1} for samples in KBr pellets [6]. Recently, IR methods using only a few micrograms of sample, such as internal microreflection [7], KBr micropellets [8] and diamond cells [9] have been proposed. However, all these techniques are only semiquantitative and are subject to interferences from molecules often present in the forensic samples.

Thin layer chromatography [1,2,8,10,11] has been widely used to separate the most important compounds that appear together with the cocaine, but the results are not always satisfactory and, moreover, the methods are not quantitative.

Gas chromatography is often used for the analysis of cocaine [12,13] with a linear temperature program in the range 190–280 °C. However, the results obtained on pure cocaine samples or on synthetic mixtures are always lower than those expected while, at the same time, a spurious peak appears on the chromatographic curves giving rise to substantial analytical errors.

HPLC is a more suitable method for cocaine analysis and many papers have been published concerning its application to the determination of cocaine and other molecules in forensic samples [14–18]. HPLC has also been used for the separation of the diastereoisomers of cocaine [19–20] and of some local anaesthetics [21–22]. Nevertheless, HPLC is not a direct method, and there are some problems concerning interaction between the mobile phases and some of the molecules during the analysis. Finally, the inorganic species cannot be analysed.

Immunological methods and especially immunoenzymatic analyses are also used for the analysis of cocaine, particulary in biological fluids. The disadvantages of these methods are the cross-reactions between the antibody and those molecules having active sites similar to those of the analysed molecules, giving overestimated results.

Therefore, even if sufficiently reliable analytical techniques are now available, it is important to have new, faster methods of analysis which are reliable and do not need any sample pretreatment.

The aim of this paper is to apply thermoanalytical techniques to the analysis of cocaine and the more common cuts found in forensic samples.

EXPERIMENTAL

Instrumentation

A differential scanning calorimeter, Perkin–Elmer DSC 2B and thermobalance TG-S2 equipped with data station, were used. The atmosphere was

nitrogen or air at a flow rate of 50–100 ml min^{-1}. Heating rates ranged between 2.5 and 10 °C min^{-1}.

Reagents

Cocaine, carbocaine, lidocaine, novocaine, tetracaine and tropocaine, in hydrochloride form, and all the other reagents, were supplied by Merck.

RESULTS

Because of the tendency of the cocaine to crystallize in compact masses, cocaine samples often contain bigger particles, where the concentration of the alkaloid is higher, together with finely subdivided powders that are much richer in cuts. Therefore, in order to obtain analytically representative sample, the mixture must be carefully ground, to obtain a perfectly homogeneous powder from which the analytical sample is removed.

To determine the calorimetric behaviour of cocaine and of the most common cuts, DSC analyses were carried out on very pure samples of: cocaine; anaesthetic cuts (carbocaine, lidocaine, novocaine, tetracaine and tropocaine); inert cuts (glucose, lactose and mannite); and caffeine. Active cuts were not considered because they are very uncommon on the illegal market.

Figures 1–10 show the DSC curves of the analysed standards, while Table 1 lists the ΔH values corresponding to the characteristic peaks of each compound.

Following the weighing of the pure substances, suitably homogenized mixtures were prepared of cocaine and each of the studied cuts. Because it has been shown statistically that mixtures sold on the illegal market are of cocaine with one cut, and that only rarely does more than one cut appear in illegal samples, two-component mixtures were examined in the first instance.

A series of synthetic cocaine–cut mixtures with variable concentrations of the cocaine, ranging between 90% and 10% in order to obtain nine points for each series, were prepared to obtain calibration curves of cocaine(%)–ΔH and of cut(%)–ΔH.

Five different samples were taken and analysed for each point and the results used to obtain the representative equations are the mean values of the five analyses.

The following values, with a confidence limit of 95%, have been obtained for the slope a and for the intercept b for the analysed mixtures:

Cocaine–carbocaine

cocaine, a: $0.450 \pm 1.2 \times 10^{-2}$; b: -0.35 ± 0.65

carbocaine, a: $0.263 \pm 6.7 \times 10^{-2}$; b: -0.19 ± 0.38.

Cocaine–lidocaine

cocaine, a: $0.438 \pm 3.1 \times 10^{-2}$; b: -0.30 ± 0.55

lidocaine, a: $0.354 \pm 7.8 \times 10^{-3}$; b: -0.21 ± 0.44.

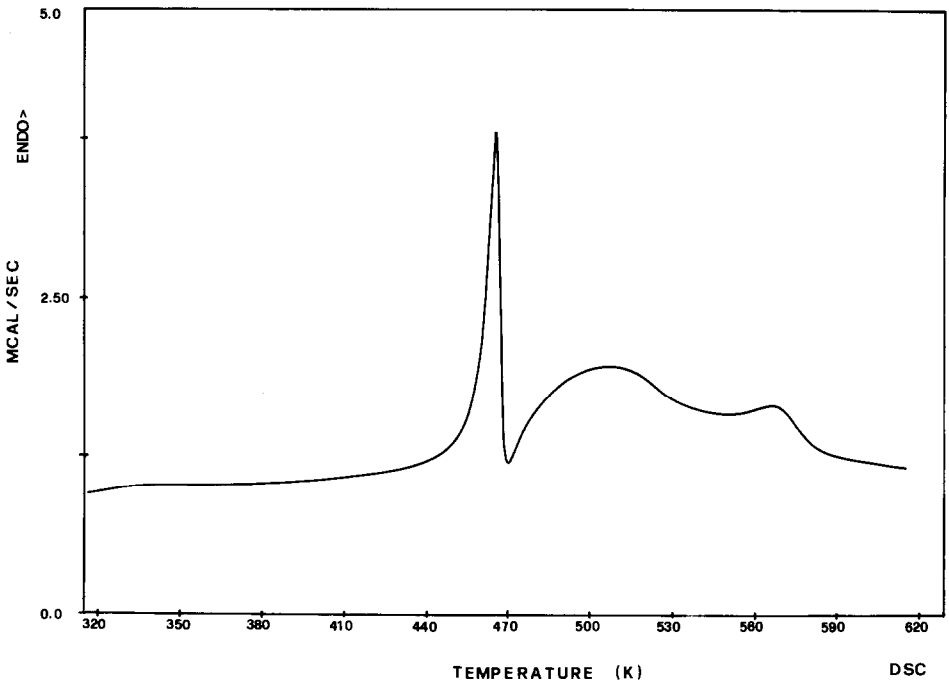


Fig. 1. DSC curve of cocaine standard. Heating rate: 10 °C min^{-1}. Atmosphere: nitrogen.

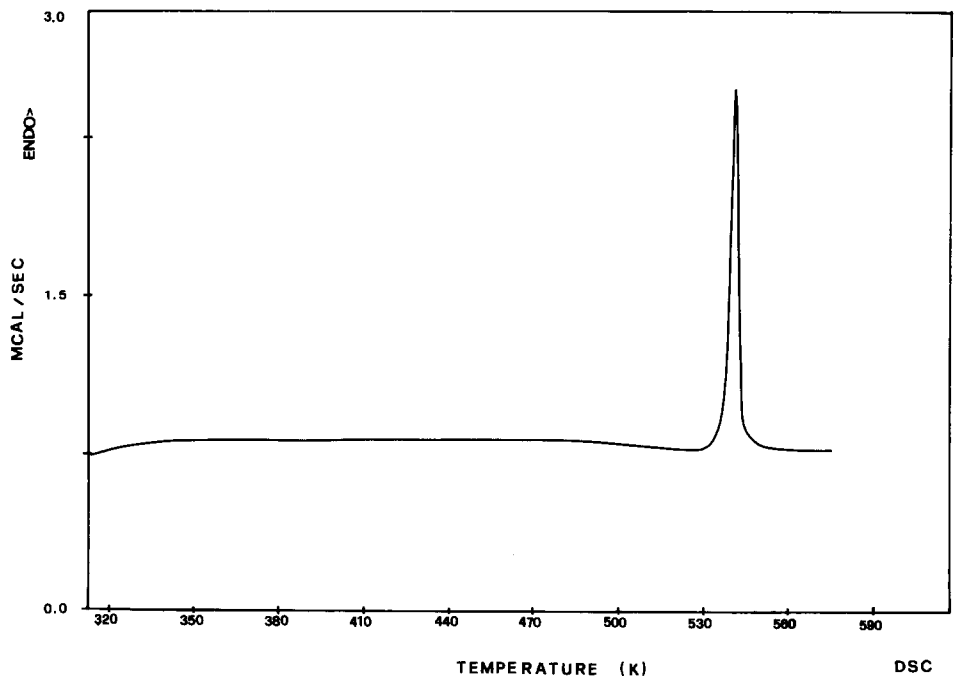


Fig. 2. DSC curve of carbocaine standard. Heating rate: 10 °C min^{-1}. Atmosphere: nitrogen.

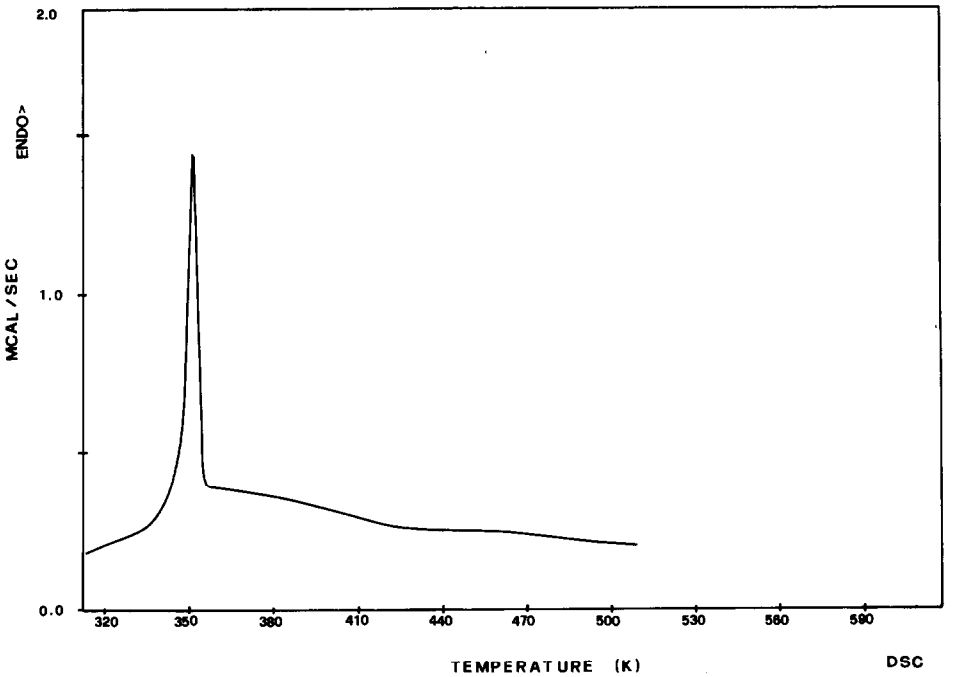


Fig. 3. DSC curve of lidocaine standard. Heating rate: 10 °C min^{-1}. Atmosphere: nitrogen.

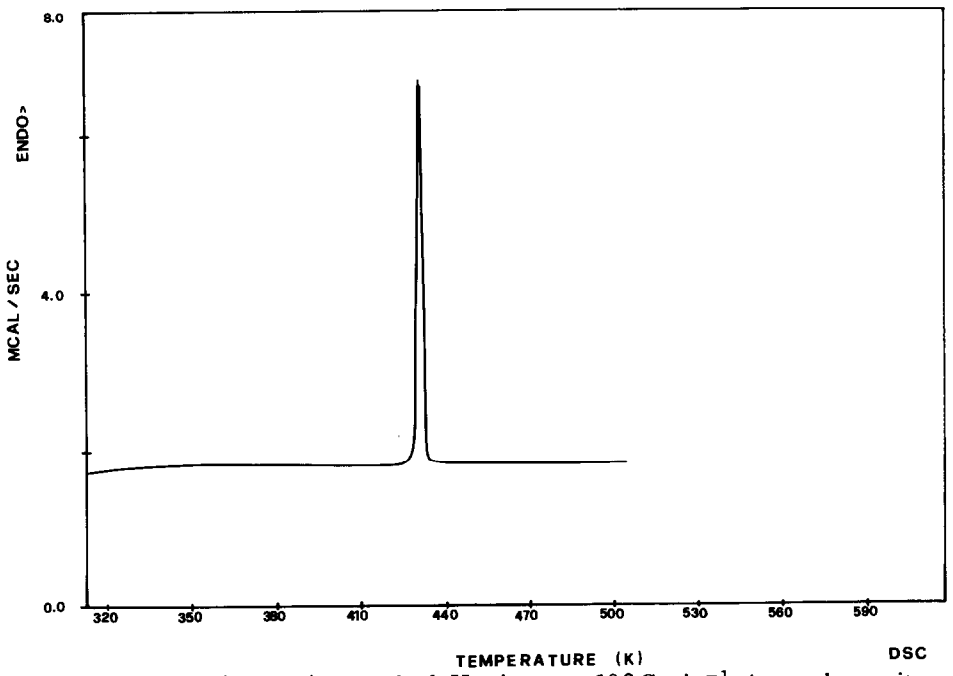


Fig. 4. DSC curve of novocaine standard. Heating rate: 10 °C min^{-1}. Atmosphere: nitrogen.

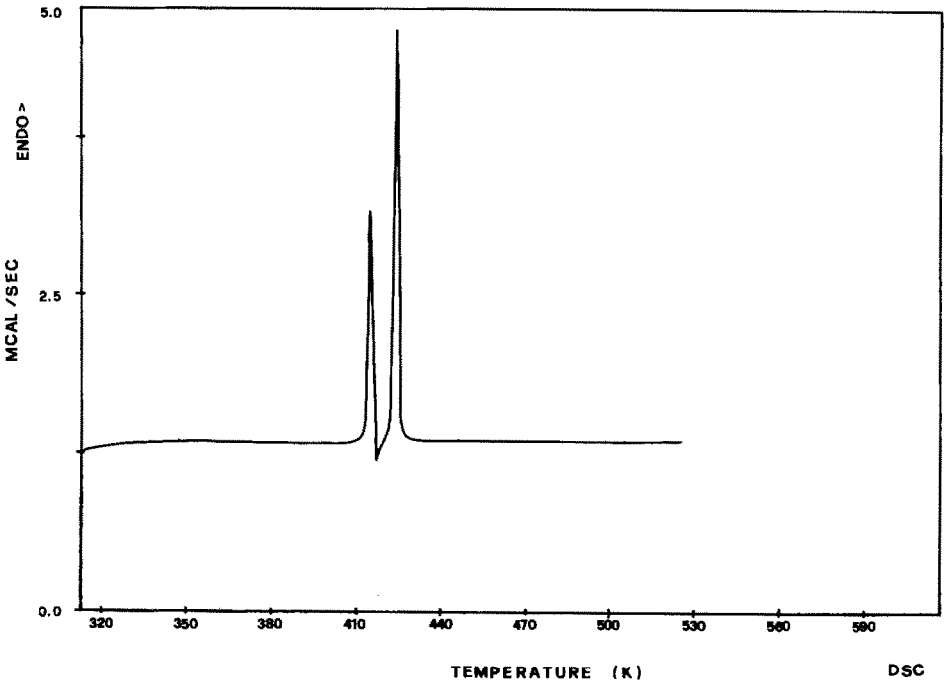


Fig. 5. DSC curve of tetracaine standard. Heating rate: 10 °C min^{-1}. Atmosphere: nitrogen.

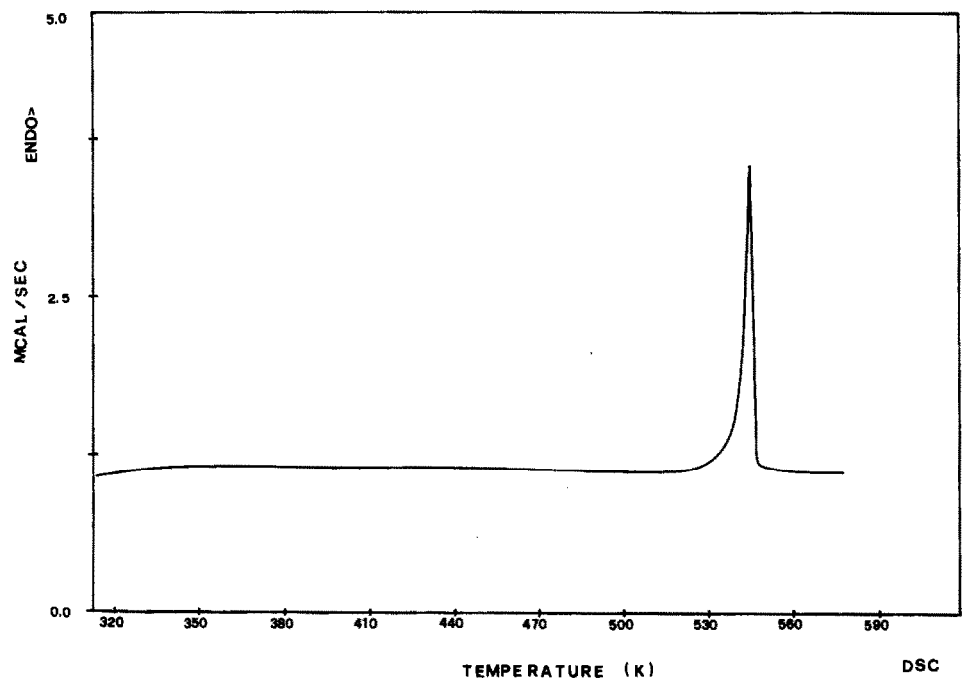


Fig. 6. DSC curve of tropocaine standard. Heating rate: 10 °C min^{-1}. Atmosphere: nitrogen.

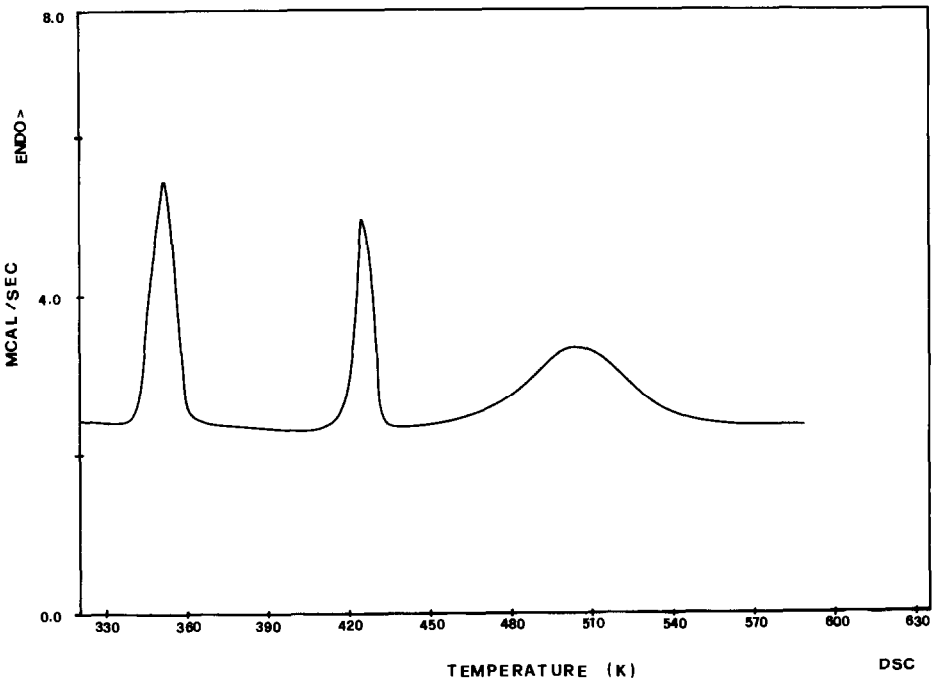


Fig. 7. DSC curve of glucose standard. Heating rate: 10 °C min^{-1}. Atmosphere: nitrogen.

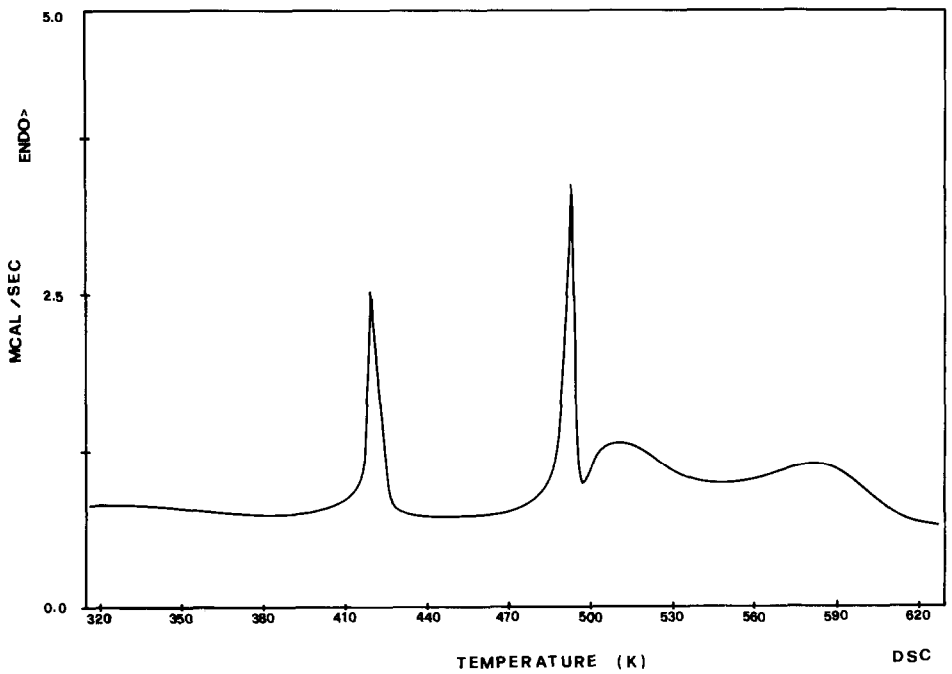


Fig. 8. DSC curve of lactose standard. Heating rate: 10 °C min^{-1}. Atmosphere: nitrogen.

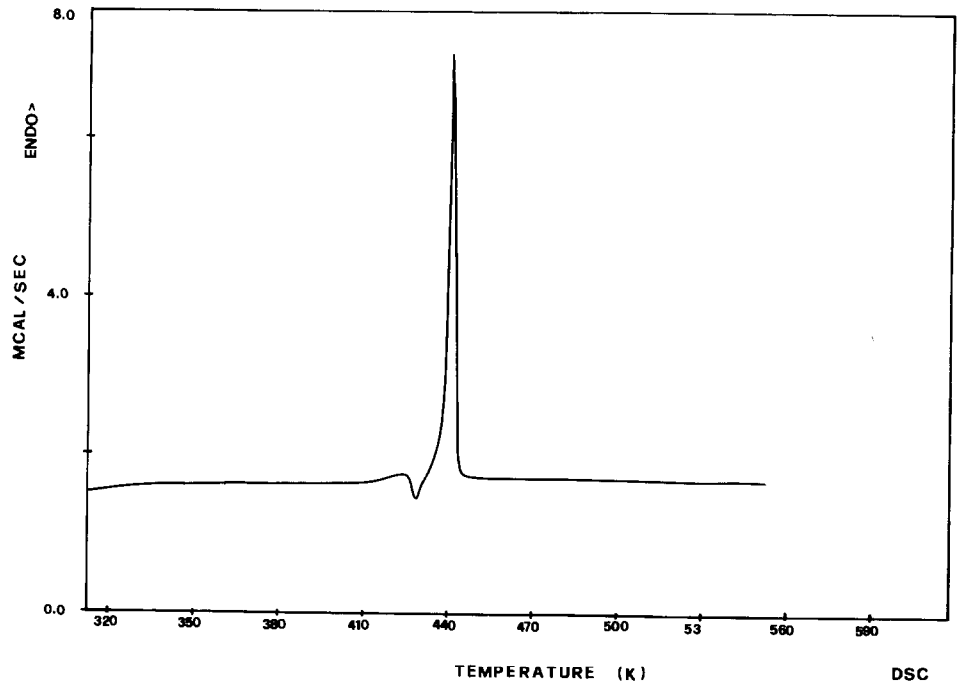


Fig. 9. DSC curve of mannite standard. Heating rate: 10 °C min^{-1}. Atmosphere: nitrogen.

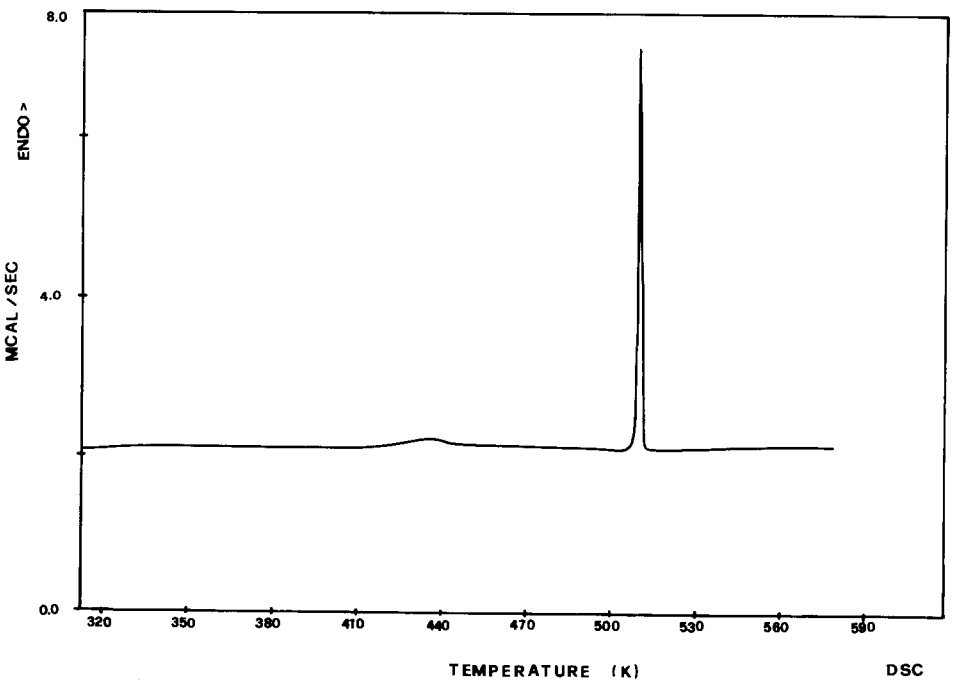


Fig. 10. DSC curve of caffeine standard. Heating rate: 10 °C min^{-1}. Atmosphere: nitrogen.

TABLE 1

ΔH values corresponding to the characteristic peaks of each compound

Standard	ΔH (cal g^{-1})
Cocaine	44.3
Carbocaine	26.2
Lidocaine	35.3
Novocaine	30.4
Tetracaine	14.7, 19.9
Tropocaine	29.1
Glucose	38.1
Lactose	34.6, 33.0
Mannite	28.4
Caffeine	19.5

Cocaine–novocaine
cocaine, a: $0.446 \pm 1.8 \times 10^{-2}$; b: -0.20 ± 1.00
novocaine, a: $0.303 \pm 1.2 \times 10^{-2}$; b: -0.11 ± 0.70.
Cocaine–tetracaine
cocaine, a: $0.428 \pm 1.9 \times 10^{-2}$; b: -0.14 ± 0.79
tetracaine, a: $0.197 \pm 2.4 \times 10^{-2}$; b: 0.12 ± 0.46.
Cocaine–tropocaine
cocaine, a: $0.448 \pm 2.1 \times 10^{-2}$; b: -0.29 ± 0.88
tropocaine, a: $0.292 \pm 1.1 \times 10^{-2}$; b: 0.14 ± 0.65.
Cocaine–glucose
cocaine, a: $0.419 \pm 2.6 \times 10^{-2}$; b: -0.22 ± 0.94
glucose, a: $0.381 \pm 3.3 \times 10^{-2}$; b: -0.06 ± 0.93.
Cocaine–lactose
cocaine, a: $0.441 \pm 2.8 \times 10^{-2}$; b: -0.23 ± 0.72
lactose, a: $0.347 \pm 3.1 \times 10^{-2}$; b: 0.18 ± 0.63.
Cocaine–mannite
cocaine, a: $0.416 \pm 2.3 \times 10^{-2}$; b: -0.20 ± 1.00
mannite, a: $0.282 \pm 1.8 \times 10^{-2}$; b: 0.08 ± 0.61.
Cocaine–caffeine
cocaine, a: $0.449 \pm 1.1 \times 10^{-2}$; b: -0.34 ± 0.63
caffeine, a: $0.195 \pm 3.3 \times 10^{-3}$; b: -0.16 ± 0.18.

Figures 11–15 show some examples of DSC curves of synthetic mixtures.

The position of the melting peak of the cocaine is sometimes influenced by the presence of the cut. In particular when the melting temperature of the cut is lower than that of the cocaine, the influence is more pronounced, although the peak area does not change. Similar behaviour can be seen for some cuts.

In contrast, the DSC behaviour of each mixture is constant, even with many different samples.

Finally, samples from the illegal market were analysed for legal purposes, and some examples are shown in Figs. 16–18.

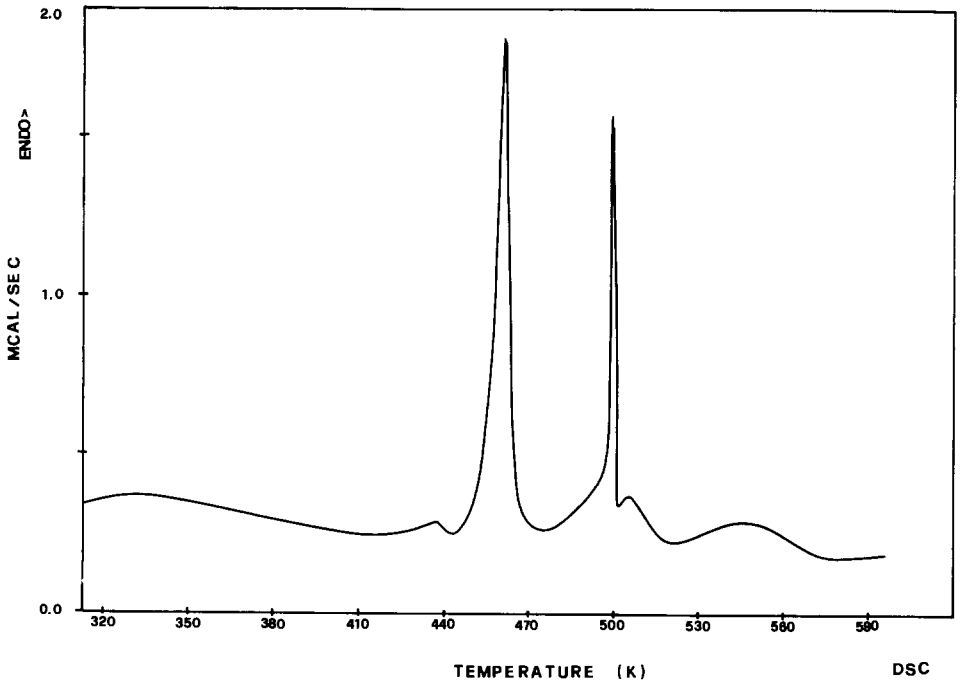


Fig. 11. DSC curve of cocaine–caffeine synthetic mixture 50:50 (w:w). Heating rate: 10 °C min^{-1}. Atmosphere: nitrogen.

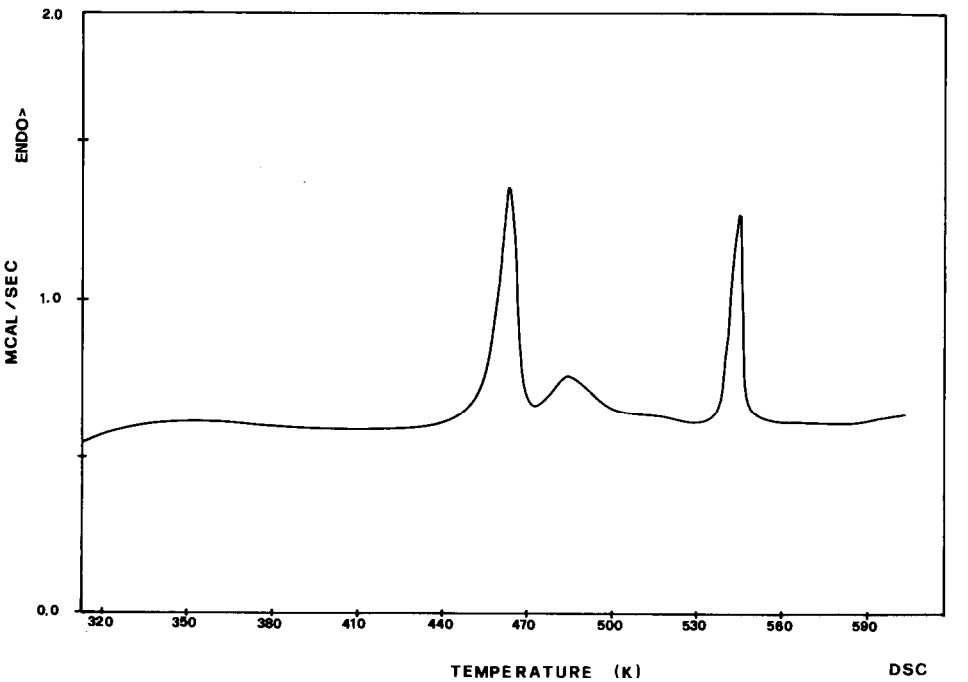


Fig. 12. DSC curve of cocaine–carbocaine synthetic mixture 50:50 (w:w). Heating rate: 10 °C min^{-1}. Atmosphere: nitrogen.

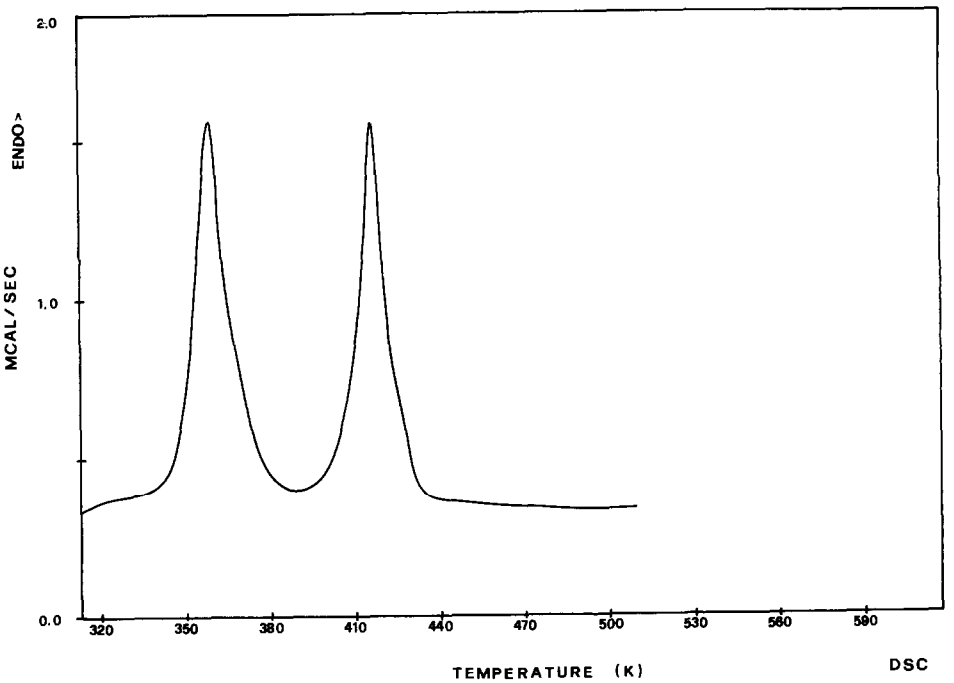


Fig. 13. DSC curve of cocaine–glucose synthetic mixture 50:50 (w:w). Heating rate: 10 °C min^{-1}. Atmosphere: nitrogen.

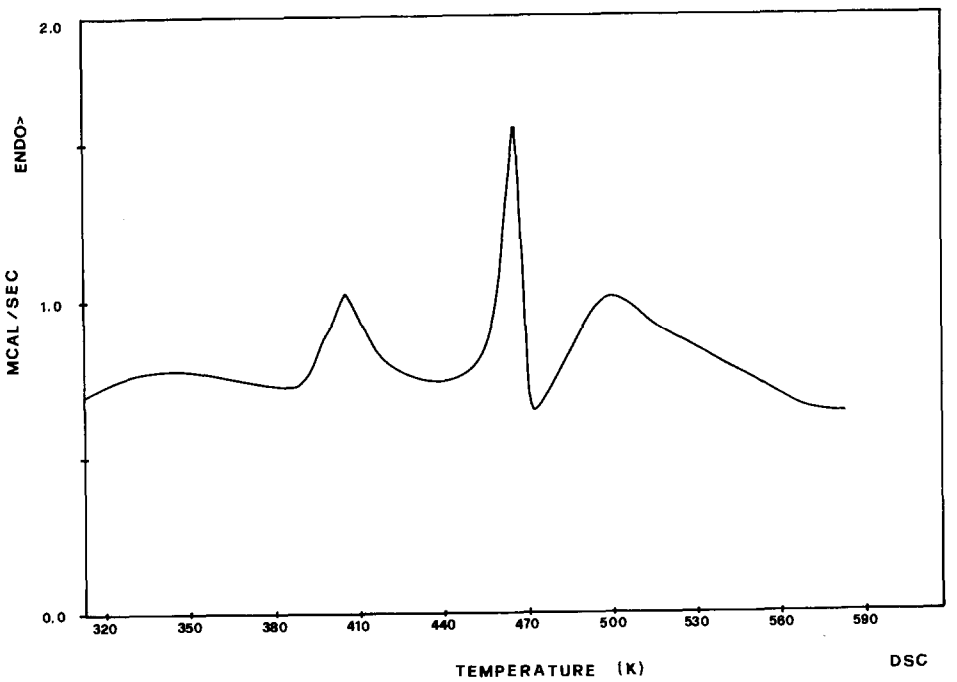


Fig. 14. DSC curve of cocaine–lactose synthetic mixture 50:50 (w:w). Heating rate: 10 °C min^{-1}. Atmosphere: nitrogen.

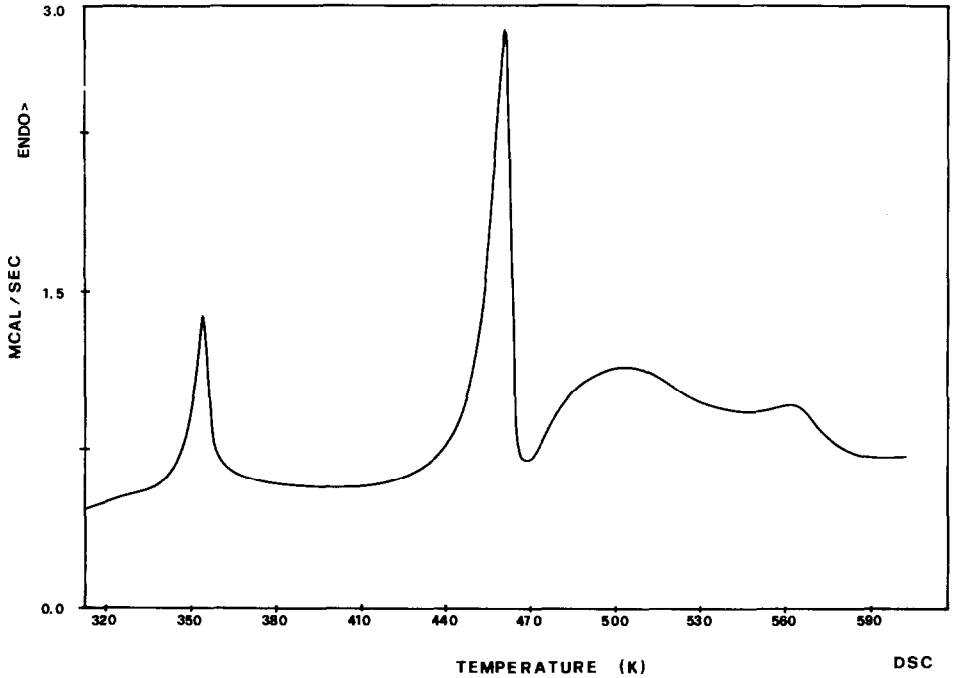


Fig. 15. DSC curve of cocaine–lidocaine synthetic mixture 30 : 50 (w : w). Heating rate: 10 °C min^{-1}. Atmosphere: nitrogen.

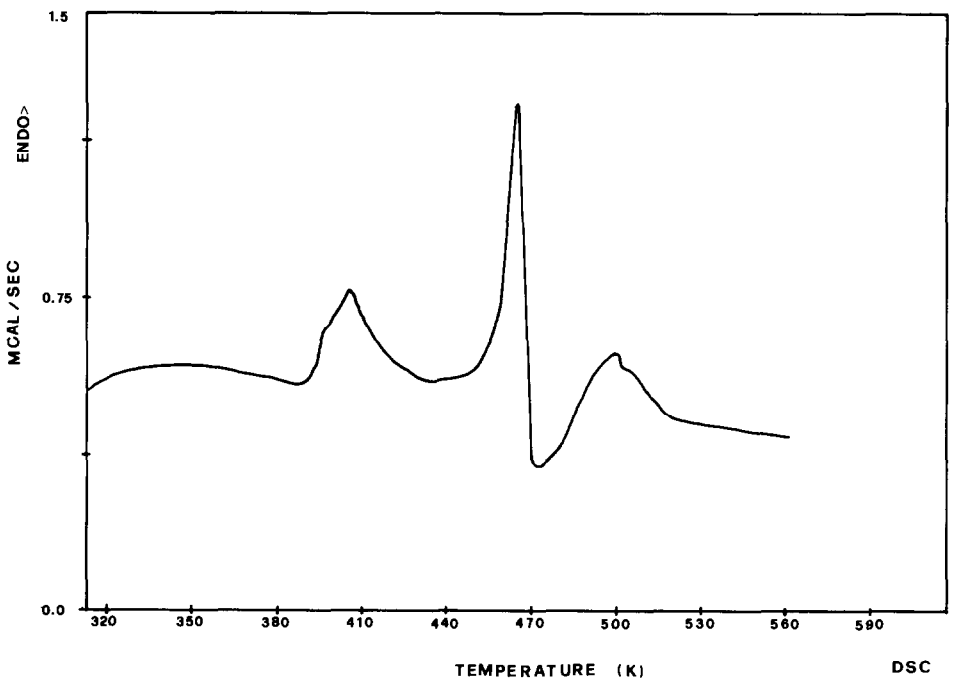


Fig. 16. DSC curve of illegal sample: cocaine 66%–lactose 34%. Heating rate: 10 °C min^{-1}. Atmosphere: nitrogen.

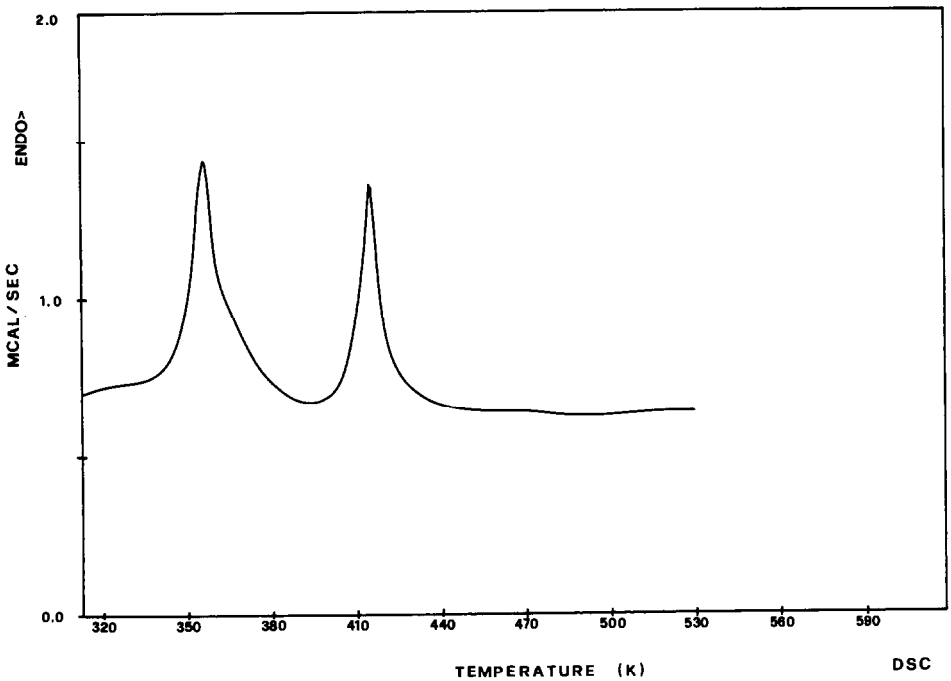


Fig. 17. DSC curve of illegal sample: cocaine 50%–glucose 50%. Heating rate: 10 °C min^{-1}. Atmosphere: nitrogen.

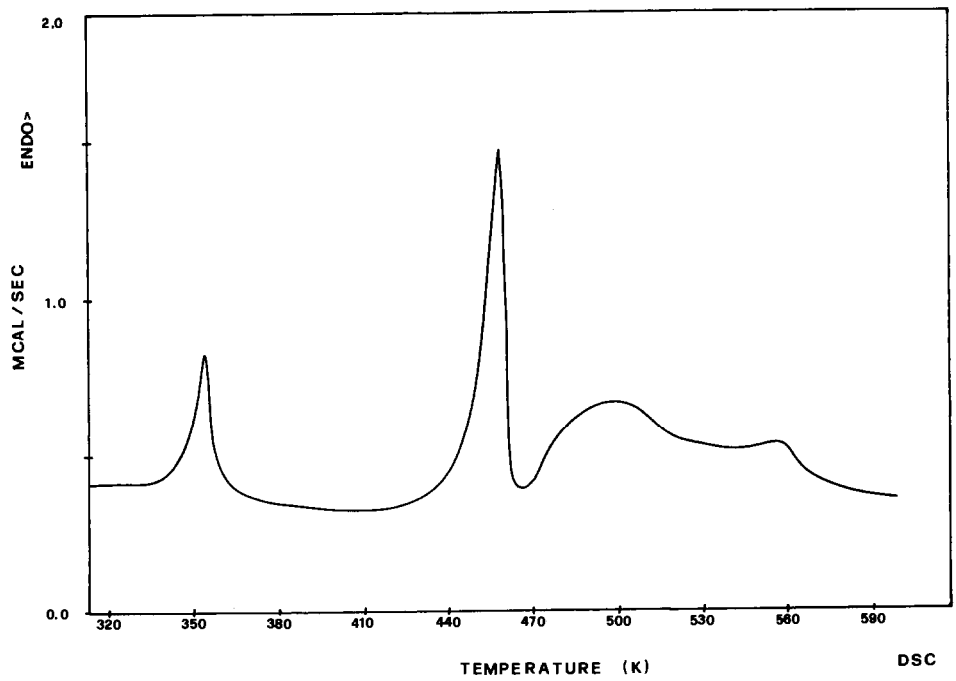


Fig. 18. DSC curve of illegal sample: cocaine 30%–lidocaine 70%. Heating rate: 10 °C min^{-1}. Atmosphere: nitrogen.

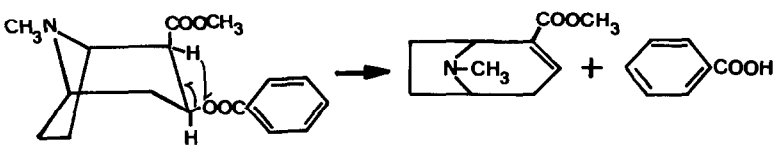
Qualitative analysis has been carried out by comparing the curves of the illegal samples with those of the pure substances and of the synthetic mixtures.

The analysis of the inorganic cuts was carried out by thermogravimetry. The TG curve of cocaine shows a main step in the range 210–290 °C and a second small step in the range 390–570 °C. Therefore, the decomposition of calcium carbonate which, especially in air, starts at much higher temperatures is not influenced by the cocaine decomposition. So a cocaine–calcium carbonate mixture gives three well-separated steps which result in a very reliable analysis.

TG can also help the resolution of a cocaine–lactose mixture because the lactose decomposes in two different processes, the first between 140 and 175 °C and the second between 240 and 560 °C. Since the first step of the lactose decomposition is clearly isolated on the TG curve of the cocaine–lactose mixture, analysis of the sugar is possible: this helps to confirm the DSC results.

DISCUSSION

The DSC curves of the cocaine show, immediately after the melting peak, a series of superimposed endothermic peaks. The first process corresponds to the break-up of the cocaine molecule to give methylecgonine and benzoic acid as described by the reaction



according to the literature and as shown by analyses on different DSC samples analysed after stopping the temperature increase at different times following the beginning of the decomposition process.

Immediately after this process, complete decomposition of the system begins, as also shown by the TG curves. The decomposition process does not give a residue for the very pure Merck cocaine, while all the samples of commercial cocaine, even for the purest samples, have some residue probably due to the salts used during the extraction and purification processes.

The described thermal behaviour of the cocaine molecule can account for the uncorrected analytical results obtained by GC, mainly due to the decomposition of the cocaine when a linear program temperature between 190 and 280 °C is used for the gas chromatographic analysis.

The DSC peaks corresponding to the cocaine and to the cuts are well separated and can very easily be used to obtain a correct qualitative analysis.

The maximum analytical error found is of the order of about 4% while the mean error is of the order of about 2%.

Analysis of the inorganic components is easily carried out by thermogravimetric analysis with a maximum error of less than 1%.

The proposed method shows a wide operative spectrum that enables the study and solution of some of the most important cocaine-related analytical problems.

In particular, the method does not require any sample pretreatment thus avoiding any uncertainties derived from artifacts due to interaction with the analytical reagents, or to the operative conditions, as in the case of gas chromatography. The method is simple, sensitive, accurate and specific, and requires only very low quantities of sample.

Finally, the time required for the analysis is very short, about 30 minutes at a heating rate of $10\,^{\circ}C\ min^{-1}$.

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