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DETERMINATION OF ALKALOIDAL NARCOTICS BY PYROLYSIS-GAS CHROMATOGRAPHY

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ABSTRACT

The alkaloidal narcotics in urine are extracted with dichloromethane and heated to evaporate the solvent. The salts of alkaloidal narcotics are pyrolyzed and analyzed by gas chromatography. By this method, the alkaloidal narcotics can be determined with high sensitivity and with good reproducibility.

Alkaloidal narcotics; gas chromatography; pyrolysis.

INTRODUCTION

Alkaloidal narcotics marketed as painkilling drugs have been analyzed by gas chromatography (GC) [1] or gas chromatography/mass spectrometry (GC/MS) [2], absorption spectrometry [3] in aqueous solution and high-performance liquid chromatography (HPLC) [4] in aqueous or organic solvents. When alkaloidal narcotics in human urine are analyzed, they have to be extracted by organic solvents under alkaline conditions. The salts of alkaloidal narcotics have high boiling points, and cannot be analyzed by GC. In this paper, the alkaloidal narcotics are pyrolyzed as alkaloid salts and the pyrolyzed compounds are analyzed by GC. We have previously reported a method of pyrolysis [5-8] which is characterized by adding metal and inorganic compound to the sample in the pyrolysis foil: by this method, organic compounds were analyzed with high sensitivity and good reproducibility. We have pyrolyzed the alkaloidal narcotics by the same method.

EXPERIMENTAL

The pyrolysis foil with a Curie point of 590°C was used to pyrolyze the alkaloidal narcotics. A mixture of iron powder and sodium carbonate anhydride (30 mg: 4:1 w/w) was first put into the pyrolysis foil. An aqueous solution of the sample was placed in the pyrolysis foil by using a 50ì l microsyringe. The foil was dried on a hot plate for 5 min at about 100°C to evaporate the water. After cooling to room temperature, the pyrolysis foil was folded up and inserted into the Curie-point pyrolyzer. The pyrolysis time was 4 s. The pyrolysis products were separated by GC and the product of 3.7 minutes' retention time was determined by measurement of the peak area. The pyrolysis products were identified by GC/MS. The pyrolysis product of morphine hydrochloride, codeine phosphate and dihydrocodeine phosphate is 3,4-dimethyl-l,2-dihydroxybenzene, which was determined. The operating conditions of pyrolysis and GC are shown in Table 1 and the pyrogram of morphine hydrochloride is shown in Fig. 1.

Selection of suitable metals and inorganic compounds

The metal powder, which is added to conduct heat from the pyrolysis foil to alkaloidal narcotics, such as aluminium, iron, chromium, zinc, manganese, nickel or copper, was put into the pyrolysis foil together with the sample and pyrolyzed. Iron powder showed the highest sensitivity of all the metal powders (Table 2).

The effect of inorganic compounds, which are added to control the pyrolysis temperature, such as sodium carbonate, potassium iodide or ammonium sulphate, added together with the iron powder to raise its sensitivity, were studied at 590°C. The results are shown in Fig. 2. The best mixture ratio of iron and sodium carbonate was between 5 : 1 and 2 : 1.

TABLE 1

Operating conditions of the instrument

Pyrolyzer	Japan Analytical Industry JHP-2
Oven temperature	150°C
Pipe temperature	200°C
Pyrolysis temperature	670°C ; 4s
Gas chromatograph	Hitachi 163
Column	10% PEG 20M Chromosorb W (AW-DMCS) 2mX3mmI.D.
Column temperature	50°C
Injection temperature	180°C
Carrier gas	Nitrogen
Detector	Flame ionization detector

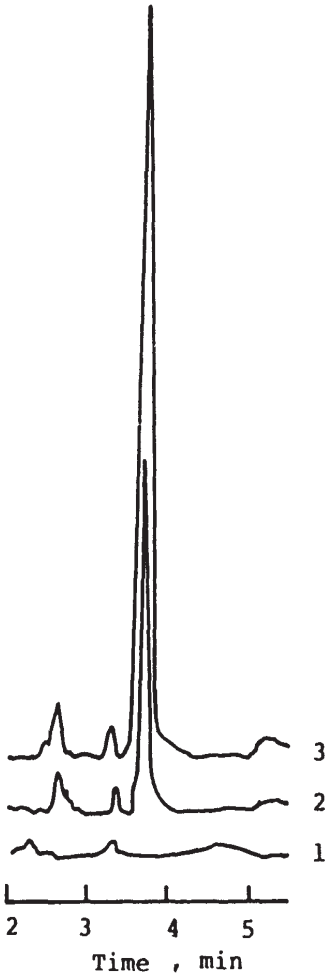

Fig. 1. Pyrogram of morphine hydrochloride (32 μg). 1: Pure; 2: 20 mg of iron; 3: addition of 30 mg of mixture powder (Fe: Na_2CO_3 = 4:1).

TABLE 2

Effect of metal (20 mg) on the pyrolysis of 32 /ìg morphine hydrochloride

Metal	Peak area (X104)
AI	3.52
Fe	19.37
Cr	17.43
Zn	4.36
Mn	7.64
Ni	0.43
Cu	1.01

Effect of amount of added mixture

The amount of the mixture added to the pyrolysis foil was varied from 6 to 50 mg. 50 mg was the maximum weight suitable for the pyrolysis foil, the optimal sensitivity was obtained between 20 and 50 mg (Fig. 3).

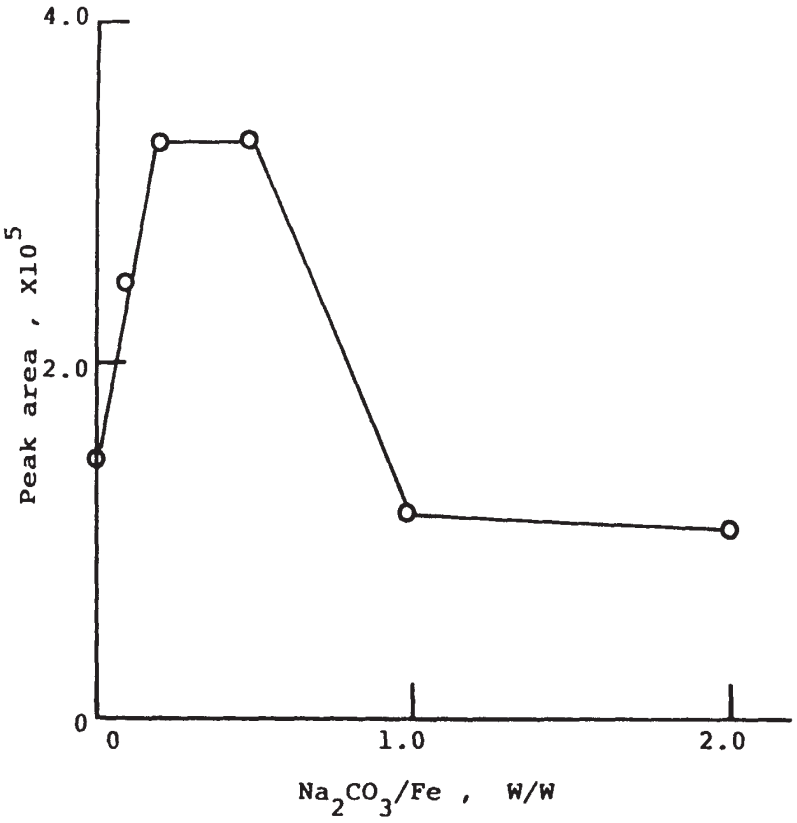

Fig. 2. Effect of a mixture of metal and sodium carbonate on the pyrolysis of 32 μg of morphine hydrochloride.

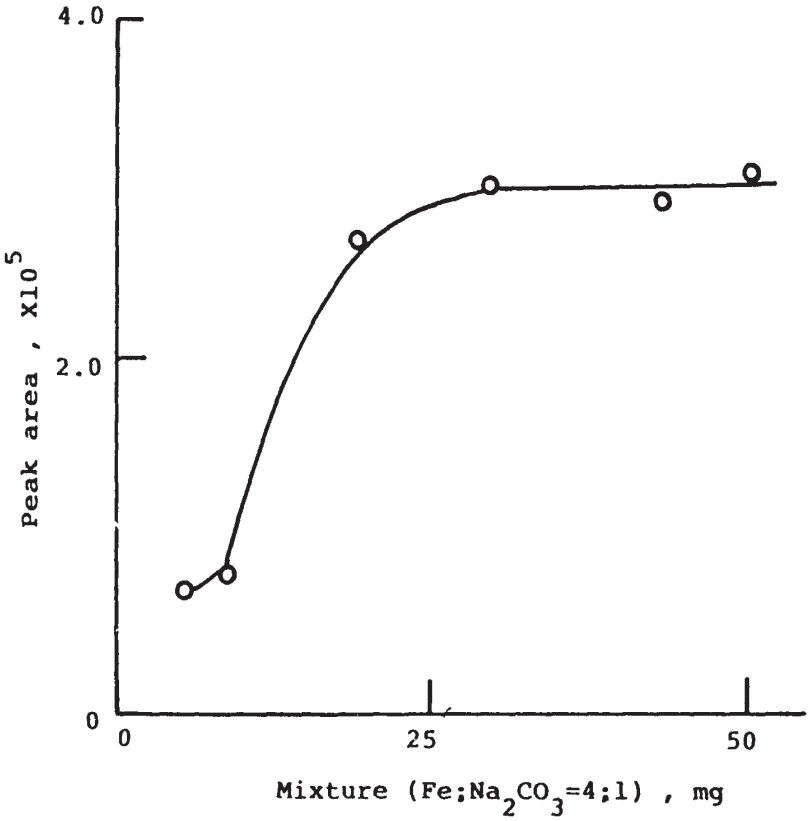

Fig. 3. Effect of an amount of added mixture powder on the pyrolysis of 32 μg of morphine hydrochloride.

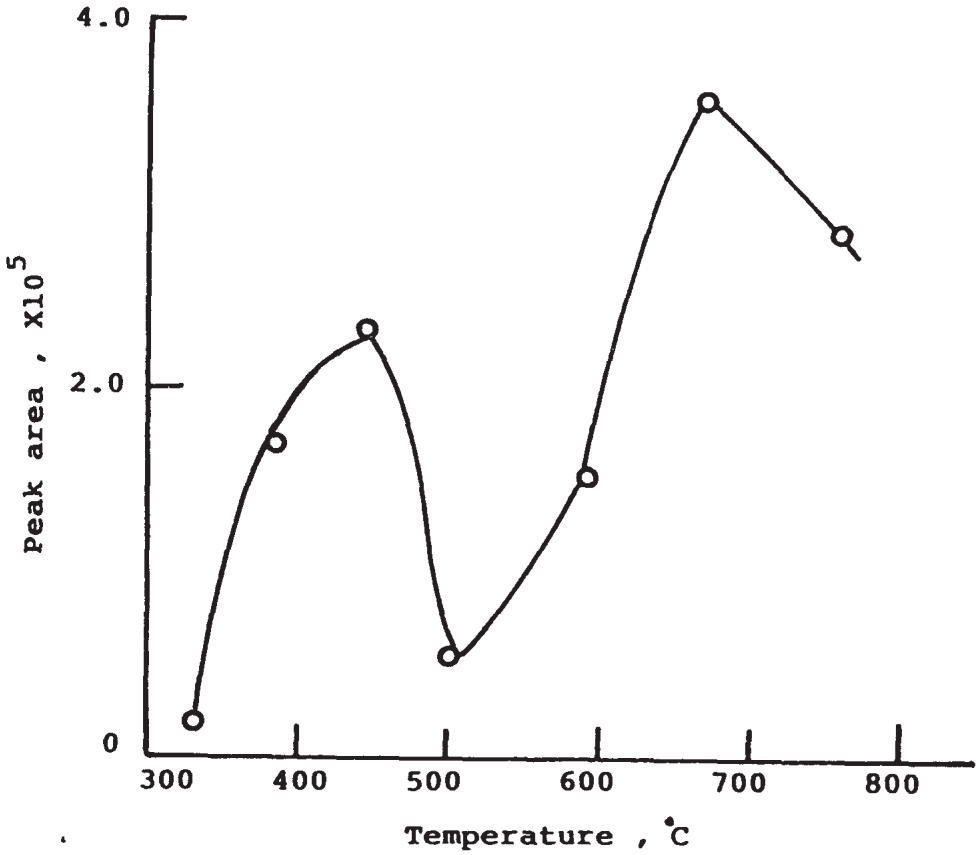

Fig. 4. Effect of temperature on the pyrolysis of 32 μg morphine hydrochloride.

Effect of pyrolysis temperature

The pyrolysis temperature was studied by using different Curie-point pyrolysis foils. When the pyrolysis temperature was 445 and 670°C, the

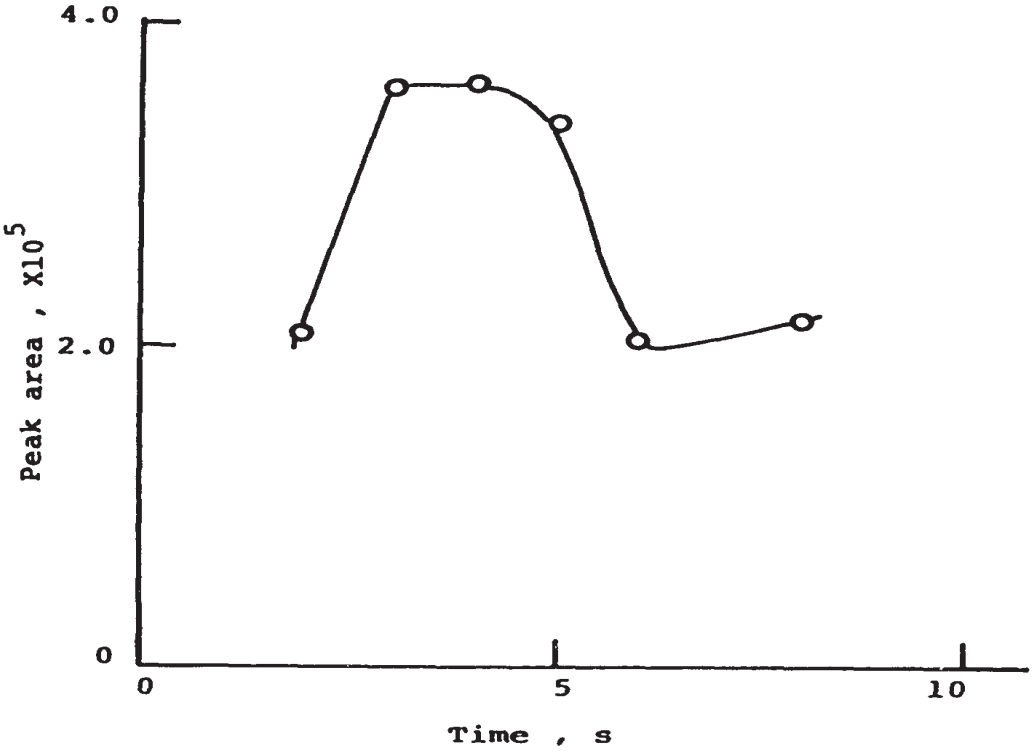

Fig. 5. Effect of time on the pyrolysis of 32 μg morphine hydrochloride.

TABLE 3

Measurement range of alkaloids

Alkaloids	Measurement range (ì g)	Retention time (min)
Morphine · HCl	2.5-40	3.7
Codeine · H_3PO_4	1.0-45	3.8
Dihydrocodeine · H_3PO_4	1.0-45	3.8
Cocaine · HC1	1.0-27	3.9

peak area was a maximum. A pyrolysis temperature of 670°C gave the maximum sensitivity, however (Fig. 4).

The pyrolysis time studied was 2, 3, 4, 5 and 8 s. The optimum pyrolysis time is 3-5 s (Fig. 5).

In this experiment, the pyrolyses of alkaloidal narcotics were carried out as follows: pyrolysis temperature is 670°C; the mixture ratio of iron and sodium carbonate is 4: 1; the amount of mixture is 30 mg; pyrolysis time is 4s.

Determination of pyrolysis products

The determination of alkaloidal narcotics by GC produces a spectrum of several peaks, one of which had a retention time identical that of to 3,4-dimethyl-l,2-dihydroxybenzene (3.7 min). The measurement range of alkaloidal narcotics was about 1-40 /ìg (Table 3). For example, the calibration curve for morphine hydrochloride (we used the commercial drugs) had a straight line with a correlation coefficient of 0.9998, and the relative standard deviation for the pyrolysis of morphine hydrochloride (32 ìg) was 2.5% (n= 10).

Extraction and pyrolysis of cocaine in human urine

The cocaine hydrochloride (13.4 /ìg) added in human urine was extracted with dichloromethane under alkaline conditions and was added to a solution of hydrochloric acid in ethanol. The solvent was evaporated on a hot plate at about 100°C and 0.05 ml of water was then added to the residue. Iron and sodium carbonate were added to the pyrolysis foil. The pyrolysis was carried out at 670°C.

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