

## TECHNICAL NOTE

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# Identification and Quantitation of Norcocaine in Illicit Cocaine Samples

**REFERENCE:** Kumar, A. and Kiser, W. O., "Identification and Quantitation of Norcocaine in Illicit Cocaine Samples," *Journal of Forensic Sciences*, JFSCA, Vol. 40, No. 3, May 1995, pp. 464-466.

**ABSTRACT:** A gas chromatographic method for determining norcocaine concentration in cocaine powder is presented. The lower detection limit was 0.01%. GC/MS was used to confirm the presence of norcocaine. Norcocaine concentrations in 170 of 198 illicit cocaine samples tested ranged from 0.01% to 3.70%, with an average of 0.54%. Norcocaine was not detected in 28 of the 198 samples.

**KEYWORDS:** criminalistics, norcocaine, gas chromatography, impurity

Norcocaine, a hepatotoxin [1], is known to form during the potassium permanganate oxidation stage in the processing of illicit cocaine (Fig. 1) [2,3]. It is also well-known as a metabolite of cocaine [4,5]. This project was initiated in 1990 in response to an inquiry by a toxicologist on the levels of norcocaine present in cocaine before it enters the body. At that time the presence of norcocaine had been reported in illicit cocaine [6], but no extensive quantitative information was available in the literature. Since then, however, several cocaine signature studies have been published that include norcocaine among the impurities of interest in illicit cocaine [7-9]. These studies have systematically quantitated norcocaine using various procedures. This technical note provides additional data, using an alternate method, on the amount of norcocaine in illicit cocaine. A temperature-programmed GLC procedure was developed to quantitate norcocaine in cocaine seizures from across the United States.

## Materials and Methods

### Chemicals

A norcocaine hydrochloride reference standard had been previously synthesized at the DEA Southeast Laboratory by oxidation of cocaine with potassium permanganate. Purity of the standard

Received for publication 7 Sept. 1993; revised manuscript received 7 July and 29 Sept. 1994; accepted for publication 30 Sept. 1994.

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Results of this study were presented at the 43rd Annual Meeting of the Academy of Forensic Sciences, Anaheim, CA, 18-23 February 1991.

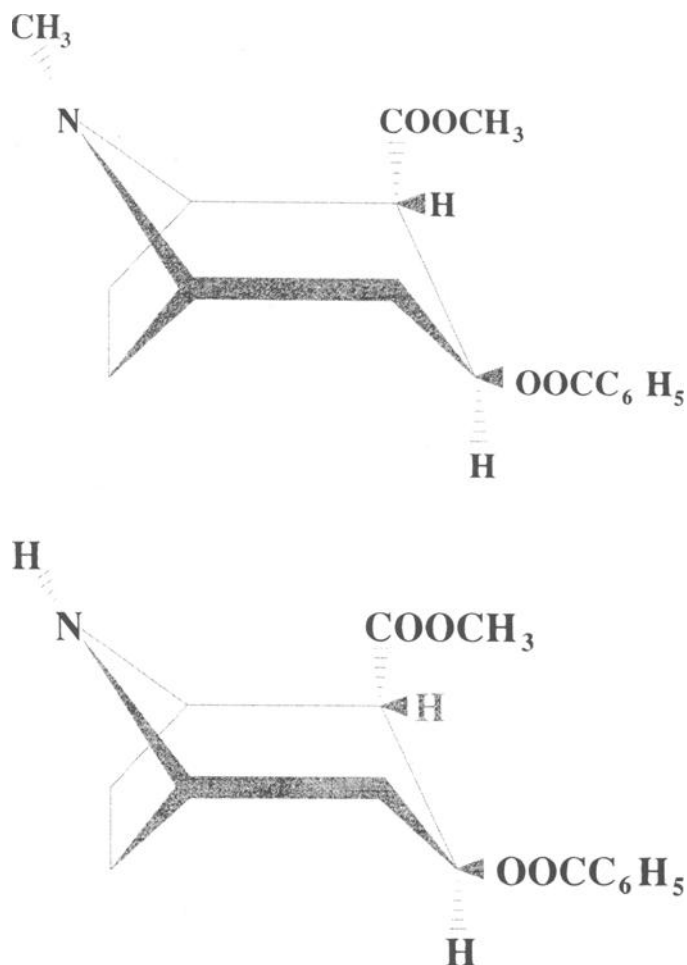


FIG. 1—Structure of (top) cocaine and (bottom) norcocaine.

(>99%) was determined by melting point and GLC. The uncorrected melting point was 113 to 115°C [10], using a Thomas Hoover capillary melting point apparatus. Norcocaine was further confirmed by GC/MS. Eicosane was obtained from Aldrich Chemical Company, Inc.

### Gas Chromatography

A Hewlett-Packard 5890A gas chromatograph equipped with an FID detector and a Hewlett-Packard 3396 integrator was used.

Samples were injected onto a 25 m × 0.20 mm i.d. capillary column coated with Ultra-2 cross linked 5% phenyl methyl silicone with a film thickness of 0.33 μm. The following temperature program was used: 180°C to 200°C at 5°/min, then 200°C to 280°C at 20°/min. The injection port temperature was 275°C. The carrier gas was hydrogen at a head pressure of 12 psi. The integrator settings were: Attenuation 0, threshold 0 and peak width 0.04.

#### Gas Chromatography—Mass Spectrometry

A Hewlett-Packard 5790 MSD interfaced to a Hewlett-Packard 5890A gas chromatograph containing a 12.5 m × 0.20 mm i.d. HP-1 (cross linked methyl silicone gum, 0.33 μm film thickness) capillary column was used. The column temperature was programmed from 150°C to 280°C at a rate of 12°C/min. The injection port temperature was 265°C, the carrier gas was helium, and the ionizing electron energy was 70 eV.

#### Sample Preparation

Kilogram packages of cocaine hydrochloride powder, free of adulterants or diluents, were used as a source of samples. The uncut cocaine hydrochloride samples of 100 mg ± 5 mg were dissolved in approximately 1 mL water. The cocaine hydrochloride was converted to cocaine base by the addition of approximately 2 mL saturated aqueous sodium bicarbonate solution. Exactly 1 mL of chloroform containing 0.5 mg/mL of the internal standard eicosane was then added. The solvents were thoroughly mixed. The aqueous layer was discarded and the chloroform layer containing cocaine base and eicosane was used for analysis. The norcocaine hydrochloride standard was dissolved in water (0.5 mg/mL) and prepared similarly.

Norcocaine was verified by GC/MSD in all samples showing a norcocaine concentration greater than 0.5%.

#### Results and Discussion

The norcocaine concentrations were plotted as a frequency distribution (Fig. 2). The concentrations ranged from 0.01% to 3.70%. The mean was 0.54% and the median was 0.39%. Norcocaine was not detected in 28 of the 198 samples. The mass spectrum (Fig.

3) shows the molecular ion peak at  $m/z$  289 and the base peak at  $m/z$  168.

Figure 4 shows chromatograms of the calibration standard and of samples with varying amounts of norcocaine. The wide peak immediately following norcocaine in the sample chromatograms is cocaine. *N*-formylcocaine and *N*-benzoylnormethylecgonine are also by-products of the potassium permanganate oxidation and are related to the formation of norcocaine (see Fig. 4, legend) [2,3,11]. Almost all samples contained a peak at a wide range of intensities, eluting just after cocaine (see Fig. 4E), that is likely to be *N*-benzoylnormethylecgonine. *N*-benzoylnormethylecgonine, an isomer of norcocaine, is formed when the benzoyl group migrates to the nor- position under basic conditions [3,8,11]. Although much of the *N*-benzoylnormethylecgonine that was observed may be inherent in the samples, it is suspected that some conversion of norcocaine to *N*-benzoylnormethylecgonine may have taken place when sodium bicarbonate was added during sample preparation. *N*-formylcocaine, which is expected to elute just before trans-cinnamoylcocaine (see Fig. 4E), was seen only at very low levels in many samples.

Processors of illicit cocaine add potassium permanganate to the cocaine as an oxidizing agent that whitens the final product by eliminating several coalkaloids, in particular *cis*- and *trans*-cinnamoylcocaine [2,3]. The cinnamoylcocaines oxidize to ecgonine, a water-soluble molecule that is easily separated from cocaine [2]. The stopping point for this oxidative procedure is critical to minimize the breakdown of cocaine and the formation of norcocaine and other impurities. If norcocaine is solely the result of the permanganate procedure, then its presence should correspond with an absence or reduction of the cinnamoylcocaines. Figure 4 depicts the general trend that was observed in the concentration of the cinnamoylcocaines as that of norcocaine increased. Although no quantitative data was generated on the cinnamoylcocaines, the following observations were noted. Significant removal of these alkaloids was apparent in all but one of 20 samples in which the level of norcocaine was greater than 2%. Of the samples with norcocaine concentrations between 1% and 2%, the extent of loss of the cinnamoylcocaines was mixed—four had significant levels, five had a significant loss, and 3 very low amounts. Five samples with less than 1% norcocaine had low amounts of the cinnamoylcocaines. And two samples with less than 0.1% norcocaine had very

### Norcocaine Concentrations Distribution Curve

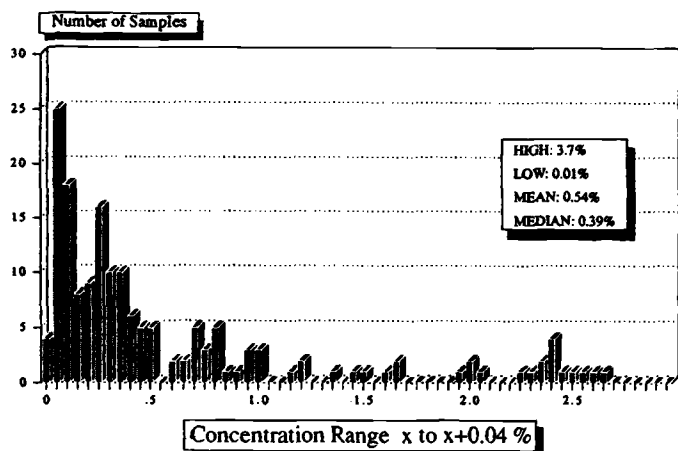


FIG. 2—Frequency distribution curve of norcocaine concentrations.

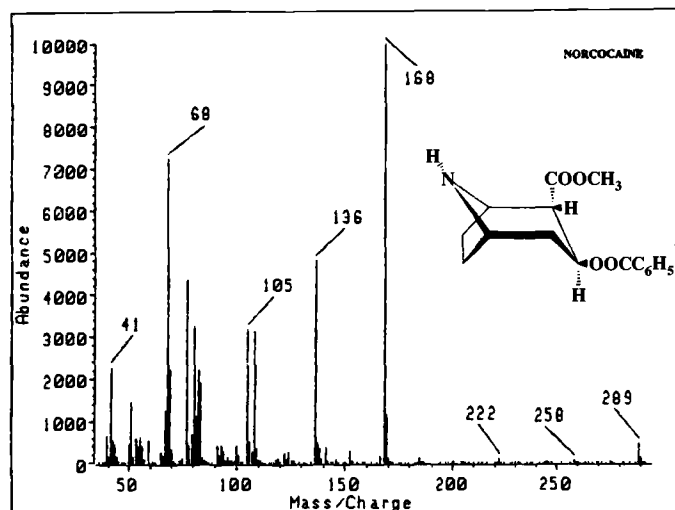


FIG. 3—Mass spectrum of norcocaine.

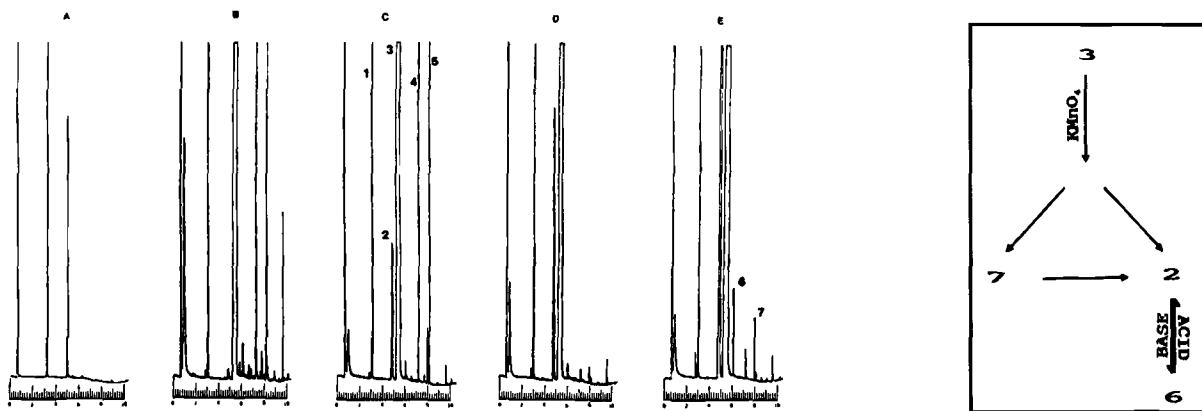


FIG. 4—Gas chromatograms of (A) a calibration standard and (B–E) samples in which the norcocaine concentration was calculated at 0.09%, 1.00%, 1.99%, and 3.70%, respectively. The peak identities are as follows: (1) eicosane, (2) norcocaine, (3) cocaine, (4) *cis*-cinnamoylcocaine, (5) *trans*-cinnamoylcocaine, (6) *N*-benzoylnormethylecgonine and (7) *N*-formylcocaine. The legend summarizes the breakdown of cocaine at the *N*-methyl position during the  $\text{KMnO}_4$  oxidation procedure.

little, and one had none. Of the 28 samples in which no norcocaine was found, all contained major amounts of the cinnamoylcocaines.

These very crude observations suggest that the origin of the norcocaine in cocaine samples is not necessarily the result of the permanganate oxidation procedure, particularly in samples in which norcocaine was detected, along with normal levels of *cis*- and *trans*-cinnamoylcocaine. LeBelle et al., also noted that significant amounts of *N*-formylcocaine were present in samples with normal amounts of the cinnamoylcocaines [11].

Although there is general agreement that the use of potassium permanganate in the processing of illicit cocaine results in the formation of norcocaine, there has been much speculation about other possible sources of the norcocaine. The norcocaine may be a result of oxidation of cocaine by peroxides that have formed in ether that is recycled over and over by processors [7]. LeBelle et al. report having identified norcocaine in coca leaves [6]. The photooxidation of cocaine into norcocaine is another explanation [12,13]. Intelligence reports indicate that cooks may be using alternate oxidizing agents to work around the inclusion of potassium permanganate in national and international chemical control laws and regulations [Sapienza, F.L., DEA Office of Diversion Control].

These are all possibilities. Whatever the explanation may be, the purpose of this project was not to study 'why?' norcocaine is found in illicit cocaine, but 'how much?' is there. This study shows that a significant amount of norcocaine may be present in a sample of cocaine before it enters the body.

#### Acknowledgment

We are grateful to Brenda Simpson, former DEA chemist, for her contributions to this study.

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