



MICROGRAM

Laboratory Division
Office of Scientific Support

BUREAU OF NARCOTICS & DANGEROUS DRUGS / U.S. DEPARTMENT OF JUSTICE / WASHINGTON, D.C. 20537

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d-desoxyephedrine in small white plastic bags marked with a floral design is reported by BNDD San Francisco Regional Laboratory. Each bag measures 17 by 8 centimeters and contains approximately 25 grams of active ingredient. Both ends of the bags are heat sealed.

Lidocaine HCl sold as cocaine has been reported by the Northern Illinois Police Crime Laboratory. The "white crystalline powder" has been found in both foil and plastic packets.

Heroin and MDA (3,4-methylenedioxyamphetamine) in combination has been reported by the Canadian Food and Drug Directorate. Exhibits consisted of #5 size capsules, each containing 64 milligrams of MDA and 4 milligrams of heroin.

Procaine (100%) is being sold as heroin in the New York area.

PCP (Phencyclidine)/Procaine mixtures are being sold as cocaine on the West Coast and inositol is used as a diluent.

LSD as a light gray powder in foil packets has been encountered by BNDD Chicago Regional Laboratory. Net weight of the packages ranged between 320 and 420 milligrams. LSD content, calculated as the base, was between 6.8 and 7.9 micrograms per milligram of powder.

Suspected DMT (dimethyltryptamine) on plant material was found, by BNDD Miami Regional Laboratory, to be phencyclidine base. The exhibit had a strong odor of peppermint, probably to mask the odor of the PCP base. Analysis revealed 7 milligrams PCP base per gram of plant material. Sachets could be made using other perfumes such as lavender, rose, etc. for smuggling or storage purposes.

Brown heroin, usually associated with the U.S./Mexico border, was recently reported as having come from Hong Kong. The material called "Brown Chunk Heroin" consists of lumps about the size of the end of a ball point pen. Analysis revealed 47.9% heroin.

Analytical methods in **Microgram** do not have official status. Use of funds for printing this publication approved by the Bureau of the Budget, April 8, 1969. **CAUTION:** Use of this publication is restricted to law enforcement agencies.

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LSD and Jalap resin in pale green tablets is reported from the Des Moines, Iowa area. The tablets, sold as mescaline, are round, biconvex, uncoated, unscored, 6.5 mm. in diameter, 2.7 mm. thick at center with bevel thickness of 1.4 mm. Weight of one tablet is 75.4 milligrams. BNDD Chicago Regional Laboratory found 66 micrograms of LSD and a quantity of Jalap resin per tablet. Jalap resin is known as a very powerful cathartic. The Iowa Drug Abuse Authority reported several admissions to the hospital following ingestion of the tablets.

NOTICE

Aerosol Sniffing: The Food and Drug Administration is investigating blood and tissue Freon levels in persons dying from aerosol sniffing. At least one gram portions of kidney, liver, brain, adrenal and blood are desired. Tissue should be quick frozen and held frozen until picked up by FDA. The interval between death and freezing should be recorded as accurately as possible. Contact Dr. Francis Marzulli, FDA, BF-154, Room 6018, 200 C Street, S.W., Washington, D.C. 20204 for further details. If samples are obtained, call collect 962-4385, area code 202.

MEETINGS

Western Conference on Criminal and Civil Problems, May 25, 26, & 27, 1972, at the Broadview Hotel, Wichita, Kansas. Contact: William G. Eckert, M.D., P.O. Box 8282 (Tele: 316-262-6211, Ext. 131), or Maj. Clyde E. Bevis, Wichita Police Department, P.O. Box 8282, Wichita, Kansas 67208.

California Association of Criminalists, Semi-annual seminar, May 18-20, 1972. Pierpont Inn, Ventura, California. For further information, contact:

Forrest Letterly
Ventura County Sheriff's Office
501 Poli Street
Ventura, California 93001

BNDD LABORATORY NOTES

DATE March 16, 1972

NO. 36

-38-

DRUG TYPE Narcotic

METHODOLOGY

Some Observations On The Quantitative Analysis Of Purportedly Pure Cocaine And Heroin Samples

by

James M. Moore
Forensic Chemist
Special Testing and Research Laboratory

This paper is a by-product of an analytical investigation into the identification of substances associated with the illicit manufacture of cocaine and heroin. It has been observed that, depending upon the quantitative method used, analytical results for some uncut cocaine and heroin samples could vary significantly. These observations were made during the past two years in dealing with illicit, uncut samples seized in Southeastern United States, Central and South America, and Southeast Asia.

In the quantitative analysis of cocaine and heroin most methodology includes either ultraviolet spectroscopic or gas chromatographic determinative steps. This paper will discuss those cases where significant differences were found using both techniques. In the samples studied it was observed that the ultraviolet results were consistently higher than those obtained by gas chromatography. Some samples were 10-15% higher. The gas chromatographic methods for cocaine (1) and heroin (2) gave the more accurate results in these cases. This paper will offer explanations to account for these quantitative discrepancies due to substances most commonly associated with illicit manufacture.

A. Cocaine

In the spectrophotometric analysis of uncut cocaine probably the most widely used technique is dissolution of the sample in dilute acid or alcohol and utilizing the maxima at either 275 or 232 μ for quantitative purposes. One substance detected in more than 25% of the samples examined has been tentatively identified as cinnamoylcocaine. This is an alkaloid indigenous to the South American coca plant. Its presence or absence in cocaine samples can be detected initially as a shoulder on the 275 μ maximum (see Figure 1). If the powdered sample containing cinnamoylcocaine is pretreated with diluted potassium permanganate the shoulder on the 275 μ band disappears. This is due to destruction of the conjugative system in cinnamoylcocaine involving the carbon-carbon double bond with the carbonyl group and also with the benzene ring. This yields a non-conjugated species that has weak absorption in the 250-270 μ range.

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Due to its high molar absorptivity at 280 μ ($E_{1\%}^{1\text{cm.}} = \text{ca. } 1000$) cinnamoylcocaine in concentrations of less than 1% can cause 15% high error in cocaine samples if the 275 μ band is used. On the other hand cinnamoylcocaine has minimal absorbance at the 232 μ cocaine maximum (see Figure 2). Using this band for cocaine quantitation close agreement with the chromatographic analysis (1) was possible. Cocaine and cinnamoylcocaine were found to be inseparable via conventional extraction techniques.

Benzoyllecgonine is a primary hydrolysis product of cocaine and has been detected in cocaine samples in quantities as high as 5%. Since benzoyllecgonine contains the same conjugated system as cocaine their ultraviolet spectra are the same. For this reason direct dilution and utilization of either the 275 or 232 μ bands is not possible. A simple basic extraction, though, would eliminate benzoyllecgonine using ether as the organic solvent.

Ecgonine and methylecgonine, also hydrolysis products of cocaine, contain no conjugative systems and so do not absorb appreciably in the near ultraviolet. Therefore, mixtures of only cocaine and these two substances could be diluted directly and the cocaine determined in the ultraviolet. It is unlikely, though, that cocaine samples would contain either ecgonine or methylecgonine without also containing benzoyllecgonine.

Though a number of other substances have been detected in uncut cocaine samples, their presence is not believed to affect quantitation significantly. It is interesting to note that cocaine seizures from different sources produced different gas chromatograms using silyl derivatization (3). Figures 3 and 4 are two uncut cocaine seizures from Miami and Panama, respectively. Both samples assayed close to 100% by direct dilution and ultraviolet methodology but by direct gas chromatographic analysis results of 89% (Panama) and 92% (Miami) were obtained. Figure 5 is a derivatized chromatogram of Ecuadorian cocaine paste. Though the exact process for manufacture of this paste is not known it is believed to be an intermediate product in the extraction of alkaloids from the coca plant and production of purified cocaine. The paste assayed 22% cocaine, 43% benzoyllecgonine, 7% ecgonine and 3% benzoic acid. It also contained other substances including significant quantities of cinnamic acid derivatives.

Detection of benzoyllecgonine, ecgonine, etc., in cocaine samples is difficult by conventional gas or thin-layer chromatography. This is due to their small quantities and their very polar nature which renders them unsuitable for most chromatographic techniques. Infrared techniques cannot detect these substances and with the exception of cinnamoylcocaine ultraviolet detection is not possible. Majlát and Bayer (4) describe a rather time consuming chromatographic method for detection of ecgonine and benzoyllecgonine in cocaine. Fish and Wilson (5) detected benzoyllecgonine in urine by methylating it with diazomethane to form cocaine and chromatographing it. A melting point determination is useful as a screening procedure for uncut cocaine samples. If a depression in the melting point is observed indicating the presence of cocaine-related alkaloids, then gas chromatography would probably yield the most accurate quantitative results.

B. Heroin

The two substances encountered most frequently and in significant quantities in heroin samples are O^6 monoacetylmorphine and acetylcodeine. The former is a primary degradation product of heroin, and the latter is an acetylation by-product in heroin which occurs due to the incomplete isolation of morphine from codeine in opium prior to acetylation. Other substances have also been detected but not in sufficient amounts to affect ultraviolet quantitation.

Direct dilution followed by gas chromatographic analysis of heroin is accurate even in the presence of these substances. Since both acetylcodeine and O^6 monoacetylmorphine absorb near heroin in the ultraviolet their presence would make direct dilution followed by ultraviolet analysis somewhat inaccurate. Nakamura and Meuron (6) isolated heroin from O^6 monoacetylmorphine, but not acetylcodeine, by column chromatography. We have quantitated acetylcodeine in heroin samples using gas chromatography (2), after insuring the absence of O^6 monoacetylmorphine as they both have the same retention time. Results have shown acetylcodeine in amounts as high as 10%. The BNDD New York Regional lab recently reported acetylcodeine at a slightly higher level. Most of the samples examined by our laboratory apparently have a S.E. Asian origin.

Detection of O^6 monoacetylmorphine and acetylcodeine is somewhat easier than for cocaine degradation products. The I.R.S. methods of analysis (7) provides TLC systems satisfactory for detection of O^6 monoacetylmorphine in heroin, but not acetylcodeine. Acetylcodeine and heroin have the same rf values in these systems. To overcome this problem Delmar (8) recently modified a method by Nakamura (9) capable of detecting acetylcodeine in heroin by thin-layer chromatography.

Conclusions

When dealing with illicit samples that originate from clandestine manufacture one must be cautious in selecting a method for quantitation. One must consider the possible presence of related substances that reflect the quality of the manufacturing process used. Substances such as benzoylecgonine and acetylcodeine can affect UV quantitation and must be eliminated to obtain the most accurate results. As an alternative, when the presence of these impurities is suspected one may proceed directly with gas chromatographic analysis.

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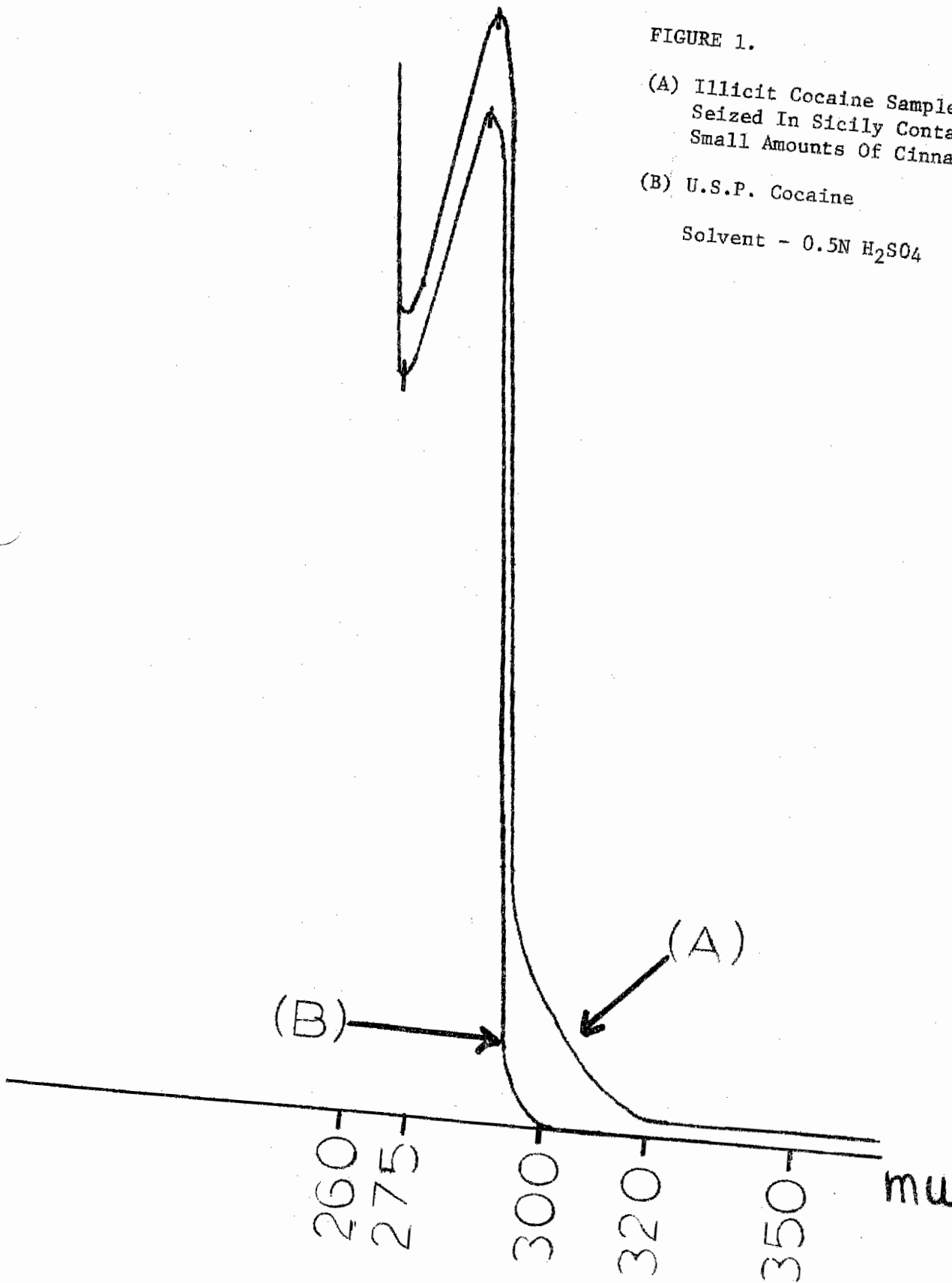
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FIGURE 1.

(A) Illicit Cocaine Sample
Seized In Sicily Containing
Small Amounts Of Cinnamoylcocaine

(B) U.S.P. Cocaine

Solvent - 0.5N H₂SO₄



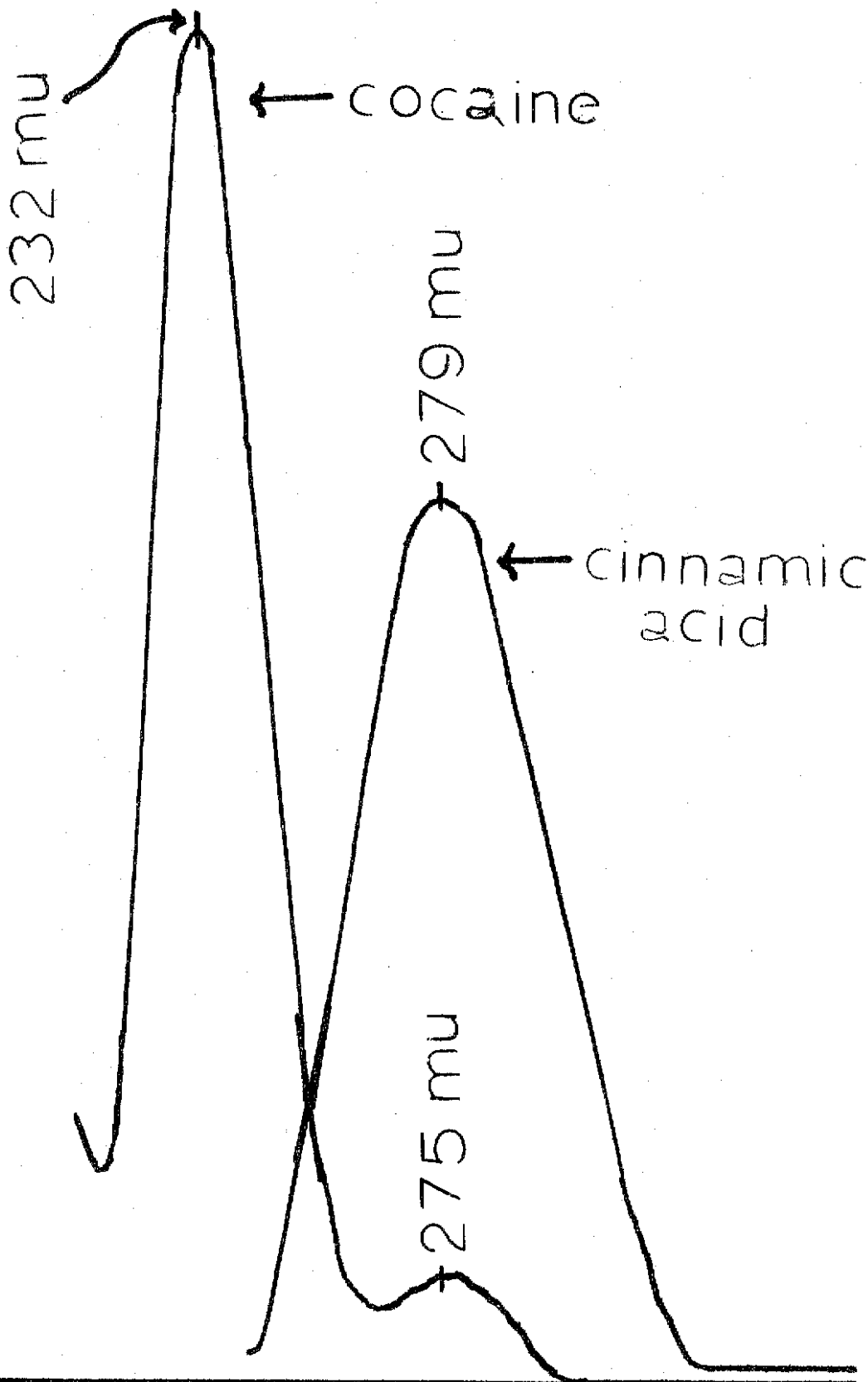


FIGURE 2. Cocaine HCl and cinnamic acid in 0.5N H₂SO₄ having concentrations of 0.02 mg./ml. and 0.004 mg./ml., respectively (cocaine ABS. at 232 mμ = 0.850)

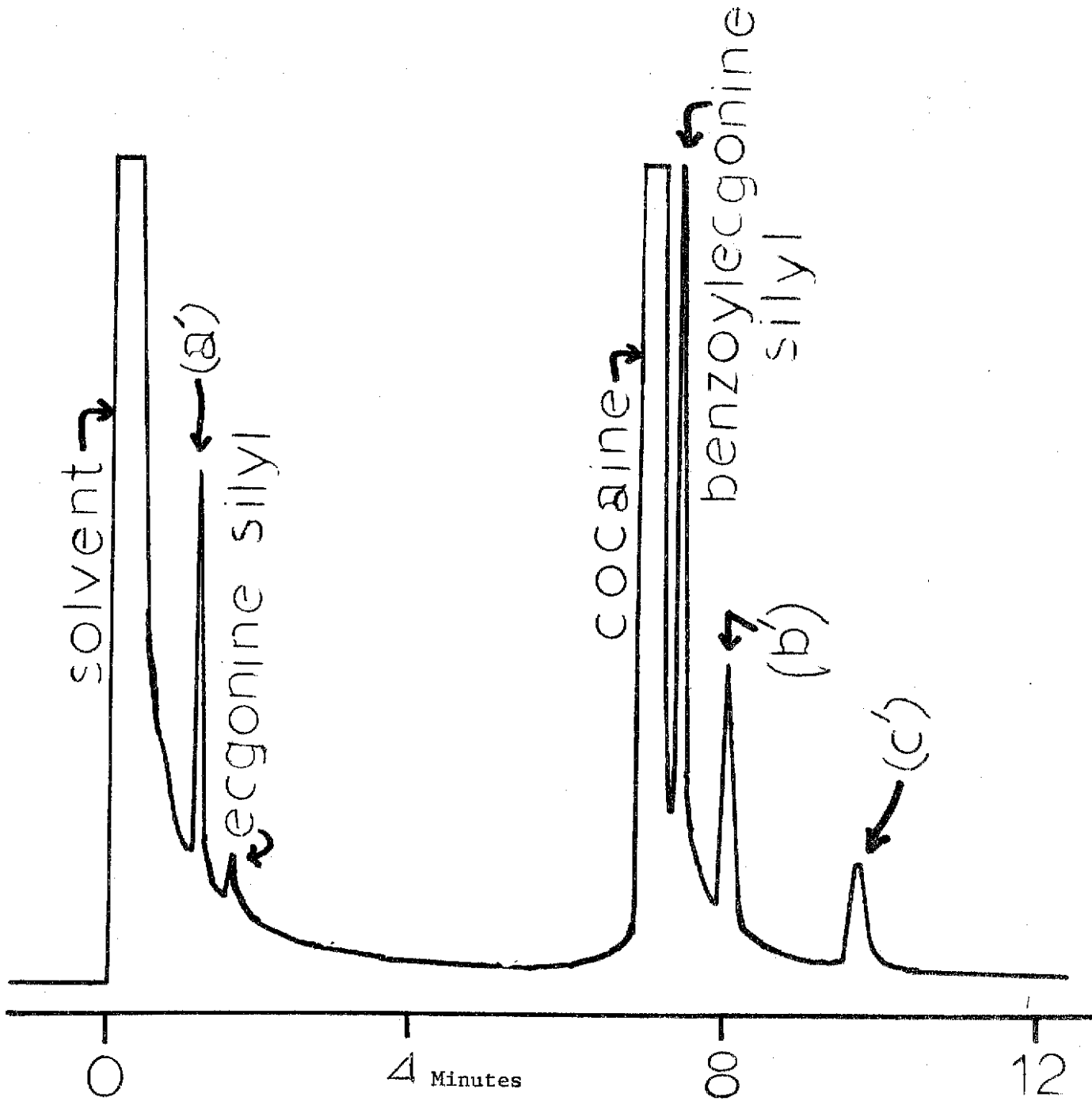


FIGURE 3. Gas chromatogram of derivatized uncut cocaine seizure from Miami, Florida.

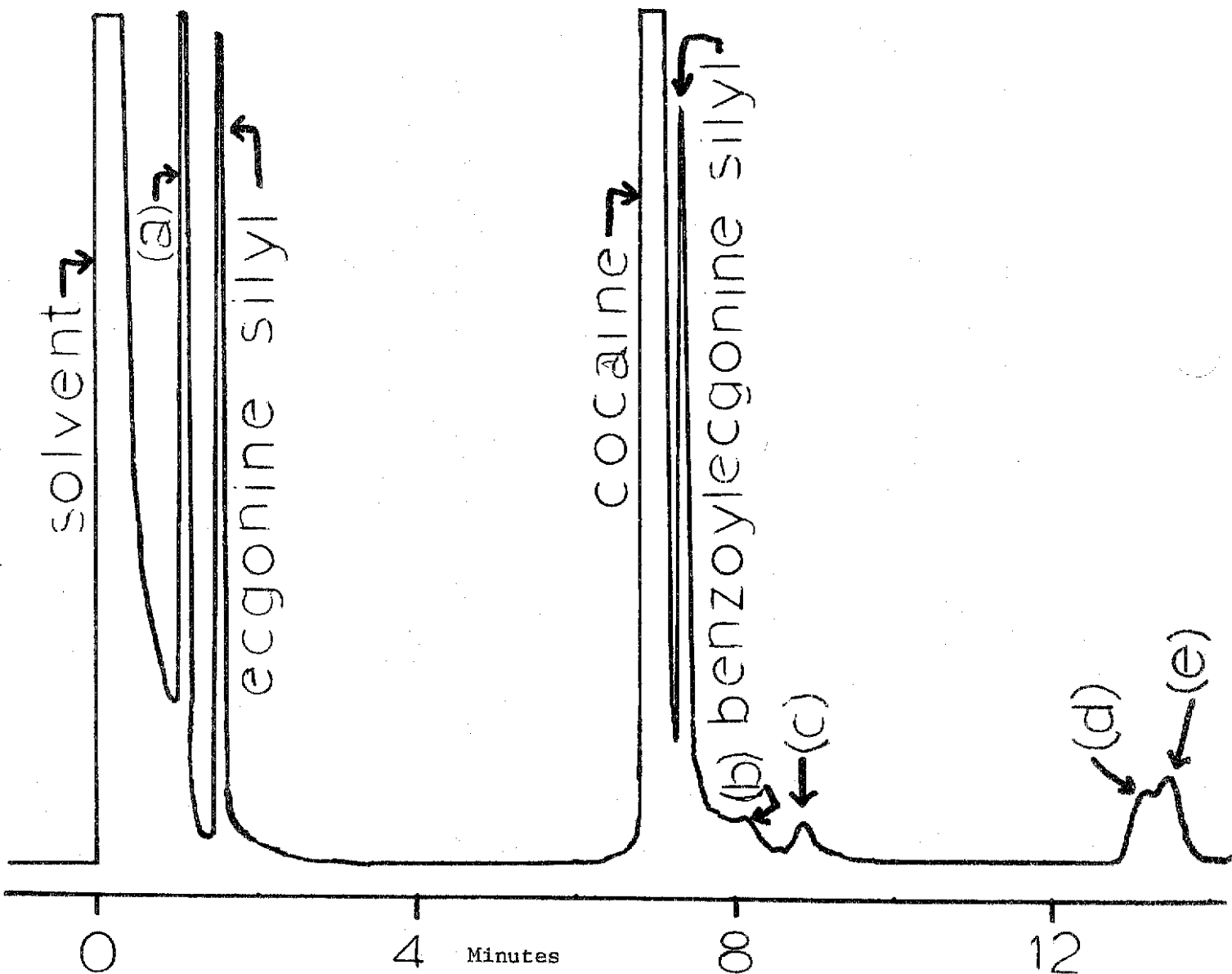


FIGURE 4. Gas chromatogram of derivatized uncut cocaine seizure from Panama.

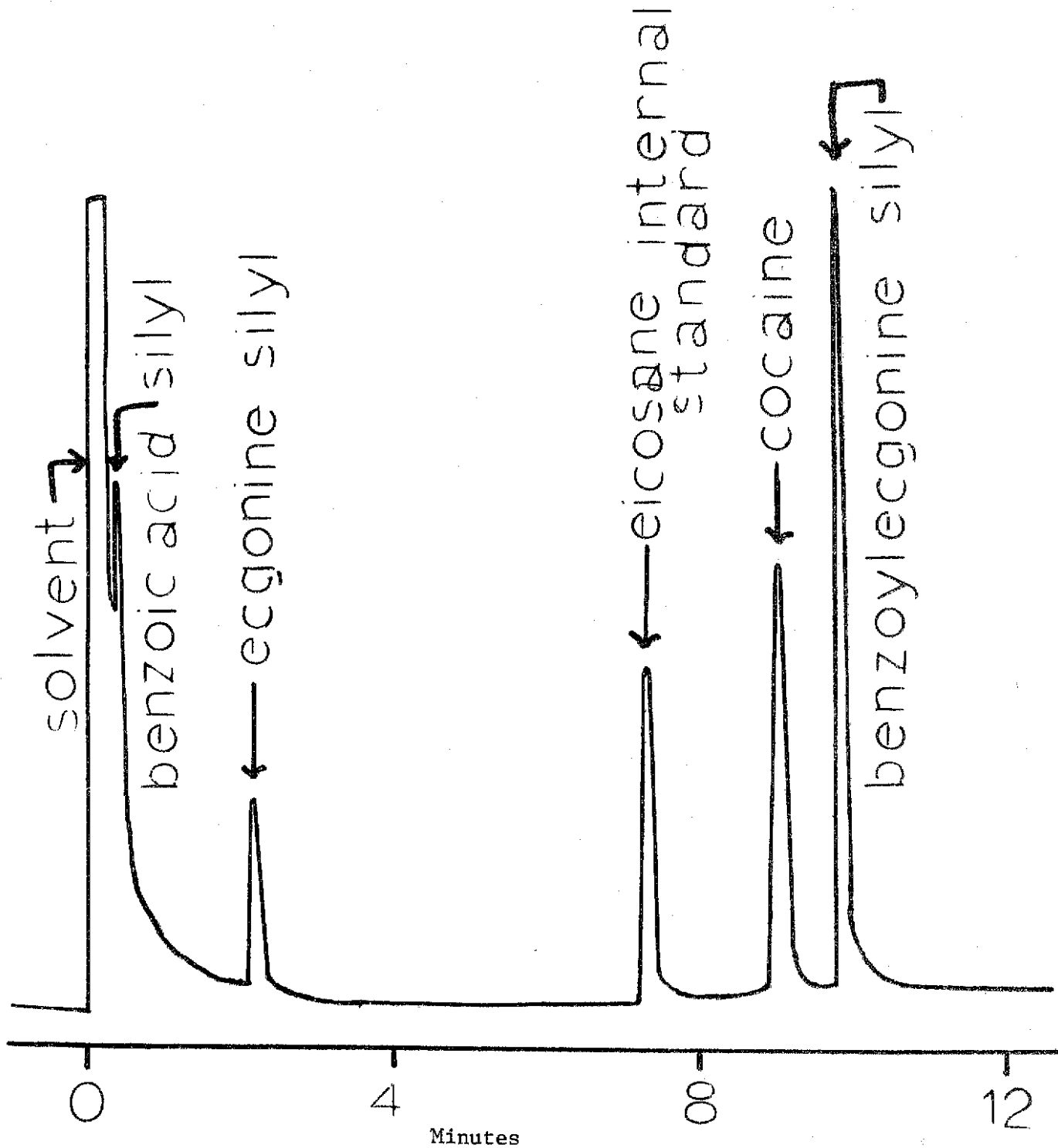


FIGURE 5. Gas chromatogram of derivatized Ecuadorian cocaine paste.