

## Unequivocal Identification of Several Common Adulterants and Diluents in Street Samples of Cocaine by Infrared Spectroscopy

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**ABSTRACT:** This paper describes an improved method for the direct identification of adulterants and diluents in street samples of cocaine using infrared spectroscopy. The proposed method requires a versatile software package designed for handling infrared data on a personal computer. The spectra of the mixtures of cocaine.HCl and several common adulterants (caffeine, procaine.HCl, lidocaine.HCl and piracetam) and diluents (glucose, lactose, sucrose, starch and mannitol) were recorded. Two regions were chosen in the infrared spectra: 1800-1500  $\text{cm}^{-1}$ , which includes all the assayed adulterants, and 960-860  $\text{cm}^{-1}$ , for sugars and polyalcohols. The display of the different spectra through the computerized program allowed the identification of the above mentioned substances even at 5% concentration.

**KEYWORDS:** toxicology, cocaine, adulterants, diluents, infrared analysis

The evergrowing abuse of drugs is a problem of great concern to government authorities and to society. These substances may be marketed in nearly pure or adulterated, diluted or contaminated forms. Spanish regulations require complete analysis of illegally distributed drug samples for Court resolution of drug abuse smuggling cases, because the sentence imposed varies according to the percent content of the active product in the sample.

The presence of adulterants and/or diluents can also help establish a common origin for otherwise unrelated seizures. Moreover, the accompanying impurities should always be considered in the adverse reactions that complicate the effects of the drug; although, according to sound experience in our laboratory [1], it is rare to find an adulterant in the street samples more toxic than the addictive substance itself.

The most frequently analysed illicit drugs are cannabis, cocaine, heroin, and the amphetamines. Of the street drug samples seized by the police and brought to National Institute of Toxicology in

Seville, Spain, for analysis, approximately 50% contain cocaine; of these, over 90% are mixtures of cocaine.HCl and a single diluent or adulterant. Based on our analytical results, the most frequently found adulterants are lidocaine, procaine, caffeine and piracetam, while the most commonly used diluents are carbohydrates such as glucose, lactose, sucrose, starch and polyalcohols such as mannitol.

Unfortunately, many of the methods used in the identification of pure cocaine cannot be applied directly to street samples due to the presence of these adulterants and diluents. The analysis of illicit substances in forensic toxicology is generally performed by gas chromatography [2,3], high pressure liquid chromatography [4] and gas chromatography-mass spectrometry [5-7]. Other less frequently used techniques include nuclear magnetic resonance spectroscopy [8] and dispersive or Fourier-transform infrared spectroscopy [9-11]. Although adulterants can be identified with these techniques, gas chromatographic identification and quantification of carbohydrate diluents requires the preparation of trimethylsilyl (or other, similar) derivatives [12] to increase their volatility.

Infrared spectroscopy is a powerful analytical technique frequently used for the qualitative analysis of drugs in forensic toxicology. Nevertheless, difficulties are encountered when using this technique for mixed street samples. The resulting spectra are usually rather complicated and the identification of the different components is quite difficult, especially minor components with concentrations of approximately 5%. However, with the combination of powerful computerized programs and infrared spectroscopy, it is now possible to resolve binary mixtures of cocaine.HCl with any of the common adulterants or diluents listed previously.

The main purpose of this paper is the application of infrared spectroscopy to the direct identification of these adulterants and diluents in cocaine.HCl street samples, using two different regions in the IR spectrum (1800-1500  $\text{cm}^{-1}$  and 960-860  $\text{cm}^{-1}$ ) and a versatile software package for handling infrared data in a personal computer. This method is not for quantitation, although this is possible with certain limitations.

### Experimental

#### Reagents

Cocaine hydrochloride, procaine hydrochloride, and lidocaine hydrochloride were obtained from Sigma-Aldrich Química, Spain. Glucose, sucrose, lactose, mannitol, starch, caffeine, piracetam and potassium bromide were obtained from Merck, Germany.

#### Apparatus

The infrared spectra were obtained with a Perkin-Elmer Model 1420 Infrared Spectrophotometer attached to a Perkin-

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TABLE 1—IR Frequencies ( $\text{cm}^{-1}$ ) of adulterants and diluents.

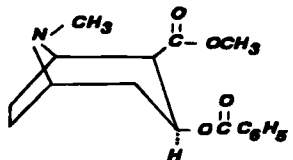
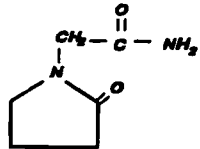
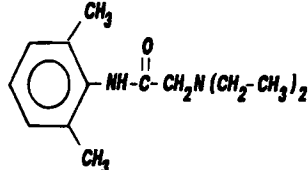
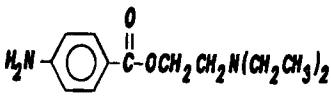
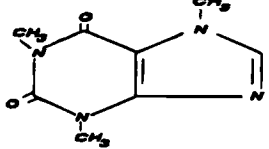
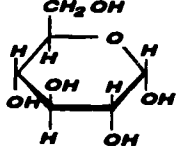
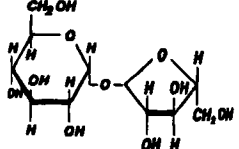
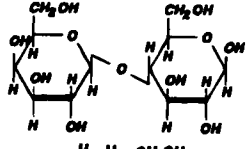
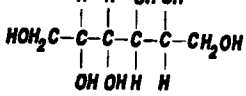
Compound	Structure	Frequency ( $\text{cm}^{-1}$ )	
		1800–1500	960–860
Cocaine		1714,1698	946,918,889
Piracetam		1692,1654	952,924,901
Lidocaine		1671,1654,1540	952,920,878
Procaine		1689,1641,1604,1571,1514	911,900
Caffeine		1690,1657,1599,1548	928
Glucose		—	910
Sucrose		—	936,905,868
Lactose		—	909,893,870
Mannitol		—	926,884,868
Starch	$(\text{C}_6\text{H}_{10}\text{O}_5)_n$	—	924

TABLE 2—IR frequencies ( $\text{cm}^{-1}$ ) of synthetic mixtures of cocaine with different adulterants and diluents.

Synthetic mixtures	Frequency ( $\text{cm}^{-1}$ )	
	1800–1600	960–860
Cocaine+Piracetam	1728,1711,1692,1651	954,925
Cocaine+Lidocaine	1726,1708,1535	953,923,895
Cocaine+Procaine	1727,1708,1693,1642,1606,1517	953,924,912,897
Cocaine+Caffeine	1725,1706,1656,1598,1549	953,924,895
Cocaine+Glucose	1726,1709	917
Cocaine+Sucrose	1726,1709	943,922,912,868
Cocaine+Lactose	1726,1709	916,899,875
Cocaine+Mannitol	1726,1709	933,891,873
Cocaine+Starch	1726,1709	953,924,896

Elmer Model 3600 Infrared Data Station. The equipment was attached to a IBM 80486 PC and a Pinwriter P22Q printer. Spectra recorded in the IR Data Station were transferred to the computer by the Software "Send IR" (Perkin-Elmer), and were handled by the IR Data Manager IRDM (Perkin-Elmer).

Potassium bromide (KBr) pellets (13 mm) were prepared with an Evacuatable KBr Die and a manual hydraulic 15 Ton Press.

#### Procedure

The typical maximum concentration of adulterant or diluent found in samples we receive is 30%; therefore, standard stock mixtures were prepared by mixing pure cocaine.HCl with 5 to 30% of the adulterant or diluent. 0.3 to 3 mg of this mixture was then added to 300 mg of KBr, and the resulting mixture was thoroughly ground in an agate mortar and pestle. A ram pressure of 10 tons was applied to prepare the pellets. Transmission spectra were recorded and the areas of interest were expanded with the IR Data Manager program.

#### Results and Discussion

Two regions of the IR spectra were used for the identification of the different components of the samples. The region between 1800 and 1500  $\text{cm}^{-1}$  provided information on stretching vibrations ( $\nu$  (C = O),  $\nu$  (C = C) in aromatic rings and in alkenes) and on in-plane bending in the  $\delta$  (NH) mode. The IR region between 960 and 860  $\text{cm}^{-1}$  corresponds to out-of-plane bending.

Figures 1 and 2 show the complete cocaine.HCl spectrum (upper traces) where a rectangle was drawn around each of the above mentioned regions; in the lower traces, each framed area has been expanded (zoom window).

In Table 1, IR frequencies of cocaine.HCl and of each of the other pure compounds are tabulated. IR frequencies of all the assayed synthetic mixtures (cocaine.HCl 70%, single adulterant or diluent 30%) are in Table 2.

#### 1800–1500 $\text{cm}^{-1}$ Region

The cocaine.HCl spectrum showed two strong bands ( $\lambda = 1714$  and 1698  $\text{cm}^{-1}$ ), attributable to stretching vibration of the two carbonyl groups  $\nu$  (C = O).

When the spectra of the synthetic mixtures of cocaine.HCl and carbohydrates were recorded, these two bands were shifted to slightly lower frequencies ( $\lambda = 1726$  and 1708  $\text{cm}^{-1}$ ) with no new signals (Fig. 3A). From these data, it was clear that if the test sample contained only cocaine.HCl, or if it was diluted only with a sugar, the identification of the diluent was not possible in this region of the IR spectrum.

In contrast, if the synthetic mixtures contained other substances (piracetam, lidocaine.HCl, procaine.HCl, or caffeine), the identification was possible (Fig. 4). The piracetam mixture showed shifted bands of cocaine.HCl, plus two additional intermediate bands at 1692 and 1651  $\text{cm}^{-1}$ . The latter was due to the  $\nu$  (C = O) vibration of amide, while the former was probably due to the  $\nu$  (C = O) vibration of the 5 member cyclic ketone of piracetam (Fig. 4A).

The spectrum of the procaine.HCl-cocaine.HCl mixture showed four new bands, two strong ( $\lambda = 1693$  and  $\lambda = 1606$   $\text{cm}^{-1}$ ) and two weak ( $\lambda = 1642$  and 1517  $\text{cm}^{-1}$ ). These corresponded to the  $\nu$  (C = O) and  $\delta$  (NH) vibrations of procaine, somewhat shifted from the pure compound (Fig. 4A).

Procaine and piracetam were unequivocally distinguished by the strong 1606  $\text{cm}^{-1}$  band of procaine, which piracetam does not display.

When lidocaine was present in the mixture, the IR spectrum showed the characteristic shifted bands ( $\lambda = 1726$  and 1708  $\text{cm}^{-1}$ ) of cocaine.HCl. A faint new band  $\lambda = 1535$   $\text{cm}^{-1}$ , attributable to the in-plane bending in the NH mode, was useful for identification (Fig. 4B).

The IR spectra of caffeine mixtures were far more complex, with a very strong band at  $\lambda = 1656$   $\text{cm}^{-1}$ , an intermediate one at  $\lambda = 1549$   $\text{cm}^{-1}$  and a faint band at  $\lambda = 1598$   $\text{cm}^{-1}$ . All three bands characterized the compound and indicated stretching vibrations  $\nu$  (C = N) and (C = O)-N (Fig. 4B). They could be used for identification purposes.

Therefore, in the 1800–1500  $\text{cm}^{-1}$  region, it was possible to identify the four most frequent adulterants of cocaine found in street sample seizures.

#### 960–860 $\text{cm}^{-1}$ Region

In this region, the cocaine.HCl spectrum showed three faint bands at  $\lambda = 946$ , 918 and 889  $\text{cm}^{-1}$ . All three are difficult to assign, but they are probably attributable to bending vibrations out-of-plane (Fig. 2).

The IR spectra of the different synthetic mixtures of cocaine.HCl and adulterants (Fig. 4) showed that the three above mentioned bands were always maintained with a slight shift to higher frequencies ( $\lambda = 954$ , 925 and 895  $\text{cm}^{-1}$ ).

Only procaine could be unequivocally identified in this region (Fig. 4C), due to a new band at 912  $\text{cm}^{-1}$ . Consequently, this region did not seem to be very useful for the identification of the adulterants considered in this study.

However, correct identification of the various diluents could be accomplished (Fig. 3B and 3C). In the synthetic mixture with mannitol, the IR spectrum maintained the characteristic band of cocaine ( $\lambda = 889$   $\text{cm}^{-1}$ ) with two new bands at  $\lambda = 933$  and

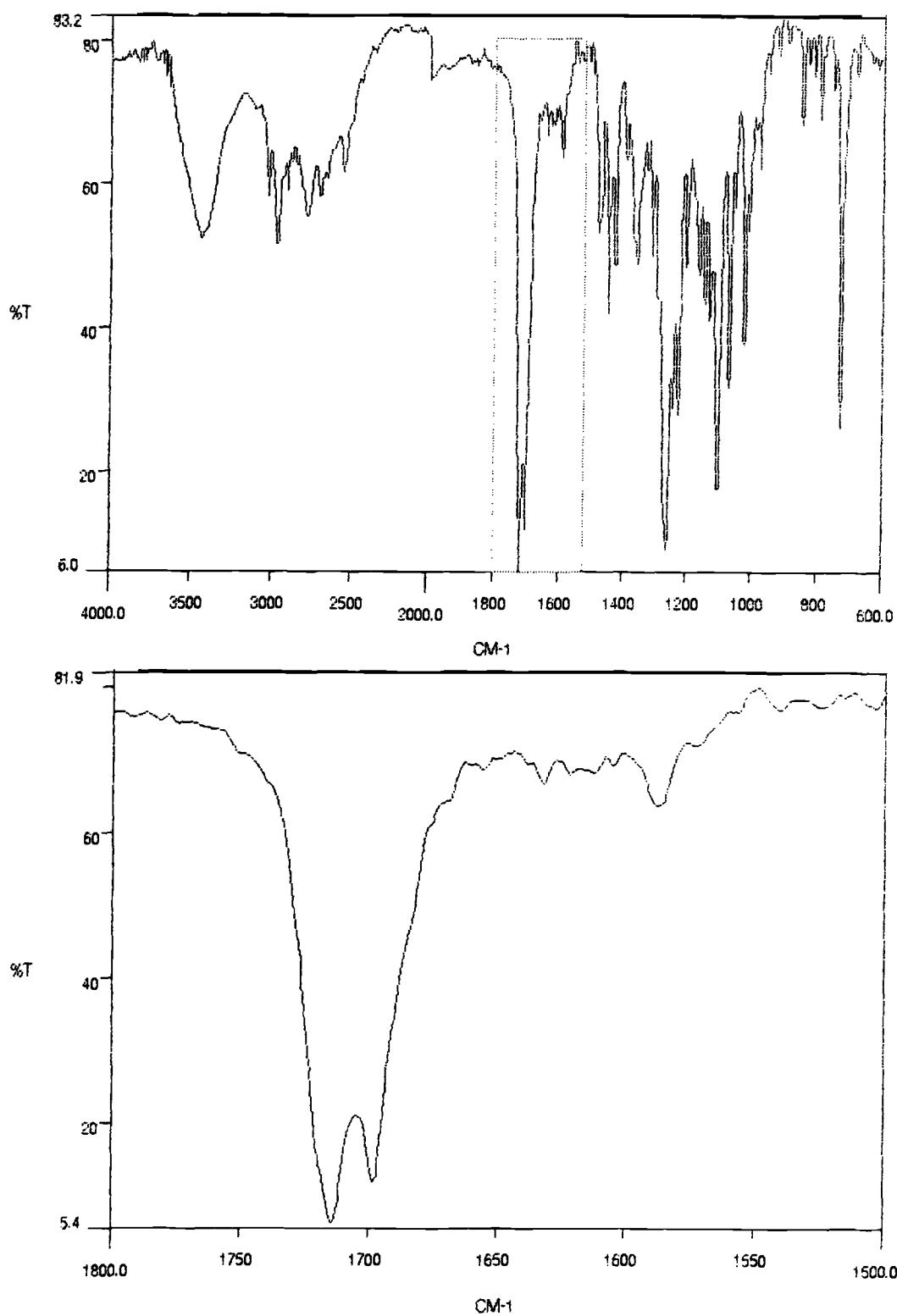


FIG. 1—Transmission spectrum of cocaine.HCl (upper trace) and expansion of spectrum at  $1800\text{--}1500\text{ cm}^{-1}$  (lower trace).

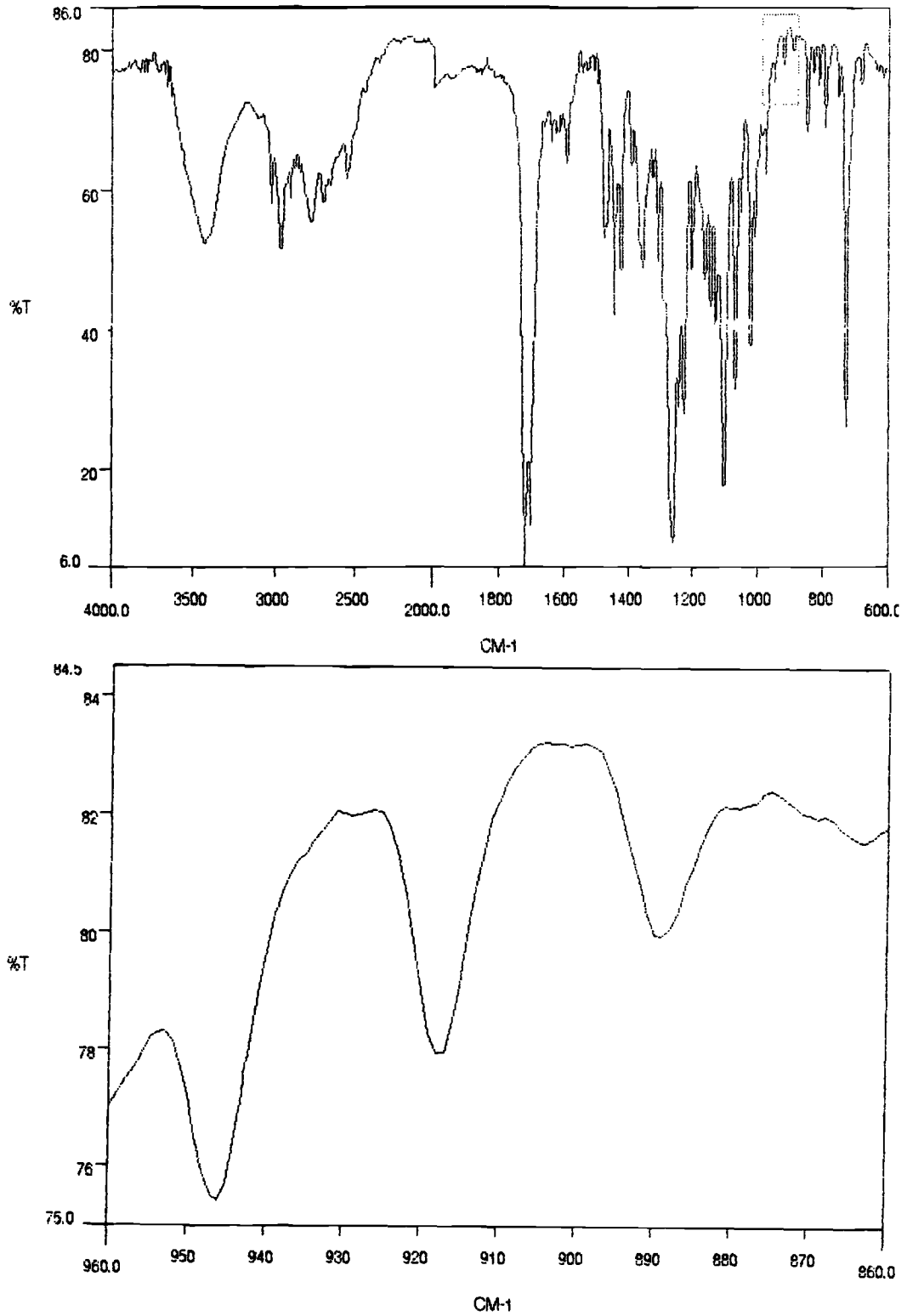


FIG. 2—Transmission spectrum of cocaine.HCl (upper trace) and expansion of spectrum at  $960\text{--}860\text{ cm}^{-1}$  (lower trace).

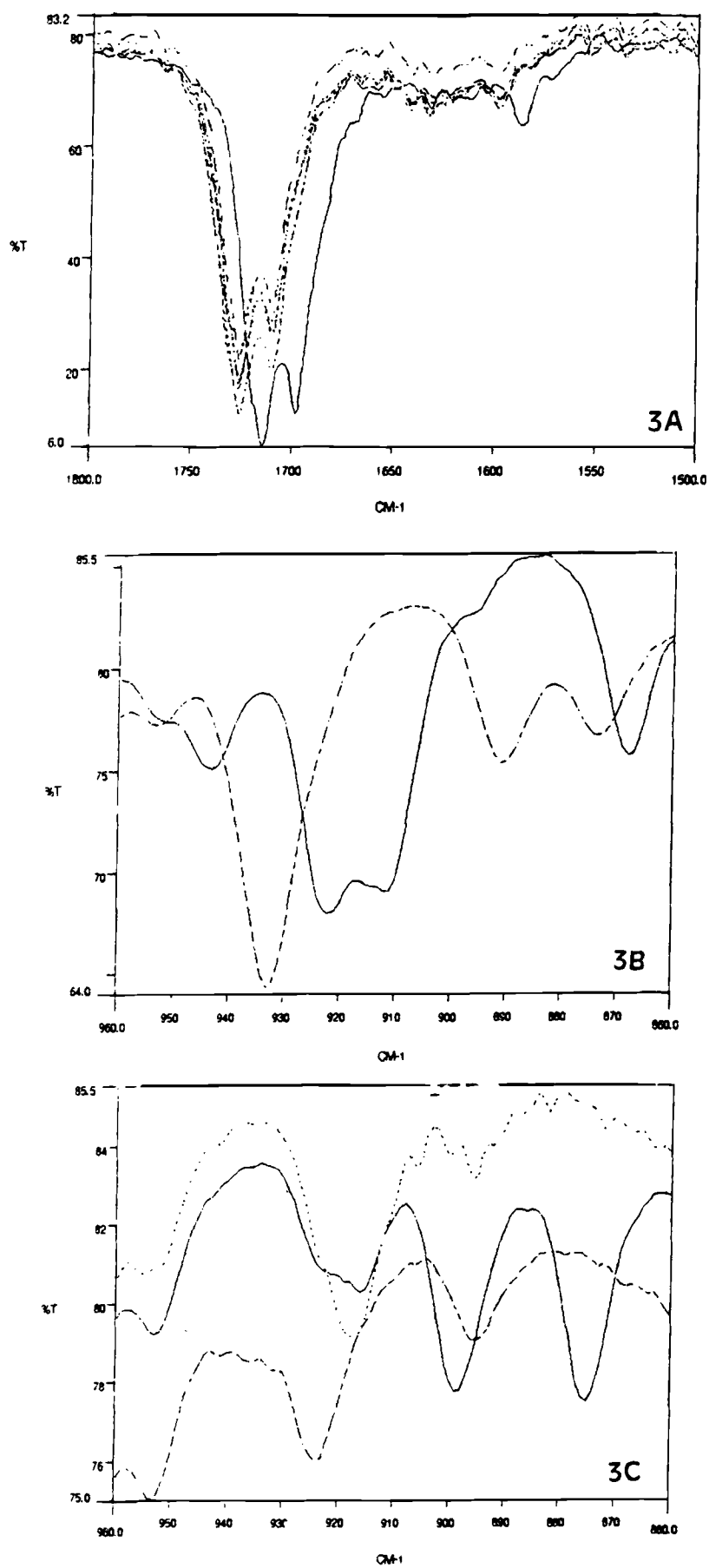


FIG. 3—Transmission spectra of synthetic mixtures of cocaine.HCl (70%) and diluents (30%): (A)  $1800$ – $1500$   $\text{cm}^{-1}$  region, all mixtures; (B)  $960$ – $860$   $\text{cm}^{-1}$ : sucrose (—), mannitol (---); (C)  $960$ – $860$   $\text{cm}^{-1}$ : lactose (—), starch (---), glucose (-.-.).

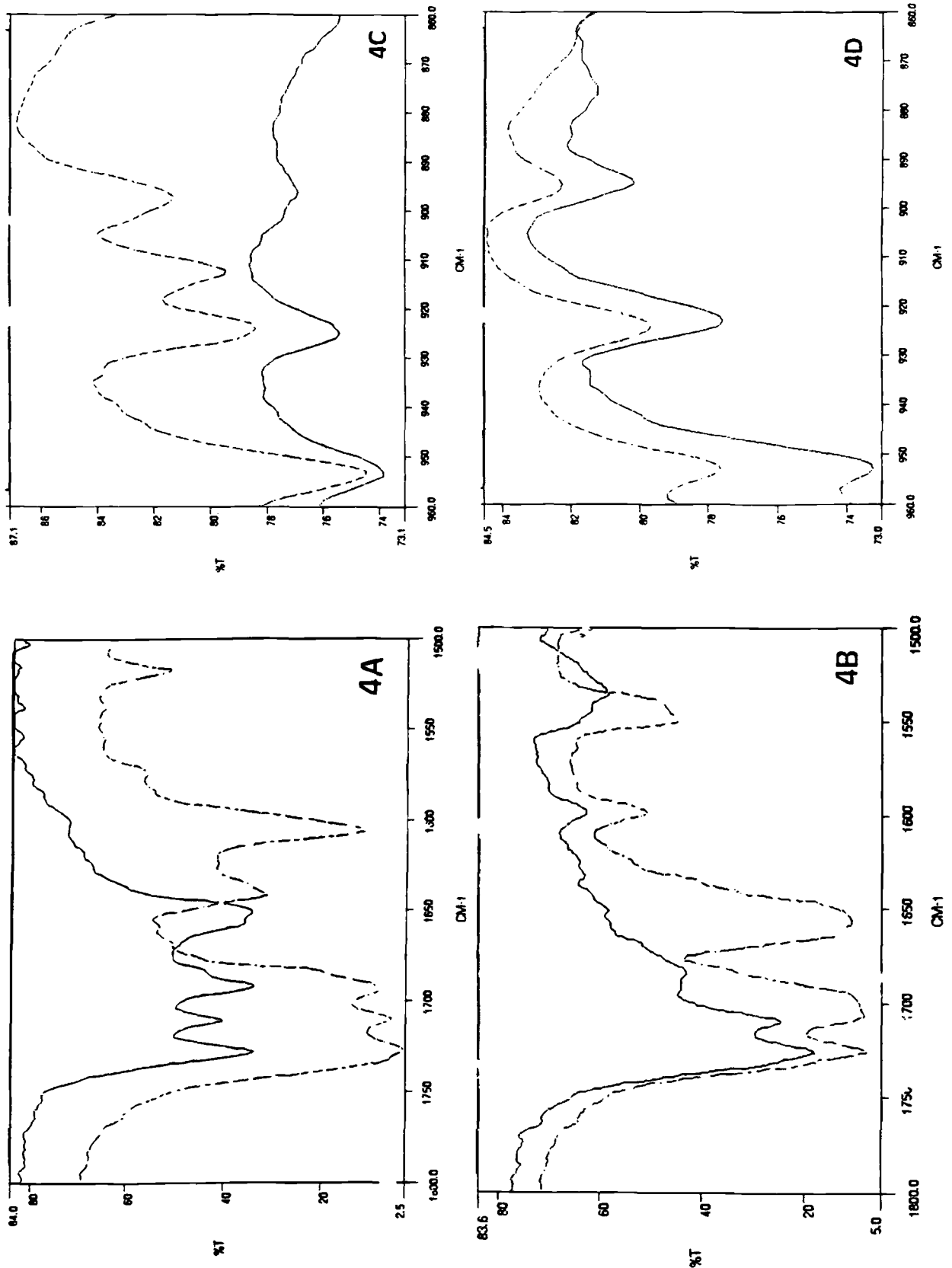


FIG. 4—Transmission spectra of synthetic mixtures of cocaine.HCl (70%) with adulterants (30%). (4A) and (4C) Cocaine.HCl with piracetam (30%), procaine.HCl (----) at 1800-1500 cm⁻¹ and 960-860 cm⁻¹; (4B) and (4D) lidocaine.HCl (----), caffeine (----), cocaine.HCl (——) at 1800-1500 cm⁻¹ and 960-860 cm⁻¹.

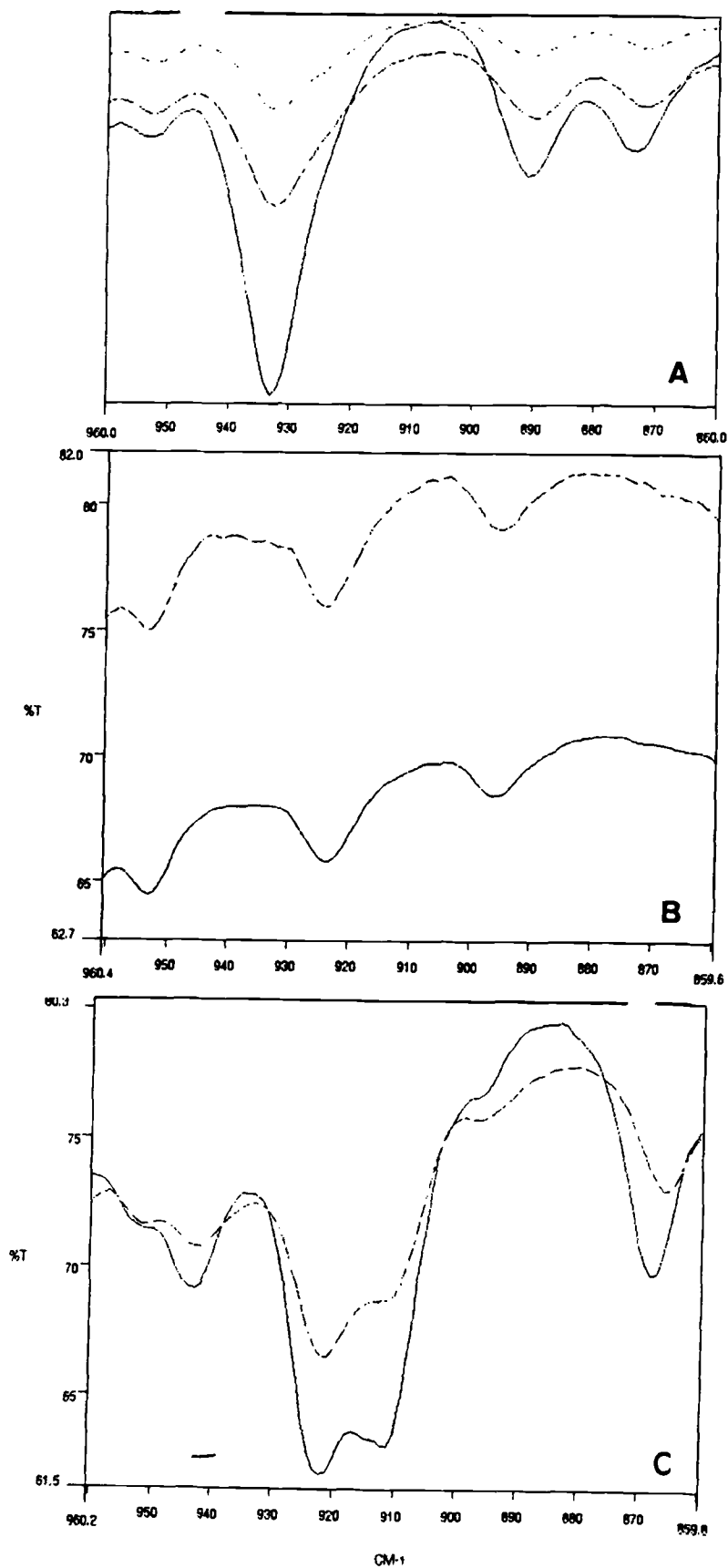


FIG. 5—Transmission spectra (960-860  $\text{cm}^{-1}$ ) of synthetic mixtures of cocaine.HCl with different content of diluents (A) mannitol 30% (—); mannitol 20% (---); mannitol 5% (-.-.-). (B) starch 5% (—); starch 30% (---). (C) sucrose 20% (—); sucrose 5% (---).



873  $\text{cm}^{-1}$  due to the polyalcohol. Sucrose was detected by the appearance of a double band at  $\lambda = 922$  and  $912 \text{ cm}^{-1}$  and a single band at  $\lambda = 868 \text{ cm}^{-1}$  while the  $889 \text{ cm}^{-1}$  band of cocaine disappeared.

The IR spectrum of lactose containing synthetic mixtures presented two bands, at  $\lambda = 899$  and  $875 \text{ cm}^{-1}$ , which was characteristic of this disaccharide. If the mixture contained glucose, the corresponding IR spectrum showed a very strong band at  $\lambda = 917 \text{ cm}^{-1}$ , probably due to the overlapping of the  $918 \text{ cm}^{-1}$  band of cocaine and the  $910 \text{ cm}^{-1}$  band of glucose; the other two bands of cocaine were not present in glucose-cocaine mixtures.

Finally, starch was easily identified by a characteristic band at  $\lambda = 924 \text{ cm}^{-1}$ .

#### *Synthetic Mixtures with Different Concentrations of Cocaine.HCl*

In order to confirm that the identification was still possible with higher proportions of cocaine, synthetic mixtures were prepared with approximately 5% content of adulterant or diluent.

The analysis of these new adulterant mixtures did not present great difficulty because identification was based on very strong bands. However, the identification of the diluent-cocaine mixtures was more complex. Some additional operations with the program were required to solve these difficulties and to confirm identifications. An attempted "overlay" of the spectra corresponding to mixtures of the same products in different concentrations could present problems if the spectra were recorded at different scales.

To overcome this difficulty, the computerized program has an arithmetic command and a new spectrum can be displayed, which is the result of the addition or subtraction of a constant to each band of the spectra. The identification is then possible and it is carried out on the expanded areas. Figure 5 shows the superposition of the IR spectra of 30%, 20% and 5% mannitol, starch and sucrose mixtures (30% and 5%) with cocaine.HCl. It can be observed that—even at 5%—the identification of these diluents is still possible.

Therefore, the method is applicable to binary samples where the contaminant ranges from 5 to 30%.

#### **Conclusions**

The data presented here demonstrate the applicability of infrared spectroscopy to the identification of five diluents and four adulterants in illicit cocaine samples. In order to obtain the necessary analytical resolution in the zones of the spectrum used for the identification, a computerized program is needed. To summarize:

- The method is best used with binary cocaine.HCl/contaminant samples.
- The 1800 to  $500 \text{ cm}^{-1}$  region is adequate to deduce the presence of the different adulterants.
- The 960 to  $860 \text{ cm}^{-1}$  region is suitable to identify the different diluents.
- The proposed method can be applied to synthetic mixtures even where the cocaine.HCl content is approximately 95%.

This procedure can also be applied to binary mixtures of cocaine

base or of heroin with the aforesaid or new contaminants, as these can be similarly handled. This will be elucidated in future publications.

#### *Acknowledgments*

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#### **References**

- [1] Soriano, T., Menéndez, M., and Repetto, M., "Principios Activos y Adulterantes en Drogas Decomisadas," *Revista Española de Drogo-dependencia*, 1994 (in press).
- [2] Jain, N. C., Chinn, D. M., Sneath, T. C., and Budd, R. D., "Simultaneous Gas Chromatographic Determination of Cocaine, Methadone, Methaqualone, Phencyclidine and Propoxyphene," *Journal of Analytical Toxicology*, Vol. 1, No. 4, July/August 1977, pp. 192-194.
- [3] Casale, J. F. and Waggoner, R. E., "A Chromatographic Impurity Signature Profile Analysis for Cocaine Using Capillary Gas Chromatography," *Journal of Forensic Sciences*, Vol. 36, No. 5, Sept. 1991, pp. 1312-1330.
- [4] Stevenson, A. J., Weber, M. P., Todi, F., Mendonca, M., Fenwick, J. D., Young, L., Kwong, E., Chen, F., Beaumier, P., Timmings, S., Woodard, D., and Kacew, S., "Determination of Procaine in Equine Plasma and Urine by High-Performance Liquid-Chromatography," *Journal of Analytical Toxicology*, Vol. 16, No. 2, March/April 1992, pp. 93-96.
- [5] Ellerbe, P., Tai, S. S. C., Christensen, R. G., Espinosa-Leniz, R., Paule, R. C., Sander, L. C., Sniegowski, L. T., Welch, M. J., and White, E., "The Certification of Cocaine and Benzoyllecgonine in a Human Urine Standard Reference Material," *Journal of Analytical Toxicology*, Vol. 16, No. 3, May/June 1992, pp. 158-162.
- [6] Platoff, G. E., Hill, D. W., Koch, T. R., and Caplan, Y. H., "Serial Capillary Gas Chromatography/Fourier Transform Infrared Spectrometry/Mass Spectrometry (GC/IR/MS). Qualitative and Quantitative Analysis of Amphetamine, Methamphetamine, and Related Analogues in Human Urine," *Journal of Analytical Toxicology*, Vol. 16, No. 6, Nov./Dec. 1992, pp. 389-397.
- [7] Cone, E. J. and Darwin, W. D., "Rapid Assay of Cocaine, Opiates and Metabolites by Gas Chromatography-Mass Spectrometry," *Journal of Chromatography*, Vol. 580, Nos. 1 and 2, September 1992, pp. 43-61.
- [8] Lukaszewski, T. and Jeffery, W. K., "Impurities and Artifacts of Illicit Cocaine," *Journal of Forensic Sciences*, Vol. 25, No. 3, July 1980, pp. 499-507.
- [9] Trinler, W. A. and Reuland, D. J., "Unequivocal Determination of Cocaine in Simulated Street Drugs by a Combination of High Performance Liquid Chromatography and Infrared Spectrophotometry," *Journal of Forensic Sciences*, Vol. 23, No. 1, Jan. 1978, pp. 37-44.
- [10] Moss, W. W., Posey, F. T. and Peterson, P. C., "A Multivariate Analysis of the Infrared Spectra of Drugs of Abuse," *Journal of Forensic Sciences*, Vol. 25, No. 2, April 1980, pp. 304-314.
- [11] Wielbo, D. and Tebbett, I. R., "The Use of Microcrystal Tests in Conjunction with Fourier Transform Infrared Spectroscopy for the Rapid Identification of Street Drugs," *Journal of Forensic Sciences*, Vol. 37, No. 4, July 1992, pp. 1134-1149.
- [12] Fuelster, R. G., "Quantitation of Sugars in Street Drug Samples," *Journal of Forensic Sciences*, Vol. 37, No. 1, Jan. 1992, pp. 77-82.

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