Jaap G. Ensing,[1] *Ph.D.; Charlayne Racamy,*[2] *M.Sc.; and Rokus A. de Zeeuw,*[3] *Ph.D.*

A Rapid Gas Chromatographic Method for the Fingerprinting of Illicit Cocaine Samples

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ABSTRACT: A gas chromatographic (GC) fingerprint method, based on the presence or absence of six congeners, was developed for illicit cocaine samples. The fingerprint utilizes the relative abundances of these congeners towards each other, disregarding cocaine as the main constituent, and can be expressed numerically or graphically in the form of pictograms for rapid visual comparison. The method can be applied directly to a solution of the sample in chloroform, without previous workup procedures. More than 70 unrelated samples were analyzed and a great variation was observed in the parameter composition. On the other hand, a remarkable similarity could be seen between related samples. The GC fingerprint method may be considered an important contribution for sample comparison, as is exemplified by a subdivision of the analyzed samples in different categories, based on the number and types of congeners found.

KEYWORDS: toxicology, cocaine, chromatographic analysis, cocaine congeners, fingerprints, sample comparison, gas chromatography, drug trafficking

Powerful analytical separation techniques, like gas chromatography (GC) and high-performance liquid chromatography (HPLC), enable the forensic analyst to unravel the composition of illicit cocaine samples. Reliable information about their total composition (that is, cocaine, minor alkaloids, extraction/processing residues, diluents/additives) may be very helpful in obtaining more knowledge about the *Erythroxylum* species from which the cocaine was extracted, about the processing technique used, and about the final preparation. For example, based on the presence or absence of the minor alkaloids and on their abundance in different cocaine samples it may be possible to determine whether these samples are derived from the same or from different sources. On the other hand, apart from the identification of cocaine itself, there is a need to compare different seized

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[1]Head, Department of Toxicology, Government Laboratory for Public Health, Willemstad, Curaçao, Netherlands Antilles; present address: Department of Analytical Chemistry and Toxicology, University Centre for Pharmacy, University of Groningen, The Netherlands.

[2]Research assistant, Department of Toxicology, Government Laboratory of Public Health, Willizmsladt, Curaçao, Netherlands Antilles.

[3]Professor of toxicology, University Centre for Pharmacy, University of Groningen, The Netherlands.

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cocaine samples to see if their fingerprint composition (that is, the presence or absence of relevant minor constituents and their relative abundance) can be matched in order to establish whether the samples have a common source.

Clark [*1*] measured the amounts of ecgonine, ecgonine methyl ester, and *trans*-cinnamoylcocaine in more than 40 samples, using hydrolysis, derivatization, and finally GC analysis.

Noggle et al. [*2,3*] used HPLC with dual UV detection wavelengths to separate and identify cocaine and some of its minor alkaloids. A similar detection technique was performed by LeBelle et al. [*4*], who demonstrated the usefulness of the described HPLC-system in comparing several cocaine samples.

Yet, despite these efforts, the comparison of cocaine samples based on the occurrence of the minor constituents (the so-called fingerprinting) is still in a premature stage, in contrast to, for example, heroin analysis, in which the fingerprint profile of the minor alkaloids not only may be used for sample comparison, but even for the determination of the geographical origin [*5–7*].

According to Morales-Vaca, the presence of different minor alkaloids in illicit cocaine may provide a clue to the area in which it originated [*8*]. Therefore, it is necessary to develop a method that allows, in a relatively simple but reliable way, the qualitative as well as the quantitative analysis of cocaine, together with its most relevant congeners.

In this paper we describe the development of such a method, which is based on the presence and relative abundance of at least six congeners, namely, three minor alkaloids and three cocaine decomposition products.

Local Situation

In The Netherlands Antilles, all material suspected of containing cocaine, seized by either the police or customs authorities, was brought to our laboratory for examination. The presence of cocaine in such seizures could be easily established by infrared spectroscopy, color tests, and other tests, but these techniques reveal little or no information about the minor components in the sample.

The latter can be clearly visualized by thin-layer chromatography (TLC) [*9*] and gas chromatography [*10*]. The frequently encountered minor alkaloids and other cocaine-related substances in the illicit cocaine samples seized in The Netherlands Antilles were the following: anhydromethylecgonine, tropacocaine, benzoylecgonine, *cis*- and *trans*-cinnamoylcocaine, norcocaine, the truxillines, *N*-benzoylnorecgonine methyl ester and *N*-formylnorcocaine. Each of these congeners will be discussed and evaluated for its use as a fingerprint parameter in cocaine analysis.

Anhydromethylecgonine (AME)

Despite its sometimes overwhelming presence during GC analysis of illicit cocaine samples, the presence of this substance could never be confirmed by TLC. Lukaszewsky et al. [*11*] already mentioned AME as an artifact originating from cocaine by thermodegradation. Another thermodegradative origin, namely, the truxillines, has been suggested recently [*9*]. Because of this artifact character, AME should not be used as a fingerprint parameter.

Benzoylecgonine (BE)

BE has been isolated from coca leaves [*12*], but is also known as one of the major hydrolysis products of cocaine [*13,14*]. Because of its relatively polar character, it has poor TLC properties. Correct GC analysis can only be performed after derivatization.

Based on the chromophoric properties of the benzoyl group, UV detection is possible and several HPLC separation procedures with UV detection have been described [2–4,15]. Yet, being a cocaine degradation product, BE is not a first choice to serve as a fingerprint parameter since its abundance may be affected by the storage and handling of the samples.

Tropacocaine (TC)

TC may occur in coca leaves [16], but has not been detected in all species [17]. Its presence in illicitly produced cocaine appears to be highly variable, but the component as such appears to be relatively stable. Using TLC on silica gel plates, TC is well separated from the other minor alkaloids [9]. Also, gas chromatographic identification may be performed easily [10]. HPLC separation followed by UV detection seems possible but has not yet been described. TC has to be considered a good fingerprint parameter.

Cis- and *Trans*-Cinnamoylcocaine (cCC and tCC, Respectively)

The compounds cCC and tCC are the best known minor alkaloids. Moore [19] was the first to identify the *cis*- and *trans*-isomers by separating them gas chromatographically, after they had been isolated from coca leaves by Giesel, as described by Liebermann [18]. HPLC separation of these isomers was first performed by Noggle et al. [2], who also noted the difference between the UV-absorbing capacities of the isomers. Having a chemical structure closely related to that of cocaine, the cinnamoylcocaines are extracted from coca leaves, together with cocaine during the extraction process. The species, the growing area, and the harvesting circumstances may be reflected in the presence of the cinnamoylcocaines in illicitly processed cocaine. On the other hand, olefinic double bonds, such as those found in the cinnamoyl group, are particularly susceptible to oxidation. Some illicit operators treat the cocaine during processing with oxidizing agents such as potassium permanganate [20], which may—at least partly—destroy the cinnamoylcocaines.

Therefore, the two isomeric cinnamoylcocaines are first-choice parameters for fingerprinting.

Truxillines (TXCs)

Although the TXCs, as potential constituents of the coca leaves, have been known for more than a hundred years [21,22], their isolation from illicitly produced cocaine was performed only recently by Moore et al. [23] and, independently, by us [9]. Formed in the coca leaves, the TXCs may accompany cocaine through the extraction process. Since no olefinic double bonds are present, the TXCs are not easily susceptible to the usual oxidizing agents.

Because of their low volatility, however, GC analysis of the intact TXCs is not possible, as this will give rise to the decomposition product AME. HPLC analysis has not been described but may be rather difficult to perform, also because of their very low UV-detection sensibility. Using thin-layer chromatography, a reasonable impression of the presence and distribution of at least five isomers can be obtained [9].

Although the TXCs may become a more useful fingerprint parameter, the lack of a reliable quantitation method makes them, at this time, less valuable.

Norcocaine (NC)

Known for several years as a human metabolite of cocaine [13], NC has recently been detected by direct GC in illicit cocaine samples [10]. Its formation may take place during

oxidation of the cocaine and is pH dependent [*24*]. A second possible formation route was observed by Singh et al. [*25*], who described the photochemical degradation of cocaine.

Gas chromatography analysis of NC is possible, although incomplete separation from cocaine may occur. HPLC detection has been described [*26*]. NC can be seen as an important fingerprint parameter, as it may (at least partially) reflect the oxidizing circumstances during the processing.

N-Benzoylnorecgonine Methyl Ester (BNEme)

As initially described by Werner et al. [*27*], BNEme may originate as a by-product when cocaine is oxidized with potassium permanganate. BNEme and NC being isomers, the latter usually predominates when the cocaine oxidation is performed under slightly acidic circumstances, whereas BNEme predominates under basic conditions [*24*]. Gas chromatography quantitation of BNEme can be easily performed [*10*], so, as with NC, this component can also be seen as an important fingerprint parameter.

N-Formylnorcocaine (FNC)

This new congener was relatively often encountered in our samples, albeit at rather low levels. Initially, as with NC and BNEme, we classified FNC as an unknown congener, but after extensive efforts to isolate sufficient amounts by TLC and HPLC, we were able to establish its identity by GC/MS, NMR, and IR [*10*]. Very recently, Brewer and Allen also described the isolation and identification of this congener [*28*]. They named the substance *N*-formylcocaine (we prefer *N*-formylnorcocaine) and reported its presence in about 60% of their sample population. This appears to agree fairly well with our observations in the Antilles, where we observed FNC in some 50% of the samples (see Table 1). The presence of FNC in cocaine samples can be due to permanganate oxidation or photooxidation in the bleaching process when the crude cocaine is exposed to sunlight [*10,28*]. Although only traces may be present, FNC appears to be relatively stable and

TABLE 1—*Gas chromatographic numerical fingerprints of 71 illicit cocaine samples.*

Sample No.	Code	S/B[a]	TC[b]	NC[c]	BNEme[d]	cCC[e]	tCC[f]	FNC[g]
1	60IIA1	B	7.4	10.0	3.0	1.5	1.2	0.9
2	60IIA2	B	8.5	10.0	1.8	1.9	2.5	1.2
3	60IIA	B	8.0	10.0	5.4	3.9	4.4	1.2
4	60IIA12	B	8.2	10.0	3.0	5.3	5.4	1.2
5	199IIB	B	1.0	1.3	–	10.0	9.8	–
6	61IIB	B	–	0.7	–	9.6	10.0	0.7
7	62IIB6	B	5.0	10.0	2.4	8.5	7.2	2.2
8	64IIA	B	–	1.4	0.7	10.0	8.4	–
9	65IIA	B	10.0	–	1.9	1.4	1.2	–
10	Mut906	B	–	–	–	10.0	8.2	–
11	58IIA2	B	10.0	7.6	2.6	3.2	3.8	–
12	58IIA4	B	10.0	8.3	2.9	5.1	6.0	0.5
13	59IIA	B	1.7	10.0	2.9	1.7	0.8	0.9
14	10IIB	S	–	–	1.5	10.0	7.4	–
15	68IIB	B	1.5	1.6	–	10.0	6.1	–
16	48IIB	B	10.0	3.9	1.8	3.8	3.2	–
17	48IIB1	S	–	4.1	–	10.0	4.7	–
18	8IIB	B	1.0	4.5	10.0	–	–	1.2
19	8IIB2	B	4.2	10.0	7.9	0.9	1.0	1.3
20	8IIB3	B	10.0	4.0	3.4	4.2	4.8	0.7

TABLE 1—*Continued*

Sample No.	Code	S/B[a]	TC[b]	NC[c]	BNEme[d]	cCC[e]	tCC[f]	FNC[g]
21	8IIB4	B	3.3	10.0	3.3	0.6	0.6	0.5
22	51IIB	S	–	10.0	–	9.1	7.3	–
23	12IIB	S	–	–	3.3	10.0	8.3	–
24	1IIA	B	10.0	6.7	6.7	3.3	2.4	5.5
25	300IIA	B	0.9	10.0	3.2	–	–	7.2
26	181IIB	B	10.0	1.6	1.2	2.7	3.0	–
27	209IIB	B	10.0	–	–	9.2	5.2	–
28	341IIA	B	1.0	10.0	2.6	0.7	0.9	1.5
29	33IIB	B	10.0	5.9	3.4	2.4	0.8	1.9
30	76IIA2	S	1.3	–	8.0	10.0	9.0	–
31	76IIB1	B	4.6	10.0	–	–	–	1.9
32	76IIB3	B	3.3	10.0	2.5	1.2	1.2	1.8
33	100IIB4	B	10.0	–	–	–	–	–
34	13IIBa	B	0.5	–	–	9.8	10.0	–
35	14IIbb	B	–	0.7	–	10.0	8.6	–
36	Mut92	B	10.0	7.7	1.8	–	–	0.5
37	Mut383	B	–	10.0	2.8	–	0.8	0.7
38	77IIA	B	4.0	4.9	3.5	10.0	8.8	0.8
39	77IIA1	B	7.1	4.2	2.9	10.0	9.7	–
40	77IIA2	B	6.2	5.2	3.4	10.0	8.7	0.8
41	15IIB	B	5.6	10.0	1.4	6.9	2.3	0.8
42	78IIA6	B	8.3	10.0	3.3	6.7	7.7	–
43	78IIB	S	9.1	10.0	–	2.2	2.4	–
44	78IIB2	S	10.0	9.4	3.1	1.8	1.6	1.3
45	79IIB1	B	4.0	10.0	10.0	3.2	1.3	2.2
46	79IIB2	B	–	10.0	–	2.4	0.9	–
47	52IIB	S	–	10.0	–	2.5	2.1	–
48	52IIB3	S	–	10.0	–	0.9	–	–
49	81IIB2	B	10.0	1.4	–	4.3	3.0	–
50	234IIB	B	10.0	9.7	3.4	–	–	0.7
51	164IIB	B	1.9	10.0	–	0.7	0.7	2.3
52	291IIB	B	1.7	8.5	10.0	–	–	1.7
53	166IIA	B	10.0	9.0	9.3	–	–	2.7
54	3IIA	S	–	–	–	10.0	9.2	–
55	35IIB	B	2.3	10.0	2.6	–	–	1.1
56	37IIB	B	3.1	10.0	3.3	–	–	0.9
57	30IIB	B	4.0	10.0	2.1	–	–	1.3
58	54IIA	B	–	–	–	10.0	7.9	–
59	Mut409	B	10.0	3.1	–	9.8	8.6	–
60	96IIA	B	1.3	10.0	2.3	8.8	7.2	1.6
61	96IIA1	B	6.4	10.0	3.3	–	–	2.2
62	99IIA2	B	1.1	1.9	0.2	10.0	8.9	–
63	103IIA	B	1.3	1.8	1.8	10.0	6.3	0.2
64	110IIA	B	0.4	–	–	10.0	7.2	–
65	113IIA	B	0.7	1.8	–	9.7	10.0	–
66	134IIB	B	1.2	0.7	–	10.0	5.6	–
67	137IIA	B	1.4	1.4	–	10.0	3.2	–
68	172IIA	B	–	2.0	0.8	10.0	4.6	–
69	200IIB	B	–	–	–	10.0	6.0	–
70	35IIB1	B	0.7	1.4	–	10.0	9.8	–
71	238IIB	B	0.4	3.0	1.3	10.0	4.6	0.2

[a]S or B indicates the sample in salt or base form.
[b]TC = tropacocaine.
[c]NC = norcocaine.
[d]BNEme = *N*-benzoylnorecgonine methyl ester.
[e]cCC = *cis*-cinnamoylcocaine.
[f]tCC = *trans*-cinnamoylcocaine.
[g]FNC = *N*-formylnorcocaine.

amenable to gas chromatography. Therefore, FNC was also selected as a fingerprint parameter.

Development of a Fingerprint Technique

Although TLC usually provides some insight in the sample composition, it is not the method of first choice for fingerprinting because it lacks adequate separation efficiency. HPLC may be more valuable in that respect, but, as indicated earlier, some components insufficiently absorb UV-light, thus inhibiting adequate detection. Furthermore, separation of all the above-mentioned parameters in one run seems rather difficult to achieve.

Gas chromatography seems to be the method of choice, and in our laboratory, three types of stationary phases were available: OV-1, OV-17, and Carbowax 20M. OV-1 is a low-polar phase with a maximal operating temperature of 350°C. OV-1 columns will elute most of the drugs of toxicological relevance and, therefore, OV-1 is preferred as a column for screening purposes. OV-17 is a moderately polar phase, also with a high maximum operating temperature. In general, compounds eluting on OV-17 columns have higher retention times when compared with OV-1 columns. Carbowax 20M is a polar phase, but is maximum operating temperature of 225°C makes it unsuitable for the proposed separation. We therefore decided to evaluate the OV-1 and OV-17 columns further for their fingerprinting potential.

Gas Chromatography

The analyses were performed using a Philips PU 4500 chromatograph (Philips/Pye Unicam, Cambridge, U.K.) fitted with dual-flame ionization detectors. The results were processed with a Beckman 427 integrator (Beckman Instruments Inc., San Ramon, California). Alternatively, a BD-II recorder was used (Kipp Instruments, Delft, The Netherlands). Two 1.52-m (5-ft) glass columns of 2-mm inside diameter were used, one packed with 3% OV-1 on Chromsorb WHP (100/120 mesh), the other with 3% OV-17 on Chromsorb WHP (100/120 mesh) (Chrompack BV, Middelburg, The Netherlands). The nitrogen carrier gas flow rate was 30 mL/min. The flow rates for detector gases were 30 mL/min for hydrogen and 300 mL/min for air, respectively. The injector and detector temperatures were maintained at 250 and 350°C, respectively. The oven temperature was held at 100°C for 2 min, then programed at 12°C/min to 320°C, and held for 5 min (Program A).

Alternatively, the oven temperature was held at 200°C for 2 min, then programed at 12°C/min to 320°C and held for 5 min (Program B).

A 1% solution in chloroform of an illicit cocaine sample containing the relevant parameters was run on both an OV-1 and an OV-17 column, and the results are illustrated in Fig. 1 left and right, respectively.

As can be seen in Fig. 1 left and right, all the compounds of interest, except the truxillines, elute on both columns and are separated reasonably well. The 3% OV-17 column provides a better separation of the compounds, so this column type was preferred for further analysis.

As the decomposition product AME can be considered an artifact, it does not contribute to the fingerprint analysis. Therefore, the initial oven temperature of the GC may be raised to 200°C, in this way shortening the analysis time without affecting the chromatographic separation. Cutting agents such as lidocaine, procaine, benzocaine, and caffeine can be easily separated and detected without interfering with the fingerprinting, as they elute in the first part of the chromatogram.

It should be noted that other potential congeners or decomposition products were not

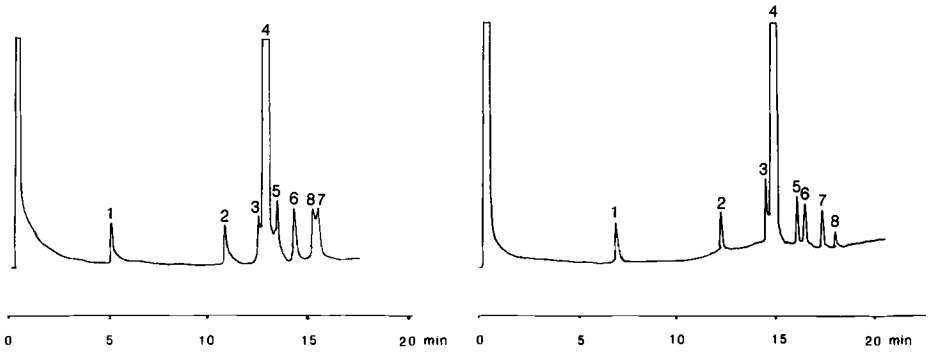

FIG. 1—*GLC spectrum of an illicit cocaine sample on OV-1* (left) *and OV-17* (right); *temperature Program A was used in both cases: 1, anhydromethylecgonine (AME); 2, tropacocaine (TC); 3, norcocaine (NC); 4, cocaine; 5,* N-*benzoylnorecgonine methyl ester (BNEme); 6,* cis-*cinnamoylcocaine (cCC); 7,* trans-*cinnamoylcocaine (tCC); 8,* N-*formylnorcocaine (FNC).*

observed under the present GC conditions. This applies, for example, to the benzoic, cinnamic, truxinic, and truxilic acids; anhydroecgonine; ecgonine; and benzoylecgonine. We assume that they either run in the solvent front, decompose upon injection, or do not elute. Methylecgonine would elute with AME, but, as the latter is not taken into account in the fingerprinting, this is of no concern.

Multiple injections of this sample showed only slight variations between the peak heights of the same components, the day-to-day coefficient of variation being less than 6.5% ($n = 8$). When tetracosane (C24) was added in a concentration of about 0.01% as an internal standard (Reference time [*Rt*] ±8 min) the coefficient of variation could be reduced to less than 4.5%. It can be noted that NC is barely separated from the large cocaine peak. The peak heights of NC were measured from the inflection point to the top.

For the expression of the fingerprint, the following system was devised: Ignoring the presence of cocaine, the peak heights of the six parameters TC, NC, BNEme, cCC, tCC, and FNC are measured. The highest peak [*H*] is given the reference value 10 and all other peaks [*h*] are then expressed as ratios of *H* and multiplied by 10.

$$h(\text{cm})/H(\text{cm}) \times 10 \qquad (1)$$

Using this system, 71 illicit cocaine samples, received over a period of a few years and believed to have no connection to each other, were analyzed. Expression of the fingerprints can be done numerically as in Table 1. Yet, for rapid visual comparison of sample compositions, we also developed so-called pictograms, which are transformations of gas chromatograms by means of Eq 1, as depicted in Fig. 2. Typical examples of pictograms are shown in Fig. 3, in which the results are expressed for Samples 31 through 40. Both the numerical fingerprints and the pictograms provide ample opportunities for building up computerized databases.

The pictograms and the data in Table 1 clearly indicate the discriminating power of the fingerprinting approach. Despite the fact that the cocaine content as such is not taken into account, the results show that a large variety of illicit cocaine samples can exist. Accepting an error window of 20% (3 × standard deviation) in the quantitation of the individual congeners, the large majority of the 71 samples investigated does not appear to be interrelated since neither the number of congeners and/or their ratios are different, the latter by a margin >20%. However, some samples resemble each other quite well

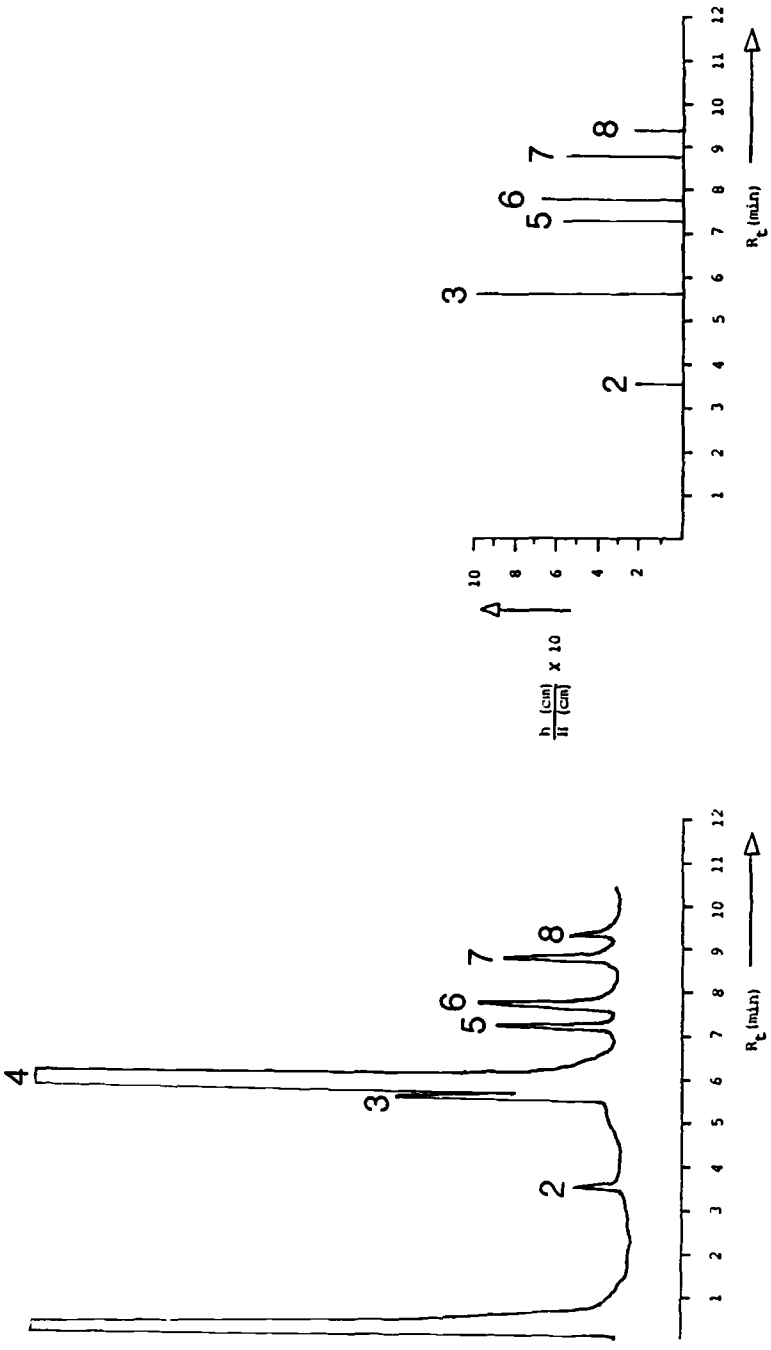

FIG. 2—*Example of a gas chromatogram of an illicit cocaine sample on OV-17, using temperature program B, and its transformation into a pictogram by means of Eq 1. Note that in the pictograms the cocaine peak is ignored.*

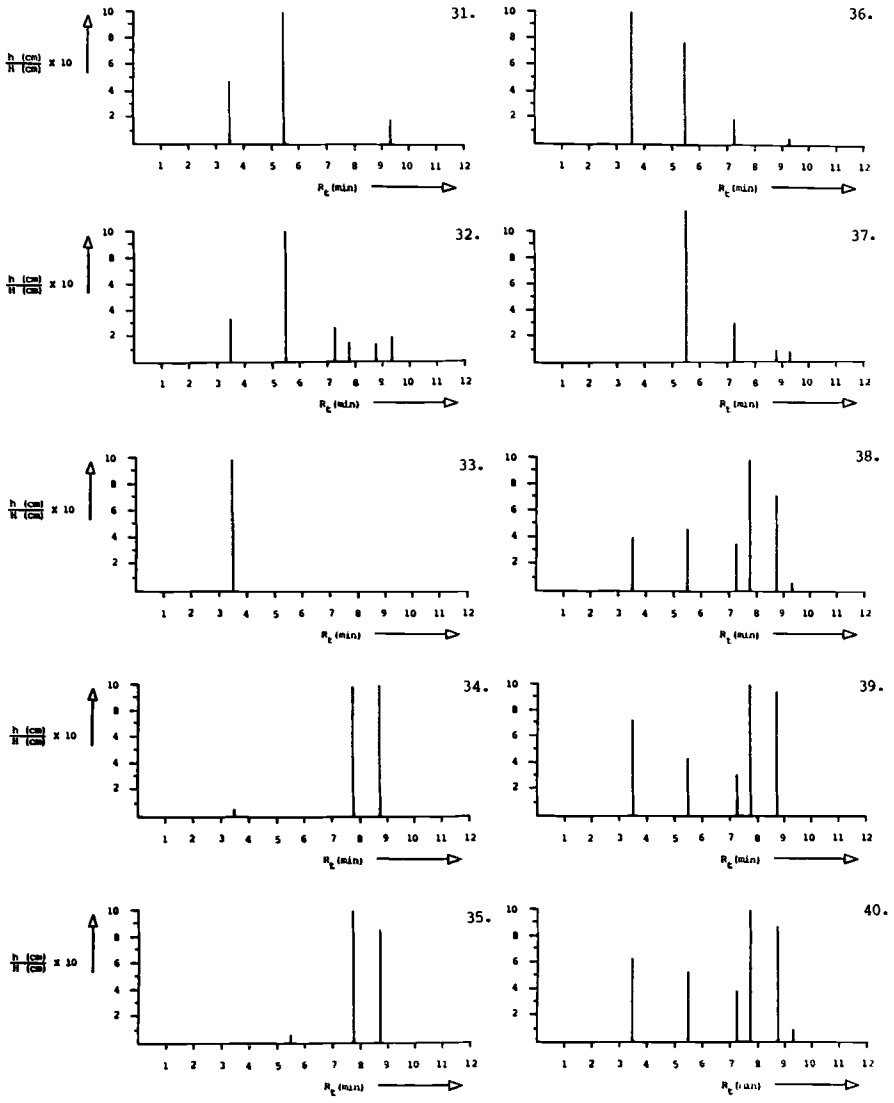

FIG. 3—*Fingerprint pictograms of Samples 31 through 40, showing typical congener patterns in illicit cocaine.*

in that they have the same number of congeners with their ratios varying less than 20% or close to 20%. This applies to sample series 10–54–58 and 5–65–70, respectively, which therefore may have a common origin. Other samples, in which one of the congeners is present in very small amounts, show marginal differences, for example, Samples 6 through 35 and 34 through 64. Also, Samples 55 and 56 differ only slightly in their ratios. In addition, if one realizes that TC, cCC, and tCC are natural by-alkaloids and that NC, BNEme, and FNC can be considered degradation products to a large extent because of the processing of the crude cocaine, some interesting observations can be made that allow a subdivision into different categories (the percentage of 71 samples is shown in parentheses.)

1. TC only: Sample 33 (1.4%).
2. cCC and tCC only: Samples 10, 54, 58, and 69 (5.6%).
3. TC, cCC, and tCC only: Samples 27, 34, and 64 (4.2%).
4. NC, cCC, and tCC only: Samples 17, 22, 35, 46, 47, and 48 (8.5%).
5. BNEme, cCC, and tCC only: Samples 14 through 23 (2.8%).
6. Without TC: Samples 6, 8, 10, 14, 17, 22, 23, 35, 37, 46, 47, 48, 54, 58, 68, and 69 (23.5%).
7. Without cCC and tCC: Samples 18, 25, 31, 33, 36, 50, 52, 53, 55, 56, 57, and 61 (16.9%).
8. With degradation products only: none (0%).
9. With degradation products except NC: Samples 9, 14, 23, and 30 (5.6%).
10. With degradation products except BNEme: Samples 5, 6, 15, 17, 22, 31, 35, 43, 46, 47, 48, 49, 51, 59, 65, 66, 67, and 70 (25.3%).
11. With degradation products, except FNC: Samples 5, 8, 9, 11, 14, 15, 16, 17, 22, 23, 26, 30, 35, 39, 42, 43, 46, 47, 48, 49, 59, 62, 65, 66, 67, 68, and 70 (38%).
12. Either cCC or tCC missing: Samples 37 through 48 (2.8%).
13. All six fingerprint parameters present: Samples 1, 2, 3, 4, 7, 12, 13, 19, 20, 21, 24, 28, 29, 32, 38, 40, 41, 44, 45, 60, 63, and 71 (31%).
14. Without degradation products: Samples 10, 27, 33, 34, 54, 58, 64, and 69 (11.2%).
15. TC and degradation products: Samples 18, 25, 31, 36, 50, 52, 53, 55, 56, 57, and 61 (15.5%).

According to these observations, the following conclusions can be drawn: The presence of only the natural by-alkaloids was found in 11.2% of all the samples, while cCC and tCC are more often present than TC (Category 1 versus Category 2).

Because no samples were found according to Category 8, the natural by-alkaloids seem fairly stable against the usual processing circumstances.

Upon degradation, NC is more common than either BNEme or FNC (Category 9 versus Category 10 and Category 11); BNEme is more common than FNC (Category 10 versus Category 11).

When comparing Category 7 and Category 15, it appears that, with the exception of Sample 33, the samples without the CCs do contain TC. The absence of CCs may be indicative for a complete conversion of these congeners into degradation products during the clandestine processing of cocaine. However, it may also be possible that *E. coca* varieties exist which do not form CCs, but only TC and other minor congeners that remain unknown so far. The latter seems to be more likely, because otherwise it would be difficult to explain the presence of a rather large Category 6, yet no representatives in Category 8.

Category 12 may be the result of nearly complete oxidation of the CCs rather than a naturally occurring species that does not form the CCs simultaneously. On the other hand, it should be mentioned that the samples in this category are unique in that, apart from a trace of one of the CCs, they do not contain other natural by-alkaloids. Had it not been for the trace of one of the CCs, the samples would have qualified for Category 8, for which no other representatives were found so far.

The presence of TC alone is also a highly discriminative feature, as only one sample was found in this category (Category 1). Other discriminative features are represented by Category 5 (two samples), Category 3 (three samples) and Category 2 (four samples).

As expected in view of the production of illicit cocaine, the large majority of the samples contained decomposition products, the ones with natural by-alkaloids representing only 11.2% (Category 14). However, of the 63 samples with decomposition products, 52 contained cCC and/or tCC, whereas 36 also contained FNC. This seems to indicate that the latter three compounds are able to withstand, at least partly, the per-

manganate or sunlight bleaching processes. On the other hand, the 11 samples with degradation products but devoid of cCC and tCC all contained FNC. These samples may be from plant varieties that do not form cCC and tCC, as mentioned above. Brewer and Allen [*28*] suggested that the absence of FNC be indicative of samples having been exposed to permanganate treatment, which would then apply to some 60% of their samples. Yet, we believe that this suggestion is incorrect and that NC and BNEme should be taken into account as well, since their formation can also be ascribed to strong oxidative treatment [*10*]. Thus, in our sample population, only the eight samples in Category 14 would not have undergone oxidative processing (11.2%). This appears to be more in line with the general belief that the large majority of illicit cocaine samples have been processed with permanganate.

On the other hand, excellent agreement between two cocaine samples was observed, both in the number and the ratio of the fingerprint parameters, as well as in cocaine content, in the following situation: An amount of cocaine base was found on a person suspected of being a cocaine dealer, and a small amount of cocaine base was also found in possession of a user. The user claimed that his cocaine did not originate from the dealer. The fingerprint pictograms of the two samples are shown in Fig. 4. Further analysis of these samples showed in both cases the presence of 75% cocaine base and no adulterants. Although these analyses do not provide definite proof that the statement of the user was incorrect, it provided useful contributing evidence in the total investigation of the case.

Thus, the above fingerprinting by GC appears to be a powerful tool for sample comparison, with regard to both naturally occurring by-alkaloids and the occurrence of different degradation products. In order to obtain an optimal sample characterization, it is

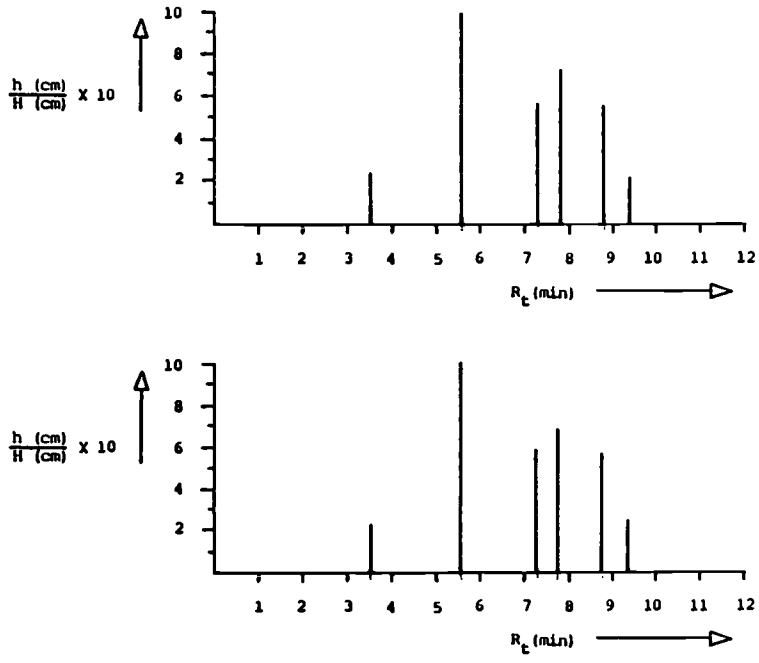

FIG. 4—*Fingerprint pictograms of two illicit cocaine samples suspected to be interrelated. See the text for details.*

clear that the cocaine content of the samples can be considered as well, together with the presence of possible cutting or diluting agents. Moreover, the presence of the truxillines can be established by TLC [9]. A mobile phase consisting of cyclohexane-toluene-diethylamine (75:15:10) will separate cocaine from the truxillines, thereby exposing valuable information on the presence of the latter.

In addition, it should be noted that the occurrence of the earlier mentioned cutting agents will not influence the GC fingerprint or the ratio of the major congener peaks versus the cocaine peak. These parameters should be constant before and after cutting, unless the samples were exposed in-between to extreme circumstances, such as heat, light, or moisture.

The composition of the above 71 samples, which were stored in the dark at room temperature, remained essentially constant over a period of at least two years.

Finally, it must be rightfully remarked that the above results were obtained in an *a posteriori* investigation with a relatively small number of samples of unknown history. Moreover, we did not have access to freshly harvested samples or to samples obtained during the processing and transport of illicit cocaine. Also, the impact of storage under different climatic conditions was not investigated. Therefore, in order to further validate the fingerprinting and characterization of illicit cocaine, it would be desirable to extend the investigations in these directions.

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Addendum

Very recently, Casale and Waggoner also addressed the fingerprinting of cocaine [29]. They used capillary gas chromatography after treating the samples with a silylating agent (BSA), thus derivatizing alcoholic, *N*-nor, and carboxylic acid functional groups. In this way, cocaine and 14 congeners could be distinguished; namely, benzoic acid, anhydromethylecgonine, anhydroecgonine, *trans*-cinnamic acid, methylecgonine, ecgonine, tropacocaine, benzoylecgonine, norcocaine, beta-truxinic acid, alpha-truxillic acid, *cis*-cinnamoylcocaine, *trans*-cinnamoylcocaine, and *N*-formylnorcocaine. The recently discovered *N*-benzoylnorecgonine methyl ester was not discussed. The potential value of this method lies in the fact that the various acidic congeners may be distinguished. The latter remain invisible in our direct approach using underivatized samples. On the other hand, as with our method, it remains to be seen in prospective studies to what extent the abundances of the various congeners are affected during harvesting, processing, manipulation, transportation, storage, and interlaboratory derivatization and analysis. Obviously, a lack of stability may impair the utility of a particular congener. In this regard, it may be noted that Casale and Waggoner had only a few samples in their population of 368 showing the presence of *N*-formylnorcocaine. In contrast, in our studies and those of Brewer and Allen [28], samples containing FNC amounted to 50% and 60%, respectively.

Finally, our approach to expressing the fingerprint in terms of relative abundances of the congeners by means of Eq 1, either numerically or as pictograms, is also applicable to the method of Casale and Waggoner.

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Address requests for reprints or additional information to
Dr. Jaap G. Ensing
Dept. of Analytical Chemistry and Toxicology
University Centre for Pharmacy
A. Deusinglaan 2
9713 AW Groningen
The Netherlands