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Cocaine Contamination of Currency in Birmingham AL

Jeremy R. Felix, Rena Hammer, and Elizabeth A. Gardner

Abstract:

Numerous studies have shown that a high percentage of currency is contaminated with nanogram to nearly milligram volumes of illicit drugs, especially cocaine. A study was conducted in the Birmingham Alabama area to determine the percentage of cocaine on dollar bills, as well the advantages and disadvantages of two extraction methods—a chloroform extraction and a chloroform extraction with an acid/base wash (chloroform/acid/base extraction). Fluorescence was examined as a potential presumptive test for cocaine on the currency. The objective was to develop a baseline determination of cocaine concentration on bills in Birmingham, a simple but adequate methods of analysis, and equally adequate methods of extraction. Two sets of twenty \$1 bills were collected from local Regions (set 1) and Wachovia (set 2) banks and subjected to a chloroform extraction and an chloroform/acid/base extraction; the results were 65% and 32% positive for set 1 and 65% and 35% positive for set 2 for a chloroform and chloroform/acid/base extraction, respectively. Analysis of the data confirms that the chloroform/acid/base extraction results in a cleaner GC/MS spectrum, is better to run on the GC column, but yields less intensity in chromatogram peaks due to sample loss through the multi-step cleaning process. Fluorescence was not found to be an accurate predictor for the presence of cocaine on dollar bills using a 254 nm UV source.

Introduction:

It has been shown through numerous studies that a high percentage of both US and international currency are contaminated with cocaine and other controlled substances.¹ After the publication of such reports, the US courts have ruled that police sniffing dogs can no longer be used in order to apprehend a suspect or confiscate what is thought to be drug related money.² However, internationally the ruling is much different. The UK allows mass spectrometric analysis of cocaine contaminated bills to be used as supporting evidence in court cases, and the technique of mass spectrometric analysis to determine cocaine contamination has been accepted by the UK Court of Appeals.³

The most obvious source of direct contamination is from the handling of large sums of cash at drug deals and the use of rolled up bills to snort cocaine.⁴ Other sources of contamination include money counting machines at banks, which have been shown to contain dust with significantly high proportions of cocaine in the mixture.⁵ Other research following these results also has shown that both counting machines as well as hand counting transfers nanogram amounts of cocaine to European banknotes.⁶

US currency paper is made up of a special mixture of 75% cotton and 25% linen, with red and blue synthetic fibers distributed throughout.³ UK sterling banknotes are also made up of cotton and linen, so it is reasonable that both should exhibit similar qualities in the ageing of the bill, as well as the transfer of cocaine to the bills.⁷ Studies have shown that through time the fibers of UK banknotes change, forming cavities in the fibers that could potentially trap contaminants, including cocaine crystals. Others have shown that the inks of the bills, grease, and chemical binding can play a role in the capture of cocaine on currency.⁶ No research could be found

on the possible contamination of bills through the passage of currency through wallets and purses, however the characteristic cavities seen in bills does not eliminate the possibility for controlled substance transfer in wallets and purses. Whether such transfer, if it occurs, yields detectible amounts is unknown.

Because of the ability of bills to pick up cocaine and other drugs from many different sources, the variable of age and wear of the bill, and the unknown amount of cocaine commonly picked up by any specific bill, it is very hard to determine prosecutable amounts of cocaine for currency and even establish a low variance baseline to distinguish background from contamination.⁸ Because of this, research has been ongoing in different countries of the world to try to create baselines for bills in specific areas of the country, states, and even cities.

Research on different methods of analyzing bills and the extraction of cocaine from the bills is also an important consideration in cocaine detection. Several methods have been developed or modified to analyze currency for cocaine contamination. Research labs have used tandem mass spectrometry (MS-MS) for the analysis of currency in which volatile substances on the bills are ionized between heat plates and pulled through the mass spectrometer.⁹ A somewhat more time consuming method is to run a GC/MS of prepared samples. This GC/MS method has also been used in research labs for the determination of cocaine on currency, and often follows a purifying step involving solid phase extraction (SPE).

GC-MS-MS methods as well as Ru(bpy)₃²⁺ ECL combined with cell electrophoresis (CE) have been developed as non-destructive methods in opposition to the destructive methods of tandem mass spectroscopy, where the part of the bill passed

through the heated plates during analysis is incinerated.¹⁰ Nondestructive methods are preferred by the scientific community, especially in crime labs where the preservation of evidence is a priority. The high sensitivity, fast analysis times, and non-destructive methods claimed by the researchers for each method gives researchers and forensic toxicologists options with results similar to those used in tandem mass spectroscopy without any destructive measures being taken.

A final concern in the analysis of currency for illicit drugs is the extraction methods employed. An Esteve-Turrillas et al.¹¹ study on a non-destructive method of cocaine determination on bills also employs a suitable, friendly, and non-destructive solvent extraction as well. It was determined that while cocaine is highly soluble in chlorinated solvents, such as chloroform, such solvents have the potential to destroy security marks and holographic strips on currency. Acetonitrile, on the other hand, is less destructive to currency, but also removes large amounts of other solid compounds with the cocaine. It was finally determined that methanol was the least destructive method and sufficient for the removal of cocaine from currency. Although these tests were performed on UK banknotes, the similar design of US and UK currency would most likely yield similar results in each of these solvents.

In this experiment, a simple yet effective way of extraction, analysis, and cocaine determination was employed. Analysis of paper currency in the Birmingham Alabama area by gas chromatography mass spectroscopy (GC/MS) was chosen due to the readily available access to a GC/MS in most research and crime labs, as well as methods previously used in earlier research, as noted above. Twenty \$1 bills were collected from a local Wachovia branch and subjected to an initial methanol extraction to remove the cocaine, yet preserve the bills. The extraction was divided so that both a chloroform extraction and a chloroform/acid/base extraction could be used in the determination of cocaine on the currency.

The GC/MS work for the collected twenty \$1 bills was preceded by a UV fluorescence test of the bills under a 254 nm handheld UV light. Labino, the maker of a UV lamp for controlled substance fluorescence, has documented that cocaine of at least 87% pure fluoresces under their UV light source.¹² According to Mercolini, cocaine has an excitation wavelength of 230 nm and emission at 314 nm,¹³ and thus the twenty \$1 bills collected were tested to see if fluorescence is an indicator of the presence of cocaine on currency.

A chloroform/acid/base extraction of cocaine works by taking advantage of the ability to change the form of cocaine by adjusting the pH above or below the cocaine pKa value of 8.6.¹⁴ By first placing the extracted contents of the currency in an acidic environment and adding chloroform, all cocaine in the sample should be in its hydrochloride form and stay in the

water layer due to its high solubility; however, most organic impurities will go into the chloroform layer. Removing the chloroform layer will remove most of the organic impurities from the sample. The sample is then made basic, turning the cocaine in the sample into the free-base form.¹⁵ Cocaine will then be soluble in the chloroform layer and insoluble in the water layer. Any salt impurities left in the sample will be dissolved in the water layer. By once again removing the chloroform layer and keeping it for analysis, a much cleaner sample containing cocaine can be run on the GC/MS.

Methods:

Materials: methanol, Fisher Scientific; Hampton, NH: Lot#001162; sodium carbonate, Acros; Geel, Belgium: Lot #B0122733; 12.1 N HCl, Fisher Scientific; Hampton, NH: Lot #065373; chloroform, Aldrich; Milwaukee, WI: Lot #JU 04354CU; chloroform, Sigma Aldrich; St. Louis, MO: Lot#09767JH; exempt cocaine standard, Cerilliant Round Rock, TX: Lot #FC032007-01A

The GC/MS analysis was performed on an Agilent Technologies 6890N Network GC System with an auto sampler. The GC was interfaced with an Agilent Technologies 5975 MSD utilizing a splitless capillary inlet and a HP 5 column (30m x 0.250mm).

Collection of Currency:

Twenty \$1 bills were collected from a Wachovia bank located in Birmingham Alabama. Each bill was collected and stored in a separate plastic bag at room temperature until analyzed.

UV Fluorescence:

An UV fluorescence test was performed under a 254 nm short wave UV light to check for a correspondence between currency fluorescence and cocaine concentration on the bill. The presence of fluorescence was recorded.

Positive and Negative Controls

A cocaine control was run at the beginning of each set of 20 samples. A blank was injected between each sample to check for carry-over from the previous run.

Methanol Extraction of Currency

Each bill was crumpled and placed into a 20 mL glass vial and 10 mL of methanol was added, covering the entire bill. They were allowed to soak overnight and were sonicated for 10 minutes in a FS20H Fisher Scientific Sonicator before removal of methanol to test tubes.

For the second set of bills, the methanol extraction was divided evenly into two test tubes per bill in order to perform a chloroform extraction and chloroform/acid/base extraction with equally concentrated samples. The methanol was then evaporated to dryness on a N-EVAP112 Nitrogen Evaporator.

Method 1 Water/Chloroform Extraction

For the first set of 20 one dollar bills, the dried residue was dissolved in deionized 1 ml water and extracted in methanol. After GC/MS analysis, the samples were again dried and then underwent a chloroform/acid/base extraction.

Method 2 Chloroform Extraction: (second set of bills only)

One ml of chloroform was added to the dry residue in the test tube and sufficiently agitated. The chloroform was pipetted into 1 ml GC vials and analyzed on the GC/MS.

Method 3 Chloroform Extraction with Acid/Base Wash (chloroform/acid/base):

One mL of deionized water was added to the test tube followed by enough drops of 12.1 N HCl to make the pH < 3.00. One milliliter of chloroform was then added to the test tube. The chloroform layer was removed as organic waste, and the pH brought to > 12.00 by the addition of saturated sodium carbonate. One mL of chloroform was then added to each the test tube, and the chloroform layer was removed and placed in GC/MS vials and analyzed by GC/MS.

Control Experiments:

All three extraction methods were performed on a Cerilliant exempt cocaine standard to first verify that all three methods were successful and to give a qualitative result of sample loss with each extraction method. From analysis of these results, it was decided that the chloroform extraction from the methanol residue was sufficient and that adding water before extracting into chloroform was not required.

Results and Discussion:

Cocaine Contamination of Currency:

The GC/MS method for cocaine was developed using the positive cocaine controls. The retention time of 9.845 ± 0.05 min. was determined and the characteristic peaks for cocaine, m/z 82, 182, and 303 were selected from the accepted literature values for cocaine.¹⁶

The presence of cocaine was determined by extracting the m/z 82, 182, and 303 from the mass spectra. The peaks resulting from the extracted ion chromatograms were much more easily distinguishable from the background noise and were determined as positives or negatives by the presence or absence of these peaks at 9.845 min. The extracted ion chromatograms (EIC) for a positive and a negative result are shown Figures 1 and 2.

In addition to the impurities in the mass spec. of the samples, there was considerable carry-over of the impurities from the chloroform extracted samples into the blank injection that followed each sample injection. While some of these impurities eluted during the retention time for cocaine, none of them were determined to be cocaine upon analysis (Fig. 3).

Sixty-five percent of the first set of the twenty \$1 bills analyzed by Hammer using a water/chloroform extraction were contaminated by cocaine. When re-analyzed with a chloroform/acid/base extraction, it was determined that 6 out of 19 samples were contaminated with cocaine with one not being analyzed due to the presence of too many impurities to safely run on the GC/MS (Table 1). Comparing percentages of 65% to 31.6% shows that the chloroform/acid/base extraction method causes sample loss through the multi-step cleaning process. However, as seen in Figure 4 and Figure 5, the chloroform/acid/base extraction resulted in a cleaner GC/MS spectrum, eliminated problems of carryover of impurities into blank injections between cocaine sample runs, and is thus better to run on the GC/MS column.

In order to qualitatively look at the loss of sample by the three extraction methods, three 200 μ l samples of a cocaine standard (1g/ml) were extracted by methods 1, 2, and 3. As illustrated in the chromatograms of the different extraction methods on the cocaine control (Figure 6), the water/chloroform extraction gave a slightly better yield than the straight extraction into chloroform, though with only one trial, this may not be a significant difference. However, the chloroform/acid/base extraction does show a significant loss of cocaine through the multiple steps of the extraction.

Another possible reason for the fewer positives between the water/chloroform and chloroform/acid/base extractions was the time between analyses. The chloroform/acid/base extraction was done approximately three months after the initial water/chloroform extraction.

A second set of twenty \$1 bills were collected from a Wachovia bank as a follow-up on the previous results. In this experiment, 65% of the samples were positive for cocaine using the water/chloroform extraction method, and 35% of the samples were positive for cocaine using the chloroform/acid/base extraction method as seen in Table 2.

Interestingly, this data corresponds to the percentage results determined from the Hammer extraction and the chloroform/acid/base extraction performed on those samples. It also shows that the chloroform/acid/base extraction results in a cleaner GC/MS spectrum, eliminated problems of carryover of impurities into blank injections between cocaine sample runs, and is thus better to run on the GC/MS column as stated before.

As seen in Table 3, and compared to the data in Table 2, there was no correspondence between the GC/MS results and the fluorescence seen under the 254 nm UV light source. This is apparent in the fact that out of the 11 bills that had at least some fluorescence only 7 of them tested positive for cocaine, and out of the 9 bills that did not fluoresce 6 of them

tested positive for cocaine. Results are even less applicable to the less sensitive chloroform/acid/base extraction method in which the two heaviest fluorescing bills, bills 5 and 20, showed no cocaine present in the chloroform/acid/base extraction. This signifies that even the most heavily fluorescing bills did not have the highest cocaine concentration and that bills that did not fluoresce still contained cocaine in the less sensitive chloroform/acid/base extraction method.

The bills were once again submitted to the UV light test after methanol extraction of the contents on the bills, and no changes in fluorescence were observed.

Conclusions:

It was determined that the results from a chloroform extraction vs. chloroform/acid/base extraction could result in a 30% difference in bills testing positive for cocaine. However, the chloroform/acid/base extraction resulted in a cleaner GC/MS spectrum, is better to run on the GC column, but yields less intensity in chromatogram peaks due to sample loss through the multi-step cleaning process. Some factors that should be taken into consideration when interpreting these results are:

1. Each methanol extraction from the second set of bills was divided in half so that the methods could be compared. If the entire volume was analyzed, the chloroform/acid/base extraction may have proved as accurate as the chloroform extraction. This could be evaluated by adding a controlled amount of cocaine to a set of bills before analysis.
2. In the extraction experiments of the controls, the analyte was already in the base form and a chloroform extraction would be the most effective method for analyzing these samples. However, cocaine on the bills would be expected to be the salt form, as that is currently the most common form encountered in crime labs. A way to test this would be to spike clean bills with both the base and salt forms of cocaine.

It was also determined that UV fluorescence at 254 nm has no preliminary determination of cocaine presence on the currency and showed that the methanol extraction method to remove contaminants from the currency had no effect on whatever material was causing the fluorescence. Further work needs to be done if a method is to be developed. The final determination of percent cocaine on bills tested in the Birmingham Alabama area using GC/MS, chloroform extraction and chloroform/acid/base extraction, and an extracted ion chromatogram for final determination showed that 65% of the bills from the chloroform extraction were contaminated with cocaine, and that 35% showed cocaine contamination from the chloroform/acid/base extraction. This data is consistent with the analysis of Hammer and the follow up chlo-

roform/acid/base extraction procedure.

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Endnotes

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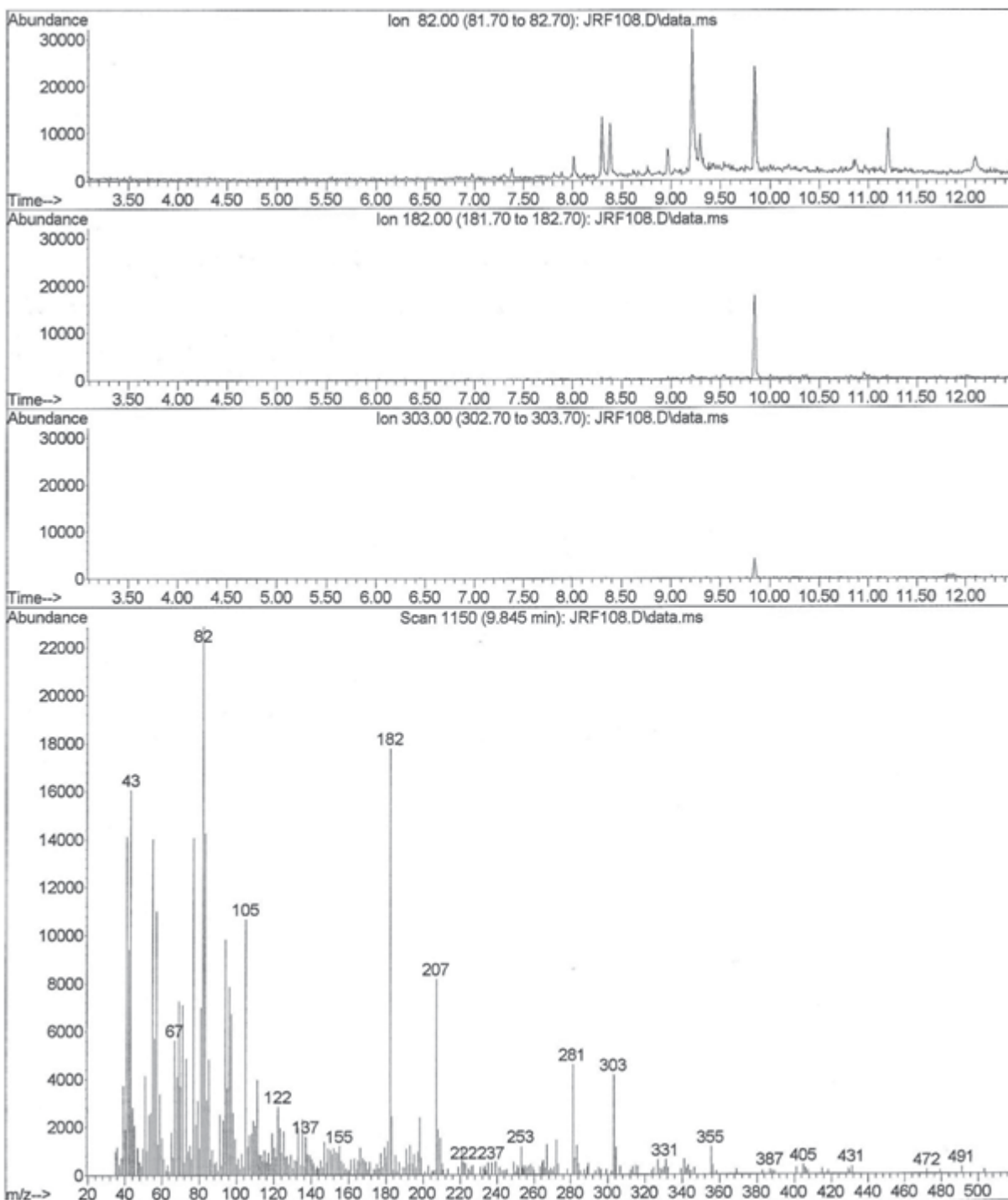
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Figure 1. Positive Cocaine Result in the Extracted Ion Chromatogram.



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Figure 2. Negative Cocaine Result in the Extracted Ion Chromatogram

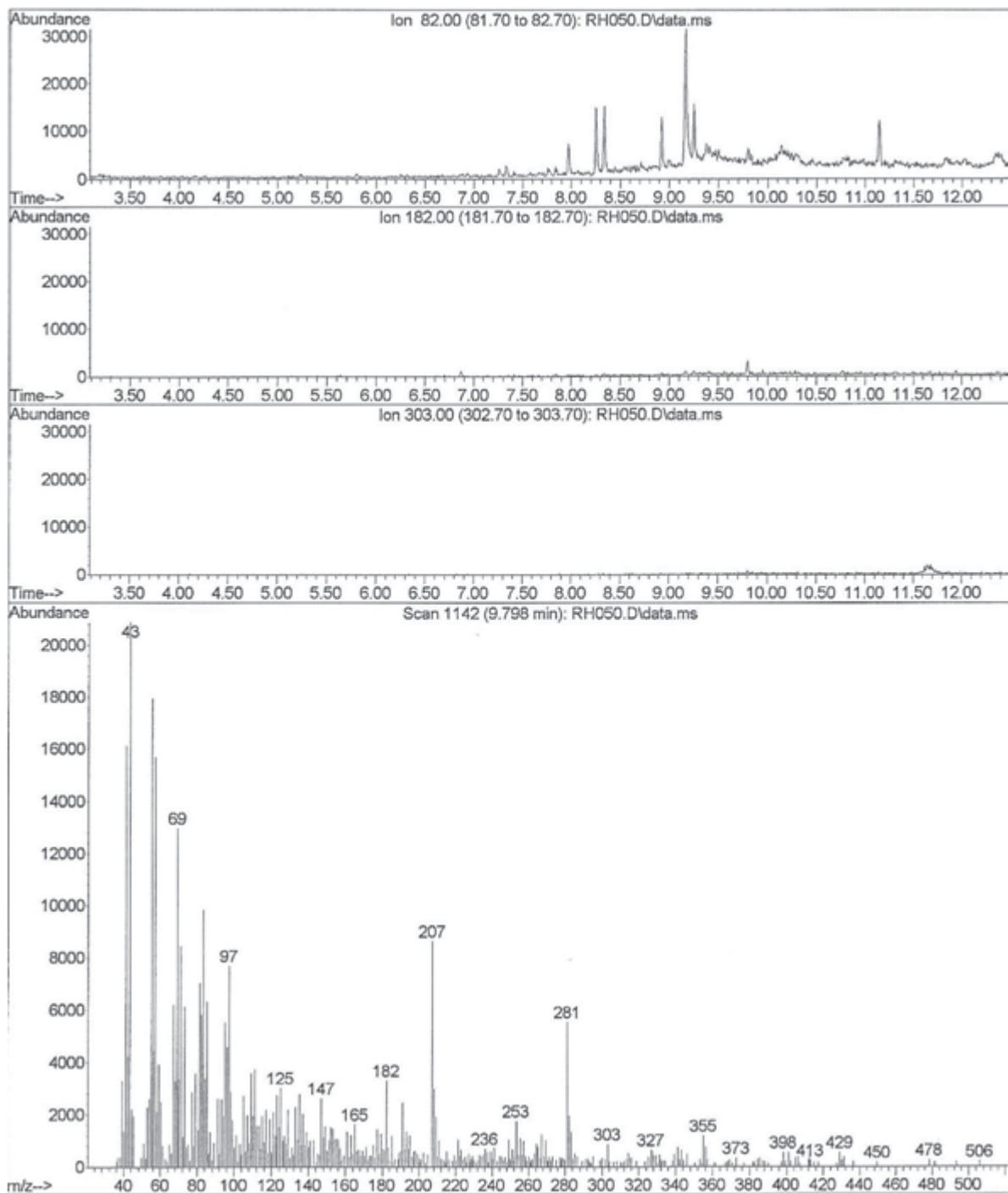


Figure 3. GC/MS of Chloroform Extraction Blank with Carry-Over at 9.839 min

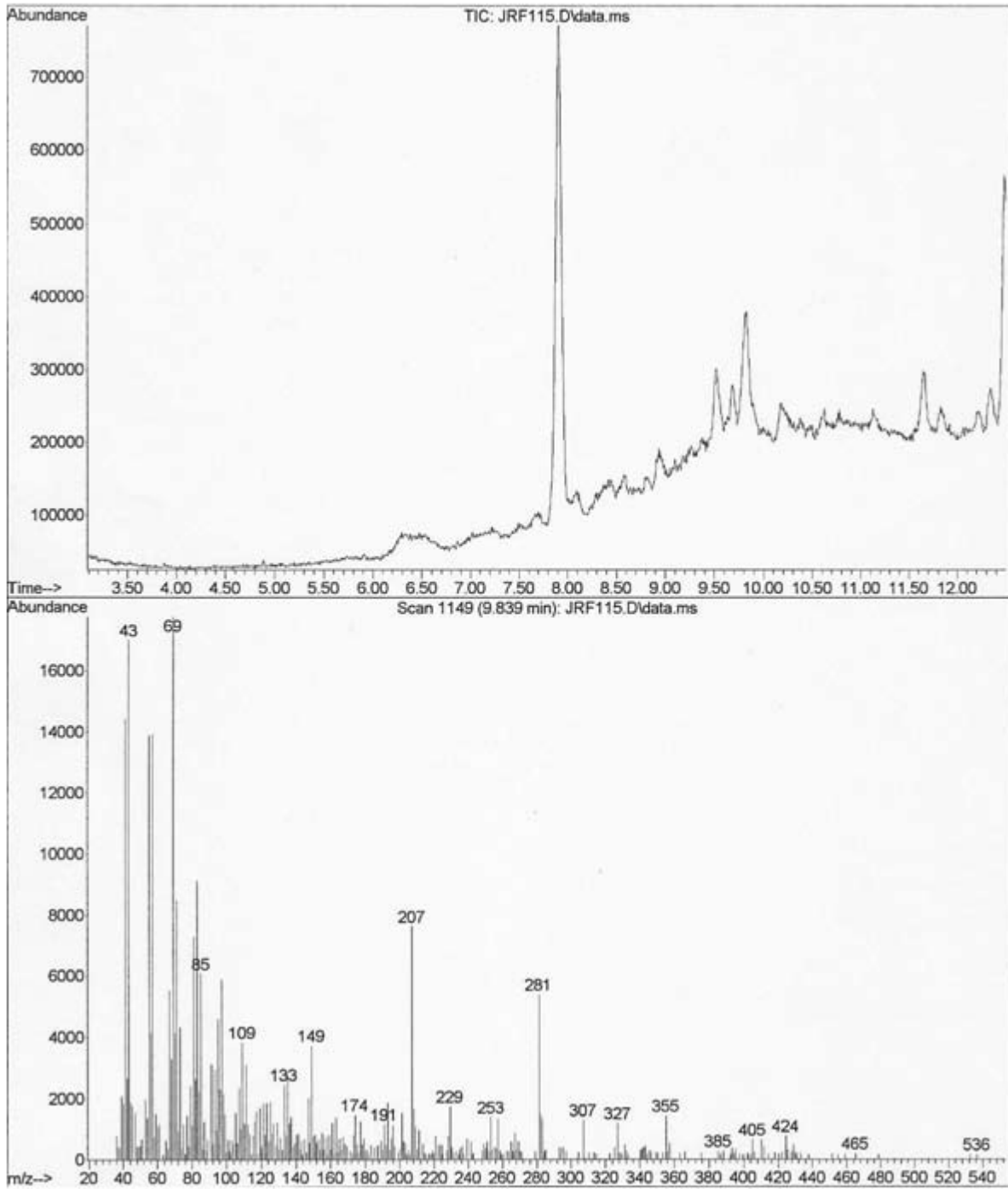


Figure 4. Chromatogram and Mass Spectrum from Chloroform Extraction (Positive for Cocaine)

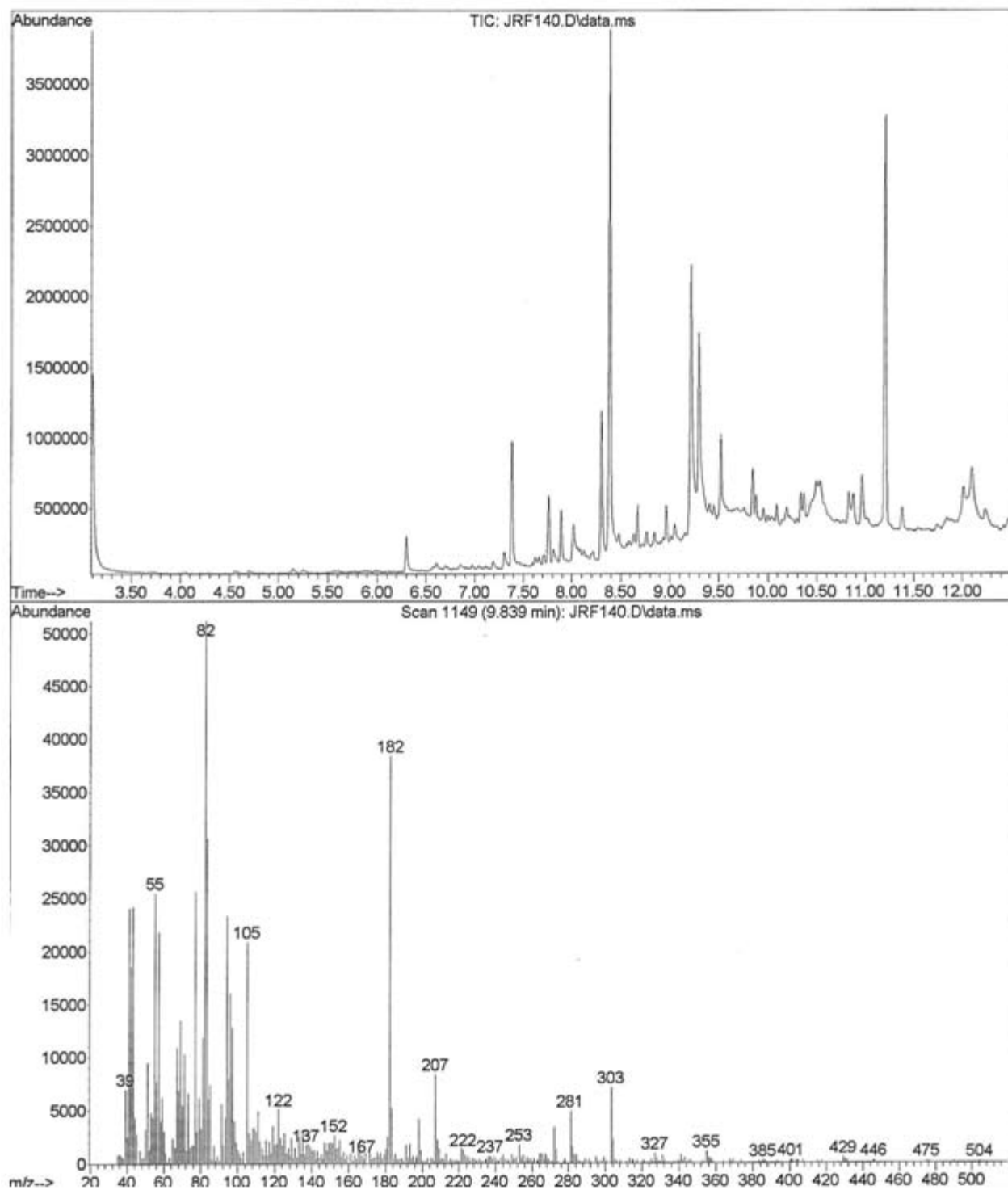


Figure 5. Chromatogram and Mass Spectrum from Chloroform/Acid/Base Extraction (Positive for Cocaine)

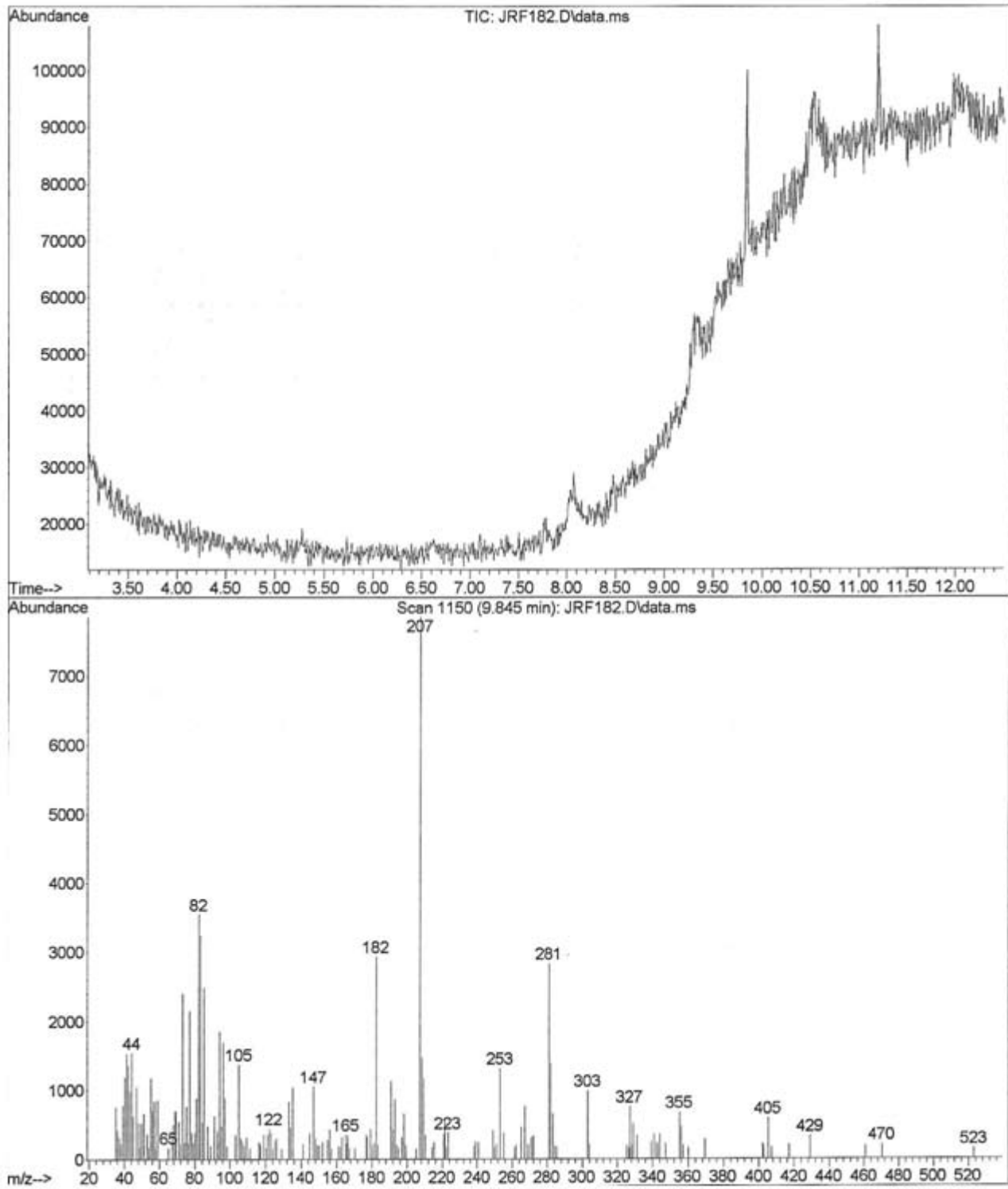


Figure 6. Chromatogram Overlay of Extraction Methods of Cocaine Standard

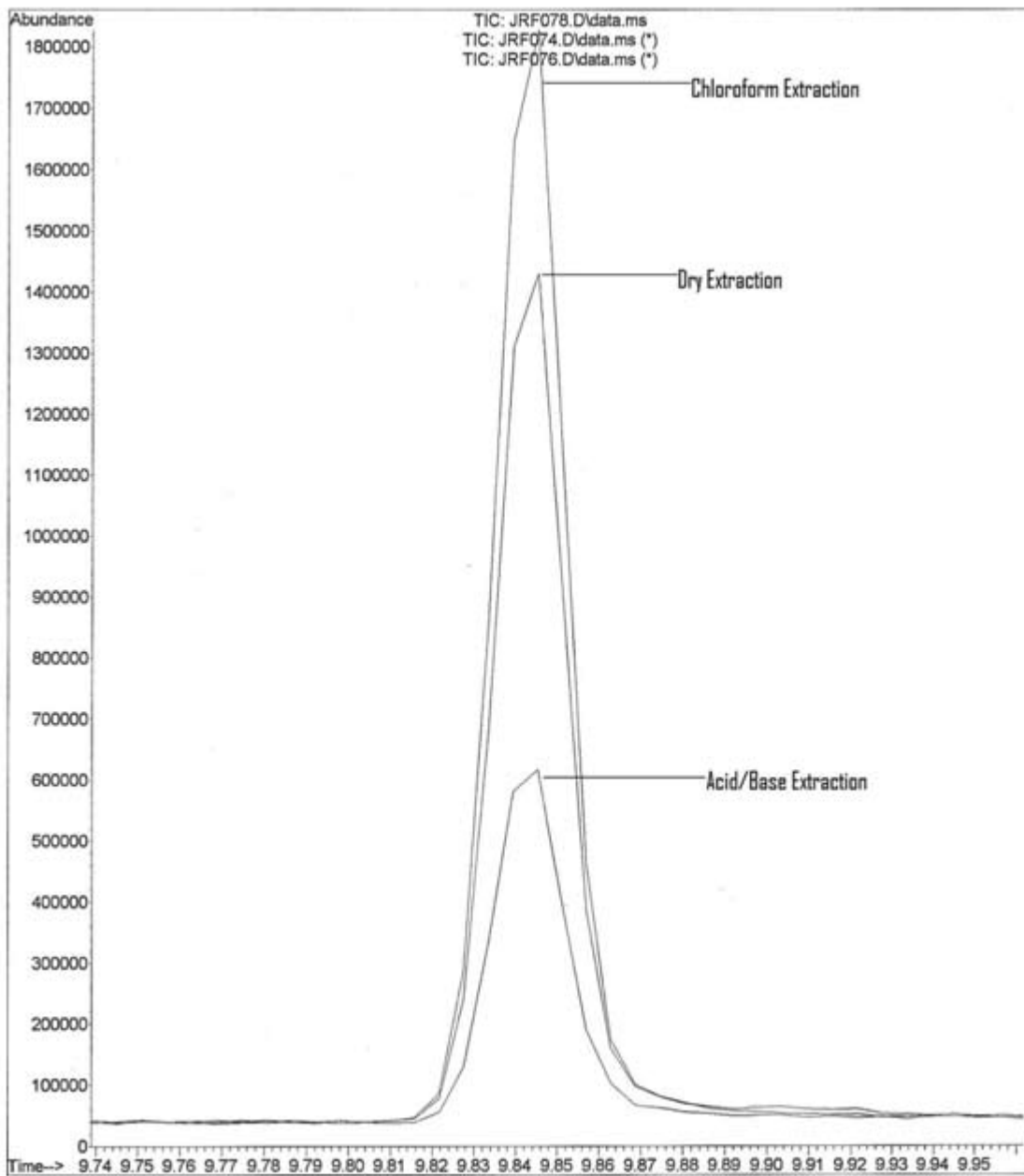


Table 1. Cocaine Analysis of Twenty \$1 Bills from Hammer and A/B Extraction Using EIC Determination

Sample	Serial Number	Series	Cocaine Dry Extraction	Cocaine A/B Extraction
1	K31639841F	2003A	No	No
2	G74352837C	2003A	Yes	No
3	L65858869F	2001	Yes	Yes
4	C43331196A	2003A	Yes	Yes
5	F29900166I	2003A	Yes	No
6	E59694877B	2003A	Yes	Yes
7	L15588053P	2003A	No	No
8	F055151816A	2006	No	No
9	D42105175A	2003A	Yes	No
10	J79320301D	2003A	No	No
11	F52780916C	2003A	Yes	Yes
12	F48991587B	2006	No	No
13	A74411471B	2003A	Yes	Not Run
14	K65247169H	1999	Yes	Yes
15	F22886476G	2003A	Yes	No
16	H09465674C	2003	Yes	No
17	K89591350B	2003A	Yes	No
18	J57336529B	2003	Yes	Yes
19	K43708395F	2003A	No	No
20	I22572086L	1995	No	No

Table 2. Cocaine Analysis of Twenty \$1 Bills Using EIC Determination

Sample	Serial Number	Series	Cocaine Dry Extraction	Cocaine A/B Extraction
1	G95919878D	2003A	No	No
2	E66746120A	2003A	Yes	Yes
3	KO1430953A	2006	No	No
4	F46387847J	2003A	Yes	Yes
5	L91961202K	2003A	Yes	No
6	H71011706A	2003A	No	No
7	F03840182K	2003A	Yes	No
8	F05931531A	2006	Yes	Yes
9	F83640498H	2003A	Yes	No
10	K01712161F	2003A	Yes	Yes
11	D09669487C	2003	Yes	No
12	G01967256I	2003A	No	No
13	E36503180A	2003A	No	No
14	D56775559C	2003A	Yes	Yes
15	H09295751A	2006	No	No
16	F54057570K	2003A	Yes	No
17	K19394902H	2003	Yes	Yes
18	L08800038P	2003A	Yes	Yes
19	B34225787C	2006	No	No
20	K53712767C	2003A	Yes	No

Table 3. UV Fluorescence at 254 nm of Currency Collected For Extraction

Sample	Serial Number	Fluorescence	Cocaine	Location On Bill
1	G95919878D	One Spot	No	Above "MER" on Back
2	E66746120A	Heavy	Yes	Around Entire Edge Front and Back. Solid Strip on Back Through "O" in Central <i>ONE</i>
3	KO1430953A	No	No	
4	F46387847J	No	Yes	
5	L91961202K	Entire Bill	Yes	Very Heavy on Entire Bill
6	H71011706A	One Slight Spot	No	Left Side of Bottom Serial Number
7	F03840182K	Slight Spots	Yes	Front Right Side of Bottom Left Hand 1, and above "N" in <i>ONE</i>
8	F05931531A	Two Small Spots	Yes	Bottom Left Back Edge
9	F83640498H	No	Yes	
10	K01712161F	No	Yes	
11	D09669487C	No	Yes	
12	G01967256I	Spots and Line	No	Front Bottom Left 1 and Edge. Strong Line on Bent Spot Diagonal of Bottom Left Hand 1
13	E36503180A	No	No	
14	D56775559C	No	Yes	
15	H09295751A	No	No	
16	F54057570K	Light	Yes	Slight Color on Front Left and Small Portion Top and Bottom Edge. Heavier and Solid Corresponding Back Side
17	K19394902H	No	Yes	
18	L08800038P	Big Spot	Yes	Spot Around Front Left Stamp. Large But Not Too Fluorescent
19	B34225787C	Spots	No	Two Spots on Left Front Edge in Middle. One Spot Top Edge Front Above <i>THE</i>
20	K53712767C	Almost Entire Bill	Yes	Heavy All Edges Both Sides and Big Spots Throughout Middle