

## CASE REPORT

### CRIMINALISTICS

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# Dancing on Coke: Smuggling Cocaine Dispersed in Polyvinyl Alcohol

**ABSTRACT:** Recent trends suggest that cocaine smugglers have become more and more inventive to avoid seizures of large amounts of cocaine transported between countries. We report a case of a mail parcel containing a dance pad which was seized at the Customs Department of Brussels Airport, Belgium. After investigation, the inside of the dance pad was found to contain a thick polymer, which tested positive for cocaine. Analysis was performed using a routine colorimetric swipe test, gas chromatography coupled with mass spectrometry and nuclear magnetic resonance spectroscopy. The polymer was identified as polyvinyl alcohol (PVA) and contained 18% cocaine, corresponding to a street value of € 20,000. Laboratory experiments showed that cocaine could be easily extracted from the PVA matrix. This case report reveals a new smuggling technique for the transportation of large amounts of cocaine from one country to another.

**KEYWORDS:** forensic science, cocaine, polyvinyl alcohol, smuggling, gas chromatography–mass spectrometry, proton nuclear magnetic resonance

Cocaine is smuggled in a variety of ways. As a solid powder, it can be hidden in vehicle parts, materials, clothing, or even in the human body (1). Recent trends suggest the use of more sophisticated methods. Smuggling cocaine in a liquid (2) or polymeric matrix (3,4) requires an extraction step before cocaine can be distributed or sold on the market. In its International Collaborative Exercises 2008 Summary Report, the United Nations Office on Drugs and Crime (UNODC) mentioned for the first time a trafficking method for cocaine involving dispersion in polyvinyl alcohol (PVA) films followed by use as lining material in backpacks (5).

PVA is a water-soluble synthetic and nontoxic polymer. It is used in many industrial, commercial, medical, and food applications, including as an adhesive and thickener material, surfactant, lubricant in eye drops, and chemical solvent barrier (6).

In this paper, we present a case report of a dance pad seized by the Customs Department at Brussels Airport, Belgium. The inside of the pad contained a thick polymer, for which preliminary colorimetric screening tests were positive for cocaine.

#### Case Report

On January 22, 2010, the Customs Department at Brussels Airport executed a routine inspection of the mail parcels from Costa Rica to Belgium. In one of the parcels, a DVD and dance pad with

the logo from “High School Musical” with connections to a PlayStation game console (Fig. 1a) were found. The parcel drew the attention of the Customs officers by its unique and strong chemical odor and was further investigated. Both the outside of the dance pad and the inside polymer (Fig. 1) were tested for cocaine with NARK II cocaine ID swipes; a discoloration of the swipe from white to blue suggests the presence of cocaine. Only the inside polymer tested positive for cocaine and this was confirmed in the Customs laboratory, where cocaine was identified in the polymeric material after extraction with methanol and analysis with gas chromatography (GC) coupled with mass spectrometry (MS).

#### Materials and Methods

##### *Chemicals and Reagents*

Cocaine hydrochloride and cocaine-*d*<sub>3</sub> hydrochloride were of analytical grade (purity >98%) and were purchased from Cerilliant (Round Rock, TX) at concentrations of 100 ng/μL in methanol (MeOH). Acetone and MeOH for GC, ethyl acetate for liquid chromatography, tetrahydrofuran for analysis and ammonium hydroxide were obtained from Merck (Darmstadt, Germany). Xylene (pure, 99%) was bought from Acros Organics (Geel, Belgium). Milli-Q water was obtained by purifying demineralized water in a Milli-Q system (Millipore, Bedford, MA). Polyvinyl alcohol (PVA) was acquired from Sigma-Aldrich (Bornem, Belgium). Deuterium oxide was obtained from Acros Organics (Geel, Belgium).

##### *Identification of the Polymeric Material*

First, simple solubility tests with different solvents were carried out to identify the polymeric material of the dance pad. Approximately 4 mL of acetone, tetrahydrofuran, and xylene was added

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FIG. 1—Left: The dance pad as found in the parcel. Middle: The dance pad with the inside polymer made visible. Right: The inside polymer of the dance pad.

separately to 500 mg of the polymer of the dance pad. Possible solubility and change in the structure of the polymer were recorded as possible evidence of polystyrene, PVC, and polyethylene. The solubility in Milli-Q water was also evaluated.

In a second phase, a  $^1\text{H}$  NMR spectrum of a sample of the polymer of the dance pad was recorded with a Varian Mercury 300 MHz spectrometer and compared with reference  $^1\text{H}$  NMR spectra of several different polymeric materials. These reference polymers were judiciously selected based on the solubility behavior of the pad in various solvents and on its  $^1\text{H}$  NMR spectrum.

#### Quantification of Cocaine in the Dance Pad

The polymeric part of the dance pad (70 × 80 cm, 2.2294 kg) was cut into nine parts: ULe, UM, UR, MLe, MM, MR, LoLe, LoM, and LoR, where U = upper, M = middle, Lo = lower, R = right, and Le = left. From each part, a small piece (about 20 mg) was collected at random and was precisely weighed. Each piece was transferred into a 10-mL test tube with screw cap, and 1 mL of Milli-Q water was added. Then, 20  $\mu\text{g}$  of the deuterated standard of cocaine (cocaine- $d_3$ ) in MeOH was added, and the test tube was closed and put in an oven at 80°C for maximum 2 h. After complete dissolution of the material in the water and a thorough mixing, 150  $\mu\text{L}$  of the solution was diluted to 1 mL with Milli-Q water. From this solution, 50  $\mu\text{L}$  was evaporated to dryness under a nitrogen stream and redissolved in 100  $\mu\text{L}$  of ethyl acetate. To evaluate possible dissolution problems of cocaine in ethyl acetate, replicate analyses of cocaine standard dissolved in MeOH and ethyl acetate were executed and peak areas in the chromatograms were compared. The ratio of the area of cocaine dissolved in ethyl acetate to the area dissolved in MeOH was 0.88 (RSD <5%). A slightly lower dissolution of cocaine in ethyl acetate was thus observed, but is negligible because of the use of cocaine- $d_3$ . The extract was analyzed on an Agilent 6890 GC system and an Agilent 7683 series automatic injector coupled with an Agilent 5973N mass selective detector (MSD) in scan mode. For the chromatographic separation, an Agilent HP-5MS capillary column (30 m × 0.25 mm × 0.25  $\mu\text{m}$ ) was used. The injection port temperature was 275°C, and the oven temperature program was as follows: 75°C for 2 min, then an increase at 15°C/min to 250°C followed by an increase to 315°C at 5°C/min (total run time 31.67 min). Helium was used as carrier gas at a constant flow of 1.0 mL/min, and the injection volume was 1  $\mu\text{L}$  in pulsed splitless mode. The ion source, quadrupole, and interface temperatures were

230, 150, and 290°C, respectively, and the electron multiplier voltage was 2012 V. The ionization energy was 70 eV, and the scanning range was 50–550 amu.

## Results and Discussion

### Identification of the Polymeric Material

No solubility or change in the physical structure of the polymeric part of the dance pad was observed upon the addition of acetone, tetrahydrofuran, or xylene. However, a structural change was observed when Milli-Q water was added and when it was heated to 80°C. Under these conditions, a complete dissolution of the polymer was observed within 2 h.

Further analysis into the identification of the polymer was performed using  $^1\text{H}$  NMR spectroscopy (Fig. 2a,b). All  $^1\text{H}$  NMR spectra were recorded at 298 K using a relaxation delay of 2.0 sec and a 45° pulse. Given the high solubility of the polymeric material in water, a 20.6 mg/mL solution was prepared in deuterium oxide ( $\text{D}_2\text{O}$ ), a common NMR solvent, and calibrated to the HDO peak at 4.8 ppm (7). The  $^1\text{H}$  spectrum clearly displays peaks characteristic for cocaine as revealed in an  $^1\text{H}$  NMR spectrum of pure cocaine hydrochloride (Fig. 2c), confirming the presence of this substance in the dance pad.

After further inspection of the spectrum, it was evident that the polymer was neither protein (e.g., gelatine) nor polysaccharide (such as agarose) in nature because the spectra lacked characteristic peaks for amide bonds (NH) (5.5–7 ppm) and sugar anomers (4.5–5.5 ppm). There were two broad peaks, at 1.4–1.7 and 3.8–4.0 ppm, which had an approximately 2:1 ratio in integrals, that were not conclusive for cocaine. At this point, an assumption was made that these peaks were related to the matrix containing the cocaine.

These two peaks with their integral ratio prompted us toward PVA. PVA is a widely available water-soluble polymer and has the molecular structure as shown in Fig. 3. A reference sample of PVA (15 mg/mL in  $\text{D}_2\text{O}$ ) was prepared, and a  $^1\text{H}$  NMR spectrum was recorded (Fig. 2d). The integral ratio between the two peaks can be explained by the ratio of nonheteroatom protons in PVA which is 2:1. The protons of the hydroxyl groups in PVA are fully exchanged with those in  $\text{D}_2\text{O}$  and are therefore not detected.

The  $^1\text{H}$  NMR spectrum of the PVA standard (Fig. 2d) not only shows two broad peaks at identical chemical shifts as observed in the sample obtained from the pad, but also displays the characteristic 2:1 integral ratio. It was concluded that the matrix is PVA, based on the

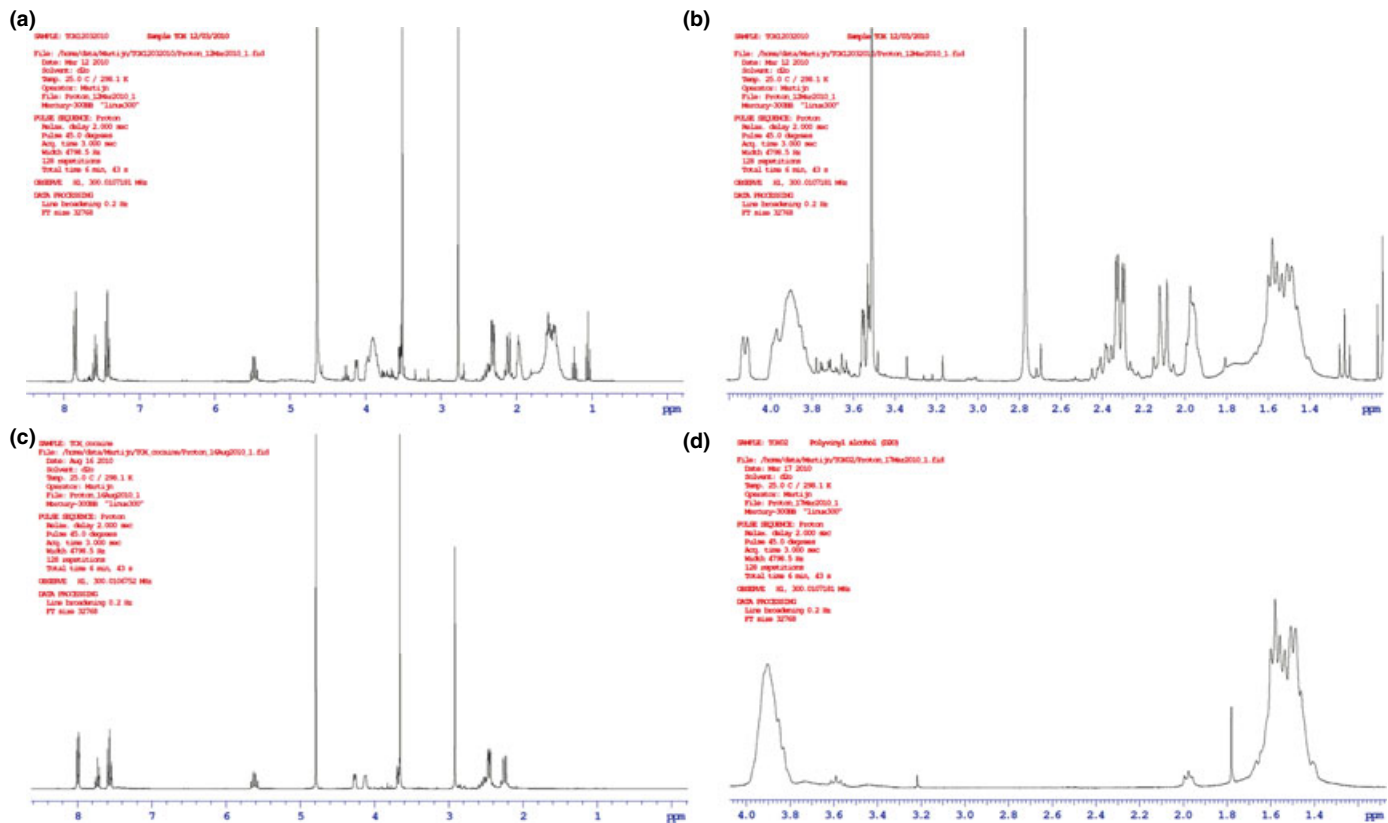


FIG. 2—(a)  $^1\text{H}$  NMR spectrum of the polymer of the dance pad. (b) Detail of  $^1\text{H}$  NMR spectrum of the polymer of the dance pad around 1–4 ppm. (c)  $^1\text{H}$  NMR spectrum of cocaine hydrochloride. (d)  $^1\text{H}$  NMR spectrum of reference sample of PVA around 1–4 ppm.

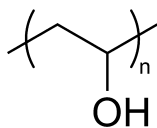


FIG. 3—Molecular structure of polyvinyl alcohol (PVA).

multiplet patterns at  $\delta$  1.4–1.7 ppm observed in the PVA standard and those from the dance pad sample (Fig. 2a,b, and d).

#### Quantification of Cocaine in the Dance Pad

In the resulting GC–MS chromatograms, the specific ions with  $m/z$  182 (cocaine) and 185 (cocaine- $d_3$ ) were monitored for quantification. The retention time of both compounds was 14.6 min (Fig. 4). Only traces of other compounds were further present: butyloctylphthalate (10.1 min), caffeine (11.0 min), cocaethylene (15.1 min), and cinnamoylcocaine (17.2 min). Standard mixtures with varying ratios of cocaine to cocaine- $d_3$  (1, 30, 100, and 300) were analyzed to evaluate the response factor between the two compounds. A response factor of 1.00 was observed in all mixtures. The amount of cocaine in each part of the polymer of the dance pad was further calculated with the following formula:

$$\text{amount of cocaine (g)} = \left( \frac{\text{area cocaine}}{\text{area cocaine} - d_3} \right) \times \text{added amount of cocaine} - d_3 \text{ (g)}$$

Table 1 gives an overview of the calculated results for each of the analyzed samples. Small variations were observed in the amount of cocaine present in each part of the polymer of the dance pad (range from 16% to 22%). The mean percentage calculated from these results was 18% with a standard deviation of 2%. An extrapolation to the complete polymer of the dance pad (2.2294 kg) suggests that it contained 404 g of cocaine with a standard deviation of 44 g. Taking into account that the average price for cocaine is € 50/g (8), this corresponds to a street value of approximately € 20,000.

#### Qualitative Information Regarding an Extraction Method for Cocaine Dispersed in PVA

An important question is how the cocaine can be extracted from the PVA to yield a form that can be sold on the illegal market, preferably as a powder. There are several extraction methodologies that can be used to extract cocaine from PVA. We used the following method. In the first step, the cocaine was separated from the PVA matrix by dissolution of the PVA matrix in Milli-Q water at elevated temperature (see experiments above). From this aqueous solution, cocaine should then be separated. As free base cocaine is nearly insoluble in water, alkalization (with, e.g., ammonium hydroxide) of the solution transformed cocaine into its free base form which was precipitated from the aqueous solution. This was then separated from the supernatant by decanting and drying. This procedure was qualitatively applied to a 500-mg piece of the dance pad. The resulting white precipitate was

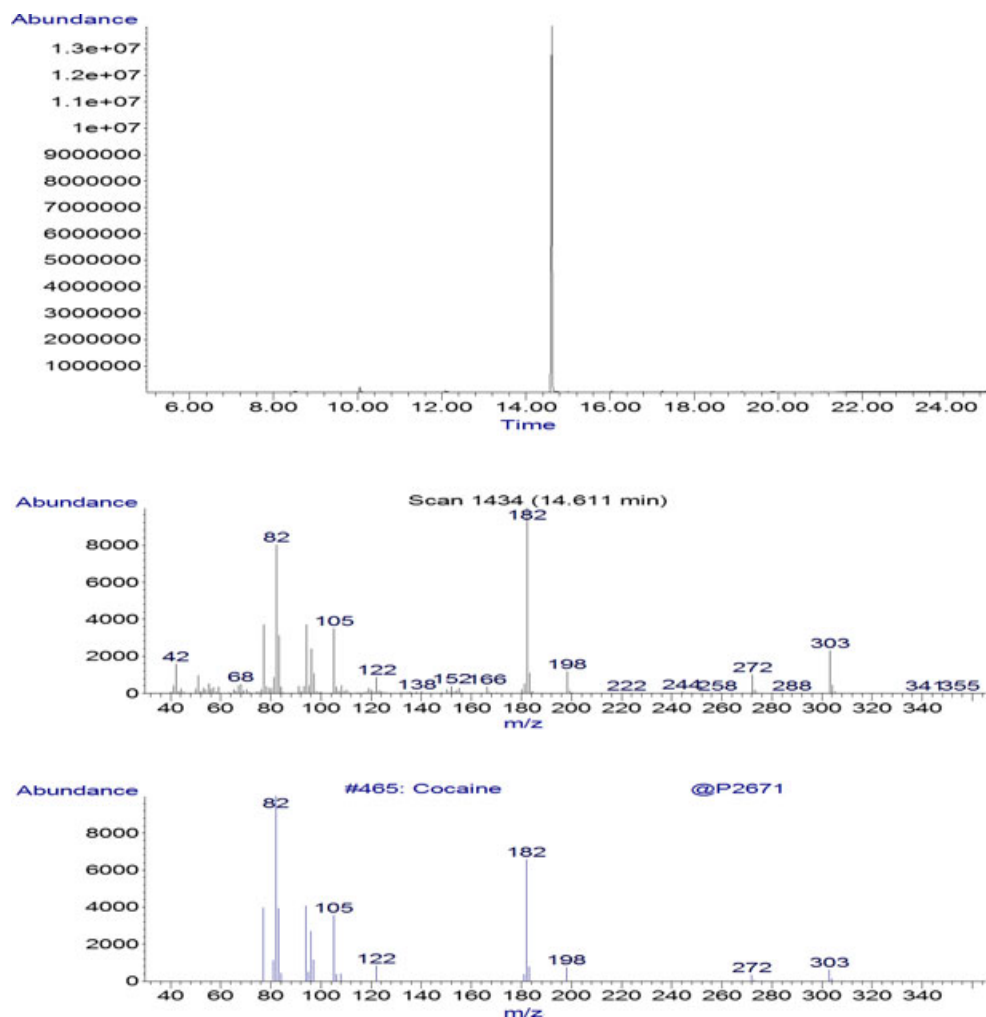


FIG. 4—Chromatogram (upper) and mass spectrum (middle) of the analysis of the middle left part of the dance pad and reference mass spectrum of cocaine (lower).

TABLE 1—Analytical results.

Part of the Pad	Weight of Analyzed Part (mg)	Amount of Cocaine in Part (mg)	Percentage of Cocaine in Part
LoLe	28.7	5.3	18
LoM	23.4	4.5	19
LoR	27.9	4.5	16
MLe	27.3	4.7	17
MM	23.9	3.6	16
MR	23.7	5.3	22
ULe	21.1	3.7	18
UM	22.1	4.1	19
URe	24.7	4.4	18

U, upper; M, middle; Lo, lower; R, right; Le, left.

dried and redissolved in methanol, and a diluted solution was analyzed with the above-mentioned GC–MS method. Cocaine was detected in this extract. This experiment shows that it is quite easy to extract cocaine from the PVA matrix. However, the presented procedure is only a suggestion, and probably other approaches can also be used.

## Conclusions

This case report shows that in an attempt to smuggle cocaine, it can be dispersed in PVA. Recovery of cocaine from the PVA

matrix is relatively easy, and these characteristics make it highly advantageous for smugglers. This case report demonstrates yet another new method developed by smugglers in their attempts to transport cocaine undetected from one country to another.

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## References

- Traub SJ, Hoffman RS, Nelson LS. Body packing—the internal concealment of illicit drugs. *N Engl J Med* 2003;349(26):2519–26.
- U.S. Department of Justice Drug Enforcement Administration. Cocaine solutions in rum bottles in Sevilla, Spain. *Microgram Bulletin* 2008; 41(11):97.
- Gostic T, Klemenc S. Evidence on unusual way of cocaine smuggling: cocaine-polymethyl methacrylate (PMMA) solid solution—study of clandestine laboratory samples. *Forensic Sci Int* 2007;169:210–9.
- U.S. Department of Justice Drug Enforcement Administration. Protective plastic cover (containing cocaine) in Colombia. *Microgram Bulletin* 2009;42(2):18.
- United Nations Office on Drugs and Crime (UNODC). International collaborative exercises 2008 summary report. Vienna, Austria: United Nations Office on Drugs and Crime (UNODC), 2008.

6. DeMerlis CC, Schoneker DR. Review of the oral toxicity of polyvinyl alcohol (PVA). *Food Chem Toxicol* 2003;41:319–26.
7. Gottlieb HE, Kotlyar V, Nudelman A. NMR chemical shifts of common laboratory solvents as trace impurities. *J Org Chem* 1997;62: 7512–5.
8. European Monitoring Centre for Drugs and Drug Addiction (EMCDDA). The state of the drug problem in the European Union and Norway. Annual Report 2009, Lisbon, Portugal, 2009, <http://www.emcdda.europa.eu/publications/annual-report/2009>.

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