CASE REPORT

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Supermarket Tampering: Cocaine Detected in Syringes and in Fruit

REFERENCE: Tomlinson JA, Crowe JB, Ranieri N, Kindig JP, Platek SF. Supermarket tampering: cocaine detected in syringes and in fruit. J Forensic Sci 2001;46(1):144–146.

ABSTRACT: Product tampering, as detailed by the Federal Anti-Tampering Act of 1983 (1), is a felony punishable by both fine and imprisonment. The rationale for product tampering ranges from pranks and attention seeking acts to extortion, terrorism, and homicide. One such case submitted for analysis involved four medical syringes found in a supermarket and suspected of being used to tamper with various products. One of the syringes was found piercing a pear while the other three syringes were found with needles exposed in other parts of the supermarket. Microscopic analysis was used to collect residue from the syringe barrels and the pear. A multidiscipline approach involving SLM, PLM, including microchemical analysis, FTIR, and GC/MS analyses, performed on the residual liquid found in the syringe barrels and in the suspect pear, confirmed the presence of cocaine. This multidisciplinary approach is often necessary when there is a possible health risk to the public and rapid response is important. With this approach, it was quickly determined which drugs or poisons were used in this tampering.

KEYWORDS: forensic science, tampering, cocaine, syringes, fruit, FTIR, GC/MS, polarized light microscopy

Case History

The Forensic Chemistry Center (FCC) of the U.S. Food and Drug Administration (FDA) routinely receives unique cases involving trace evidence analysis of poisons related to pharmaceuticals and foods. Unusual and/or complex matrices often complicate sample analysis, especially when the sample involves food products. In this case, a sample containing four syringe barrels and one pear was submitted to the FCC by the FDA's Office of Criminal Investigation (OCI) working in conjunction with a local law enforcement department in Lincoln, Nebraska. All the syringe barrels were received with needle covers. The needles were not present in the shipped sample and were not available for analysis. The syringes were allegedly used in a tampering incident at a supermarket. One syringe was found on the floor with the needle exposed, while two syringes were found in a deli case with needles exposed. The last syringe was found in the produce department with the needle portion of the syringe piercing a pear.

When the samples arrived at the FCC, a visual examination was performed to determine if any residual liquid or crystals were present in the syringe barrels. Examination was also performed to determine if the skin of the pear had been punctured with a syringe needle. The visual examination revealed that the syringe barrels did contain residual liquid and crystals. One puncture hole was found in the pear. When the FCC suspects tampering with an unknown adulterant, a multidisciplinary screening procedure for drugs and poisons is routinely performed. Various instrumental techniques including Fourier transform infrared spectroscopy (FTIR), stereoscopic, and polarized light microscopy (SLM, PLM) and gas chromatography/mass spectrometry (GC/MS) were used to detect and identify possible toxins and/or drugs in the residual liquid and pear.

Materials and Methods

Visual Examination

Examination of each of the four syringe barrels and the pear was conducted using a Nikon SMZ-U 1:10 Zoom Stereo Light Microscope (SLM). The microscope had a trinocular head fitted with a Sony MDX-760C 3^{CCD} camera. The camera was coupled to an Image 1 Analyzer controlled by a Gateway 2000 computer. The imaging system was used to capture and store the images used in the analysis. Nikon Crescent® 150 and Intralux® 5000 fiber optic light sources provided the lighting needed for observation and photodocumentation.

Examination of the pear as received revealed a triangular shaped puncture measuring ~4 mm in longest dimension. There was a slight discoloration to the flesh of the produce where it appeared to have oxidized from exposure to air. Upon viewing with higher magnification a single hole, measuring 1 mm in diameter was observed (Fig. 1). A core was removed containing the hole of the produce. A cut along the radius of the puncture was made to expose the region of the produce used for further instrumental analysis (Fig. 2).

The four syringe barrels were a common type of insulin syringe with a printed volume of 1.0 mL. The plungers were present in all syringe barrels. The needles were previously removed and not available for analysis. Examination of the four syringe barrels revealed what appeared to be liquid droplets and crystalline residue remaining in each barrel. The liquid droplets appeared colorless. A portion of the droplets was removed from each syringe barrel with

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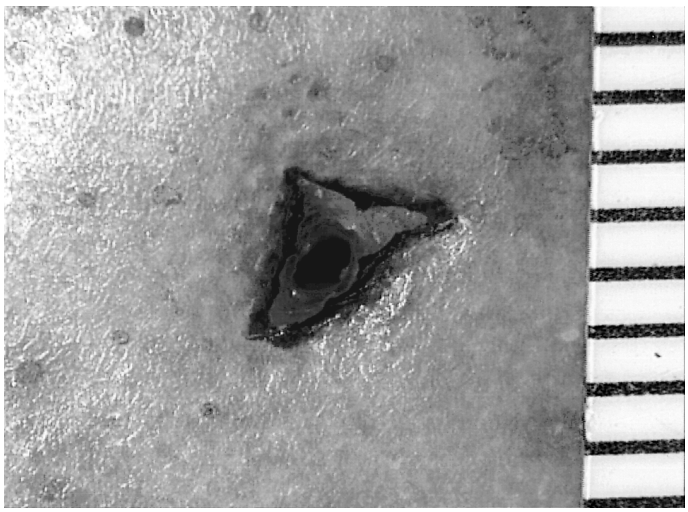

FIG. 1—*Puncture hole in skin of pear. The skin has slightly pulled away from the hole.*

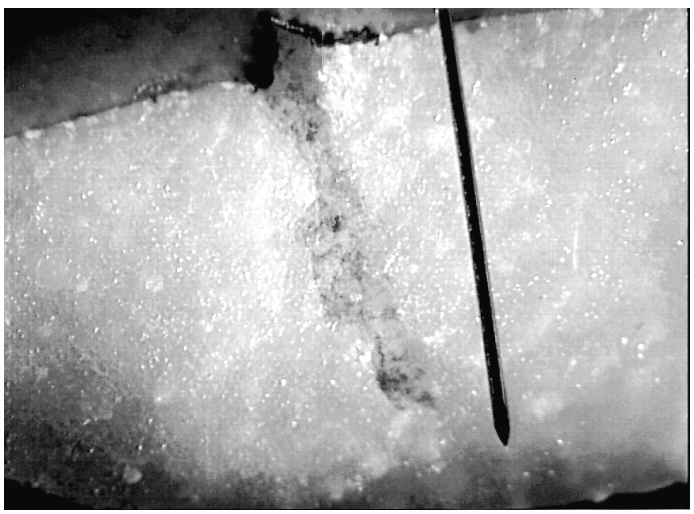

FIG. 2—*Cross section of puncture in pear. A control needle is pictured next to cross section of hole. Oxidation has taken place in the hole so the needle bore is more visible.*

a clean glass rod. This collected drop was transferred to a cleaned microscope slide and used for other analytical techniques.

A study of the migration of an injected contaminant in the pear flesh was necessary to determine an appropriate sampling area. When the flesh of the questioned pear was sectioned for instrumental analysis, the size of the section needed to be large enough to include the injected substance but small enough to insure a concentrated sampling. A diffusion study was therefore developed using a colored dye to observe the possible migration of aqueous solutions in the pear flesh. A range of volumes was used to demonstrate the migration pattern. This study was conducted using syringes similar to those in the questioned sample. The visual results of the study can be seen in Fig. 3. The suspect syringe had a 1.0 mL capacity. Using the study as a guide and assuming that as little as 10 μL or less of solution could be injected into a pear from a syringe, a 4.6 g aliquot of the flesh (without skin) was removed from the sample pear and transferred to a vial for GC/MS analysis.

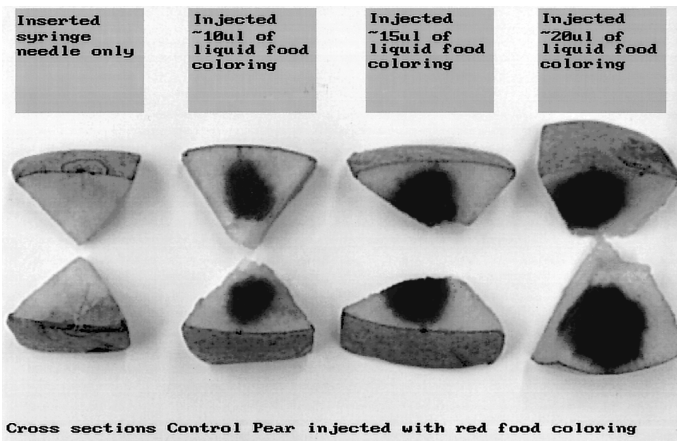

FIG. 3—*Diffusion study showing the migration of food coloring through the pear flesh. The volumes used were 5, 10, and 15 μL of food coloring. The volume (if any) of product injected into the pear was unknown. This study helped determine the amount of sample that was to be dissected from the pear for GC/MS analysis.*

Polarized Light Microscopy (PLM) and Microchemical Analysis

A Nikon Opti-Phot Pol polarizing light microscope with a Javelin ChromaChip II RGB camera coupled to a Sony color video printer was used for microcrystalline observation and recording. Gold chloride reagent was prepared by dissolving 3.0 g of tetrachlorauric [III] acid (Sigma Chemical Co.) in 100 mL of DDI H_2O acidified with a few drops of hydrochloric acid (Fisher Scientific) (2,3). This is a microchemical test used to determine the presence of cocaine.

The portion of the dried residue from the microscope slide was transferred with a glass rod to a second clean microscope slide. The residue was dissolved in a drop of the gold chloride reagent and covered with an 18-mm diameter glass cover slip.

A laboratory cocaine standard was prepared by dissolving 0.5 mg of cocaine hydrochloride (Sigma Chemical Co.) in 5.0 mL of methanol (Fisher Scientific). Using a glass rod, a drop of the solution was transferred to a glass microscope slide and dried like the suspect samples. A small amount of the dried residue was removed and treated with the gold chloride reagent as previously described.

Each preparation was immediately examined by crossed polarized light microscopy for crystal formation using a 40X objective lens. The crystals are normally delicate rosettes. When the cocaine crystals form slowly, they are long rods with many short arms running out at nearly right angles from the main axis. Note that the shape varies greatly according to the cocaine concentration (2). The sensitivity for this method has been reported up to 1:20,000 (2).

Fourier Transform Infrared Spectroscopy (FTIR)

A Nicolet Magna-IR 550 spectrometer interfaced with a NicPlan infrared microscope measured the FTIR spectra. Settings of the spectrometer were as follows: resolution 4 cm^{-1}, number of scans 64, apodization function was Happ-Genzel, mirror velocity was 1.8988 cm/s, detector was MCT/A, the aperture was 100 and the gain was 2. The instrument accesses the Aldrich Condensed Phase spectral library and the Toronto Forensic spectral library utilizing OMNIC spectral libraries software.

Approximately 1 μL of a colorless liquid was retrieved from each of the four syringe barrels and transferred to four sites on a single

barium fluoride (BaF_2) window (25 mm in diameter by 4 mm in thickness) using a 10-μL syringe. The liquids were observed to dry rapidly in air, depositing a residue on the window site. The BaF_2 window with the four-dried residue sites was transfered to the Nic-Plan microscope and the infrared spectrum was measured.

A small amount of solid material was transferred from the microscope slides. The solid material was prepared by placing it on a diamond anvil cell and compressing the solid into a thin film. The cell was then taken apart and a single diamond window containing the thin film was transferred to the Nic-Plan microscope where the infrared spectrum was measured.

Gas Chromatography/Mass Spectrometry (GC/MS)

GC/MS experiments were performed using a Varian 3400 GC directly interfaced to a Finnigan MAT ITS-40 ion trap mass spectrometer. The GC was equipped with a J&W Scientific DB-5msidt column, 30 m × 0.25 mm × 0.25 μm. The temperature program was: 75°C (1 min hold) to 300EC at 25°C/min (5 min hold). Injector and transfer line temperature were both 300°C and the mass spectrometer manifold temperature was 250EC. The injection port was operated in the splitless mode. Helium was the carrier gas with a flow rate of 28.3 cm/s (300°C). The mass spectrometer was operated in the electron impact (EI) mode, scanning from 40 to 650 amu in 1 s. The mass spectrometer ionization control was automatic. The acquisition time was 15 min.

Only one half of the dissected portion of the pear, weighing 2.5 g, was prepared for analysis. The other half of the pear weighing 2.1 g was refrigerated pending analysis. The pear was prepared by compositing the pear flesh and then adding 4 mL of $CHCl_3$ (Fisher Scientific) to the sample, sonicating for 10 min, followed by centrifugation at 2100G for 5 min. After centrifugation, the $CHCl_3$ layer was drawn off and reduced to dryness at 110°C under dry air. The residue was then reconstituted with 0.5 mL of MeOH and filtered (0.2 μm PTFE Gelman).

Discussion

A multidisciplinary approach was undertaken to identify the unknown substance found in the suspect syringe barrels. This approach was also employed to determine if other drugs or poisons were present in the syringe barrels or in the pear. All three techniques identified the substance in all four syringe barrels as cocaine. The FTIR analysis also detected the presence of inositol in the liquid contained in the syringe barrels. The GC/MS analysis determined that cocaine was present in the pear. Further discussion of the analytical results follows.

In the PLM experiment, introduction of the gold chloride reagent to each preparation produced a visible white precipitate. Crossed polarizing light microscopy analysis of the precipitates from all preparations showed the formation of crystals in the form of delicate rosettes (four suspect and one control preparation). The crystals produced from the four suspect preparations were found consistent with the crystals produced in the control preparation for cocaine hydrochloride.

The FTIR analysis produced infrared absorbance spectra of the liquids and solids that were retrieved from the syringe barrels. The infrared spectra of the four liquid samples were visually compared to a standard infrared spectrum of cocaine hydrochloride. All four suspect liquid sample spectra exhibited spectral features consistent with those found in the standard cocaine hydrochloride infrared spectrum. Specifically, the suspect spectra exhibited peak maxima which corresponded to the major infrared absorbance bands of cocaine hydrochloride between 1800 to 800 cm^{-1}. Infrared spectra were also obtained for the solid materials recovered from two of the syringe barrels. The infrared spectra of the solid materials was identified as inositol. When the suspect sample spectra were visually compared to a library spectrum of inositol, the suspect spectra exhibited peak maxima that corresponded to the major absorbance bands of inositol. Further visual inspection of the suspect spectra, however, revealed the precence of a carbonyl absorbance band at approximately 1730 cm^{-1} and other absorbance bands between 1000 to 800 cm^{-1} which were not observed in the standard inositol spectrum. Based on the position of these additional absorbance bands in the suspect solid spectrum and that cocaine hydrochloride was observed in the suspect liquid spectra, it was determined that small amounts of cocaine hydrochloride were present in the suspect solid materials. This was confirmed by comparing a standard spectrum of a mixture of cocaine hydrochloride and inositol to the suspect solid spectra.

In the GC/MS analysis, the residual crystals from the syringe barrels resulted in the identification of cocaine with a mass spectral library match. Analysis of a 1 μg/mL standard of cocaine hydrochloride confirmed that the major peak in the suspect samples' total ion chromatogram corresponded to the retention time and mass spectrum of the cocaine standard. Both the sample and the standard spectra exhibited the characteristic ions at m/z 82, 182, and 303 expected for cocaine (4).

The pear sample was prepared and analyzed by GC/MS to determine the presence of cocaine. Both samples taken from the pear were confirmed to contain cocaine. The first half of the pear that was analyzed contained approximately 306 ng/g of cocaine. The second half of the pear contained approximately 843 ng/g of cocaine. The discrepancy in the concentration in the two pear samples was attributed to the method of sampling and the heterogeneous distribution of the cocaine within the pear flesh around the injection site.

Conclusions

The FCC applies a team/multidisciplinary approach to solving problems. Although the analysis of cocaine is not unique to any of the techniques utilized in this case, cocaine is not commonly found in a pear matrix. This parallel multidisciplinary approach produces an accurate identification with a quick turn-around time that is essential when there is a possible health risk to the public. Although this tampering was a single act, and no suspect was apprehended, it was unknown at the time if other supermarkets in the same area were under the same threat of tampering.

Acknowledgments

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