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Development of Test Material for Narcotics Detection Equipment: Sand/Drug Mixtures

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ABSTRACT: This study outlines the preparation and testing of a reliable test material for the evaluation of cocaine and heroin detectors based on chemical systems. The test material is simple to prepare and use. It consists of a homogeneous sand/drug mixture that can be transferred reproducibly to a surface for subsequent sampling and analysis. The ratio of sand to drug can be varied easily, allowing for the testing of instruments with varying sensitivities to the drugs of interest.

KEYWORDS: forensic science, test material, chemistry, detection, street drug detection instruments

The Laboratory and Scientific Services Directorate of Revenue Canada, Customs, Excise and Taxation, in collaboration with the Enforcement Directorate, has a mandate to develop and evaluate drug detection equipment to be used by Customs Officers at various points of entry into Canada.

Two basic types of instrumentation are presently being deployed in the field for the detection of contraband drugs (1). The first type is based on the bulk detection of the material of interest by subjecting suspect items to electromagnetic or ionizing radiation (for example, X-rays, gamma radiation, or neutron activation). The second type is based on chemical detection. These instruments rely on either vapor or particle sampling of the substances of interest, with subsequent analysis using a tandem separation/detection technique (for example, ion mobility spectrometry, gas chromatography or mass spectrometry).

The separation/detection systems in current use are based on technology commonly used in laboratory equipment. The instruments have been modified to render them amenable for field use; one of the major modifications involves changes to the inlet of the instruments, to allow the introduction of field samples. The systems normally consist of a sample collector (using either suction or physical wipe), a thermal desorber, a heated inlet and an analyzer. These latter type instruments are the subject of this discussion.

Cocaine and heroin, two drugs of high interest to Customs authorities worldwide, have low vapor pressures (2); furthermore,

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the vapor pressures of cocaine hydrochloride and heroin hydrochloride, the forms normally intercepted by Customs officers, are much lower, making detection of their vapors non-viable. Thus, most cocaine and heroin detectors have instead been designed to detect microscopic particles of these drugs, which may be present on the surfaces of suspect items. The particles are collected using either suction or wiping, placed in the inlet of the instrument and thermally desorbed. The resulting vapors are then entrained into the analyzer unit of the equipment by means of an inert carrier gas.

Test materials are required to properly evaluate these types of systems and to monitor the efficiency of the sampler and/or the analyzer. Although test materials have been developed for explosive vapors (3-5) and explosive particles (6), no such materials yet exist for drugs. Tests on the detection limits of some drug detection equipment have been performed using solutions and solid mixtures (7-9); however, no test protocol that includes the sampling step has been devised. A narcotics assessment program (10,11) involving a number of U.S. and Canadian drug enforcement agencies is currently under way to evaluate narcotic detection systems. As part of this assessment, a solid test material is required.

Said test material must fulfill a number of requirements; it must be homogeneous, must be transferable to surfaces in a reproducible manner, must be simple to use and should be easily recovered from the surface by suction or wiping. In addition, the amount of drug present in a set quantity of the test material must be well established, and should fall somewhere between the minimum detection level of the equipment and its saturation point.

Experimental Materials and Methods

Gas Chromatography

The gas chromatograph was a Hewlett-Packard 5890 Series II GC with a 7673A autosampler and an HP 3365 Chemstation, equipped with a flame ionization detector operating at 300°C. A 25 m × 0.32 mm i.d. fused silica capillary column coated with 1.05 μm DB-5 was employed. Helium was the carrier gas, at approximately 8 psi, at a flow rate of 1.2 mL/min @ 55°C. The injector port was maintained at 250°C, and samples (1 μL sample volume) were injected in splitless mode using a Hewlett Packard Model 7673 auto injector. The oven temperature was programmed as follows: initial temperature, 55°C; hold, 1 min.; temperature program rate, 30°C/min; final temperature, 300°C. The total run time was 10 min.

Gas-Chromatography—Mass Selective Detector

The GC-MS was a Hewlett Packard 5890 Series II GC equipped with a Series 5970B Mass Selective Detector. The system was

controlled by a 59940A MS Chemstation (HP-UX Series). A 12.5 m × 0.20 mm i.d. fused silica capillary column coated with 0.33 μm HP1 was employed. Helium was the carrier gas, at approximately 8 psi, at a flow rate of 1.0 mL/min @ 50°C. The injector port, sample introduction and temperature programming parameters were identical to those described in the Gas Chromatography section. The transfer line temperature was 310°C. Mass spectra were acquired in the electron ionization (EI) mode at 70 eV. The spectral range was 39 to 400 amu at 1.51 scans/s. Autotune parameters were used.

Scanning Electron Microscopy (SEM)

The SEM was an AMRAY 1800T. Parameters of the SEM (for example, working distance, spot size, apertures) were optimized for each sample. The accelerating voltage was 20 kV. The samples of the sand and sand/drug mixtures were gold-coated.

Chemicals

Cocaine hydrochloride and butacaine (3-(dibutylamino)-1-propanol-4-aminobenzoate, used as an internal standard) were purchased from Sigma Chemical Co. Heroin hydrochloride (McFarlan & Smith) was obtained from Health and Welfare Canada. These chemicals were used without further purification. The sand used in the preparation of the test material was Sand, Washed and Dried, purchased from Anachemia. The methanol and hexane used were HPLC Reagent Grade from J. T. Baker, Inc. The acetone and the chloroform used were Assurance Grade from BDH, Inc.

Experiments

Separation of Sand into Different Particle Sizes

A tungsten carbide holder with two tungsten carbide balls was filled with approximately 20 g of sand and placed on a Spex Industries Inc. Mixer/Mill for 10 minutes. The crushed sand was then sieved in series through 100 micron, 63 micron, 45 micron and 20 micron sieves (Buckbee Meers Co.), using approximately 150 mL of acetone as a solvent to facilitate the sieving procedure. The different sized sand particles were used to determine the relative efficiency of the vacuum sampler.

The crushed sand was also sieved in series through the 100 and 20 micron sieves. The portion of sand trapped on the 20 micron sieve (that is, 20–100 micron size) was used in the preparation of the sand/cocaine mixture. The portion of sand of size less than 20 micron was used in the preparation of the sand/heroin mixture.

Preparation Sand/Drug Mixtures

Sand (approximately 5 g) of the appropriate size was placed on a filter paper and washed three times with 25 mL each of hexane, chloroform, and methanol to remove organic impurities. The sand was left to air dry.

Three separate cocaine standards were prepared by adding 10 mL of a cocaine hydrochloride solution in methanol (1.002 mg/mL) to 1 gram of sand (20–100 micron particle size) in a 50 mL round bottom flask. The mixture was evaporated to dryness on a rotovap (Buchi Rotavapour R), using water aspirator vacuum, and the solid was removed and ground lightly in a mortar and pestle to break up any clumps of sand.

Three heroin standards were prepared in the same way, using a solution of heroin hydrochloride in methanol (1.098 mg/mL) and sand particles less than 20 microns.

Analysis of Sand/Cocaine and Sand/Heroin Mixtures

Aliquots of different weights of the cocaine/sand mixture or heroin/sand mixture (5, 10 and 20 mg) were placed in individual 3.5 mL vials. To each aliquot was added 1.0 mL of a butacaine internal standard in methanol (50 μg/mL). The mixture was shaken for 30 seconds on a Vortex to dissolve the drug and left to settle. The supernatant was transferred into an autosampler vial for analysis using the GC-MSD system. The GC/FID was used for the quantitation of the sand/heroin mixtures.

Loose Powder Recovery

All weighings were performed on a Mettler AE200 Electronic Balance, accurate to 0.1 mg. Glass vials, (2.6 mL, plastic cap, Fisher Scientific) with an open bottom polyethylene stopper, were used to hold 5, 10 or 25 mg of sand of particle size 20 to 100 micron or less than 20 micron. With the caps on the bottles, the vials were shaken to ensure good contact of the powder with all the surfaces inside the vial. Without removing the caps, the vials were tapped a few times to bring the particles to the bottom. The contents of the vial were then emptied on a piece of weighing paper (Fisher Scientific) by tapping the opened vial three times against the paper. The amount of powder transferred to the paper was weighed. The percentage of sand transferred was calculated:

$$\% \text{ transferred} = (\text{wt sand on paper} / \text{wt sand in vial}) \times 100$$

These experiments were repeated 20 times for each weight of sand by a number of different persons.

Efficiency of Sampler

A vacuum sampler for one of the drug detectors was used to collect particles from a surface. A known amount of particles of known size was placed on a specific, pre-cleaned area of a laboratory bench. The collecting filter on the sampler was weighed before (blank filter) and after sampling the surface for 30 seconds (sampled filter). The percent efficiency of the sampler was calculated as:

$$\left[\frac{(\text{Wt of sampled filter} - \text{Wt of blank filter})}{\text{Weight of particles deposited}} \right] \times 100$$

Results and Discussion

The drug detection equipment for which this test material was designed includes a vacuum sampler to collect large amounts (that is, 5 to 25 mg) of extraneous materials such as sand and dust, which may contain small amounts (that is, nanograms to micrograms) of cocaine or heroin. Sand was chosen as the bulk support in the test material because it is inert, cannot thermally desorb, and will not cause chemical interferences or chemically suppress the signal normally produced by the drug molecules.

Efficiency of Vacuum Sampler

Sand of a specific size range (less than 20 microns and 45 to 63 microns) was deposited on a surface and sampled. The results

(Table 1) indicate that the efficiency of the sampler was lowest for particles less than 20 micron and reached a plateau at particle sizes 45 to 63 micron and 63 to 100 micron. The lower efficiency of the sampler for smaller particles is caused by static (that is, attractive) forces between the particles and the plastic surfaces and brushes of the sampling head, as evidenced by the presence of white powder on the surfaces of the sampler. Thus, the size of the particles will affect the amount of sample collected for eventual analysis by the detector, and proper control of this parameter is important to obtain consistent results.

Previous work by Revenue Canada and the U.S. Customs Service indicated that heroin particles from seized samples are rarely larger than 20 microns in diameter, while cocaine particles are often larger than 20 microns, sometimes reaching 400 microns.² The sand/drug mixtures were therefore prepared with sand sieved through a 20 micron sieve for heroin and equal parts of sand sieved through a 100 micron, a 63 micron, a 45 micron sieve and caught in a 20 micron sieve for cocaine. This minimized differences in sampling caused by the variation of the sampler efficiency as a function of particle size.

To determine the make up of the sand/drug mixtures, SEM photographs were obtained on the sand particles (Fig. 1a) and on the drug/sand particles resulting from a mixture containing 1 mg of the drug per 10 mg of sand (Fig. 1b for cocaine/sand mixture). Both drugs are present mainly as a coating of small particles on the sand matrix, that is, not a mixture of drug particles intermixed with the sand. Thus, the size of the sand/drug mixture realistically

²Hoglund, DE, US Customs Service, Washington, DC, personal communication, 1994.

TABLE 1—Efficiency of sampler as a function of particle size.

| Particle size (micron) | Number of Readings | Mean Efficiency | Standard Deviation |
|------------------------|--------------------|-----------------|--------------------|
| <20 | 10 | 48.8 | 5.6 |
| 20 to 45 | 10 | 64.2 | 4.1 |
| 45 to 63 | 9 | 91.2 | 6.6 |
| 63 to 100 | 10 | 91.7 | 5.3 |

mimics that of the pure drug substances. It is assumed that the sand/drug mixtures prepared at higher and lower drug concentrations will behave identically to those investigated in this study.

Homogeneity of Sand/Cocaine Mixture and Sand/Heroin Mixture

Cocaine or heroin was extracted from three different weights of the sand/drug mixture using methanol containing added butacaine as an internal standard. The extract was analyzed by GC-MS. This experiment was repeated for three different preparations of the mixtures. Figure 2 shows the cocaine to butacaine signal ratio as a function of the weight of the sand/cocaine mixture. The straight line obtained for each preparation indicates that each preparation is homogeneous. The superposition of the lines also indicates that the amount of cocaine present in each preparation is consistent. Thus, the procedure reproducibly yields homogeneous mixtures of cocaine and sand. The reproducibility was observed for cocaine/sand mixtures containing as little as 50 ng of the drug. Similar results were obtained for the sand/heroin mixtures. The % recovery of the extraction procedures varied between 95 and 99.3%.

Loose Powder Recovery

To ensure that a certain amount of the sand/drug mixtures can be transferred reproducibly to a surface, different persons attempted the transfer of sand particles from glass vials to a surface. These experiments were repeated for three different amounts of sand (5, 10 and 25 mg), for two particle size distributions (<20 microns and 20–100 microns). The results are shown in Table 2. The best reproducibility is obtained when transferring 25 mg of the sand/drug mixture (error of 4%); however, this is a larger amount of dust than would typically be sampled. Transferring 10 mg amounts yields a larger error in the amount of drug transferred (8%), but represents more realistically the typical amount of dust collected from most surfaces with the samplers of the current drug detectors. Using 5 mg of the sand/drug mixture raises the error to 19%, which is unacceptable for use as a testing standard. Thus, the use of 10 mg of sand/drug mixture is recommended. The amount of

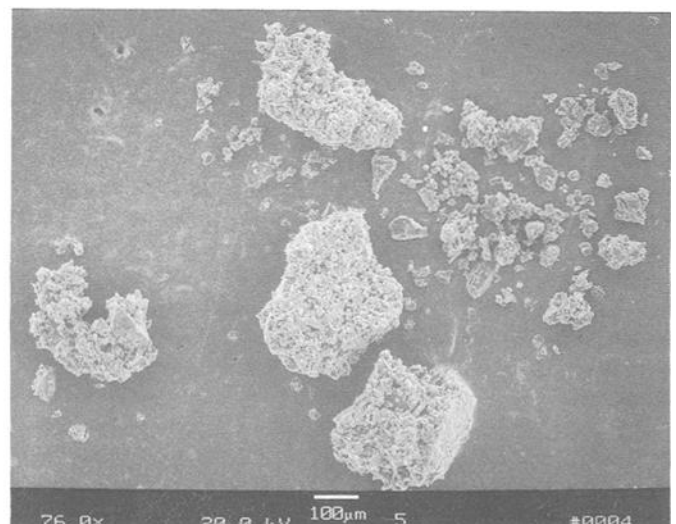
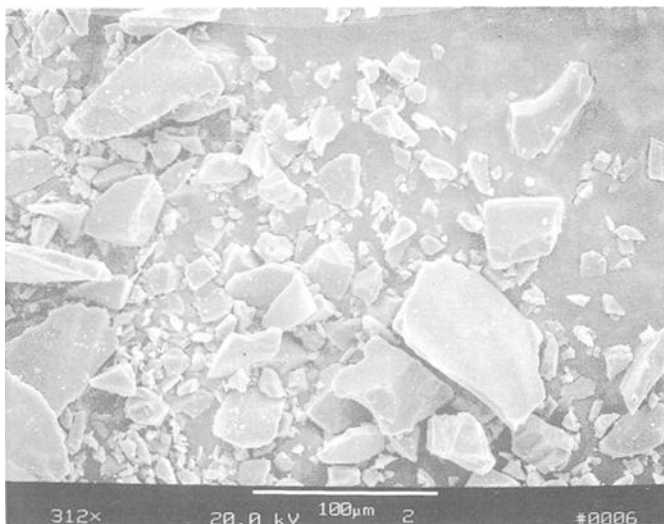


FIG. 1—Scanning electron micrographs of sand (a) and sand/cocaine mixture (b).

drug in the mixture can be varied to give the proper amount for optimum detector response.

Shelf-life of Standard

Laboratory studies of the shelf life of the sand/drug mixtures indicated stability for a maximum time span of four months. The drug signal decreases after this time period.

The examination of the cocaine/sand and the heroin/sand mixtures under an optical microscope showed no signs of moisture, even after leaving the mixtures on a surface for a period of three weeks. However, these experiments were performed in a low humidity environment (air-conditioned room); because it is known that finely divided cocaine hydrochloride and heroin hydrochloride are hygroscopic, it is recommended that the material be placed on the surface immediately prior to sampling.

Conclusions

The sand/drug mixtures described herein suffice for the evaluation of chemical detection systems for the detection of cocaine and heroin. The test material is homogeneous and can be prepared in a reproducible manner. The transfer to a surface for eventual removal by suction or wiping can be performed reproducibly. The amount of drug in the test material can be varied easily. The materials used are inexpensive and the preparations of the standards are relatively simple. It is expected that this test material and the protocol for its use will be adopted for the continuous evaluation of existing and new technologies for drug detection.

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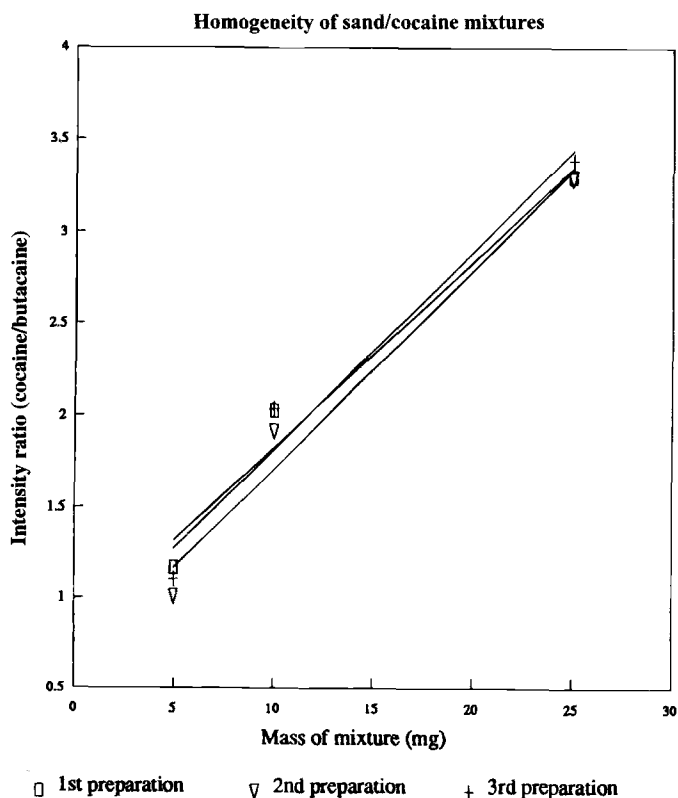


FIG. 2—The cocaine to butacaine signal ratio as a function of the weight of the sand/cocaine mixture.

TABLE 2—Range of values of % powder transferred from vial.

| Nominal Weight in Vial of 5 mg | | | |
|--------------------------------|---------------------|------------------------------|---------------------|
| Particle size < 20 microns | | Particle size 20–100 microns | |
| Person | Range of Values (%) | Person | Range of Values (%) |
| 1 | 78.4–86.8 | 1 | 83.0–94.1 |
| 2 | 87.5–94.1 | 2 | 77.8–93.3 |
| 3 | 83.0–92.6 | 3 | 79.2–90.4 |
| 1,2,3 | 78.4–94.1 | 1,2,3 | 77.8–94.1 |

| Nominal Weight in Vial of 10 mg | | | |
|---------------------------------|---------------------|------------------------------|---------------------|
| Particle size < 20 microns | | Particle size 20–100 microns | |
| Person | Range of Values (%) | Person | Range of Values (%) |
| 1 | 89.9–94.4 | 1 | 88.7–93.3 |
| 2 | 89.8–95.0 | 2 | 87.1–93.1 |
| 3 | 90.5–96.1 | 3 | 86.3–91.7 |
| 4 | 87.9–95.2 | 1,2,3 | 86.3–93.3 |
| 1,2,3,4 | 87.9–96.1 | | |

| Nominal Weight in Vial of 25 mg | | | |
|---------------------------------|---------------------|------------------------------|---------------------|
| Particle size < 20 microns | | Particle size 20–100 microns | |
| Person | Range of Values (%) | Person | Range of Values (%) |
| 1 | 95.2–98.4 | 1 | 95.2–96.9 |
| 2 | 94.8–97.6 | 2 | 93.1–96.1 |
| 3 | 95.5–97.6 | 3 | 94.4–96.8 |
| 1,2,3 | 94.8–98.4 | 1,2,3 | 93.1–96.9 |

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