Analysis of Bank Security Device Chemicals

1 Scope

Redacted

This procedure applies to Chemistry Unit (CU) personnel that are qualified and authorized to examine evidence for the presence of bank security device chemicals.

2 Equipment/Materials/Reagents

- Common laboratory glassware and equipment
- Analytical balance
- Acetone

Redacted

- Chloroform
- Redacted
- Methanol (MeOH)
- 1-Methylaminoanthraquinone (MAAQ)
- Orthochlorobenzalmalononitrile (CS tear gas)
- Toluene
- Evaporator
- Silica gel Thin-Layer Chromatography (TLC) plate and TLC tank
- Polyethylene glycol (PEG, 550 average molecular weight)
- Time-of-flight mass spectrometer with direct analysis in real time ionization source (DART/TOFMS)
- Gas chromatograph/mass spectrometer (GC/MS) equipped with electron impact ionization and a 30 meter DB-5 column (or equivalent)
- Gas chromatograph/mass spectrometer (GC/MS) equipped with chemical ionization and a 30 meter DB-5 column (or equivalent)

3 Standards and Controls

3.1 Negative Control

The same volume of solvent from the same source and lot used to extract the questioned item(s) and within a similar container (e.g., test tube, vial) will be used as the Negative Control. If swabs are submitted as evidence, a blank swab extracted in the same manner as the questioned item(s) will be used as the Negative Control. In some instances an extract from a portion of the item(s) which does not contain a stain of interest may be selected for use as a Negative Control.

3.2 Positive Controls

- MAAQ Stock Solution (1 mg/mL):

  Prepared by dissolving 10 mg of MAAQ in 10 mL of an appropriate solvent (e.g. acetone, MeOH). This solution will be stored in a freezer.

- MAAQ/CS Positive Control Solution (50 ug/mL):

  Prepared by weighing out 5 mg of orthochlorobenzalmalononitrile (*Lachrymator- use caution when handling), adding 5 mL of the above MAAQ Stock Solution (1 mg/mL), and diluting with an appropriate solvent to a final volume of 100 mL. This solution will be stored in a freezer and is verified with each use. This solution may be further diluted (e.g., 5 ug/mL) to prevent overloading an instrument.

Redacted

4 Sampling

Typically, one or more samples (e.g., cuttings, swabbings) are selected from the stained area(s) of the questioned item. When multiple samples are selected from the same item, the samples are typically combined prior to extraction.

Multiple items that are packaged together or otherwise in contact with each other will typically be sampled as one collective item. For example, if ten bills of currency are packaged together, one or more of the bills will be sampled and the selected samples will be combined prior to extraction.

When non-statistical sampling is utilized on a heterogeneous item, the results of examinations will be clearly limited to the sample(s) that were selected and analyzed.

5 Procedure

Refer to *General Chemistry Instrument Parameters* (GenChem 34) for specific instrument settings and decision criteria.

a. Thoroughly examine items for red or pink stains, Redacted Redacted

b. If a red or pink stain is observed, cut a small section of the item which contains the stain of interest and transfer the cutting to a labeled test tube. Multiple cuttings from the same item may be combined. Use an empty, labeled test tube as a Negative Control.

c. If the stain is not conducive to cutting, remove a sample of the stain by rubbing a cotton swab that has been wetted with a few drops of an appropriate solvent (e.g., acetone, MeOH) over the stain. If the stain is very dark and has a powdery appearance, it can be sampled with a dry cotton swab (or scraped directly into a test tube). Transfer the swab to a labeled test tube. Additionally, transfer an unused swab from the same source (dry or wetted with the same solvent) to a labeled test tube as a Negative Control.

d. If the item is dark in color such that a red and/or pink stain could be obscured, rub cotton swabs (dry or wetted with an appropriate solvent) over the item. Examine the swab for any red or pink color that may have transferred to the swab. Swab as necessary until either the entire item has been swabbed or until a red or pink color has transferred to the swab. Transfer the swab(s) to a labeled test tube. Additionally, transfer an unused swab from the same source (dry or wetted with the same solvent) to a labeled test tube as a Negative Control.

e. If no red or pink stains are observed on an item, or if no stain was transferred to a swab for a dark colored item (step d), then additional exams may be omitted.

f. Test the solubility of the stain using an appropriate amount of solvent (e.g., acetone, MeOH) added to the test tube containing the selected sample(s). Do not use acetone if the item is plastic. Spot check a small portion of the plastic substrate with chloroform. If the plastic does not dissolve in chloroform, then chloroform may be substituted for acetone. If the chloroform dissolves the plastic, use MeOH. The Negative Control sample(s) shall be extracted in the same manner as the selected sample(s).

g. Transfer the extracts to new labeled test tubes. Note the color of the extracts, to include the Negative Control(s).

h. If the extract(s) is colorless or faint/light pink, concentrate the extract(s) under N_2 (g) flow at ~60 ºC. The extract(s) should not be taken to dryness due to the possible loss of CS tear gas. Concentrate the associated Negative Control(s) in the same manner as the extract(s) from the questioned item(s). If the extract(s) is colorless after concentration then the analysis is complete.

i. Analyze extracts by DART/TOFMS in the positive ionization mode by sampling the extracts with the closed end of a glass capillary. Analyze the Negative Control(s), the MAAQ/CS Positive Control, and PEG within the same data collection file. Redacted

Redacted Redacted If a questioned item extract does not indicate the presence of MAAQ or by DART/TOFMS then additional exams may be omitted.

j. As an alternative to DART/TOFMS, the extracts may be analyzed by TLC. Fill a TLC tank with an appropriate amount of toluene and allow it to equilibrate. Spot 5 to 10 uL of the extracts at the origin of a silica gel TLC plate (typically ≥ 1 cm from bottom of TLC plate). Spot the MAAQ/CS Positive Control on the same TLC plate. Redacted Redacted Allow the spots to dry. Place the TLC plate into the TLC tank and allow the mobile phase to migrate ~ 10 cm up the plate. Remove the TLC plate from the tank, mark the location of the mobile phase solvent front and allow the plate to dry. Record and/or photograph the results. Calculate the retardation factor (R_f) for any pink/red spots that are observed. If a questioned item extract does not indicate the presence of MAAQ Redacted then additional exams may be omitted.

k. Analyze the extracts and MAAQ/CS Positive Control by GC/MS using electron impact (EI) ionization mode. Incorporate a solvent blank between each sample. Redacted

Redacted

l. Analyze the extracts and MAAQ/CS Positive Control by GC/MS using negative ion chemical ionization (NICI) mode. This will be conducted even if the above analysis by GC/MS (EI) was negative for CS tear gas since NICI is the more sensitive technique. Incorporate a solvent blank between each sample. Redacted

6 Calculations

- R_f = (distance spot center traveled from origin) / (distance of solvent front from origin)
- Distances traveled are measured from the origin. Distances are considered approximate and the R_f value is not treated as a significant measurement.

7 Measurement Uncertainty

Not applicable

8 Limitations

- CS tear gas is present in a smaller concentration in bank security devices than MAAQ and is a volatile chemical.
- In instances where items are negative for MAAQ or where visible pink/red color stains are absent, no further examinations are performed for bank security device chemicals.
- MAAQ strongly binds to polymeric materials (e.g., styrene, methylmethacrylate). This may limit solvent choices and the ability to extract MAAQ.

The following conclusions apply to the analysis of bank security device chemicals:

- Identification (i.e. identified)
- Consistent with
- Not identified
- Inconclusive

Refer to *Chemistry Unit (CU) FBI Approved Standards for Scientific Testimony and Report Language for General Chemistry* (GenChem 32, ASSTR), *General Approach to Report Writing in General Chemistry* (GenChem 27), and *Department of Justice Uniform Language for Testimony and Reports for General Forensic Chemistry and Seized Drug Examinations* (GenChem ULTR) for examples of reporting examination conclusions and the associated limitations and decision criteria.

Refer to *General Chemistry Instrument Parameters* (GenChem 34) for instrumental limitations and decision criteria.

Refer to *General Chemistry Guidelines for Comparison of Mass Spectra* (GenChem 33) for mass spectra comparison decision criteria.

9 Safety

- Take standard precautions for the handling of all chemicals, reagents, and standards. Some of the chemicals may be carcinogenic. Refer to the *FBI Laboratory Safety Manual* for the proper handling and disposal of all chemicals. Personal protective equipment should be used when handling any chemical and when performing any type of analysis.
- CS tear gas is a lachrymator and should be handled carefully.

10 References

Martz RM, Reutter DJ, Lasswell LD. A comparison of ionization techniques for gas chromatography/mass spectroscopy analysis of dye and lachrymator residues from exploding bank security devices, *J Forensic Sci* 1983; 28: 200-207

Verweij AMA, Lipman PJL. Comparison of mass spectrometric techniques for the analysis of trace amounts of 1-Methylaminoanthraquinone used as smoke dye in exploding money suitcases. *J Chromatography A* 1993; 653: 359-362

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Kataoka M, Seto Y, Tsuge K, Naomi M. Stability and detectability of lachrymators and their degradation products in evidence samples. *J Forensic Sci* 2002; 47: 44-51

Jagardeo E, et al. Analysis of trace amounts of bank dye and lachrymators from exploding bank devices by solid phase microextraction and gas chromatography-mass spectrometry. *J Chromatogr Sci* 2006; 44: 86-90

General Chemistry Instrument Parameters; FBI Laboratory Chemistry Unit – General Chemistry SOP (GenChem 34)

Guidelines for Comparison of Mass Spectra; FBI Laboratory Chemistry Unit – General Chemistry SOP (GenChem 33)

FBI Laboratory Safety Manual

Rev. #	Issue Date	History
3	01/15/20	Revised title. Removed previous section 1 (Introduction), section 3 (Principle), and section 6 (Calibration), and renumbered sections accordingly. Edited new section 1 for clarity and to include personnel. Defined 'Chemistry Unit' as 'CU'. Changed lettered listing in section 2 to bullets and revised the list. Edited new section 3.1 to add detail. Changed lettered listing in section 3.2 to bullets and edited section for clarity. Detail added to new section 4 (Sampling). Section 5 edited to add more details. Removed use of ultraviolet light to observe for fluorescence. Changed previous section 9 to sections 6 and 6.1 and added detail. Removed TLC information from section 8 and revised entire section for clarity and to allow for flexibility. Minor edits to sections 9.1 and 9.3, added section 9.2. Changed title of section 10 (was 'Limitations of Procedure'); removed previous 1st bullet and added new 1st, 2nd, and 4th bullets in section 10. Removed approximate LODs from Limitations sections. Updated references section (content and format).
4	Mm/dd/yy	Section 1- added "and authorized". Section 2- removed "deionized water". Section 4- added "on a heterogeneous item". Section 5- added first sentence; edited steps (g), (h), (j), (k), and (l) for clarity; step (k)- changed last sentence from "may" to "will". Added detail to section 6 and clarified that the distance measurements are approximate and thus measurement uncertainty is not applicable for R_f values. Deleted previous sections 6.1, 8 (Instrumental Conditions) and 9 (Decision Criteria). Section 8- added content below the bulleted list. Section 10- added GenChem 34; added "(GenChem 33)" to SOP title.

Approval

Chemistry Unit Chief: Redacted - Signatures on File Date: 03/31/2021

General Chemistry Technical Leader: Date: 03/31/2021