Comparison of Inks

1 Scope

This procedure allows for the analysis of writing, marking, or other inks from various matrices (e.g., paper, cardboard, cloth). Comparisons are made between questioned and known ink items, which allow conclusions to be reached regarding the possible common origin of the inks. Identification of inks by manufacturer and dating of inks are beyond the scope of this procedure.

This procedure applies to Chemistry Unit (CU) personnel that are qualified and authorized to compare inks.

2 Equipment/Materials/Reagents

- Common laboratory glassware and equipment
- Stereo microscope
- Digital microscope
- Ultraviolet (UV) light source
- CrimeScope CS-16 light source
- Video Spectral Comparator (VSC)
- Whatman HP pre-coated silica gel TLC plate (10 cm x 10 cm) (or equivalent)
- TLC tank
- Blunt-tipped sampling device (e.g., core sampler)
- n-Butanol
- Deionized water
- Ethanol
- Ethyl acetate
- Methanol
- Pyridine, low water

3 Standards and Controls

3.1 Negative Control

A Negative Control will be prepared from an area of the questioned item where no ink is present. If there are no unmarked areas of the item, a solvent blank will be used as a Negative Control. If there is printing on the opposite side of the item (e.g., security printing on the inside of an envelope) then the Negative Control will be sampled from a portion of the questioned item that contains the printing. It is left to the discretion of the examiner as to what constitutes an adequate Negative Control.

3.2 Positive Control

Since this procedure is based on comparative tests, positive controls are typically not applicable. However, when a known ink will be deposited on a matrix to facilitate a comparison, the matrix will be similar to the matrix of the questioned item. Blank samples from the matrix will also be sampled. Subsequent extraction of the known ink and matrix will serve as a Positive Control.

4 Preparation of Solvent Systems

Volumes indicated below may be scaled up or down as long as the volume ratios remain the same.

4.1 Solvent System I

Prepared by combining 70 mL of ethyl acetate, 35 mL of ethanol, and 30 mL of deionized water (14:7:6 volume ratio) in a beaker and mixing thoroughly. Transfer an aliquot of Solvent System I to a TLC tank and allow it to equilibrate for 15 minutes.

4.2 Solvent System II

Solvent System II is used when samples were not differentiated by Solvent System I. Solvent System II is prepared by combining 50 mL of n-butanol, 10 mL of ethanol, and 15 mL of deionized water (10:2:3 volume ratio) in a beaker and mixing thoroughly. Transfer an aliquot of Solvent System II to a TLC tank and allow it to equilibrate for 15 minutes.

5 Sampling

Ink samples are screened with a combination of light sources (e.g., visible, UV, CrimeScope, VSC) to ensure homogeneity before collecting plugs.

When performing this procedure on printer-related evidence (e.g., ink cartridges), ink samples obtained from printing with the device are preferred. For a full color inkjet printer, samples will include multiple punches of each available color (typically cyan, magenta, yellow, and black) when possible.

Statistical sampling is performed according to the General Chemistry *Sampling Guidelines for Bulk Materials and Multi-Unit Populations* (GenChem 21).

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.

6 Procedure

a. View the ink sample and record relevant observations. Observe the sample under magnification to determine whether the writing was produced by a ballpoint or non-ballpoint device or machine produced (e.g., inkjet printed). Ballpoint pen writing will usually show signs of skipping, gooping, and burr striations. Record observations with photography or digital imaging if possible.

b. If an item is a writing or printing device, prepare a Positive Control by using the device to deposit a sample of the ink onto a matrix that is similar to the matrix of the questioned item. Allow the sample to dry. Perform step (a) on the Positive Control to the extent necessary. An ink sample may be directly removed from the device if it is not possible to use the device as intended.

c. Place the matrix (e.g., document) on a cutting mat and use a core sampler to individually remove ~1 mm diameter plugs (typically 5 to 10 plugs) from an area of the matrix which does not contain ink for use as a Negative Control. Transfer the plugs to a labeled test tube or vial ensuring each of the plugs is transferred. If the matrix is not conducive to removing plugs with a core sampler, obtain samples via cutting or other method ensuring similar areas are obtained for all items.

d. Perform step (c) for each area that contains an ink sample of interest, as well as any Positive Control(s) from step (b), ensuring that the same number of plugs is collected for all samples. Blank plugs from the Positive Control matrix will also be collected.

e. Add 7 to 15 uL of solvent (e.g., pyridine, methanol) to each of the test tubes. Vortex and allow the extracts to sit for ~2 minutes. The amount of solvent may need to be varied for non-plug samples. Dilute any ink extract in the initial solvent if the extract is substantially darker in color than the comparison solution. The goal is to obtain consistency in extract concentrations among the ink samples. Ideally, an ink extract will have a distinct color and be transparent.

f. Record the colors of the extracts. If an extract is clear and colorless additional exams may be discontinued.

g. Spot a portion of each of the extracts ~1 cm from the bottom of a TLC plate. Allow the spots to dry. If additional sample is needed, repeat the spotting process until the desired spot intensity is achieved. Typically, it is unnecessary to repeat the spotting process. The TLC plate will have sample spots from the Negative Control(s) and questioned ink sample(s), as well as any applicable Positive Control(s) and associated matrix blank(s).

h. Record the color of all of the spots that were deposited on the TLC plate.

i. Transfer the plate into the Solvent System I TLC tank.

j. After ~10 minutes, remove the plate from the TLC tank and allow it to dry.

k. Record observations [e.g., any visibly separated components, colors of the components, relative concentrations, relative distances (R_f values)]. Photographs should be taken with a ruler in the field of view.

l. View the TLC plate under alternate light sources (e.g,. UV light, CrimeScope, VSC) and record observations.

m. If differences are observed between comparison samples (e.g., different ink component R_f values), then only Solvent System I is necessary.

n. If additional sample extracts remain, use it to spot a new TLC plate as described in step (g) and record the color of all of the spots that were deposited on the TLC plate. Otherwise, repeat steps (c) through (h).

o. Transfer the new plate into the Solvent System II TLC tank.

p. Repeat steps (j) through (l) for the new plate.

7 Calculations

- Distances traveled are measured from the origin. Distances are considered approximate and the R_f value is not treated as a significant measurement.

- R_f = (distance spot center traveled from origin) / (distance of solvent front from origin)

8 Measurement Uncertainty

Not applicable

9 Decision Criteria

9.1 Visual Observations

9.1.1 Indistinguishable Samples

If no distinguishable characteristics are observed between the ink samples, this will be recorded and TLC will be performed.

9.1.2 Differentiated Samples

If differences are observed between ink samples by visual and/or microscopic exams, this will be recorded and no further exams are necessary. Photography or digital imaging will be used to record the differences if no further exams will be conducted.

9.2 TLC

9.2.1 Writing Inks

9.2.1.1 Indistinguishable Samples

Ink samples are considered indistinguishable if all separated colorant components, relative concentrations, and R_f values correlate well between the samples in both solvent systems.

9.2.1.2 Differentiated Samples

If differences are observed in the general appearance of any separated colorant components, relative concentrations, and/or R_f values, this will be recorded and the samples will be reported as differentiated. If this occurs with Solvent System I, analysis with Solvent System II is not required.

9.2.2 Inkjet Inks

9.2.2.1 Indistinguishable Samples

Ink samples are considered indistinguishable if all separated colorant components, relative concentrations, and R_f values correlate well between the samples in both solvent systems. There may be instances when an inkjet colorant (e.g., cyan, magenta, yellow, black) is not present on an item. The absence of a colorant in a comparison should not be used to distinguish samples in these instances.

9.2.2.2 Differentiated Samples

If differences are observed in the general appearance of any separated colorant components, relative concentrations, and/or R_f values where comparable colors (e.g., cyan, magenta, yellow, black) were sampled, this will be recorded and the samples will be reported as differentiated. If this occurs with Solvent System I, analysis with Solvent System II is not required.

10 Limitations

This procedure is limited to writing inks (e.g., pens, markers) and inkjet inks. The available sample size may limit or preclude the analysis from being performed. Items that have small amounts of ink may not be able to be analyzed by this procedure. Certain matrices (e.g., plastics, clothing) may hinder or prevent adequate extraction and/or separation of the ink components.

The following conclusions apply to the comparison of inks:

- Cannot be differentiated
- Excluded
- 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.

11 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.

12 References

ASTM E1422-05 – Standard guide for test methods for forensic writing ink comparison (Withdrawn 2014).

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Sampling Guidelines for Bulk Materials and Multi-Unit Populations; FBI Laboratory Chemistry Unit – General Chemistry SOP (GenChem 21)

Chemistry Unit (CU) FBI Approved Standards for Scientific Testimony and Report Language for General Chemistry – General Chemistry SOP (GenChem 32)

General Approach to Report Writing in General Chemistry; FBI Laboratory Chemistry Unit – General Chemistry SOP (GenChem 27)

Department of Justice Uniform Language for Testimony and Reports for General Forensic Chemistry and Seized Drug Examinations (GenChem ULTR)

FBI Laboratory Safety Manual

Rev. #	Issue Date	History
3	05/04/20	Removed previous sections 1 (Introduction), 3 (Principle), 6 (Calibration), and 10 (Instrumental Conditions); renumbered sections accordingly. Edited new section 1 for clarity and to include personnel. Changed lettered listing in new section 2 to bullets and revised the list. Minor edits to sections 3.1 and 3.2. Added new section 4 (was contained within procedure section). Added significant detail to section 5. Section 6 was edited throughout for clarity and flexibility. Minor edit made to section 7 for clarity. Changed new section 8 title from 'Uncertainty of Measurement'. Changed formatting, made minor edits, and added content covering inkjet inks to section 9. Changed formatting, made minor edits, and added content including conclusions and references to ASSTR, ULTR, etc. to section 10. Updated references in section 11.
4	Mm/dd/yy	Section 1- added "and authorized". Section 4- added sentence. Section 5- added "on a heterogeneous item". Section 6- added line spacing between each step for ease of reading (did not mark this with change indicators as content did not change); step (f)- added last sentence. Added detail to section 7 and clarified that the distance measurements are approximate and thus measurement uncertainty is not applicable for R_f values.

Approval

Redacted - Signatures on File

Chemistry Unit Chief: Date: 03/31/2021

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