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The potential for application of ink stable isotope analysis in questioned document examination



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ABSTRACT

We investigated a novel application of stable isotope abundance analysis of nitrogen (¹⁵N), carbon (¹³C), hydrogen (²H), and oxygen (¹⁸O) to characterize pen ink. We focused on both ballpoint and gel pen inks. We found that the isotope ratios of ink from pens purchased together in a package were similar and within-package stable isotope ratio variability was not significantly larger than the variability of isotope reference materials used during analysis. In contrast, the isotope ratios of ink from pens of the same brand purchased in three states of the continental USA were significantly different from each other and there was isotope ratio variation among pens of the same brand but different, unknown production periods. The stable isotope ratios of inked paper were statistically distinguishable using measured δ^{15} N values. Paper inked with different gel pens was statistically distinguishable using measured δ^{2} H values. The capacity of stable isotope ratios to differentiate among ballpoint inks as well as gel inks shows that stable isotope analysis may be a useful and quantifiable investigative technique for questioned document examination, although current sample size requirements limit its utility. Application of the technique in casework will require the development of micro-scale sampling and analysis methods.

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1. Introduction

Understanding the authenticity and origins of documents is of widespread commercial and legal interest. As such, questioned document examination (QDE) is an important forensic discipline because it focuses on answering questions related to a document's history [1,2]. Examiners often investigate paper documents or records to determine authenticity, such as the Hitler diaries "discovered" in East Germany in 1983 [3] or counterfeit currency surfacing in the global marketplace [4]. Document examination can also be useful in investigations of material origin, as when the FBI searched for the origins of the 2001 Amerithrax letters [5].

Questioned document examination is a comparative science in which trained examiners observe characteristic features of two or more samples in order to compare and contrast different documents. Casework investigations may involve scrutiny of the applied media (ink) and the substrate (paper), both of which can be examined using a variety of non-destructive and destructive analysis techniques. Non-destructive examination often relies on optical observation via microscopy, photography, and additional spectral analysis methods [6–9]. Destructive QDE techniques typically rely on chemical analysis

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methods; examples include chromatography [10,11], elemental analysis [12], and mass spectrometry [13–15].

Chromatography-specifically, high performance thin-layer chromatography (TLC)-is among the most common destructive analysis techniques used in QDE for identifying ballpoint pen inks because analysis is relatively straightforward and results are rapidly generated [16–19]. Yet the identification of gel pen inks via TLC is often not possible [20]. This is because gel pen inks contain pigment-based colorants as opposed to the dve-based colorants found in most ballpoint pen inks [21]; these pigments are not soluble in the organic solvents associated with TLC analysis methods. Given the reduced potential for tampering, gel ink pens are marketed as an appealing choice for signing documents like wills or contracts. As such, document examiners frequently encounter gel inks during investigations [20]. However, authentication of text written with a gel ink pen is challenging because of (1) the difficulty in removing pigmented ink from the substrate once it is applied and (2) the lack of validated chemical analysis techniques to distinguish different gel inks. Several methods for characterizing and differentiating gel inks have been investigated [20,22-24], but to date no single approach has been deemed preferable for the discrimination and identification of gel ink pens.

In this study we explored a novel chemical analysis technique for pen inks: stable isotope ratio analysis. One of the key features of stable isotope analysis is the ability to relate and distinguish chemically identical materials through measurement of naturally occurring small

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differences in the stable isotope abundances within the materials. Stable isotope analysis can provide an additional isotope "fingerprint" to further characterize a piece of evidence. Measurement of stable isotope ratios has previously proven useful in the investigation of many different materials of forensic interest [25–27]. For example, stable isotope analysis has been used to differentiate packaging tapes [28,29] and paints [30] as well as drugs [31–33] and explosives [34–36]. Related to QDE, recent work by Jones et al. focused on the stable isotope analysis of commercially available office paper and demonstrated that carbon isotope ratios could be used to discriminate different papers [37–39].

Here we show the potential for stable isotope analysis to be applied as a quantitative testing method for characterizing pen inks during questioned document examination. We first investigated ink isotope ratio variation within packages of pens, by purchase location, and among pens of various ages before measuring the stable isotope ratios of pen inks surveyed in one location. We then focused on the stable isotope analysis of inks on paper. Finally, we present some limitations of the technique as explored in this work and discuss future work to further develop stable isotope analysis for application in QDE casework.

2. Materials and methods

2.1. Stable isotope analysis and statistical analysis

Samples were analyzed for nitrogen (N), carbon (C), hydrogen (H), and oxygen (O) element concentrations and stable isotope ratios. Stable isotope ratios are reported in δ -notation, where $\delta = R_A/R_{STD} - 1$ and R_A and R_{STD} are the ratios of the rare to common stable isotopes (e.g., $^{15}N/^{14}N$, $^{13}C/^{12}C$, $^{2}H/^{1}H$, and $^{18}O/^{16}O$) in the sample and an international standard, respectively. The international standard for nitrogen is atmospheric air (AIR); for carbon, it is Vienna-Pee Dee Belemnite (V-PDB). The international standard for both hydrogen and oxygen is Vienna-Standard Mean Ocean Water (V-SMOW). Stable isotope ratios reported as δ -values are presented in "per mil" on the basis of (for example) $-4.56 \times 10^{-3} = -4.56\%$.

Stable isotope ratios in samples were measured using a MAT 253 isotope ratio mass spectrometer (ThermoFinnigan; Bremen, Germany). For the measurement of nitrogen and carbon, samples were weighed as described below and then introduced to an elemental analyzer (EA; ThermoFinnigan) via a zero-blank autosampler (Costech Analytical; Valencia, California, USA). For the measurement of hydrogen and oxygen, samples were weighed as described below and then introduced to a high temperature conversion elemental analyzer (TC/EA; ThermoFinnigan) via a zero-blank autosampler.

Samples were analyzed alongside two primary laboratory reference materials that were used to (1) correct for potential memory, time, and/ or peak area effects during the analytical sequence and (2) normalize measured sample data to international isotope scales. Another laboratory reference material was analyzed as an unknown; comparison of this secondary reference material's corrected δ -value to its calibrated δ value was used to verify corrections and normalization. All samples within an analytical sequence were reanalyzed if the secondary reference material did not correct/normalize to within analytical uncertainty of its calibrated δ -value. Laboratory reference materials used for carbon and nitrogen isotope analysis were glutamic acids. Hydrocarbon reference materials were used for hydrogen isotope analysis and benzoic acids were used for oxygen isotope analysis.

Primary glutamic acid laboratory reference materials were calibrated using the international isotope reference materials USGS40 and USGS41 to give reference values for $\delta^{15}N_{AIR} = +49.63\%$ and -4.56% and $\delta^{13}C_{VPDB} = +23.96\%$ and -28.18% for UU-CN-1 and UU-CN-2, respectively. The primary laboratory hydrocarbon reference materials were calibrated using the international isotope reference materials IAEA-CH-7, V-SMOW, and SLAP to give reference values for $\delta^2 H_{VSMOW} = -35.8\%$, and -248.7% for n-C₂₄ and n-C₂₈, respectively. Benzoic acid primary laboratory reference materials were calibrated against the

international isotope reference materials IAEA-601 and IAEA-602 to give reference values of $\delta^{18}O_{VSMOW} = +37.02\%$ and -3.71% for UU-OH-5 and UU-OH-7, respectively. Analytical precision—defined as the standard deviation of the secondary laboratory reference material—was 0.22‰ for N (UU-CN-3; $\delta^{15}N_{AIR} = +9.30\%$, n = 40), 0.06‰ for C (UU-CN-3; $\delta^{13}C_{VPDB} = -12.35\%$, n = 40), 3.5‰ for H (PARA; $\delta^{2}H_{VSMOW} = -99.8\%$, n = 33), and 0.41‰ for O (UU-OH-6; $\delta^{18}O_{VSMOW} = +26.15\%$, n = 34).

Statistical analyses were completed using Prism for Mac OS X (Version 5.0c, GraphPad Software Inc.; La Jolla, California, USA). The significance level for all statistical tests was set at $\alpha = 0.05$. When samples were analyzed more than once, replicate analyses were averaged and the mean value used in tests.

2.2. Collection of inks

To investigate the isotope ratio variability among pens, we purchased 1 package each of black, blue, and red ballpoint pens of two common brands (Bic® and Papermate®) in Utah, USA. In addition, we purchased 1 package of black ballpoint pens of the same two brands in New Hampshire and Louisiana, USA. The black ballpoint pens from three different states were also used to investigate isotope ratio variation based on purchase location. To investigate the isotope ratio variation among inks of different ages, we collected 7 Bic® Round Stic® ballpoint pens from the assortment of pens accumulated at one author's home.

We also purchased a variety of ballpoint and gel ink pens in June– August 2012 from a large office supply store and a university bookstore located in Salt Lake City, Utah, USA. Pens were purchased both individually and as packages. We purchased various combinations of ink types, brands, and colors to collect a total of 27 ballpoint ink pens and 19 gel ink pens.

To extract all the ink from pens, we removed the ink reservoir from the pen barrel and then removed the pen tip from the reservoir. The reservoir was placed inside a 12-ml round-bottom Exetainer® vial (Labco Limited; Lampeter, Ceredigion, United Kingdom). When present, we trimmed the "grease plug" [21] from the gel pen reservoir. The reservoir was centrifuged at 720 RCF for 5 min to pool ink at the bottom of the test tube. We assumed centrifugation homogenized the ink sample. The reservoir was discarded and the ink was stored in the capped vial (placed upright in the lidded boxes used for shipping the Exetainer® vials) at room temperature.

2.3. Preparation of inks for stable isotope analysis

Samples were weighed by dipping a metal wire into the ink, then touching the wire to the bottom of a 3.5×5.0 mm capsule (Costech Analytical). We initially weighed ~2 mg of each ink into tin capsules for nitrogen and carbon analysis and ~0.3 mg of each ink into silver capsules for hydrogen and oxygen analysis. Initial mass was recorded to the nearest 0.001 mg. Capsules were left open and placed in a brass rack that was heated at 40 °C for a minimum of 24 h to allow the ink to dry. After drying, capsules were weighed again then crimped closed and analyzed, as described above, to determine element concentrations.

From the initial and final mass data, we calculated mass loss associated with drying. Using the mass loss and element concentration data, we reweighed all inks so that gas peak areas generated by the combustion or pyrolysis of dried inks would be consistent within an analysis sequence. Initial masses ranged from 0.75 to 2.17 mg for carbon and nitrogen analysis and from 0.050 to 0.300 mg for hydrogen and oxygen analysis. Reweighed inks were analyzed, as described above, to determine stable isotope ratios. All ballpoint and gel pen inks were analyzed once each for carbon, nitrogen, hydrogen, and oxygen element concentrations and stable isotope ratios; 5 of the 19 purchased gel pens were analyzed in duplicate for hydrogen and oxygen element concentrations and stable isotope ratios. Download English Version:

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