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The forensic analysis of office paper using oxygen Isotope Ratio Mass Spectrometry, part 2: Characterising the source materials and the effect of production and usage on the $\delta^{18}O$ values of cellulose and paper

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ABSTRACT

For casework applications, understanding the source processes used to create a material and the effects of those sources on the results obtained by Isotope Ratio Mass Spectrometry (IRMS) of a bulk material is important. Likewise, understanding the effect of environment, home/office printing processes and some forensic testing in at least a basic context, ensures that in casework, enough information on the effects of these variables is available during comparison and interpretation.

In this study, which focuses on oxygen isotopic abundance measurements, both fractionation and mixing effects were observed within the pulping and production process. Also observed in the carbon isotopic experiments, sampling that included toner changed the measured isotopic abundance values of the paper and should be avoided in casework. Inkjet printing processes were not shown to have an effect on the paper oxygen abundance values. Samples that were treated for fingerprints using 1,2-Indandione-Zn prior to sampling showed the greatest risk for misinterpretation of whether two samples had originated from the same source. While this study provides a good basis and understanding of the effects of a range of factors on document paper oxygen isotope values, further testing for a range of specific casework scenarios is required and should be undertaken on a case by case basis as the need arises.

1. Introduction

Isotope Ratio Mass Spectrometry (IRMS), though still uncommon in routine casework, is an emerging capability within forensic science for the comparison and discrimination of a range of materials [1–3]. Particularly with respect to organic materials, variability has been demonstrated that is both consistent and predictable [4–9] demonstrating a clear potential for comparison and discrimination between different source materials. The work undertaken in environmental studies in particular [10] presents a fundamental basis for further applications of this technology in other fields, including forensic science.

The aim of this and previous work by the authors is to develop and test the parameters of a method for the use of IRMS in the measurement and comparison of document papers. This work has included method development and validation studies [11], measurement of the expected background variability of the Australian and New Zealand market [12,13] and an examination of the effects of the production process, environment and common usage on the bulk measurements of carbon isotopes in paper [14]. It is the later variability that is the focus of this study, with these experiments designed to understand the effect of a range of production and usage variables on the bulk oxygen isotopic abundance values of document papers. This holistic approach to understanding the variables within the entire isotopic system is consistent with the recommendations of Gentile et al. [15] and the Forensic Isotope Ratio Mass Spectrometry network [16].

A minimum value for discrimination was experimentally defined based on the inter and intra ream homogeneity of paper reams in part one of this series of papers [13], to inform the comparison process. The definition of this value however, was experimentally defined using clean unused papers. For casework, the paper samples under examination have typically undergone some form of handling, writing or printing process. Having a general understanding of the effect of these processes is essential to inform interpretation and reporting.

For measurements of bulk materials, as undertaken for papers, this general understanding also needs to be extended to the effect

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of the production process on the isotopic abundance values. The production of paper is an industrial process which utilises heat, pressure and harsh chemicals to strip the cellulose fibres from whole wood chips [17]. The fibres are then placed through a series of whitening and refinement stages to remove residual contaminants and to brighten the fibres, using ozone, peroxide and caustic soda [18].

After cellulose fibre production has been completed, refined short fibres (in the majority) are mixed with a long fibre source to promote bonding and stability of the formed sheet. Included in this mixture is a filler material, typically a calcium carbonate or similar, which is used to fill the spaces between fibres to form a flat and smooth sheet. The mixture is suspended in a large proportion of water, which is poured on to a moving web to form a continuous sheet [19]. This is then dried, polished and sealed using a number of surface additives, selected for the particular purpose of the paper being produced.

Isotopically, fractionation is defined as any chemical or physical reaction or process that shows a bias between the heavy and the light isotope [20]. These reactions are chemical in nature and occur due to differences in the physiochemical properties of molecules or during chemical reactions [21]. Overall this changes the isotopic abundance values of a material between the reactants and products of a given reaction. Similarly, but reversibly, mixing of one or more sources of material will change the isotopic abundance measured.

The experiments in this study aim to examine the effect of paper pulping and production, and usage of toner and inkjet printing processes on $\delta^{18}O$ values. In addition, a short experiment was undertaken to determine the effect of environment, including the measurement of papers that have been in contact with dirt/dust, have been charred with an open flame and have been heavily handled. These experiments sit alongside the testing of papers that have other forensic testing undertaken on them prior to isotopic measurement which, as for the previous carbon experiments, included tape lifting for trace DNA collection and the detection of fingerprints using 1,2-Indandione-Zn [22].

The broader aim of this work is to develop, adapt and validate a protocol for the examination of document papers within the Australian Federal Police (AFP) laboratory. Future work will be focussed on incorporating IRMS within a more holistic paper examination protocol that includes light, physical and isotopic comparisons.

2. Materials and methods

2.1. Standards and samples

International standards, IAEA-601 and IAEA-602 were purchased from the International Atomic Energy Agency (IAEA, Vienna) and run in all analytical sequences to correct unknown samples. These benzoic acid standards (with published isotopic abundance values of $\delta^{18}O_{VSMOW}$ 23.3 and 71.4‰ respectively) were weighed to 250 μg ± 20 μg and placed in replicates of five at the start and the end of the analytical sequences. International standard cellulose (IAEA-CH-3) was utilised as a quality control material for the purposes of accepting or rejecting the results of an analytical sequence. The laboratory derived mean and standard deviation values for this material were determined to be $\delta^{18}O_{VSMOW}$ 31.93 ± 0.3‰ over a series of more than fifteen analytical sequences.

The following samples (which are the same as measured for their $\delta^{13}C_{VPDB}$ values [14]) were collected from the Australian Paper Mill (Maryvale, VIC, Australia) in 2011. These samples were measured for their $\delta^{18}O$ abundance value from different stages of the production process, with their abbreviated titles in brackets:

- Whole Eucalyptus wood chip (Wood Chip)
- Post-digester unbleached Eucalyptus pulp (Unbleach Euc)
- Samples from within the bleaching/whitening process
  - Post oxygen wash (Ex O)
  - Post ozone and peroxide wash (Ex ZD)
  - Post caustic soda, oxygen and peroxide wash (Ex EOP)
  - Post chlorine dioxide wash (Ex D)

- Refined bleached eucalyptus (Refined Bleach Euc)
- Refined bleached pine
- Directly from the paper decal roll, post paper production (Paper Decal)
- Paper packed into reams for shipping (Paper Packed)
- Bulk measurements for packed paper and paper decal
- Paper filler material—Calcium Carbonate ($CaCO_3$)

To maintain consistency across the production process, cellulose extraction was undertaken, followed by measurement at the University of California at Berkeley. Additional bulk samples were measured at the AFP laboratory. All measurements were traceable to international standards and as such, are comparable to demonstrate the effect of the production process on sample values. Any difference in sample measurement (for those samples measured by both laboratories) observed would indicate instrumental or correction differences between the two laboratories, which are not unexpected, and can be used to inform the comparison between the extracted and bulk values.

For the printing process samples, 250 μg of sample was taken from a selection of the office printed samples previously measured [14], with a 2 mm micropunch (Harris Unicore, LabSciTech, Australia). The number of samples measured in this experiment was reduced in comparison to the carbon experiments, to remove repetition of brand and model. For oxygen, the number of unique samples measured is 22 for the toner experiment and 8 for the inkjet samples. The samples measured for their oxygen isotopic content are shown in Table 1 (toner printers) and Table 2 (inkjet printers). For ease of comparison the sample numbers for these samples were retained from the carbon experiments [14].

Triplicate samples were taken from the non-image areas of the printed pages (i.e. from the blank sections) and from directly on top of heavily inked areas that had been printed using a bold font (to simulate a worst case scenario). These samples were compared to the plain unprinted paper results measured in the background population study to determine whether there was any effect on the $\delta^{18}O$ of the papers measured from having undergone a printing process. The printed samples measured will be used to give a preliminary indication of whether IRMS may be a suitable technique for discrimination of the toner or inks, if a suitable technique to remove samples from the page can be developed.

In order to investigate the effects of typical forensic science examinations on the measurement of isotopic abundances, samples were punched from paper that had been subjected to fingerprint treatment using 1,2-Indandione-Zn and DNA collection via tapelifting.

Additionally, samples were taken from three usage effects tests, where paper had been subjected to dirt/dust contamination, charred using an open flame and heavy handling. To create these samples, the following was undertaken:

- *Dirt/Dust*: The sheets were soiled by placing them on an outside concrete surface and applying pressure to maximise contact and adhesion of contaminants. Loose particles were dusted from the page prior to sampling from areas of visually identified as soiled.
- *Charring with open flame*: The sheets of paper were charred by placing them above an open flame until mild discolouration occurred.