



# The forensic analysis of office paper using oxygen isotope ratio mass spectrometry. Part 1: Understanding the background population and homogeneity of paper for the comparison and discrimination of samples



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## ABSTRACT

Isotope ratio mass spectrometry (IRMS) using carbon isotopes has previously been shown to be a robust and discriminating technique for the comparison of document papers. This study aims to examine the inter and intra sample variability for oxygen isotopes measured in standard 80gsm white document papers, to inform the comparison of document papers in forensic casework.

123 paper samples collected from Australia and New Zealand over a 24-month period were measured for their bulk oxygen isotopic abundance and were found to sit within a range of 15 ‰. A homogeneity study was undertaken which included examining the variability of samples at the sheet, ream and brand source levels. The results of this study were used to construct guidelines for sample comparison and as such, 95% confidence intervals were observed to be inappropriate for use given the high intra sample variability. Instead, a 1.4 ‰ discrimination range (0.7 ‰ either side of the measured value) was defined for use as a benchmark for discrimination when samples were measured in the same sequence. Utilising this value, 82% of the samples could be discriminated using a paired comparison, demonstrating a strong potential for use within forensic casework.

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## 1. Introduction

Isotope ratio mass spectrometry (IRMS) as a forensic technique is gaining traction for the comparison of materials that are unable to be discriminated using traditional forensic techniques. It has been used in a range of evidence types including the comparison of drugs, explosives, paints, soils, polymers including tapes, organic materials including fibres and matches and in human provenancing. A number of articles of note provide a holistic review of the research undertaken in the forensic IRMS discipline [1–3]. In general, the majority of the published studies are focussed on proof of concept studies that include an assessment of the homogeneity of a particular material. While these studies provide the basis for comparison and discrimination, in most cases there still remains a

need for location-based studies to be undertaken and local databases to be constructed.

The primary reason that the measurement of stable isotopes is useful is based on the observed variability of materials due to both their photosynthetic pathway and location of growth for organic materials, or due to source material differences and/or production process fractionation. Understanding not just the variability of the material but the effects of external or production process, particularly for bulk stable isotope measurements, is key in being able to interpret the abundance values.

For an organic sample type such as paper, the cellulose content of the material lends itself towards the use of oxygen and hydrogen isotopes in addition to the carbon isotopes previously studied. These two isotopes, and hydrogen in particular, come with inherent problems related to absorption and exchange of isotopes from the atmosphere to the surface of the cellulose molecules. There also remains debate within the stable isotope community about how to correct or control for hydrogen isotopic exchange, with a number of different strategies proposed [4–6]. Given this, oxygen was selected

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as a more robust isotope to add to carbon in an attempt to increase the discriminability of IRMS as a forensic tool [7].

This study aims to build on the carbon isotopic research previously conducted [8–10], by building a background population of the oxygen isotopes of document papers in the Australia and New Zealand region. This primarily includes measuring the same background paper samples as previously measured for their oxygen isotopic abundance. As was identified in the carbon study, document paper is a relatively inhomogeneous material isotopically and requires careful comparison and interpretation.

To assist with this, an examination of the homogeneity of seven brands of paper was undertaken at the sheet, ream and brand source levels. The results of this experiment will be used to inform the interpretation process for comparison of values, particularly to determine whether traditional statistical tests or, as for the results presented in the carbon studies [8–10], to define an appropriate benchmark value for comparison and discrimination of samples.

## 2. Materials and methods

### 2.1. Standards and samples

To correct all paper samples, international benzoic acid standards IAEA-601 and IAEA-602 (purchased from the International Atomic Energy Agency, Vienna) were run in replicates of 5 at the start and the end of all analytical sequences. The published  $\delta^{18}\text{O}_{\text{VSMOW}}$  values of these standards are 23.3 and 71.4 ‰ respectively [11,13]. International standard cellulose IAEA-CH-3 was used as a quality assurance material. While no internationally accepted value exists for the oxygen isotopic abundance of this material, inclusion of it in each run allowed for a laboratory value to be determined over time and comparison of correction between sequences to be undertaken.

The background paper samples utilised in these experiments were taken from the samples measured in Part 1 of the carbon series previously published [8] and are included in Table 1. This table also includes brand details, countries of manufacture and packaging date (where available). All papers were collected from Australia and New Zealand and were marketed as 80gsm (grams per square metre) standard office paper, typically in a ream of 500 sheets. Collection was over a period of 24 months and consisted of 46 unique brands, with 123 samples in total being measured. None of the papers in this sample set were advertised as containing recycled material. All samples were run in triplicate, with one sample taken from three random sheets collected from each ream.

As a preliminary assessment and a comparison against papers manufactured with virgin pulp, seven reams of paper that contained varying levels of recycled content were measured for their  $\delta^{18}\text{O}_{\text{VSMOW}}$  abundance value. 5 samples were marketed as containing 10% recycled pulp with the other two samples containing 50% recycled content. The details for these papers, including brand names, are included in Table 2.

The paper samples measured for the homogeneity experiments are detailed in Table 3. Seven reams from seven brands from a range of production locations purchased at the same time were utilised for these experiments.

A secondary study was undertaken to observe the inter brand homogeneity of paper samples. A change was made to the samples utilised for the second round of homogeneity testing (experiments focussed on measuring seven samples from seven reams from the same brand), with HP Everyday and Paper One branded samples (originating from Brazil and Indonesia respectively) replaced by Double A and Olympic (Thailand and Australia) branded samples. All samples are detailed in Table 3.

Following the protocol used in the carbon experiments [8] the summary below outlines the sampling utilised for the two rounds of homogeneity testing.

To test the homogeneity of a single ream, and to inform sampling, with a total of over 5% of a single ream measured:

- 3 samples from one page, in one location;
- 3 samples from one page, in random locations;
- 7 samples from one page, in one location;
- 7 samples from one page, in random locations;
- 7 samples from 7 different pages;
- 25 samples from 25 different pages (representing 5% of the ream).

To test the homogeneity of a single brand produced and therefore measured at a single time:

- 7 samples, from 7 single pages, from 7 individual reams (49 samples in total).

### 2.2. Instrumentation, equipment and method

A Genius ME5 (Sartorius, Goettingen, Germany) analytical balance was used to weigh the international benzoic acid standards IAEA-601 and IAEA-602, and international cellulose IAEA-CH-3 to a sample size of  $250 \mu\text{g} \pm 20 \mu\text{g}$ . Paper samples were prepared using a combination of a 1.2 mm and 2 mm Harris Uni-core micro-punches (Proscitech, Queensland, Australia) where appropriate up to a sample size of  $250 \mu\text{g}$ . Samples were placed into  $3.3 \text{ mm} \times 4 \text{ mm}$  silver capsules for solids (Thermo Fischer Scientific, Sydney, Australia) and stored in a Perspex desiccator with self-indicating orange silica gel until measurement.

The standards and samples measured in these experiments did not include active drying prior to measurement, but were held in a desiccator at room temperature before being immediately transferred to a sealed, helium purged auto-sampler.

Individual samples were dropped from a helium purged Costech Zero Blank autosampler (Thermo Finnigan, Bremen, Germany) into the graphite furnace of a TC/EA packed with glassy carbon, as recommended by the manufacturer (Thermo Finnigan). The combustion furnace was set to a temperature of  $1400 \text{ }^\circ\text{C}$  and was connected to a 0.5 m packed molecular sieve heated to  $60 \text{ }^\circ\text{C}$ . Helium carrier gas was fed through the TC/EA at a pressure of 120 psi to a ConFlo III and into a DELTAplus XP IRMS (Thermo Finnigan). The sample peaks were scaled against pulses of CO reference gas with a purity of 99.999%, set at a peak height of approximately 4000 mV, with helium dilution switched on during the sample elution window. Reference gas pulses were set to 20, 200, 240 and 280 s (for 20 s duration), with a total measurement time of 340 s.

### 2.3. Data treatment

The  $\delta^{18}\text{O}_{\text{VSMOW}}$  values produced by the Isodat (IRMS control) software were exported into Microsoft<sup>®</sup> Excel. Isotopic composition is expressed in delta notation as an oxygen isotope ratio ( $\delta$ , expressed in ‰) relative to known standards (for oxygen this is Vienna Standard Mean Ocean Water – VSMOW). This is expressed as:

$$\delta^h E_{\text{std}} = (R_{\text{Sample}}/R_{\text{Std}}) - 1$$

where 'h' refers to the heavy isotope, 'E' refers to the element being measured, 'std' refers to the standard material being referenced against and 'R' is the ratio of the light and heavy isotope. For this

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