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# Background survey of polyethylene in the Australian Capital Territory – A demonstration of variability in isotopic abundance values and their application to forensic casework

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## ABSTRACT

Plastics including adhesive tapes, cable ties, and packaging are common evidence types encountered in forensic investigations and casework. Traditional examination techniques such as Fourier Transform Infrared (FTIR) spectroscopy lack specificity and are unable to discern differences within the same polymer structures leaving the analyst with a generic identification. High quality manufacturing methods further amplify the limitations in detecting variability between samples. Isotope Ratio Mass Spectrometry (IRMS) has been shown to be a valuable technique in further discriminating plastics. Discrimination is achieved by analysing the relative abundances of stable isotopes within a sample, with differences detected in isotope ratios possibly attributed to the source of raw materials and fractionation during the manufacturing process. A survey of cling wraps and re-sealable zipper storage bags collected in the Australian Capital Territory was undertaken to assess the variability in carbon and hydrogen isotope ratios of different brands and samples. The results of this research are discussed, particularly with respect to within and between brand trends, and a case study is presented as an example of the value of including IRMS in a casework context.

## 1. Introduction

Plastics are a ubiquitous material, with 269 million tonnes globally produced in 2015 alone. Market demand is driven by agriculture, the automotive industry, building and construction, and packaging. Polyethylene continues to be produced in high volume to support common uses such as food packaging, bags, trays, and containers [1].

Plastic products such as re-sealable zipper storage bags and cling wraps are generally produced from polyethylene, polyvinyl acetate or polypropylene. These materials are produced by polymerisation of ethylene monomers in the presence of metal oxide catalysts, that have generally been derived from petrochemical sources [2]. Polymer products that have been produced from materials such as cellulose and starch (termed biopolymers) are increasing their market share and therefore may also start emerging in forensic casework [3]. To produce a polymeric film, beads of a specified polymer are melted and put through a process called blown film extrusion, whereby the polymer is extruded through a circular die in a continuous tube. This tube is either cut on one edge to form a flat film, or in the case of plastic bag manufacture, heat sealed at intervals and cut to form a bag shape [4].

Forensic chemists are commonly requested to conduct comparison

examinations in an attempt to link an offence such as drug importation, with a product seized from a suspect or residence. Polymer films including clear polymer substrates are becoming more prevalent in the professional printing industry and will emerge as a means to counterfeit polymer-based currency, presenting new and emerging opportunities for chemical examinations to add value in other forensic disciplines such as Document Examination.

Where traditional chemical examination techniques conclude at an identification of the polymeric structure, further comparison of the isotopic abundances of polymers allows discrimination based on the variability in the source of the carbon and hydrogen isotopes incorporated into the film during manufacturing. Variability in isotopic abundance may also be derived from the stages in the production process. Manufacturing steps that include heat or chemical processes typically induce fractionation (any separation or reaction process that alters the isotopic abundances of a material). In addition to this, isotopic abundance variability may arise when multiple sources of the target isotope are introduced to achieve the final product.

Current protocol for the comparison of polymers includes chemical identification using Fourier Transform Infrared Spectroscopy (FTIR) [5,6] and examination of the striation and other manufacturing marks

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using microscopy and polarised light [7,8]. While an examination of the manufacturing marks and birefringence patterns captured on the plastic has been shown to be discriminating [9,10], evidence that is physically small (e.g. is only part of a plastic bag or a small piece of tape) or is obscured (e.g. counterfeit currency which has been heavily printed) lends itself more easily to comparison using isotopic abundance. The addition of a chemical technique adds weight to the evidence presented and can allow for the combination of results into a likelihood ratio to express the overall strength of the evidence.

The comparison of polymeric materials using Isotope Ratio Mass Spectrometry (IRMS) is an emerging technique in forensic science. A range of previous studies have explored the applications of IRMS to various materials of forensic significance [11,12]. Petrochemicals themselves have been shown to be isotopically variable [13–15], providing a strong basis for the isotopic comparison of materials produced from these source materials. In addition to gaining an understanding of the source materials and production process used to manufacture a material, the variability between packages and homogeneity within a single source also need to be defined to inform comparison and discrimination processes. In general, the approach when seeking to incorporate stable isotopic measurements into forensic casework is detailed in Gentile et al. [16].

The interpretation of isotopic comparison results, requires databases of materials for two fundamental reasons. Firstly, the development of a database containing known samples enables the assessment of variability of the material within the commercial market from which a casework sample has been derived. This allows the examiner to define whether the values express adequate variability for differentiation and to inform the parameters for discrimination. The second purpose of a well-constructed and characterised database is to allow some statistical measure of strength to be assigned to the comparison undertaken for casework reporting. This measure could be based on statistical tests of difference such as the comparison of standard deviation values [17] or for calculating a likelihood ratio to inform the strength of the evidence opinion provided [18]. Additional to these fundamental reasons, a third and emerging use of databases is for use in forensic intelligence frameworks, where an isotopic abundance value of an unknown or questioned item is compared to a database to inform the source (i.e. the location of production or brand of the sample). This is applicable only if the database is representative of the geographical region or market for which the unknown item was located [19–21].

The purpose of this background survey was to understand the isotopic variability of common plastic products sourced within the Australian Capital Territory (ACT), Australia. Further work to broaden this study is planned to determine how representative this database is of the Australian market. A study of the variability of polymers within the Australian region has not previously been undertaken, and the results of this research provide a basis for understanding the variability and homogeneity of polyethylene materials in this market, ready for use in forensic casework.

## 2. Materials and methods

A total of 26 packages of re-sealable zipper storage bags (herein referred to as “re-sealable bags”) were purchased from outlets within the ACT in a single day, in 2014 (Table 1). In the same outlets, 26 cling wrap samples that varied between 15 and 150 m in length were also purchased (Table 2). As the purpose of this study was to examine between source variability, a limited within sample variability study was conducted for the re-sealable bags.

All re-sealable bag samples and cling wrap samples were examined using an iS50 Nicolet Attenuated Total Reflectance - Fourier Transform Infrared (ATR-FTIR) spectrometer. Identification of samples as polyethylene was achieved by comparing spectra to commercial databases using Omnic software.

Triplicate samples were taken from three separate re-sealable bags

from each 26 re-sealable bag package. Samples were taken from random locations on the largest portion of the re-sealable bag, avoiding any printed areas and the section where the zipper was located. This sampling process for re-sealable bags was duplicated to enable measurement of both carbon and hydrogen isotopic composition. Each cling wrap sample was measured in replicates of four for carbon and five for hydrogen isotopes.

Two micro-punches (Harris Unicore, Proscitech, Australia) were used to produce the appropriate sample size for isotopic measurement. For carbon isotopes 100 µg of sample was placed into a tin capsule and for hydrogen isotopes 150 µg of sample was placed into a silver capsule (Thermo Fischer Scientific, Sydney, Australia). Samples were crimped and stored in a desiccator prior to analysis. Given the structure and stability of polyethylene, no controls for hydrogen exchange were utilised other than storage of samples over desiccant and the use of a helium purged Costech Zeroblank autosampler.

Isotopic abundance measurements were made on a Thermo Finnigan Delta<sup>plus</sup> XP instrument, coupled to a ConFlo III. Helium carrier gas and reference gases (carbon dioxide and hydrogen) were analytical grade and sourced from Coregas (ACT, Australia).

Delta notation ( $\delta$ ) is used to express the results of the measurement of isotopic abundances by calculating the isotopic ratio of a sample relative to the known isotopic ratio of a standard. All delta values are expressed in per mil (‰) and are scaled using standards to a master or internationally recognised scale. For carbon measurements this scale is Vienna Pee Dee Belemnite (VDPB) and for hydrogen it is the Vienna Standard Mean Ocean Water/Standard Light Arctic Precipitation (VSMOW/SLAP). Delta values are expressed as:

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

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.

Carbon isotope ratio measurements were undertaken by placing samples into a helium purged Costech Zeroblank autosampler attached to a FlashEA 1112 (Thermo Finnigan, Bremen, Germany) packed with a silvered cobaltous/cobaltic oxide and copper oxide. The reaction column was held at 900 °C and a reduction furnace containing reduced column was held at 680 °C. A packed GC column at 45 °C was used to further separate peaks prior to introduction into the ConFlo III. International standard materials IAEA-CH-7 polyethylene and IAEA-CH-6 cellulose were used to correct raw values to the VPDB scale (International Atomic Energy Agency, IAEA, Vienna). IAEA-CH-3 cellulose was used as a quality assurance check material in each analytical sequence.

Hydrogen isotope ratio measurements were made by placing samples in a helium purged Costech Zeroblank autosampler attached to a High Temperature Conversion Elemental Analyser (TC/EA) packed with glassy carbon. The reactor of the TC/EA was set to a temperature of 1450 °C, with a 0.5 m packed molecular sieve heated to 60 °C. International standard materials IAEA-CH-7 polyethylene and IAEA-NBS-22 oil were used to bracket the polyethylene samples at the start and the end of the sequence and to correct raw hydrogen values to the VSMOW2/SLAP scale.

Isotopic corrections were completed using Microsoft Excel and statistical tests were conducted with Graphpad Prism. No uncertainty measurements have been calculated from these results but will be included in future procedures where casework samples are compared to the database.

## 3. Results and discussion

### 3.1. Re-sealable bags

Table 1 details the measured  $\delta^{13}C_{VPDB}$  and  $\delta^2H_{VSMOW}$  (‰) values for

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