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Stable isotope ratio mass spectrometry and physical comparison for the forensic examination of grip-seal plastic bags

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Abstract

Plastic bags are frequently used to package drugs, explosives and other contraband. There exists, therefore, a requirement in forensic casework to compare bags found at different locations. This is currently achieved almost exclusively by the use of physical comparisons such as birefringence patterns. This paper discusses some of the advantages and shortcomings of this approach, and presents stable isotope ratio mass spectrometry (IRMS) as a supplementary tool for effecting comparisons of this nature. Carbon and hydrogen isotopic data are presented for sixteen grip-seal plastic bags from a wide range of sources, in order to demonstrate the range of values which is likely to be encountered. Both isotopic and physical comparison (specifically birefringence) techniques are then applied to the analysis of rolls of bags from different manufacturing lots from a leading manufacturer. Both approaches are able to associate bags from a common production batch. IRMS can be applied to small fragments which are not amenable to physical comparisons, and is able to discriminate bags which could be confused using birefringence patterns alone. Similarly, in certain cases birefringence patterns discriminate bags with similar isotopic compositions. The two approaches are therefore complementary. When more than one isotopically distinct region exists within a bag (*e.g.* the grip-seal is distinct from the body) the ability to discriminate and associate bags is greatly increased.

Keywords: Plastic materials; Polyethylene; Plastic bag examination; Birefringence; Isotope ratio; Isotope ratio mass spectrometry (IRMS)

1. Introduction

In 2003 there were 30,000 seizures of class A drugs in England and Wales involving over 2.7 tonnes of heroin and 6.8 tonnes of cocaine [1]. Such drugs are inevitably seized together with the materials in which they are packaged, the packaging type varying according to the quantity and nature, or physical form, of the drug. For example, small quantities of drugs are typically wrapped in cigarette papers and/or cling film [2] whilst larger quantities may be contained in plastic bags or any number of other containers. As with many other packaging products, grip-seal bags are ubiquitous in modern society and are common packaging for many types and quantities of drugs. It is, therefore, necessary to find ways to differentiate or associate samples, especially when exhibits have been physically deformed or only fragments exist. Grip-seal bags were originally developed by Dow Chemicals as Ziploc™ bags [3] and are known by many other names such as zip lock bags or resealable bags. Previous research has demonstrated the potential of isotope ratio mass spectrometry (IRMS) to characterise packaging materials such as cling film [4] and pressure sensitive adhesive tape [5] *via* the stable isotopic composition of these materials or their constituents. An increased interest in forensic applications of IRMS has lead to the publication of a number of reviews [6,7].

Grip-seal bags are made almost exclusively from low density polyethylene (LD-PE), although a few are manufactured from poly(vinyl chloride) (PVC). The manufacturing process [8] begins with raw plastic pellets that are melted and mixed with additives, such as pigments, plasticisers and emulsifiers. The mixture is then extruded through a die, often incorporating the

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Table 1
Physical and isotopic characteristics of sixteen assorted grip-seal bags

Bag #	1	2	3	4	5	6	7	8	9	10	11	12[a]	13[a]	14	15	16
Approximate width (mm)	88	200	113	115	100	154	134	100	120	200	112	73	73	100	323	227
Approximate length (mm)	130	280	127	127	195	248	200	175	190	305	168	100	100	170	342	340
Grammage ($g\ m^{-2}$)[b]	41	51	51	52	50	58	83	48	57	49	55	60	62	116	55	50
$\delta^{13}C$ data																
Top	−29.5	−27.3	−27.8	−27.8	−28.8	−28.4	−30.0	−27.2	−27.4	−32.1	−29.2	−29.3	−29.3	−28.7	−27.7	−27.7
Middle	−29.6	−27.3	−27.9	−27.8	−28.9	−28.5	−30.0	−27.2	−27.4	−32.1	−29.3	−29.3	−29.4	−28.8	−27.7	−27.7
Seam	−29.6	−27.2	−27.9	−27.8	−29.1	−28.4	−29.9	−27.2	−27.4	−32.1	−29.3	−29.4	−29.4	−28.7	−27.7	−27.7
Grip-seal	−29.6	−27.2	−27.8	−27.9	−29.2	−28.4	−28.3[c]	−27.2	−27.4	−32.1	−29.2	−29.4	−29.4	−28.8	−27.7	−27.7
Average	−29.6	−27.3	−27.9	−27.8	−29.0	−28.4	−30.0	−27.2	−27.4	−32.1	−29.3	−29.4	−29.4	−28.7	−27.7	−27.7
S.D. (n = 8)	0.04	0.07	0.07	0.08	0.14	0.03	0.04	0.03	0.03	0.05	0.07	0.04	0.06	0.03	0.06	0.06
$\delta^{2}H$ data																
Top	−101	−66	−66	−61	−75	−62	−84	−79	−66	−46	−74	−62	−61	−93	−54	−47
Middle	−102	−62	−65	−64	−75	−59	−80	−70	−63	−46	−70	−56	−61	−97	−52	−54
Seam	−107	−63	−67	−64	−76	−59	−84	−80	−60	−49	−70	−59	−58	−103	−59	−59
Grip-seal	−107	−69	−69	−66	−77	−62	−82[c]	−85	−61	−52	−74	−62	−60	−104	−54	−55
Average	−105	−65	−67	−64	−76	−60	−83	−79	−62	−48	−72	−60	−60	−99	−55	−53
S.D. (n = 8)	3	3	2	2	1	2	2	6	3	3	2	3	2	5	3	5

$\delta^{13}C$ value reported as permil versus VPDB (Vienna PeeDee Belemnite). $\delta^{2}H$ value reported as permil versus VSMOW (Vienna Standard Mean Ocean Water).
[a] Believed to originate from the same source.
[b] Calculated from the size and weight of the bag, making no allowance for the zip.
[c] The value for the zip was not included in the average.

grip-seal profile, by cast extrusion (not blown film). The resulting sheet is allowed to cool, sealed to form bags of a required size and wound into a roll. During the manufacturing process the plastic comes into contact with a number of rollers which produce manufacturing marks [9].

Previous research has examined a range of physical and spectroscopic techniques for the classification of plastic films but, in general, has focused on the characterisation of production and handling marks [8–14]. Although the marks left on extruded plastic by machines are often visible with no enhancement it is generally accepted that birefringence patterns have greater potential for characterising clear plastics as more detail can often be seen using polarising filters [10]. It has been noted that the comparison of manufacturing marks is made possible, but also limited, by changes as machine parts become contaminated and wear, with some additives contributing to the deterioration [9].

Table 2
Isotopic characteristics of six boxes of Tesco grip-seal bags

Box #	A	B	C	D	E	F
Batch identification	2005/07/30C	2005/07/30C	2004/06/21B	2004/06/21B	2004/09/03C	2004/06/12C
$\delta^{13}C$ data						
Top	−37.2	−37.0	−28.6	−28.7	−29.5	−28.6
Middle	−37.2	−37.3	−28.7	−28.6	−29.5	−28.6
White panel	−36.3	−36.5	−28.7	−28.7	−29.6	−28.6
Seam	−37.1	−37.2	−28.5	−28.6	−29.5	−28.6
Red grip-seal	−38.1	−38.0	−38.2	−38.2	−30.7	−38.1
Blue grip-seal	−37.9	−38.0	−33.6	−33.5	−30.8	−28.7
Average[a]	−37.2	−37.2	−28.6	−28.7	−29.5	−28.6
Range[b]	0.6	0.3	0.3	0.1	0.2	0.2
$\delta^{2}H$ data						
Top	−43	−44	−62	−62	−73	−49
Middle	−43	−43	−63	−62	−65	−49
White panel	−49	−49	−65	−65	−70	−51
Seam	−49	−49	−64	−66	−74	−48
Red grip-seal	−48	−48	−61	−60	−80	−48
Blue grip-seal	−43	−48	−60	−55	−76	−47
Average[a]	−46	−46	−64	−64	−70	−49
Range[b]	9	11	12	5	10	5

$\delta^{13}C$ value reported as permil versus VPDB (Vienna PeeDee Belemnite). $\delta^{2}H$ value reported as permil versus VSMOW (Vienna Standard Mean Ocean Water).
[a] Calculated for the four areas sampled from the inner most bag (n = 8) excluding data for red and blue zips.
[b] calculated for the middle area of 24 contiguous bags (n = 96).