Quantifying the Biobased Content of Plastics Using ASTM-D6866
ASTM-D6866 is a standardization of radiocarbon dating methods used to determine the age of fossils, artifacts, and materials.
Topics

- Understanding Radiocarbon Dating
- Methods: ASTM D6866-04a
- Accuracy & Precision
- Reporting
- Working Examples: Surprises
Topics

• Understanding Radiocarbon Dating
Understanding Radiocarbon Dating

STEP 1: On-going formation and decay of radiocarbon within the atmosphere

- Nitrogen ($^{14}\text{N}$) + cosmic neutrons → Radiocarbon ($^{14}\text{C}$)
- Radiocarbon immediately oxidizes → Carbon Dioxide ($^{14}\text{CO}_2$)

The radiocarbon immediately starts to decay ($T^{1/2} = 5730$ years)

"Constant" amount of radiocarbon in the atmosphere as $\text{CO}_2$ (~ 14.7 dpm)
STEP 2: Radiocarbon is removed from the atmosphere by plants

Plants take in the $^{14}$CO$_2$ during photosynthesis

While alive, they have the same radiocarbon content as the air around them (equilibrium with the atmosphere is maintained).

$^{14}$CO$_2$ uptake $\leftrightarrow$ $^{14}$C Decay
Understanding Radiocarbon Dating

STEP 3: Disequilibrium begins upon “death”

Upon harvest – carbon uptake ceases

Radiocarbon within the plant is no longer being replenished

The $^{14}$C Decay continues

The plants are no longer in equilibrium with the atmosphere

The “Radiocarbon Clock” is set to zero and starts ticking
Understanding Radiocarbon Dating

Biobased Content Analysis using Radiocarbon Dating
Understanding Radiocarbon Dating

Food comes from nature. Why not the container?

Perimeter departments like deli, bakery, meats and produce are the heart of your brand’s difference. Non-100% corn-based NatureWorks™ PLA helps drive traffic to high-value areas, boosting customer loyalty. Strong and durable to reduce shrinkage costs. Great optics enhance visual display. Approved for food contact in the United States, Canada and Europe.

If it were 100% petroleum derived

If it were 50% corn-based & 50% petroleum derived

Biobased Content Analysis using Radiocarbon Dating
Topics

- Methods: ASTM D6866-04a
Biobased Content Analysis using Radiocarbon Dating

Radiocarbon Methods: ASTM D6866-04a

Method A
CO2 Absorption
Routine by the 1970s
SAMPLE
\[ \text{CO}_2 \]
Absorbed into Counting Solution

Method C
Benzene Synthesis
Routine by 1960s
SAMPLE
\[ \text{CO}_2 \]
Lithium Carbide
Acetylene
\[ \text{Benzene} \]

Method B
AMS (Accelerator Mass Spectroscopy)
Routine by the 1980s
SAMPLE
\[ \text{CO}_2 \]
Reduced to Graphite

Increasing cost of analysis, Increasing price to manufacturer

LSC $25,000

AMS $1.5 - 3 million

Biobased Content Analysis using Radiocarbon Dating
## Radiocarbon Methods: ASTM D6866-04a

<table>
<thead>
<tr>
<th>Method</th>
<th>ADVANTAGES</th>
<th>DISADVANTAGES</th>
</tr>
</thead>
</table>
| CO₂ Absorption | Low cost chemistry lab  
|              | Standard LSC detection  
|              | Rapid Through-put                                      | Very low precision (+/- 10 %)   
|              | High carbon content requirement                       | High chemical overhead              |
| Benzene      | Good precision (<= 2% absolute)  
|              | Standard LSC detection  
|              | Rapid Through-put                                      |                                        |
| AMS          | Good precision (<= 2% absolute)  
|              | Very small sample requirements                         | High detector overhead              |
Radiocarbon Methods: ASTM D6866-04a

CO₂ and BENZENE LABORATORIES

Biobased Content Analysis using Radiocarbon Dating
Radiocarbon Methods: ASTM D6866-04a

AMS LABORATORY

Biobased Content Analysis using Radiocarbon Dating
Topics

• Accuracy & Precision
A Test of Accuracy - Known Ethanol Concentrations in Heptane verified by Radiocarbon Dating

Accuracy & Precision

% Ethanol per 14C  % Ethanol per Chemistry
Variables that can be controlled in the lab

- Quantitative combustion of all available carbon in the product
- The yield of carbon through the chemical conversions
- The methodology used: Method A, B, or C
- How long the sample is measured in the detector
Variables that can not be controlled in the lab

- The homogeneity of the biomass components within the product
- Component loss during manufacturing ("fractionation")
- Collection parameters
- Storage parameters
Biobased Content Analysis using Radiocarbon Dating

Reporting

Simple Visual Report

Easy Inter-comparison

Instinctively Obvious

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Biobased Content Analysis using ASTM-D6866

**Submitter:** ABC Company
**Submitter Label:** Gas Bag 1
**Laboratory Number:** BETA-00001
**Material Analyzed:** CARBON DIOXIDE
**Date Received:** October 13, 2006
**Date Reported:** October 17, 2006

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**Biomass CO2:** 73% *

*(carbon-neutral CO2)*

Proportions Biomass CO2 vs. Fossil CO2 indicated by C14 content

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* ASTM-D6866 cites precision on the mean Biomass CO2 Result as +/- 3% (absolute). This is the most conservative estimate of error in the measurement of complex biomass containing solids and liquids based on empirical results. Real precision for readily combustible and homogenous materials (e.g. gasoline) and especially samples received as CO2 (e.g. flue gas or CEMS exhaust) can be as low as +/- 0.5-2%. The result only applies to the analyzed material. Fluctuations in carbon content within a batch of product, gasoline or flue gas must be determined separately (e.g. averaged measurements of multiple solids or liquids, and single measurement of the combination of gas aliquots collected over time). The accuracy of the result as it applies to the analyzed product, fuel, or flue gas relies upon all the carbon in the analyzed material originating from either recently respired atmospheric carbon dioxide (within the last few decades) or fossil carbon (more than 60,000 years old). "Percent biomass" specifically relates % renewable (or fossil) carbon to total carbon, not to total mass or molecular weight. Mean Biomass CO2 estimates greater than 100% are assigned a value of 100% for simplification.
Topics

• Working Examples: Surprises
The manufacturer submitted 3 samples

Radiocarbon Dating Results were . . .

<table>
<thead>
<tr>
<th>Product</th>
<th>Biobased Percentage</th>
</tr>
</thead>
<tbody>
<tr>
<td>Product A</td>
<td>69%</td>
</tr>
<tr>
<td>Product B</td>
<td>78%</td>
</tr>
<tr>
<td>Product C</td>
<td>70%</td>
</tr>
</tbody>
</table>

After the analyses, the manufacturer informed us that A, B, & C were all the same product and an error must be present in the result for Product B.

The $^{14}$C dating determined the biobased content & revealed a quality control issue.
The manufacturer submitted 2 samples

Radiocarbon Dating Results were . . .

Product A  ➔  96 % Biobased
Product B  ➔  77 % Biobased

After the analyses, the manufacturer informed us that Product B was Product A diluted with water and sold under a different name.

Their formulators investigation revealed Product B contain 2 petroleum derivatives TEA-99 and Polyol, with a total fossil C contribution to the product of ~ 20 %.

The correct biobased contents were identified and the marketing of Product B has to be reconsidered.
USDA BioPreferred Program

- Preferred Procurement Program for US Federal Agencies and their Contractors

- Voluntary Labeling Program for the broad scale consumer marketing of biobased products

Both programs require ASTM D6866 certification
Key Points and Considerations

Radiocarbon Dating works for comparing biobased content between products

Basic assumption: all carbon in the product is either present day or fossil

It also provides an added quality control measure.

Accuracy relies heavily on homogeneity and quantitative extraction of all available carbon.

http://www.betalabservices.com/biobased.html