

Quantifying the Biobased Content of Plastics Using ASTM-D6866

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Biobased Content Analysis using Radiocarbon Dating

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

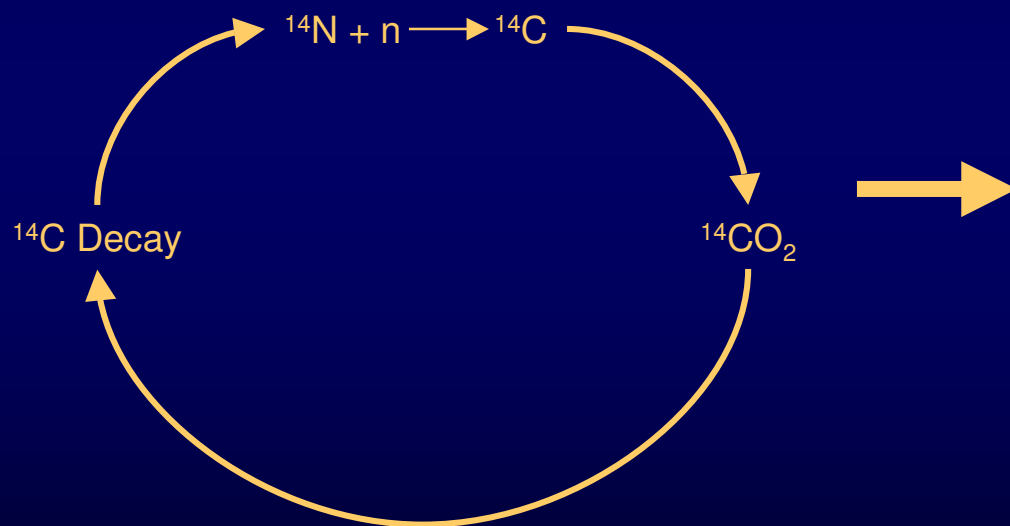
- Understanding Radiocarbon Dating

Understanding Radiocarbon Dating

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



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

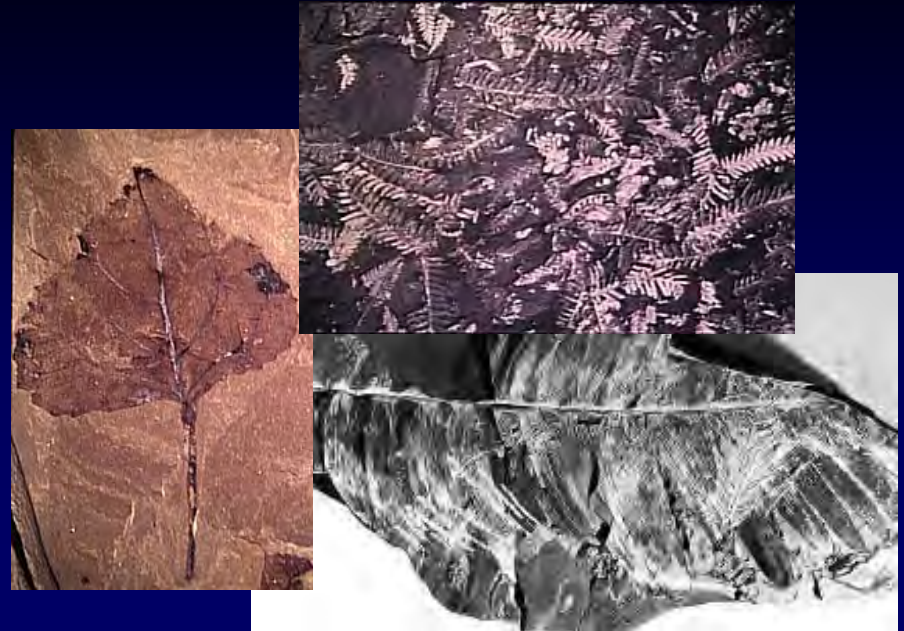


“Constant” amount of radiocarbon in the atmosphere as CO_2 (~ 14.7 dpm)

Understanding Radiocarbon Dating

STEP 2: Radiocarbon is removed from the atmosphere by plants

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



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

$^{14}\text{CO}_2$ uptake \rightleftharpoons ^{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

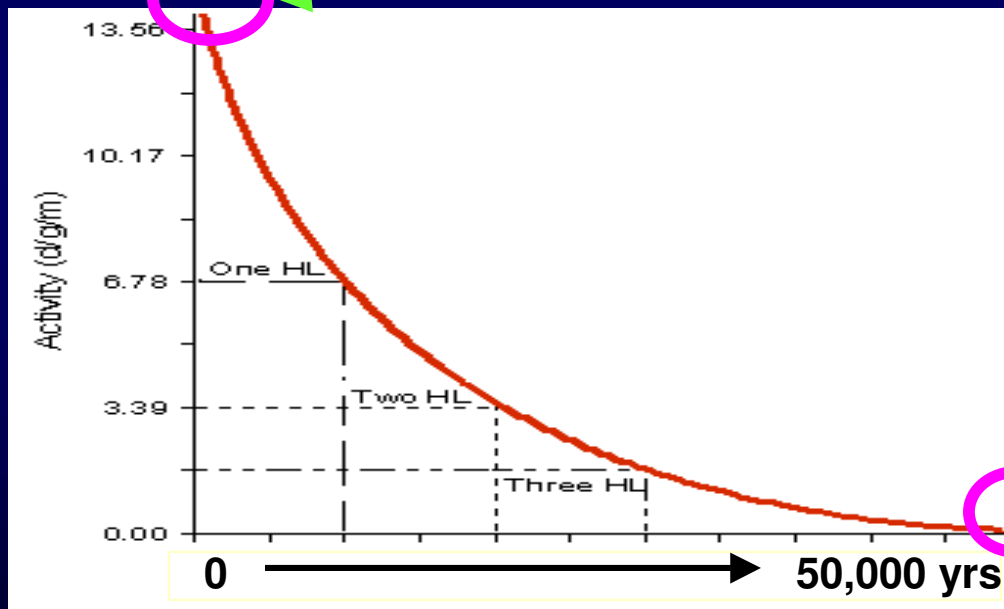
The ^{14}C Decay continues

The plants are no longer in equilibrium with the atmosphere

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



Understanding Radiocarbon Dating



Understanding Radiocarbon Dating

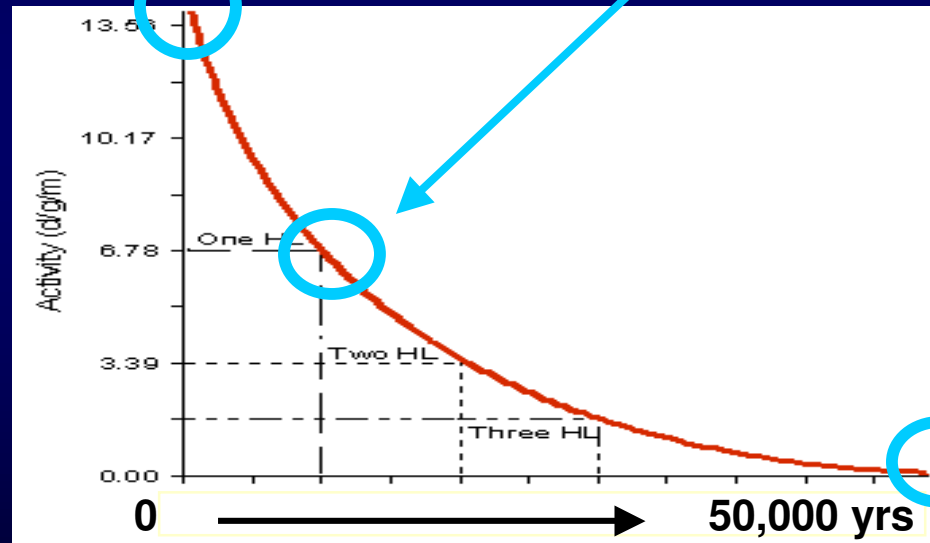
Food comes from nature. Why not the container?

Perimeter departments like deli, bakery, meats and produce are the heart of your brand's differentiation. **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



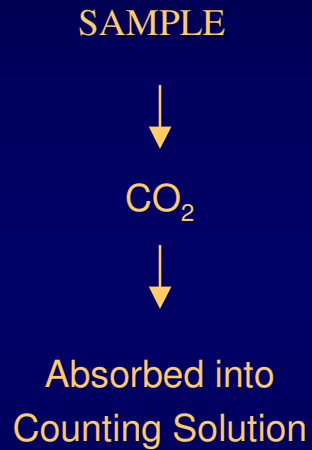
Topics

- Methods : ASTM D6866-04a

Radiocarbon Methods : ASTM D6866-04a

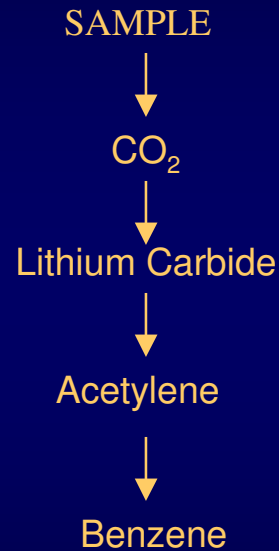
Method A
CO₂ Absorption

Routine by the 1970s



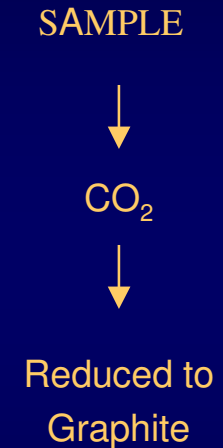
Method C
Benzene Synthesis

Routine by 1960s



Method B
AMS
(Accelerator Mass Spectroscopy)

Routine by the 1980s



Increasing cost of analysis, Increasing price to manufacturer

LSC → \$25,000

AMS → \$1.5 - 3 million



ADVANTAGES

DISADVANTAGES

CO₂ ABSORPTION

Low cost chemistry lab
Standard LSC detection
Rapid Through-put

Very low precision (+/- 10 %)
High carbon content requirement

BENZENE

Good precision (<= 2% absolute)
Standard LSC detection
Rapid Through-put

High chemical overhead

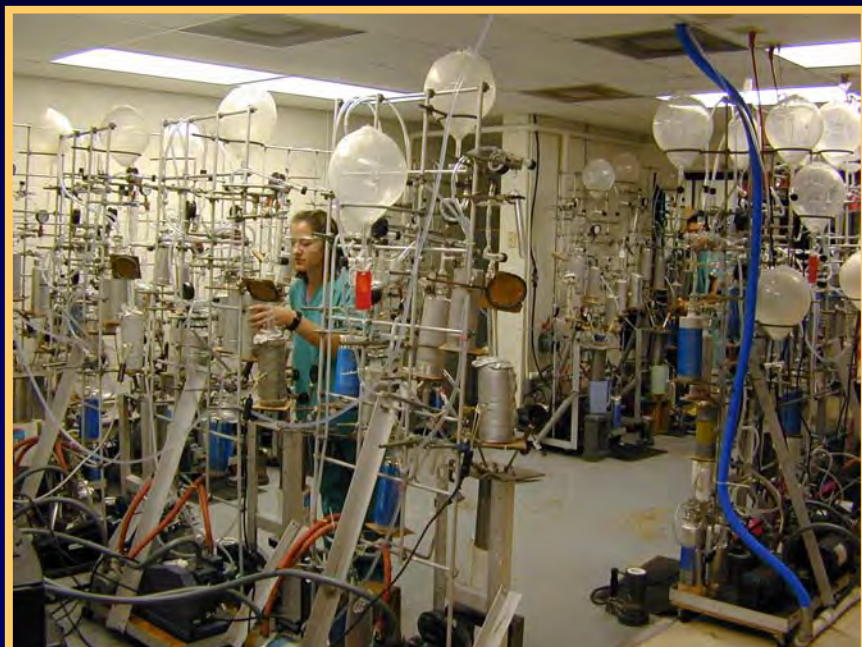
AMS

Good precision (<= 2% absolute)
Very small sample requirements

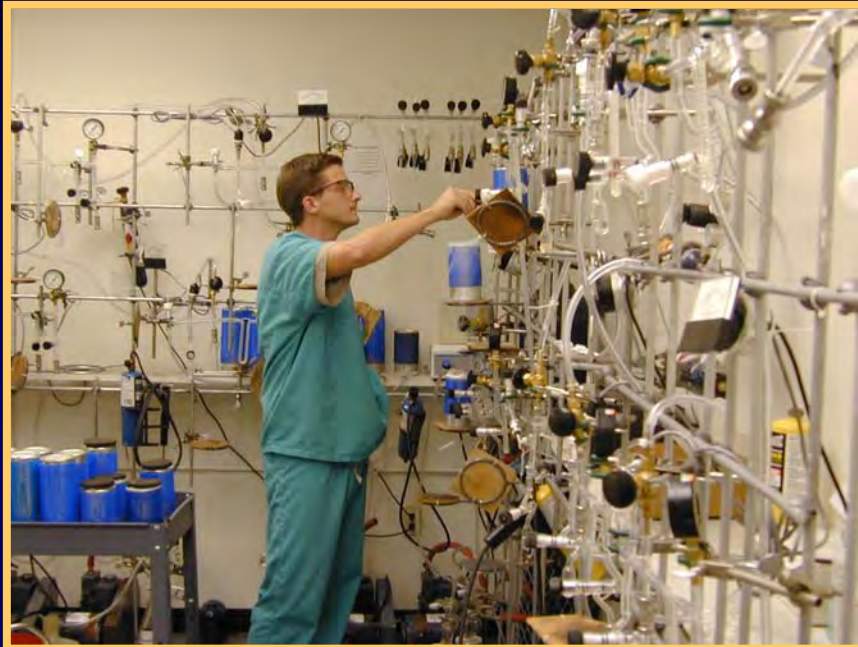
High detector overhead



CO₂ and BENZENE LABORATORIES



AMS LABORATORY

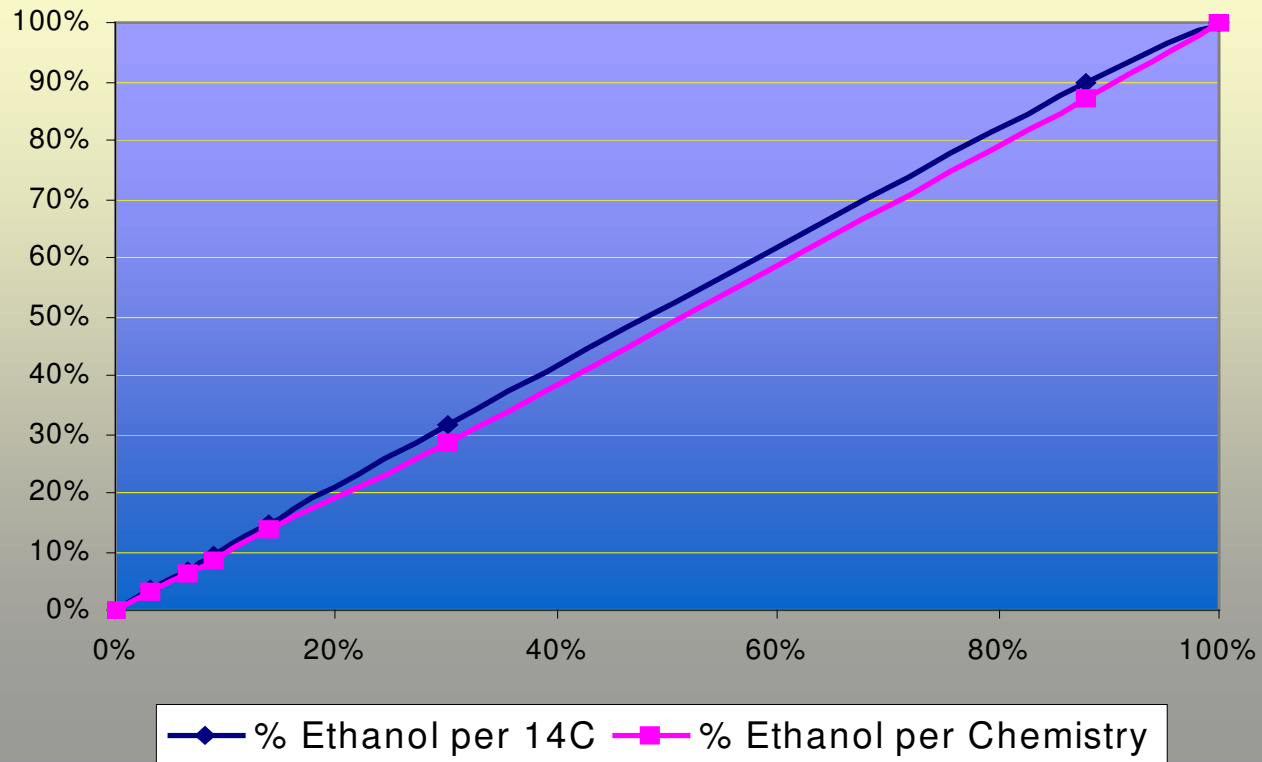


Topics

- Accuracy & Precision

Accuracy & Precision

**A Test of Accuracy - Known Ethanol Concentrations in Heptane
verified by Radiocarbon Dating**



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

Reporting

Simple Visual Report

Easy Inter-comparison

Instinctively Obvious

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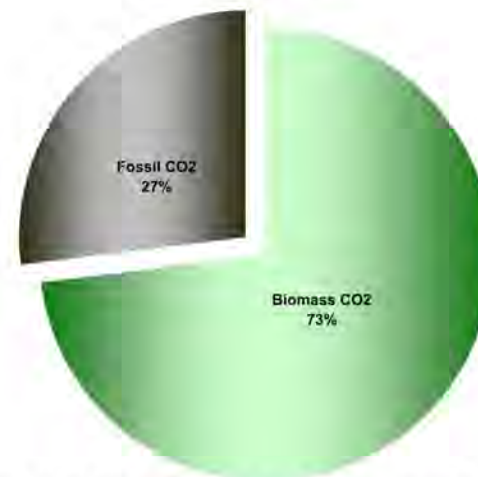
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Report of Biomass CO₂ Content Analysis using ASTM-D6866

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

Biomass CO₂: **73% ***
(carbon-neutral CO₂) (renewable carbon to total carbon)

Proportions Biomass CO₂ vs. Fossil CO₂
indicated by C14 content



* 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 50,000 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.

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Biobased Content Analysis using Radiocarbon Dating

Topics

- Working Examples : Surprises

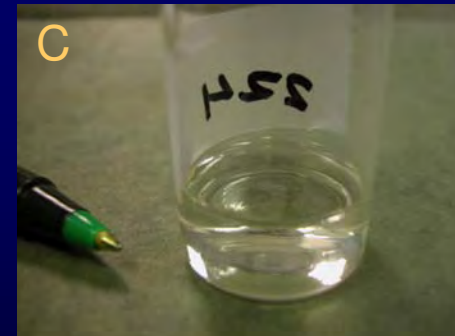
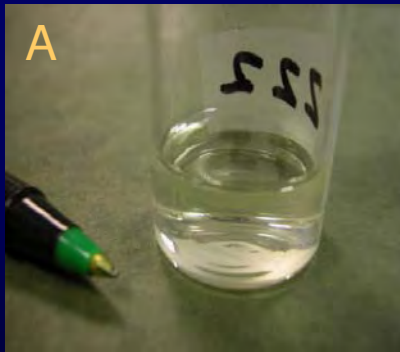
Working Examples : Surprises

The manufacturer submitted 3 samples

Radiocarbon Dating Results were . . .

Product A	→	69 % Biobased
Product B	→	78 % Biobased
Product C	→	70 % Biobased

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.

Working Examples : Surprises

The manufacturer submitted 2 samples

Radiocarbon Dating Results were . . .

Product A	→	96 % Biobased	(19% difference)
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>

