Bio-base Product Determination by ASTM Method 6866-08 Using Liquid Scintillation Counting and Benzene Synthesis: Progress and Performance in an Expanding Market.

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Outline:

- Mandate for Bio-based products and testing
- Bio-based product Research
- Challenges since 2005
- Liquid Scintillation Counting: Bio-based product methodology and performance
- Comparison: LSC and AMS for heterogeneous sample types
- Summary
- Market trends and future research

- Mandate for Bio-based products and testing
  - 2002 U.S. Farm Security Act authorizes Federal Biobased Preferred Products Procurement Program (FB4P) – rather than petroleum based products.
  - 2005 U.S. Dept. of Agriculture published guidelines for identifying and evaluating bio-based products.
  - ~2008 European Committee for Standardization (CEN) develops standards for bio-plastics, bio-polymers and bio-lubricants.

Bio-based Products Research

2000, Currie, Klinedinst, Burch, Feltham and Dorsch, **Authentication and dating of biomass components of industrial materials; links to sustainable technology**. Nucl. Instr. and Meth. in Phys. Res. B 172, 281-287.

2005, Noakes, Norton, Culp, Nigam and Dvoracek, **A comparison of analytical methods for the certification of biobased products**. In: *LSC* 2005, Advances in Liquid Scintillation Spectrometry 259-271.

2005, Norton and Devlin, **Determining the modern carbon content of biobased products using radiocarbon analysis**. Bioresources Tech.

2006, Dijs, van der Windt, Kaihola and van der Borg, **Quantitative Determination by 14C analysis of the biological component in fuels.** Radiocarbon, Vol 48, Nr 3, 315-323.

2006, American Society for Testing and Materials (ASTM), **Standard test methods for determining the biobased content of natural range materials using radiocarbon and isotope ratio mass spectrometry analysis.** (Method D6866-06).

2008, Edler, **The use of liquid scintillation counting technology for the determination of biogenic materials**. In: *LSC* 2008, Advances in Liquid Scintillation Spectrometry 261-267.

2008, Culp and Noakes, **Evaluation of biobased content ASTM method 6866-06A: Improvements revealed by liquid scintillation counting, accelerator mass spectrometry, and stable isotopes for products containing inorganic carbon.** In: *LSC* 2008, Advances in Liquid Scintillation Spectrometry 269-278.

2008, American Society for Testing and Materials (ASTM), **Standard practice for collection of integrated samples for the speciation of biomass (biogenic) and fossil-derived carbon dioxide emitted from stationary emissions sources**. (Method D7459-08).

Challenges since 2005

- Low carbon content:
  Spray cleaners, sealants & carpet - addressed with AMS technique

- Dilution with water or alcoholic solution:
  Various cleaning solutions, lubricants - requires two-step combustion.

- Inorganic carbon (Calcium carbonate) exclusion:
  Paints, dyes, ceiling tile - requires expensive two-step AMS analysis

- Decreasing atmospheric ^{14}C activity level:
  Uptake by photosynthesizing Bio-base plants

- Sample heterogeneity:
  Advantageous to use gram size quantities and LSC

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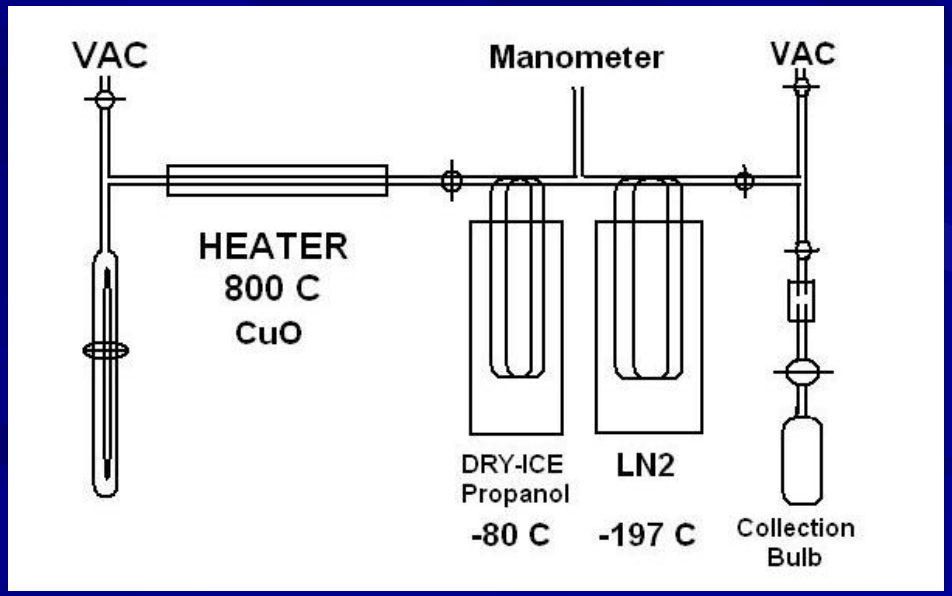

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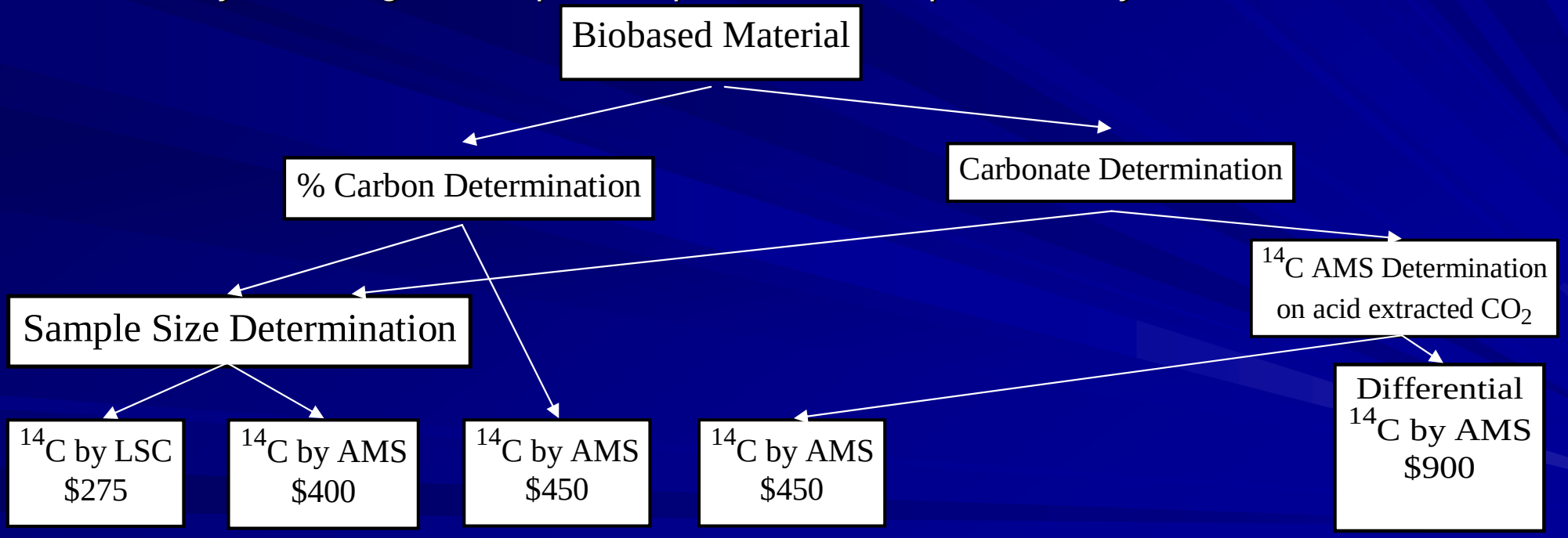


BioPreferred Designated Items – January 2010

	Min. Biobased Content
Construction and Industrial	
Carpets	7%
Chain and Cable Lubricants	77%
Composite Panels:	
Acoustical	37%
Interior Panels	55%
Plastic Lumber	23%
Structural Interior Panels	89%
Structural Wall Panels	94%
Concrete and Asphalt Release Fluids	87%
Forming Lubricants	68%
Fluid-Filled Transformers:	
Synthetic Ester-Based	66%
Vegetable Oil-Based	95%
Hydraulic Fluids:	
Mobile Equipment	44%
Stationary Equipment	44%
Industrial Cleaners	41%
Metalworking Fluids:	
General Purpose Soluble, Semi-Synthetic, and Synthetic Oils	57%
High Performance Soluble, Semi-Synthetic, and Synthetic Oils	40%
Straight Oils	66%
Parts Wash Solutions	65%
Plastic Insulating Foam for Residential and Commercial Construction	7%
Roof Coatings	20%
Water Tank Coatings	59%
Wood and Concrete Sealers:	
Membrane Concrete Sealers	11%
Penetrating Liquids	79%
Miscellaneous	
Bedding, Bed Linens, and Towels	12%
Firearm Lubricants	49%
Hand Cleaners	64%
Hand Sanitizers	73%
Lip Care Products	82%
Films: Non-Durable	85%
Semi-Durable	45%

	Min. Biobased Content
Food Service	
Disposable Containers	72%
Disposable Cutlery	48%
Food Cleaners	53%
Facility Operations and Maintenance	
2-Cycle Engine Oils	34%
Corrosion Preventatives	53%
Diesel Fuel Additives	90%
Dust Suppressants	85%
Fertilizers	71%
Gear Lubricants	58%
General Purpose De-Icers	93%
Greases:	
Food Grade	42%
Multipurpose	72%
Other	75%
Rail Track	30%
Truck	71%
Penetrating Lubricants	68%
Sorbents	89%
Janitorial	
Adhesive and Mastic Removers	58%
Bathroom and Spa Cleaners	74%
Carpet and Upholstery Cleaners:	
General Purpose	54%
Spot Removers	7%
Floor strippers	78%
General Purpose Household Cleaners	39%
Glass Cleaners	49%
Graffiti and Grease Removers	34%
Laundry Products:	
General Purpose	34%
Pretreatment/Spot Removers	46%
Multipurpose Cleaners	56%

Decreasing atmospheric ^{14}C activity level

^{14}C Pathway

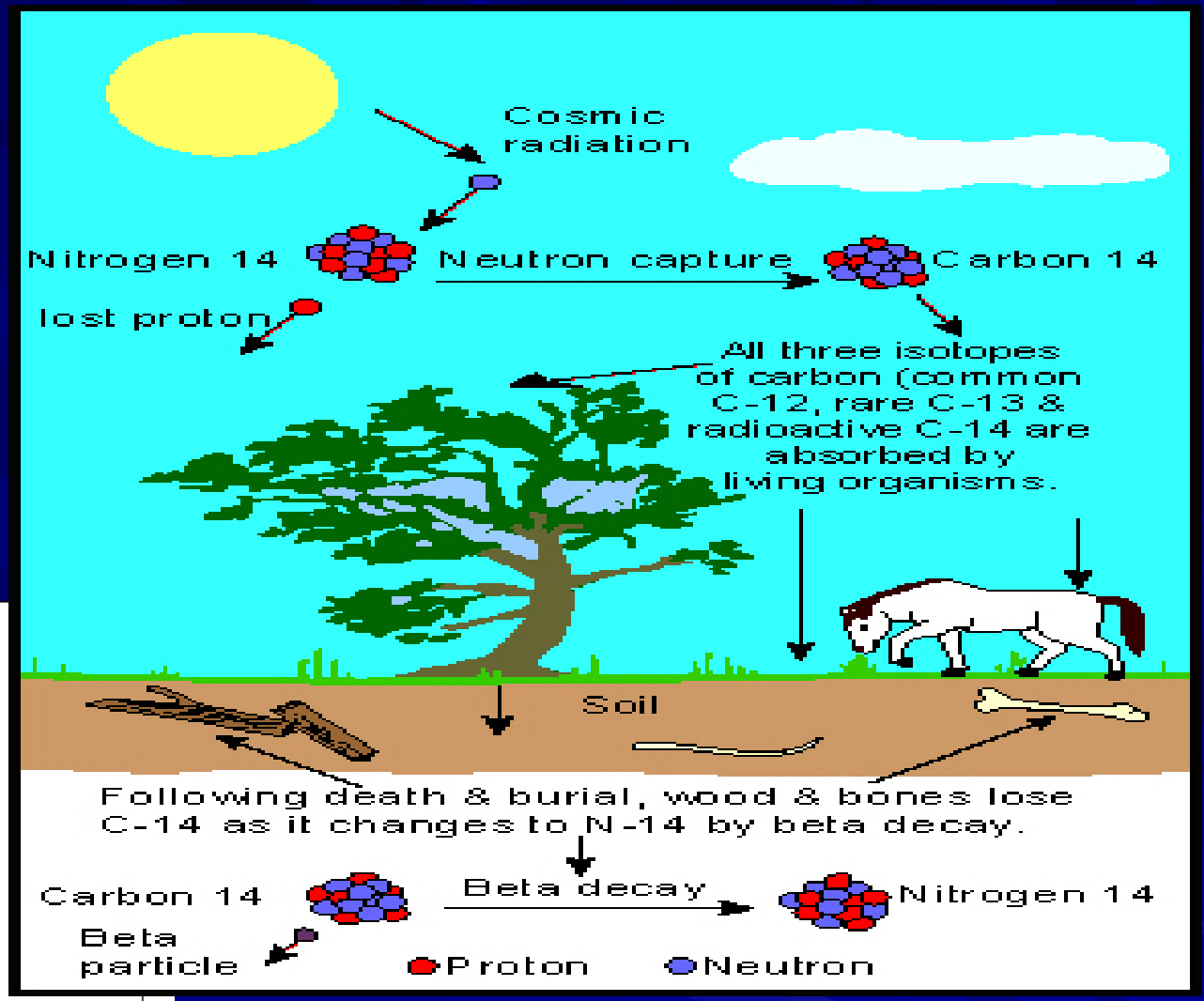
Atmospheric Bomb testing effect

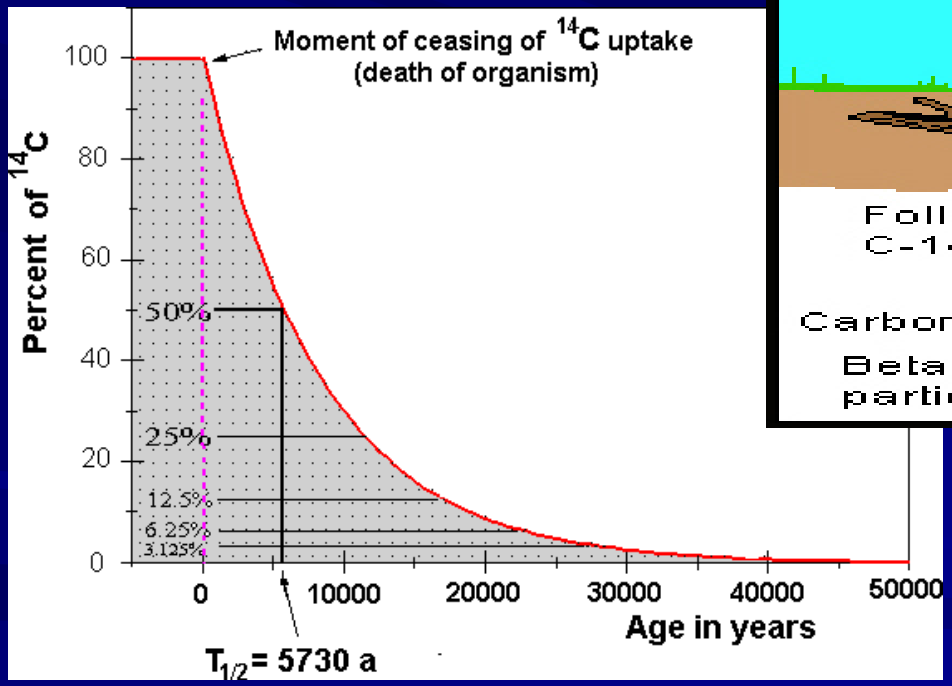
Recent decreasing ^{14}C activity level

*Modify ASTM 6866 to reflect today's ^{14}C activity

ASTM6866-10 (2010) now in use

^{14}C Pathway





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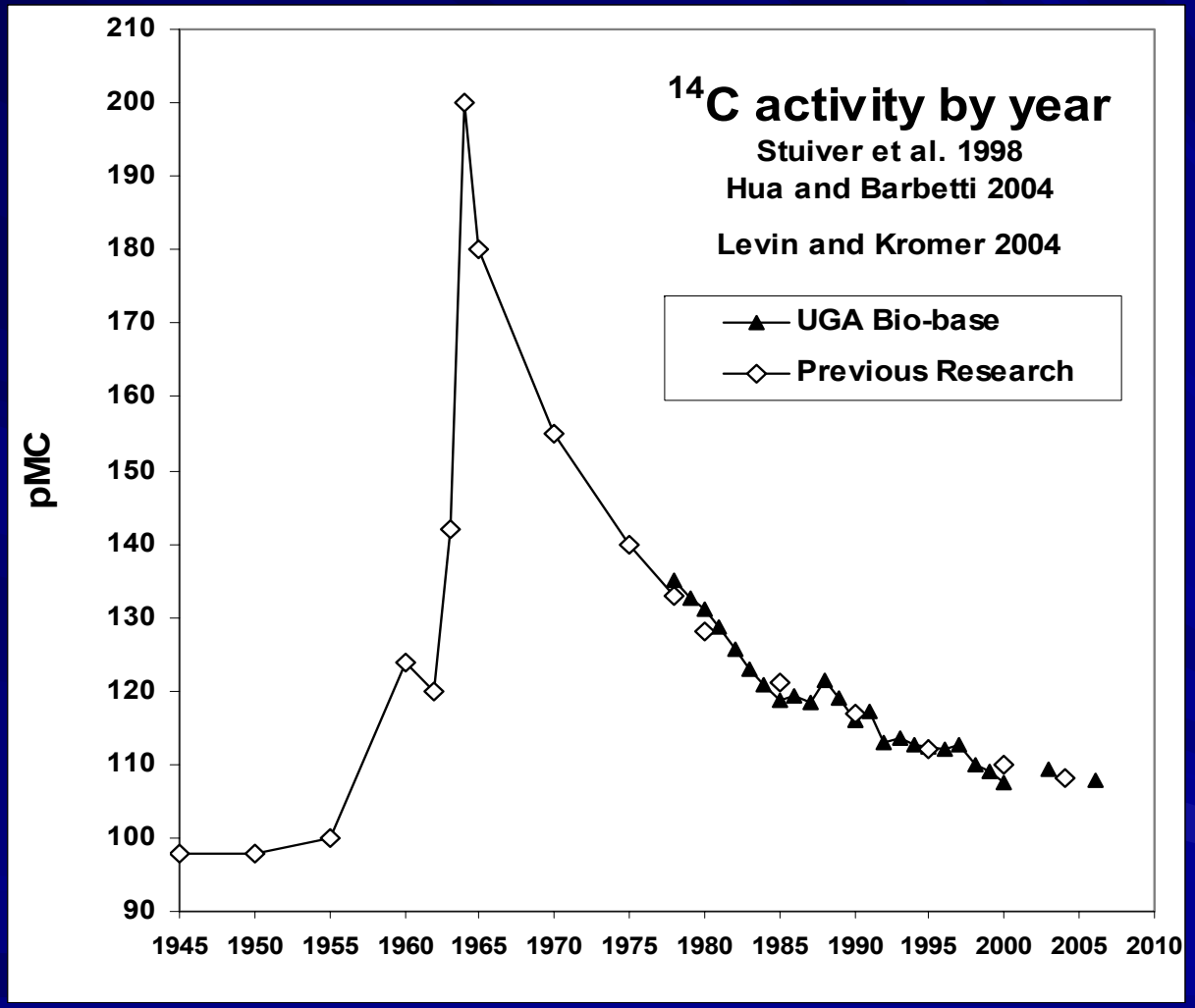
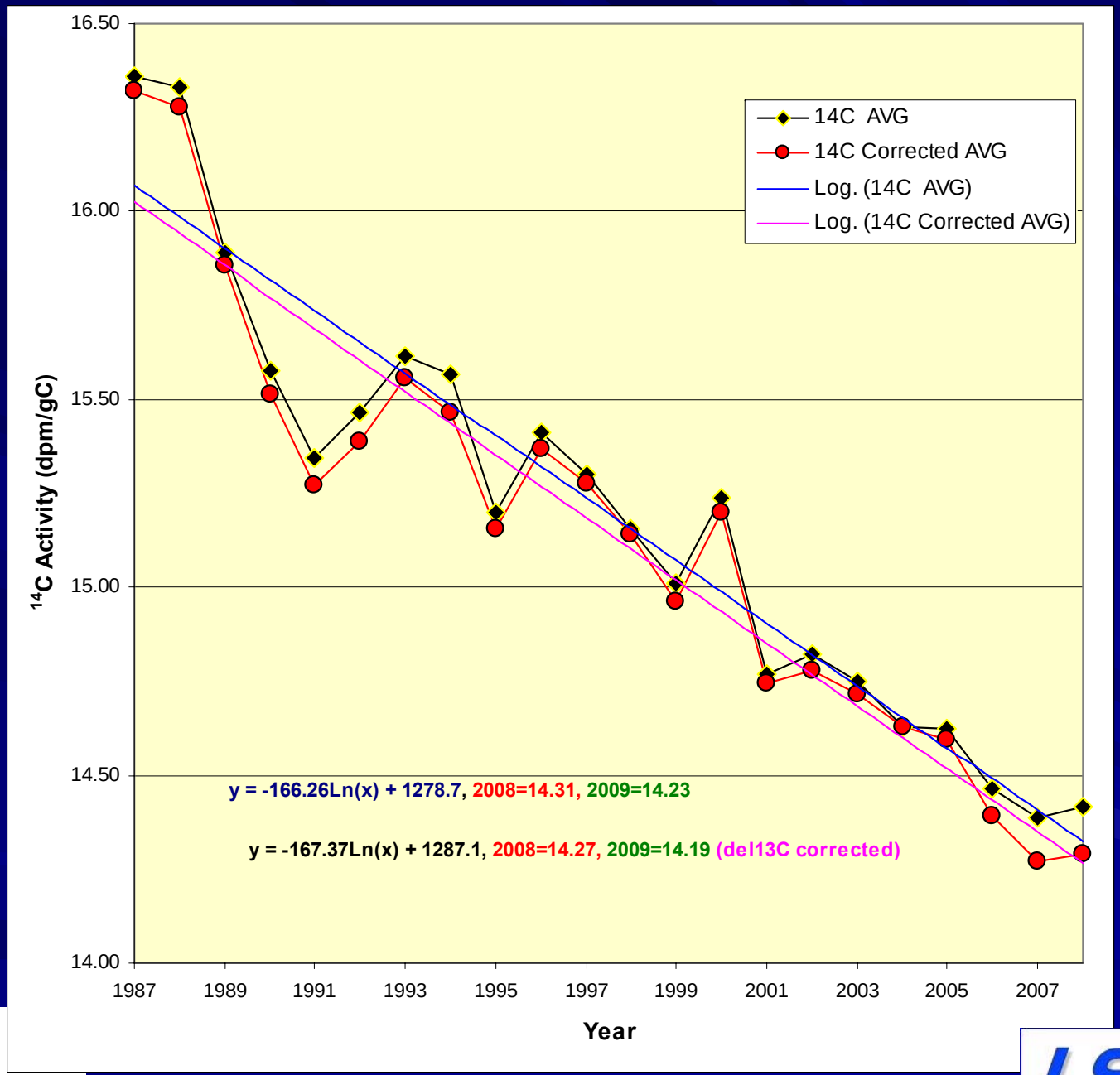
Atmospheric ^{14}C activity since 1945



Bio-based product ^{14}C activity: 1987-2007



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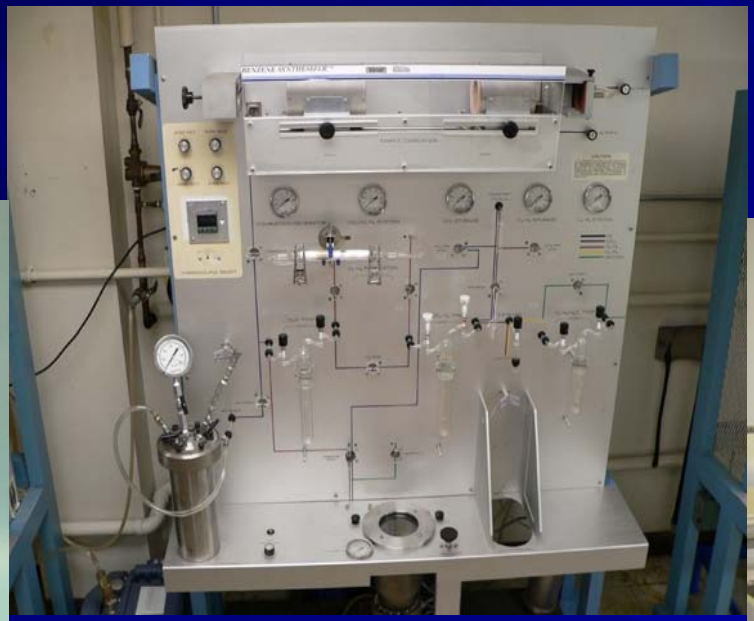
LSC Bio-based Product Methodology and Performance

- Instrumentation for Bio-base testing of heterogeneous samples
- Mass dependency tests – eleven samples
- Benzene synthesis chemistry
- Intermediate compound efficiency
- Overall yield vs Mass

BIO-BASE PRODUCT DETERMINATION ASTM 6866-08 Part C:

1. Parr Bomb Combustion
2. Benzene Synthesis
3. Liquid Scintillation Counting



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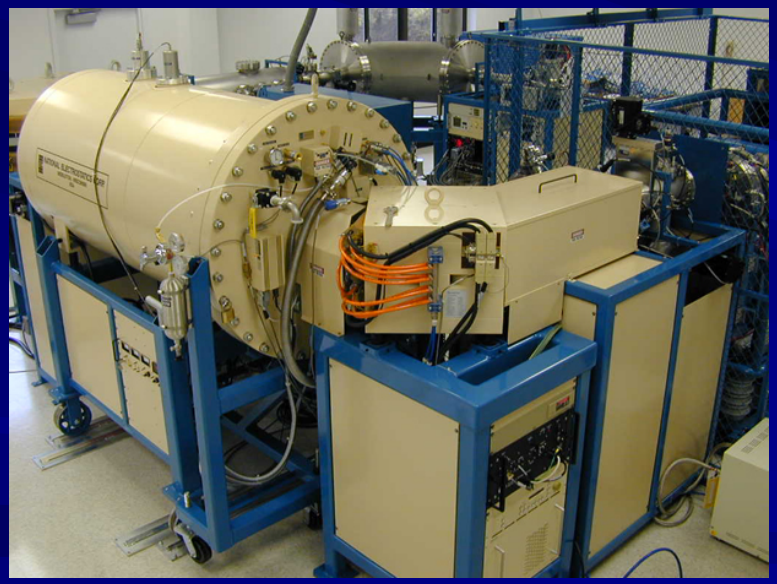
Supporting Analytical Instrumentation

For small samples <1 gram, dilute samples <10% in solution, and volatiles

Accelerator Mass Spectrometer

NEC 0.5 MeV Pelletron Tandem:

ASTM 6866-08 Part B



Stable Isotope Mass Spectrometer

Finnigan MAT 252 IRMS:

δ13C stable isotope correction

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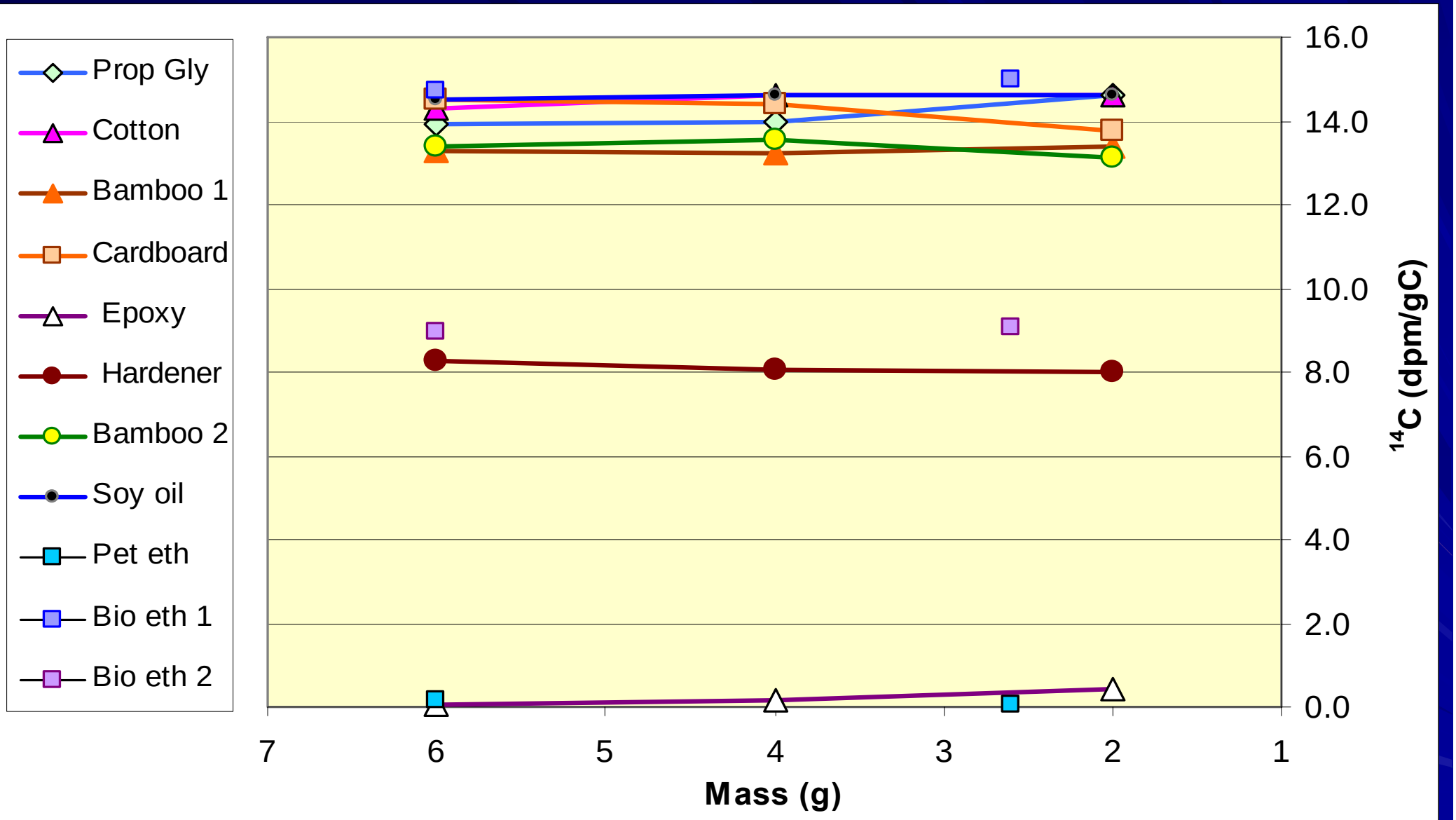
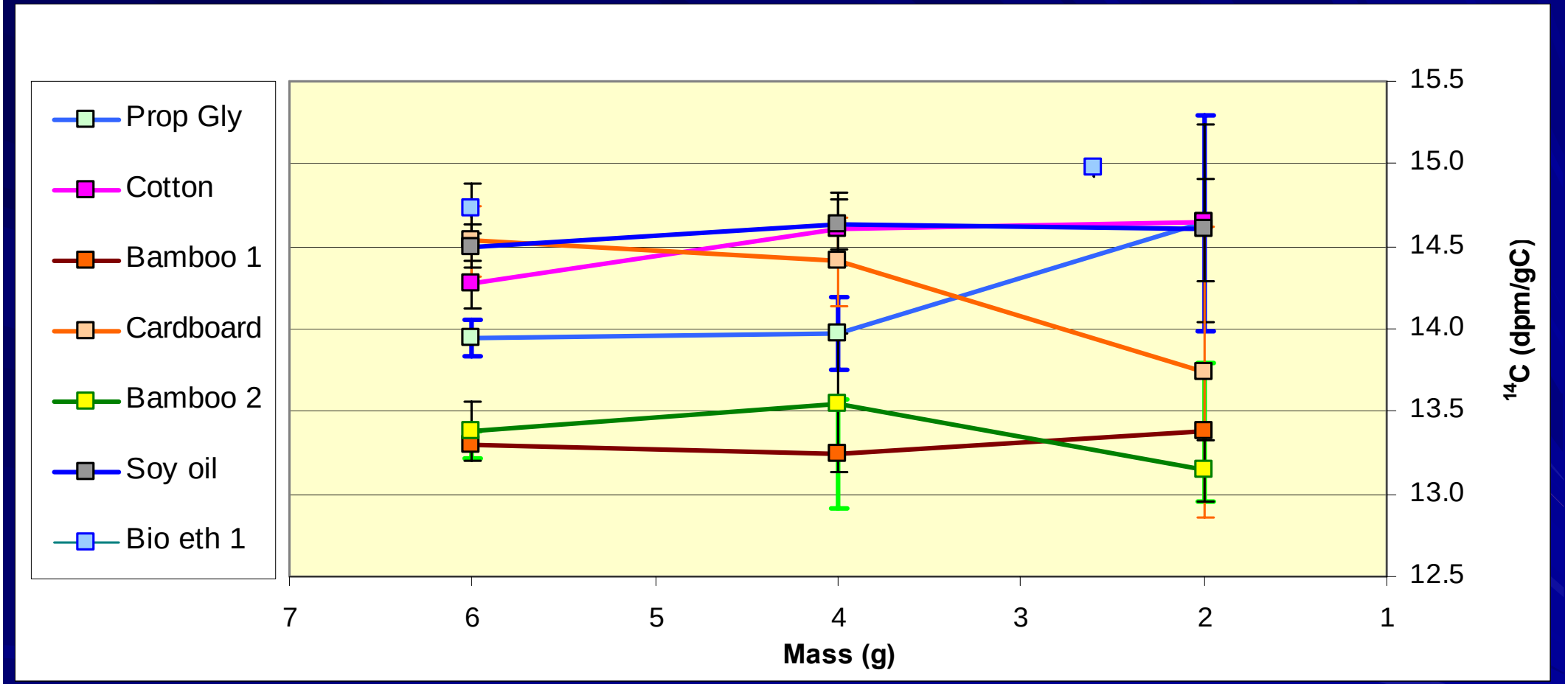
Eleven Samples: LSC ^{14}C Activity vs Mass (C)



Seven Modern Samples: LSC ^{14}C Activity (+/- 1σ) vs Mass (C)



Benzene Synthesis

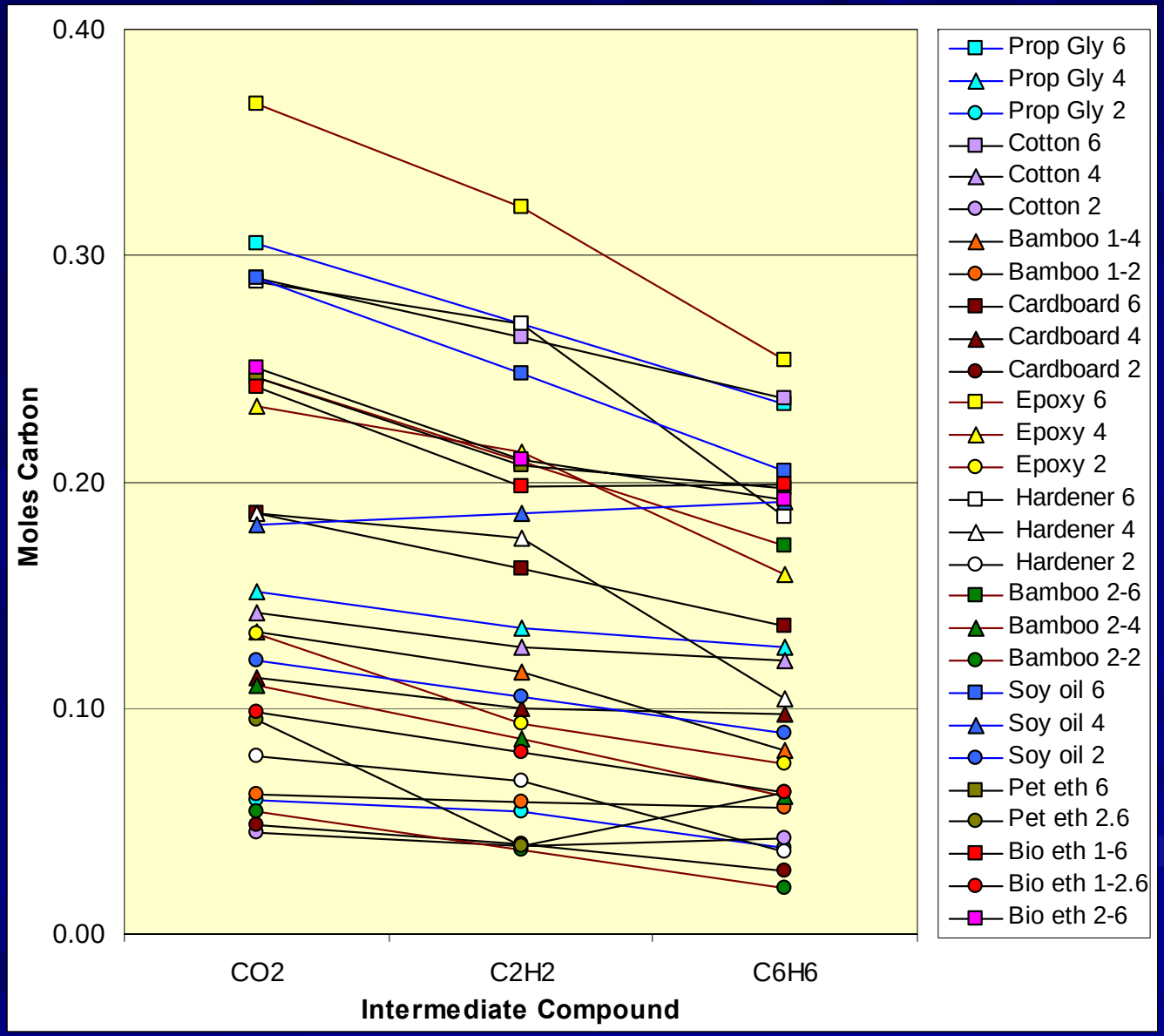
$$^{14}C_nH_{2n}O_n \xrightarrow{(\Delta,\ O_2)} n\ CO_2 + H_2O$$

$$10\ Li + 2\ CO_2 \xrightarrow{(\Delta)} Li_2C_2 + 4\ LiO$$

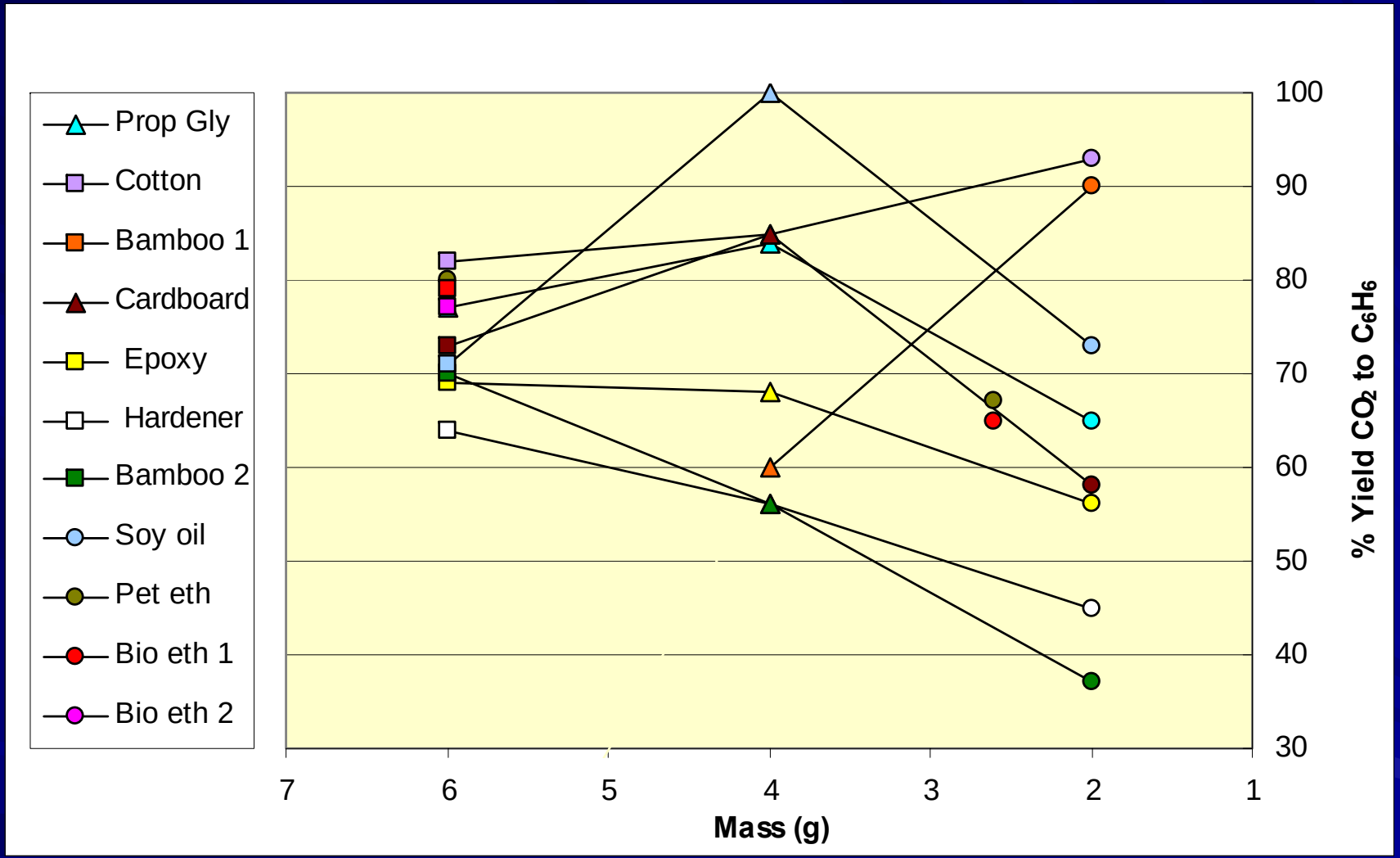
$$Li_2C_2 + 2\ H_2O \xrightarrow{(H2O)} C_2H_2 + 2\ LiOH$$

$$3\ C_2H_2 \xrightarrow[(Catalyst)]{} {}^{14}C_6H_6$$

Benzene Synthesis: Intermediate Compound Conversion Efficiency



Benzene Synthesis: Overall Yield vs Mass (C)



^{14}C Activity (+/- 1σ) LSC vs AMS

	Mass	LSC	error	AMS	error
Pro Gly	6	13.94	0.11		
	4	13.97	0.22	14.43	0.08
	2	14.64	0.65	13.82	0.10
Cotton	6	14.27	0.14		
	4	14.61	0.22	14.40	0.08
	2	14.64	0.60	14.36	0.08
Bamboo-1	6	13.30	0.08	13.30	0.08
	4	13.24	0.33	13.40	0.08
	2	13.38	0.42	13.28	0.08
Cardboard	6	14.53	0.21		
	4	14.41	0.27	14.12	0.08
	2	13.74	0.88	14.15	0.08
Bamboo-2	6	13.38	0.18	13.23	0.08
	3	13.55	0.42	13.20	0.08
	2	13.14	0.18	13.21	0.08
Soy oil	6	14.50	0.13	14.52	0.10
	4	14.63	0.15	14.49	0.08
	2	14.60	0.31	14.24	0.08
Bio eth 1	6	14.73	0.15	14.47	0.10
	3	14.98	0.35		
Hardener	6	8.25	0.12	8.50	0.06
	4	8.06	0.14	8.45	0.06
	2	8.00	0.26	8.48	0.06
Bio eth 2	6	8.96	0.13	8.88	0.08
	3	9.09	0.24		
Epoxy	6	0.05	0.11	0.04	0.02
	4	0.17	0.08	0.04	0.02
	2	0.43	0.17	0.20	0.02
Pet eth	6	0.15	0.11	0.13	0.02
	3	0.06	0.37	0.07	0.02

Summary

- LSC method exhibits uniform ^{14}C activity for wide range of masses
- ^{14}C activity independent of wide range of benzene synthesis yields
- Precision decreases with lower mass without considerable loss in accuracy
- Excellent agreement between LSC and AMS methodologies
- Wide range of capability to access Bio-base materials

Market trends and future research

- Fuel oils and lubricants
- Bio-fuels – octane enhancers
- Greases, cleaners and sealants
- Food service consumables
- Flue gas analysis for bio-base fuel apportionment (ASTM7459)
- Bio-degradable - Bio-base products

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