*AN024*

Picarro's Combustion Module-CRDS Quickly Distinguishes Between Renewable and Fossil Fuel Plastics

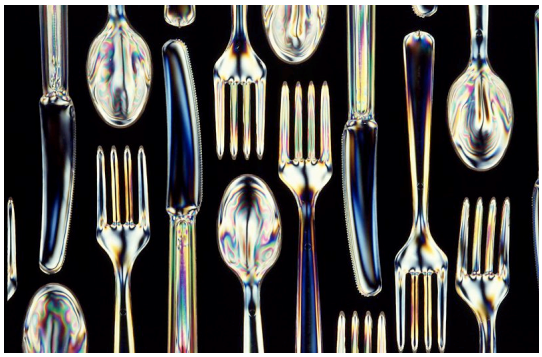
# A fast screening method for supply chain management and QA/QC


**Keywords:**

Material: Plastic, bio-plastic, renewable, plant, corn
Process: Stable isotopes, $\delta^{13}C$, CM-CRDS

**Summary and Relevance:**

Plastics derived from annually renewable (bio-based or plant-based) carbon are used in a growing variety of products – from disposable cutlery and cups to chip bags and soft drink bottle products. So-called bioplastics (bio-based plastics, organic plastics, renewable plastics) are purported to provide significant reductions in greenhouse gas emissions and energy use[1]. The market for bioplastics was estimated at 360,000 metric tons for 2007 and growing by 38% annually[2].



Current methods to test for bio-based content (ASTM D6866-08[3]) require radiocarbon ($^{14}C$) analysis through liquid scintillation counters (LSC) or accelerator mass spectrometers (AMS). LSC is generally considered a low precision tool and typically requires extensive sample prep, such as dissolving plastics in a chemical 'cocktail'. Although AMS is considered a high-precision instrument, the capital and operating costs required to run an AMS unit are prohibitive to most users. For both techniques, per sample costs ($250 - $400) are considerably higher than typical per sample costs for stable isotope analyses ($20 - $100).

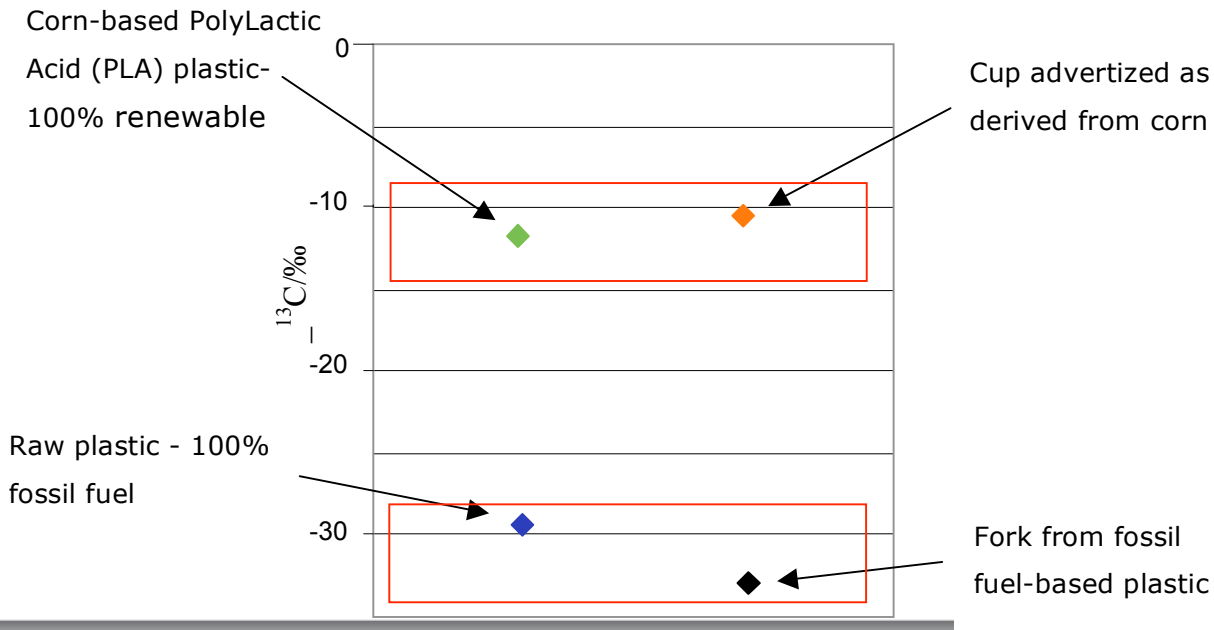
Picarro's Combustion Module-Cavity RingDown Spectroscopy (CM-CRDS) platform can be used to test for bioplastic content in raw materials and finished products such as disposable cups and forks. The CM-CRDS relies on the measurement of the stable (non-radioactive) carbon isotopes, $^{12}C$ and $^{13}C$. The measurement process is simple. Small amounts of any solid or liquid can be placed in a tin capsule and dropped into the Combustion Module. The carbon in the sample is converted to $^{12}CO_2$ and $^{13}CO_2$ which are then analyzed using Picarro's time-based, high-precision spectroscopic analyzer to provide the ratio of $^{13}C$ to $^{12}C$. This value, $\delta^{13}C$, is a measure of the plant to fossil fuel content of the carbon in the material.

**Process:**

Small shavings of commercially available bioplastic pellets and store-bought plasticware were loaded into the autosampler of the CM-CRDS system. Using $N_2$ as the carrier gas, the $CO_2$ produced by the combustion of the plastic samples was driven and collected in bellows inside the Liaison™ interface, ensuring isotopic homogeneity. From there the sample-generated $CO_2$ gas is routed into the isotopic $CO_2$ gas analyzer. The shavings were not washed, weighed or pre-treated in any other way.

**Results:**

Figure 1 below shows the $\delta^{13}C$ values obtained from two sets of samples. The first set, upper and lower left of the figure are raw plastics, purchased as 100% corn-based and 100% fossil fuel materials.



The second set of samples, to the right, represent consumer products advertized as corn-based plastic cup (top) and fork (bottom) with zero bioplastic content. From Figure 1 its very clear that the raw material and the consumer product advertised as containing bioplastic are differentiated from the raw material and products made from fossil fuel-based plastics. In addition, the difference between the two sets of values shows that mixed products containing percentages of both bio- and fossil fuel plastic can also be analyzed and measured.

**Comments:**

This study confirms that bioplastic content can be analyzed and verified using Picarro's CM-CRDS system. The differentiation is clear and the samples are easy to run, requiring no sample preparation. Additional work to analyze plastics based on other plant materials (pea, potato and other starches) will be required to map out the full carbon stable isotope measurement range. However, it is clear that this tool will be invaluable as a supply chain test as bioplastics sourcing and use continues to grow.

**References:**


1. See for example, The eco-profiles for current and near-future NatureWorks® polylactic acid (PLA) production, E.T.H. Vink, D.A. Glassner, J.J. Kolstad, R.J. Wooley, R.P. O'Connor, *Industrial Biotechnology*, **2007**, 3(1): 58-81.
2. L. Shen, Product Overview and Market Projection of Emerging Bio-Based Plastics, PRO-BIP 2009, Final Report, June 2009
3. ASTM D6866-08 Standard Test Methods for Determining the Biobased Content of Solid, Liquid, and Gaseous Samples Using Radiocarbon Analysis, American Society for Testing and Materials.


Figure 1: Carbon stable isotope ratios, $\delta^{13}C$, from raw plastic and consumer products.