

VINEGAR INDUSTRY PRODUCT INTEGRITY PROGRAM

The Vinegar Institute has been active during the past few years in the identification of analytical procedures that can be used to detect adulteration in vinegar products. The following outline will provide a basic description of the application of these analytical procedures, and the interpretation of results for evaluating various kinds of vinegars.

Carbon Stable Isotope Ratio Analysis by Mass Spectrometry

Stable isotope Ratio Analysis of Carbon (SIRA) has an established use in the food industry for adulteration detection, and is being applied to maple syrups, honey, vanilla, soy and animal protein and fruit juices. SIRA evaluations provide information on physical properties that are not affected by processing techniques. These evaluations look at the Carbon 13 and Carbon 12 (^{13}C and ^{12}C) isotopes, which are fixed into the plant through the process of photosynthesis. Photosynthesis is accomplished by three different pathways, and each pathway will result in different Carbon isotope ratios. With the accumulation of baseline data on individual agricultural products, average SIRA values for various plant types can be derived.

The average recorded literature values for SIRA evaluations of various raw ingredients for vinegar products are indicated in Table 1. These values are reported as per mill deviations from a limestone standard or a " $\delta^{13}\text{C} \%$ " value. When a combination of raw materials is used in the manufacture of the vinegar product, the analytical results will reflect an average of the expected values for these raw materials. Consequently, a range of values may result for a particular type of vinegar. An example would be that of a white distilled vinegar with a value of -10.0 blended with an apple cider vinegar having a value of -25.0 . The blended product would have a value for $\text{C}^{13/12}$ between -10 and -25 , depending on the mixture amount.

Values for SIRA that can be used as indicators of adulteration are recorded in Table 2.

Natural Radiocarbon Activity Measurement

Petrochemically derived products are readily distinguishable from agricultural products by measurement of the ^{14}C activity of the Carbon. These analyses are being used for quality control purposes in alcoholic and carbonated beverages, flavorings, fragrances and other products. Radiocarbon measurement has been applied to vinegar products to determine whether the acetic acid in the vinegar is derived from an agricultural product or from added glacial acetic acid.

Radiocarbon (^{14}C) is an unstable isotope that declines by a predictable factor over a period of time. Agricultural products grown over the past few years will have a ^{14}C activity level that reflects levels of ^{14}C in the atmosphere during their growth.

Substances that have been dead for millions of years (i.e., petrochemically based) will have no ^{14}C activity. Any mixing of substances from these two categories can be readily determined. The natural radiocarbon activity is reported as "counts" or "disintegrations per minute" (cpm or dpm) per gram of Carbon, or as a percentage of the expected radiocarbon activity.

As indicated in Table 1, the average value for natural radiocarbon activity in the 1986 growth year is approximately 16.00 dpm/gC. Because of above ground nuclear testing, the average value for ^{14}C will be higher than 16.00 dpm for previous years, and will decline somewhat over the next few years. As yet, there are no studies to determine interlaboratory variation on ^{14}C values for vinegar products, but a range of ± 1 dpm can be expected in any one year. To account for this variation, a level of 14.5 dpm/gC (15% below the average value for radiocarbon activity) has been defined as a lower limit for adulteration detection.

TABLE 1
Average Recorded Literature Values

	SIRA	¹⁴C activity, dpm/gC (for 1986 growth year)
Corn or Corn Sugar Sources	-9.7	16.00
Sugar Cane Sources	-11.5	16.00
Sugar Beet Sources	-24.2	16.00
Wheat Sources	-25.0	16.00
Barley Sources	-25.0	16.00
Apple Sources	-25.4	16.00
Rice Sources	-26.0	16.00
Grape Sources	-26.8	16.00
Sulfite Liquor Alcohols	(a)	16.00
Petrochemical Alcohols	-25.0 to -40.0	0.00
Acetic Acid	(b)	0.00

(a) Insufficient database to determine average values.

(b) Insufficient database to determine average values.

TABLE 2
Expected Results for Vinegar Products

	SIRA	¹⁴C activity, dpm/gC
Apple Cider Vinegar	-22.0 to -27.5	14.5 or higher
Wine Vinegar	*	14.5 or higher
Malt Vinegar	*	14.5 or higher
Corn Sugar Vinegar	-9.0 to -10.5	14.5 or higher
White Distilled Vinegar	*	*
Rice/Rice Wine Vinegar	-22.0 to -28.0	14.5 or higher

*Results of testing may vary significantly because of raw components permitted in manufacturing this vinegar. This analysis should not be used as an indication of adulteration, but can be helpful in identifying actual ingredients or ingredient blends.