

¹⁴C IN AUSTRIAN WINE AND VINEGAR

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ABSTRACT. I analyzed wine from the vicinity of Vienna for ¹⁴C and ³H, using an ultra-low-level liquid scintillation counter. A series of certified samples from 1955 to 1987 was used to establish a calibration curve, which was applied successfully to a sample of apricot brandy. I used a simple extraction method to isolate acetic acid from vinegar, which I measured directly after mixture with a scintillation cocktail. A sample labeled as manufactured from wine contained too high a concentration of ¹⁴C, and thus may have been adulterated. Analytical- and technical-grade acetic acid also showed different concentrations of ¹⁴C, although it is unlikely that they are produced from organic material.

INTRODUCTION

Large amounts of ¹⁴C and ³H were released during atmospheric nuclear tests in the 1950s and 1960s. Since the test moratorium, concentrations of both radionuclides have declined characteristically. Both radionuclides are assimilated into plant material. Fermentation of carbohydrates in grapes yields alcohol; thus, the concentration of ¹⁴C and ³H in alcohol reflects the concentration in the atmosphere. ¹⁴C and ³H determinations can provide information about the natural origin of many substances, including alcohol and vinegar, which can be used to determine the age of alcoholic beverages of a certain vintage. The aim of this study was to establish reliable calibration curves for alcoholic beverages and to investigate the possibility of measuring ¹⁴C in acetic acid isolated from vinegar.

METHODOLOGY

For this study, I used two ultra-low-level liquid scintillation Quantulus counters. Superior counting performance can be achieved with these instruments, as active and heavy passive shielding result in very low background. The counting system allows for a very low detection limit and shorter measurement times to enhance sample throughput.

Schönhöfer (1989) described the sample preparation procedure and the optimization of counting conditions for analysis of ¹⁴C and ³H from alcoholic beverages. For ¹⁴C determinations, ethanol from wine is concentrated in a two-step distillation procedure to about 90% (volume). I mixed 10 ml of this ethanol with 10 ml of cocktail (Quickszint 400) in a PET- or PTFE-lined polyethylene vial. Background is determined using ¹⁴C-free ethanol of the same concentration. I determined counting efficiency for all samples using an internal standard of n-hexadecane in absolute ethanol. For ³H measurements, pure water is distilled from the residue of the ethanol distillation, and ³H is determined by mixing 8 ml of this water with 12 ml of Quickszint 400 in a PTFE-lined polyethylene vial.

For ¹⁴C measurements in vinegar, acetic acid was isolated by continuous extraction with di-isopropyl ether and subsequent distillation (Schmid, Fogy & Kenndler 1977). Concentrated acetic acid was used as such. Measurement conditions were optimized for miscibility, efficiency and background; 4 ml of the sample were mixed with 6 ml Quickszint 400 in a PTFE-lined polyethylene vial. Efficiency was determined by adding an internal standard of n-hexadecane. Background was 0.65 cpm in the optimized window, efficiency was 47%, and the figure of merit was 3405. For 1000-min measuring time, the 3 σ error was <1%.

RESULTS FOR ¹⁴C AND ³H IN WINE

Schönhöfer (1989) already discussed some factors influencing the concentration of ¹⁴C and ³H in

wine. For this study, I obtained wine samples from HBLVA Klosterneuburg, a school for viticulture near Vienna; the samples were cultivated in the same small area and were guaranteed to be from a single harvest year, over the range 1955–1987.

Figure 1 shows ¹⁴C results for these samples; Figure 2 shows ³H results. All values represent at least triplicate analyses; in all cases, measurement time was 500 min. 3 σ error bars are presented.

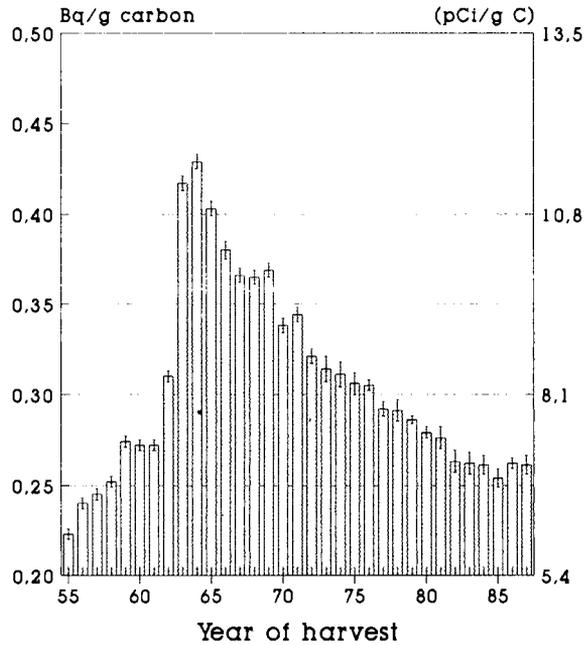


Fig. 1. ¹⁴C in wine. HBLVA Klosterneuburg

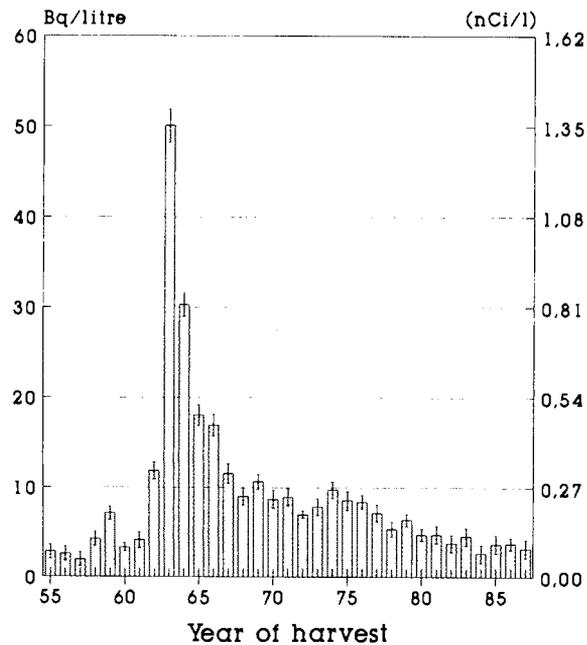


Fig. 2. ³H in wine. HBLVA Klosterneuburg

These data sets show a much smoother trend than previous data (Schönhofer 1989). One reason might be that initial measurements were made on commercial samples; another might be that our current use of an internal standard allowed for a more precise efficiency determination than parallel standards run with approximately equal ethanol concentrations.

I observed no significant ^{14}C and ^3H differences between wines produced from different grape varieties of the same year, nor between red and white wines.

The calibration curve was successfully tested on a sample of apricot brandy. The year of distillation was unknown to the analyst, but was known to have been produced from a single harvest year. In principle, the possibility of different ^{14}C concentrations in the brandy might be explained by different assimilation of apricots. Thus, based on measured ^{14}C and ^3H concentration, I cautiously assigned a range of 1962–1965; the brandy sample was actually distilled in 1963. Figures 1 and 2 show that relatively precise age determinations can be made over the range 1955–1975; after 1975, smaller annual ^{14}C and ^3H differences preclude age determination more precise than 5–7 yr.

RESULTS FOR ^{14}C IN VINEGAR

For ^{14}C determination in acetic acid, a background sample containing ^{14}C -free acetic acid was required. Several samples of analytical- and technical-grade acetic acid were tested for use as background, because it was likely that they were produced from petroleum hydrocarbons. At first, I found no sample free of ^{14}C , perhaps because ^{14}C -labeled acetic acid had been added. Finally, "Riedel-deHaen" acetic acid proved to be ^{14}C -free, and was used for background determination.

Figure 3 summarizes the ^{14}C concentrations in different acetic acid samples. L1, L2 and D were isolated from vinegars labeled as produced by fermentation from wine; "Merck" was analytical-grade acetic acid; "Neuber" and "Techn" were technical-grade acetic acid; "Lenzing" was produced from wood. "Old" acetic acid was produced long before atmospheric nuclear testing (it was found in a chemical institute; label and bottle shape indicated production long before World War II). All samples were measured in triplicate; error bars represent 3σ .

The "Old" sample reflects the natural concentration of ^{14}C before nuclear weapons testing. L1 and L2 results correspond to the ^{14}C concentration in wine of recent years. Thus, I concluded that these

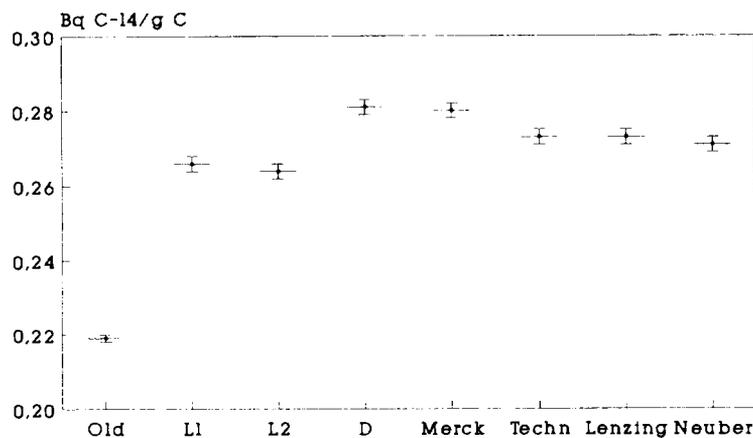


Fig. 3. ^{14}C in acetic acid

± 3 sigma error

vinegars probably originated from wine, although other fruit sources cannot be excluded. "Neuber" and "Techn" technical-grade acetic acids have a ¹⁴C concentration similar to that of "Lenzing" wood-derived acetic acid, approximately 0.27 Bq g⁻¹ C, suggesting that the two technical-grade acetic acids may have derived from wood. This activity corresponds to the 1980 level (Fig. 1), indicating that 10-yr old trees may have been used to manufacture these technical-grade acetic acids. On the other hand, ¹⁴C concentration of ethanol produced from wood in 1988 was 0.30 Bq g⁻¹ C, suggesting the use of 15–20-yr-old wood in its manufacture. This is difficult to verify, as the factory closed recently. Artificial labeling also cannot be excluded.

The "Merck" sample shows an even higher concentration of ¹⁴C, although it seems unlikely that analytical-grade acetic acid is produced from wood.

The D sample, labeled as originating from wine, has a ¹⁴C concentration higher than in samples L1, L2 and contemporary wine, indicating that it was not produced from wine. Its activity corresponds to 1980 wine. Normally, wine would not be kept for 10 years to produce vinegar, nor would vinegar be kept for 10 years until sold. Both possibilities would have resulted in a high price – but this D-sample vinegar had a suspiciously low price. Acetic acid derived from relatively old wood may have been used to produce the D sample; a more likely possibility is dilution of analytical-grade acetic acid, labeled artificially with ¹⁴C. Earlier comparative studies of ¹⁴C and ³H concentrations and ¹³C/¹²C ratios showed that ¹⁴C concentration in a sample of analytical-grade acetic acid corresponded to the biogenic concentration; ³H concentration did not. The ¹³C/¹²C ratio indicated a non-biogenic origin for this analytical-grade acetic acid (Schmid 1977, 1978a,b).

CONCLUSIONS

Ethanol and acetic acid can be measured directly and precisely in an ultra-low-level liquid scintillation counter, thus avoiding expensive, time-consuming chemical preparations such as benzene synthesis.

Measurements of ¹⁴C and ³H concentration allow age determination of wine and other alcoholic beverages from approximately the last 35 years. False labeling may also be detected from these analyses. ¹⁴C analysis of vinegar may verify its origin and may uncover adulterations.

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