



## Forensic applications of $^{14}\text{C}$ bomb-pulse dating

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### Abstract

After a brief review of the basics of  $^{14}\text{C}$  bomb-pulse dating, this paper presents two unique forensic applications. Particular attention is dedicated to the use of the  $^{14}\text{C}$  bomb-pulse to establish the time of harvest of illicit drugs such as heroin and opium. Preliminary measurements of  $^{14}\text{C}$  concentrations in milligram samples taken from seized drugs are presented.  $^{14}\text{C}$  bomb-pulse dating can determine whether drug distribution originates from stockpiles or recent manufacture, and support the action of law enforcement authorities against criminal organisations involved in drug trafficking. In addition, we describe the dating of wine vintages for a number of authenticated single label vintage red wines from the Barossa Valley – South Australia. Our results show that radiocarbon dating can be used to accurately determine wine vintages and therefore reveal the addition of unrelated materials of natural and synthetic origin.

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### 1. Introduction

More than 50 years ago, humanity entered the nuclear era. This was a turning point in the history of the 20th century. One of the consequences of the atmospheric nuclear weapon tests during the 1950s and early 1960s was the abundant production of anthropogenic radionuclides such as  $^{14}\text{C}$ . In the Northern Hemisphere, the 1963–1964 atmospheric  $^{14}\text{C}$  concentration reached a level nearly 100%

higher than the pre-bomb level. Since the Nuclear Test Ban Treaty came into effect in 1963, the  $^{14}\text{C}$  concentration has been decreasing due to the exchange with the biosphere and the oceans (with minor perturbations due to sporadic nuclear tests). Presently, the  $^{14}\text{C}$  level has declined to about 10% greater than the pre-bomb level. The shape and intensity of this *bomb-pulse* has been determined by measuring  $^{14}\text{C}$  in atmospheric  $\text{CO}_2$  [1,2] and tree rings [3]. This well-determined temporal change of  $^{14}\text{C}$  provides a clock for dating biological materials formed after 1955 AD, and leads to interesting forensic applications [4].

The use of accelerator mass spectrometry (AMS) extends the applicability of the  $^{14}\text{C}$

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bomb-pulse method, allowing the analysis of  $^{14}\text{C}$  in sub-milligram organic samples. Specific molecular compounds extracted from bones, hair, skin and other carbon bearing substances of forensic significance can now be dated, enhancing the sensitivity and reliability of chronological determinations.

## 2. The authentication of wine vintages

The authentication of Australian wine vintages and the detection of unauthorised additives and wine ‘forgeries’ are of major importance to the industry. In Europe, methods such as site specific isotope fractionation [5] and carbon dating [6] have been used to distinguish the addition of materials of natural and synthetic origin to foods and wines. However, these studies have not considered the usefulness of the non-alcoholic components in age or authenticity determination. Although the amount of top-up permitted by legislation is small, the measurement of the radiocarbon concentration in a single component does not necessarily provide unequivocal proof of vintage. For this reason, the unambiguous determination of a wine vintage requires the measurement of the ages of a range of wine components, the greater the number, the greater the degree of certainty.

Candidate compounds for age determination include those components of higher concentration such as ethanol and tartaric acid. Other candidates include various phenolic components naturally present in the grape and succinic acid and glycerol produced as a yeast-derived fermentation products of glucose. Fig. 1 shows the scheme that has been used to isolate these different components for carbon dating. It is noted that further separation and purification of individual compounds within each of these fractions can be carried out using different types of chromatography. Legitimate additions of grape juice concentrate and tartaric acid may distort the vintage arrived at if the age of only ethanol or tartaric acid were used. Similarly, the phenolic components of the wine may originate not only from the grapes, but also from oak treatments and from the introduction of oenotannins. For this reason a fractionation process, based on the method of Oszmianski et al. [7] has been used to isolate different types of phenolic components whose ages may be individually determined. The technical aspects of these procedures have been described elsewhere [8].

For this study we measured 20 alcohol and three tannin samples extracted from a number of authenticated single label vintage red wines from the Barossa Valley (South Australia) ranging from 1958 to 1997. Usually, red wines have tannins added to them during the winemaking process.

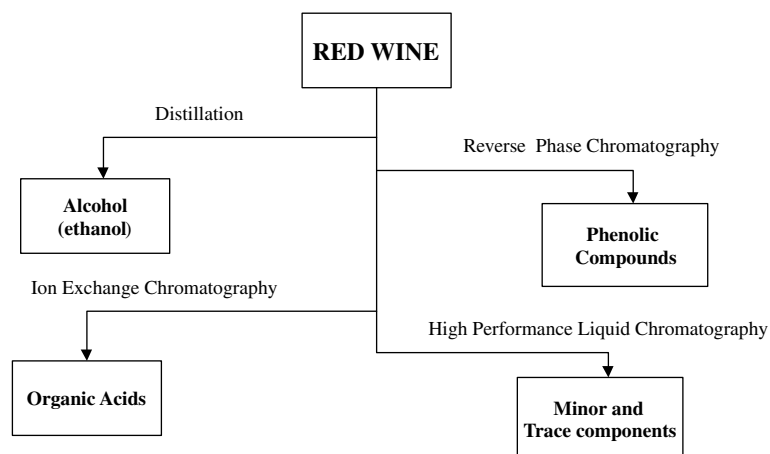


Fig. 1. Scheme for the separation of classes of compounds in red wine.

These tannins can come from the heartwood of trees or from galls and grape seeds. Furthermore, red wines can also pick up oak tannins from the barrels they are stored in. The use of older heartwood would result in a tannin  $^{14}\text{C}$  concentration corresponding to the pre-bomb-pulse period. Galls and grape seed tannins predominantly originate from the previous vintage and thus should result in a “1 year older”  $^{14}\text{C}$  concentration. For this study we selected wines that had no contact with oak and were prepared with tannins derived from galls and grapes.

All samples were measured at the ANTARES AMS facility at ANSTO [9,10].  $\Delta^{14}\text{C}$  concentrations are listed in Table 1 and plotted in Fig. 2. Calibrated age ranges were determined using the compiled Southern Hemisphere bomb curve [11] and the ‘calibrate’ calibration software [12]. In Fig.

2, the measured  $\Delta^{14}\text{C}$  concentrations are plotted at January 1st, the midpoint of the growing season in the Southern Hemisphere. The agreement between the predicted vintage year based on our measured  $^{14}\text{C}$  results and the vintage indicated on the bottle label is very good and, apart from the 1966 and one 1969 sample, is within the 1–2 sigma calibrated age error. Of particular interest is year 1969, which beleaguered the industry with the inconvenience of a particularly wet growing season and a lesser wine quality. One of the three different 1969 vintage wines shows a  $^{14}\text{C}$  calibrated age matching either the 1963–1964 or the 1974–1975 growing season. For that particular wine, the calibrated age for the tannin fraction corresponds to September 1963  $\pm$  2 months or January 1974  $\pm$  4 months, respectively. Knowing that the wine under investigation was prepared using tannins derived from galls and

Table 1  
The measured  $\Delta^{14}\text{C}$  values for alcohol and tannin samples

ANSTO code	Sample type	Year (bottle label)	$\delta^{13}\text{C}$ (‰)	$\Delta^{14}\text{C}$ (‰)	Calibrated age range
OZE722	Alcohol	1958	-24.8	69.9 $\pm$ 4.6	Feb 1958 $\pm$ 3 months
OZE725	Alcohol	1963	-28.1	248.6 $\pm$ 4.7	Sep 1962 $\pm$ 3 months
OZE727	Alcohol	1965	-28.9	609.7 $\pm$ 5.6	Jan 1965 $\pm$ 4 months
OZE715	Alcohol	1966	-24.1	575.9 $\pm$ 6.5	Jun 1964 $\pm$ 2 months Dec 1967 $\pm$ 3 months
OZE738	Alcohol	1968	-25.4	553.7 $\pm$ 6.5	Sep 1968 $\pm$ 5 months
OZG353	Tannin	1969 (1)	-28.5	424.6 $\pm$ 4.9	Sep 1963 $\pm$ 2 months Oct 1973 $\pm$ 4 months
OZE721	Alcohol	1969 (1)	-23.2	389.4 $\pm$ 6.3	Aug 1963 $\pm$ 2 months Feb 1975 $\pm$ 6 months
OZF903	Tannin	1969 (2)	-28.0	585.5 $\pm$ 5.9	Sep 1967 $\pm$ 3 months
OZF904	Alcohol	1969 (2)	-25.9	540.4 $\pm$ 6.0	Feb 1969 $\pm$ 7 months
OZF905	Tannin	1969 (3)	-27.3	574.0 $\pm$ 5.8	Jan 1968 $\pm$ 3 months
OZF906	Alcohol	1969 (3)	-25.2	530.8 $\pm$ 6.0	Jul 1969 $\pm$ 7 months
OZE735	Alcohol	1971	-24.7	491.8 $\pm$ 7.0	May 1971 $\pm$ 7 months
OZE726	Alcohol	1973	-25.5	463.2 $\pm$ 4.7	Sep 1972 $\pm$ 4 months
OZE720	Alcohol	1974	-26.1	448.3 $\pm$ 5.5	Feb 1973 $\pm$ 4 months
OZE716	Alcohol	1978	-24.7	336.8 $\pm$ 7.5	Mar 1977 $\pm$ 9 months
OZE730	Alcohol	1980	-28.1	300.8 $\pm$ 4.6	Apr 1979 $\pm$ 5 months
OZE728	Alcohol	1982	-28.6	240.3 $\pm$ 6.7	Oct 1982 $\pm$ 8 months
OZE719	Alcohol	1985	-25.0	214.9 $\pm$ 4.6	Sep 1984 $\pm$ 9 months
OZE729	Alcohol	1989	-27.3	174.0 $\pm$ 4.6	Aug 1988 $\pm$ 13 months
OZE718	Alcohol	1991	-21.5	160.8 $\pm$ 5.2	Apr 1990 $\pm$ 17 months
OZE724	Alcohol	1993	-26.6	141.3 $\pm$ 3.6	Nov 1991 $\pm$ 15 months
OZE723	Alcohol	1995	-25.3	117.0 $\pm$ 3.8	Mar 1995 $\pm$ 11 months
OZE717	Alcohol	1997	-26.7	120.6 $\pm$ 4.3	(a)

For 1969 we measured three different wines (labels (1), (2) and (3)). Note that, as explained in the text, tannins measured in this study are expected to provide a ‘1 year older’  $^{14}\text{C}$  concentration.

(a) Outside calibration curve.

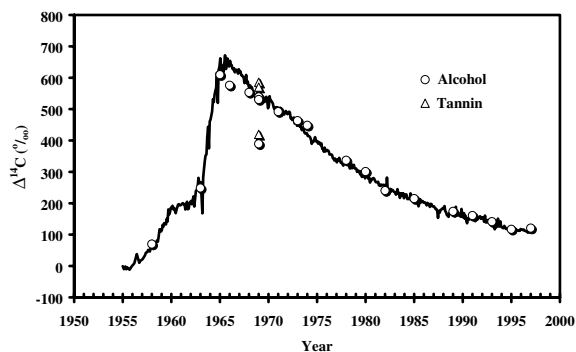


Fig. 2. Comparison between  $\Delta^{14}\text{C}$  values for alcohol and tannin samples (this work) and the compiled Southern Hemisphere bomb curve by Hua and Barbetti [11]. Note that, as explained in the text, tannins measured in this study are expected to provide a '1 year older'  $^{14}\text{C}$  concentration.

grape seeds we can conclude that it is compatible with a 1975 vintage, and not 1969 as shown on the label. Of course, this depleted  $^{14}\text{C}$  level might also be present in a 1969 wine containing a larger than usual amount of low  $^{14}\text{C}$  top-ups. In any case, this shows the strength of our method in identifying suspect wines.

We note that the atmospheric  $\Delta^{14}\text{C}$  is decreasing exponentially halving approximately every 16 years [13]. Presently, the annual differential in  $\Delta^{14}\text{C}$  is at most 5 permil/year, a factor of 2 greater than the precision level for the  $^{14}\text{C}$  AMS technique. Due to seasonal variations being larger than the magnitude of this decreasing trend, dating to the nearest year of biological materials formed after 1990 is very difficult. However, aged wines are usually the most expensive and their value is rapidly increasing. Wine trading is attracting more investors and the authentication of wine vintages will become more relevant. Radiocarbon dating is an effective tool for verifying the vintage of wines produced from the peak of the  $^{14}\text{C}$  bomb-pulse in 1965 up to about 1990.

### 3. Radiocarbon dating of illicit drug samples

Using appropriate analytical methods, complex chemical profiles can be obtained for different drug samples and compared to characteristic chemical

signatures. These profiles may contain natural components, impurities, precursors, by-products and cutting agents. Examination of all the components of a sample, in theory, provides its complete 'history'. Chemical links between samples can be established, and material from different seizures can be classified into groups of related samples. Consequently, and most useful for law enforcement authorities, specific links between manufacturers, suppliers and users can be established, drug distribution patterns and networks can be built, and the source, including the geographic origin of drug samples may be identified. The Australian Forensic Drug Laboratory (AFDL) has developed a detailed methodology for characterisation of all major drugs seized in Australia (Heroin, Cocaine, Methamphetamine and MDMA) and currently employs this for tactical comparison of illicit drug samples to assist in prosecution and strategic intelligence.

Radiocarbon dating of illicit drug samples represents the extension of this approach and has potential to significantly impact drug characterisation. It could provide vintage (age) of the illicit drug samples and answer questions such as when the naturally derived drug samples were produced, and hence if they have been stockpiled or directly transferred to the Australian market. The production year of the samples could also help law enforcement agencies to estimate the extent of the opium and heroin production in areas such as the 'Golden triangle' in South East Asia, the 'Golden Crescent' in South West Asia, cocaine production in South America. This information could also impact on global intelligence capabilities. The United Nation Office on Drugs and Crime (UNODC) in cooperation with the developed nations is placing significant effort and material resources to fight drug production in the developing world by replacing the drug-bearing plants with regular crops. According to the latest UNODC figures [14], in 2002 Afghanistan was the world's number one opium producer with 3400 metric tonnes on 74000 hectares. The figures obtained in such surveys are usually based on analysis of satellite images and extensive fieldwork, which can only be obtained with full cooperation of the respective governments. The accuracy of such surveys must

then be verified with additional independent scientific methods. Radiocarbon dating could provide the tool to effectively monitor those processes especially in countries in which governments are uncooperative or corrupt.

Illicit drugs such as cocaine, opium, morphine and heroin are derived from plants. Therefore, their growing season can be determined using the bomb-pulse radiocarbon dating technique. Of vital importance for an accurate age determination is the extraction of sample material containing only the carbon that was naturally fixed during the growing season and not derived from the chemicals used during drug synthesis which may have a different  $^{14}\text{C}$  content. Cocaine (refined from coca plants), opium and morphine (extracted from poppy plants) are relatively simple cases because no exogenous carbon is added during treatment in clandestine laboratories. Heroin is synthesised from morphine through the addition of two acetyl groups, thus introducing exogenous carbon. In order to be dated, heroin must undergo deacetylation without further contamination. The resulting morphine is purified using column chromatography, homogenised and dried in vacuo to remove solvents.

For this study we measured the  $^{14}\text{C}$  concentration in nine different samples (see Table 2). Cocaine samples OZG080, OZG081 and OZG082 arrived in Australia in 1992, 1993 and 1995 on various flights from South America and were

seized by Customs. Both opium samples OZG086 and OZG087 were seized in 1998 on separate flights from Thailand to Australia. Morphine sample OZG085 was extracted from poppies grown in legally controlled operations in Tasmania during the 2000/2001 growing season and made available by the pharmaceutical company 'Tasmanian Alkaloids'. Sample OZG079 is an opium standard material used to calibrate drug strengths and concentrations. It was synthesised in 1988. Finally, cocaine base samples OZG083 and OZG084 were purified in two different occasions (1995 and 1998, respectively) from a cocaine sample seized in 1993. When this process (counter current extraction and re-crystallisation) was performed it was not anticipated that radiocarbon dating would be carried out, and no particular effort was made to avoid carbon contamination from organic solvents. This fact highlights the problems we might be facing when dealing with heroin samples. Particular care will be necessary to avoid contamination from solvents used during the deacetylation process.

The results displayed in Fig. 3 show that, in the case of naturally produced drugs when no exogenous carbon is added during treatment, it is possible to obtain an accurate age. As noted before, due to the particular trend of the  $^{14}\text{C}$  bomb-pulse, dating to the nearest year of biological materials formed after 1990 is very difficult. Nevertheless, especially in the case of verifying the conversion to

Table 2  
The measured  $\Delta^{14}\text{C}$  values for natural and synthetic drug samples

ANSTO code	Sample type	Year of seizure	$\delta^{13}\text{C}$ (‰)	$\Delta^{14}\text{C}$ (‰)	Calibrated age range
<i>Naturally produced drugs</i>					
OZG080	Cocaine	1992	-34.8	$147.1 \pm 4.0$	Jul 1991 $\pm$ 15 months
OZG081	Cocaine	1993	-34.5	$126.7 \pm 4.1$	Jan 1994 $\pm$ 12 months
OZG082	Cocaine	1995	-34.2	$113.9 \pm 3.6$	Jun 1995 $\pm$ 11 months
OZG086	Opium	1998	-29.6	$102.7 \pm 4.8$	(c)
OZG087	Opium	1998	-30.6	$101.9 \pm 4.9$	(c)
OZG085	Tasmanian morphine	2001 (a)	-29.8	$86.0 \pm 4.0$	(c)
<i>Synthetic drugs</i>					
OZG079	Opium standard	1988 (b)	-27.7	$-26.3 \pm 3.7$	
OZG083	Cocaine base	1993	-34.4	$378.5 \pm 5.3$	Jun 1992 $\pm$ 14 months
OZG084	Cocaine base	1993	-34.7	$135.1 \pm 4.7$	

(a) Growing season; (b) year of synthesis; (c) outside calibration curve.

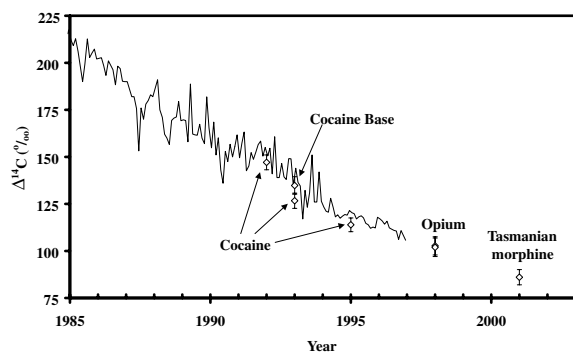


Fig. 3. Comparison between  $\Delta^{14}\text{C}$  values for drug samples (this work) and the compiled Southern Hemisphere bomb curve by Hua and Barbetti [11]. Note that, in order to enhance the plotting resolution of data points close to the calibration curve, samples OZG083 ( $378.5 \pm 5.3\text{‰}$ ) and OZG079 ( $-26.3 \pm 3.7\text{‰}$ ) are not plotted.

alternative crops, a two-year resolution is sufficient.

#### 4. Conclusions

The cases discussed in this paper demonstrate the potential of AMS analysis in modern forensic science. The use of the  $^{14}\text{C}$  bomb-pulse to reveal forgeries and frauds is a well-established technique. The investigation of criminal activities related to drug smuggling is still at the planning stage and its implementation will require a close dialogue between scientists and the intelligence/police community.

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