

## TOWARDS ACHIEVING LOW BACKGROUND LEVELS IN ROUTINE DATING BY LIQUID SCINTILLATION SPECTROMETRY

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**ABSTRACT.** International radiocarbon intercalibration studies have revealed that radiometric laboratories using liquid scintillation (LS) spectrometry of benzene reported, on average, younger ages for near-background standards than either gas proportional counter (GPC) or accelerator mass spectrometry (AMS) laboratories. These studies suggested that the younger LS ages are probably related to the use of spectrophotometric benzene as a background standard. An analysis of successive 110-ka subfossil wood (Airedale Reef Ancient Wood: ARAW) standards shows that vacuum line memory effects occur in LS spectrometry and, consequently, must be corrected to obtain accurate  $^{14}\text{C}$  dates. ARAW standards, measured at monthly intervals in the Waikato laboratory, are used to provide blank corrections for both research and routine dating applications. The strong correlation between the ARAW  $\Delta^{14}\text{C}$  data and the sample activities that preceded the standards may provide an opportunity to obtain sample-specific blank corrections. Lithium carbide synthesis is likely to prove a source of contamination. This work suggests that reproducible background levels for routine dating of less than 0.1 pMC (55 ka  $^{14}\text{C}$  yr) are achievable.

### INTRODUCTION

International radiocarbon intercalibration studies have revealed that radiometric laboratories using liquid scintillation (LS) spectrometry of benzene reported, on average, younger ages for near-background standards than either gas proportional counter (GPC) or accelerator mass spectrometry (AMS) laboratories (e.g. the near-background FIRI Kauri standards A and B, Scott et al. 2003)—see Figure 1. These studies suggested that the younger LS ages are probably a function of laboratory standards and, in particular, relate to the use of spectrophotometric benzene to determine background count rates.

Accurate  $^{14}\text{C}$  determinations by all 3 methods, especially of near-background samples, requires the establishment of accurate and reproducible background levels, obtained from materials containing no  $^{14}\text{C}$  (background blanks). Anthracite, ancient wood, or ancient carbonates are commonly used as “dead” carbon sources for this purpose. Many benzene LS laboratories utilize spectrophotometric benzene derived from a petrochemical source to provide background activities for the scintillation vials. It appears that some laboratories are utilizing these values as background blanks and ignoring contamination levels in their vacuum systems.

Long and Kalin (1992) reported that the Arizona LS laboratory utilized spectrophotometric benzene as the background for routine precision, stating that with 3 mL (2.4 g) benzene counted for 2 k min, differences in  $^{14}\text{C}$  activity between spectrophotometric benzene and anthracite are “statistically invisible” (Long and Kalin 1992: 355). However, Long and Kalin (1992) found significant differences in activity between spectrophotometric benzene and anthracite using large benzene volumes (11.5 g) and longer counting times (12 k min). Four successive anthracite blank samples were processed and a decreasing level of memory effects was observed, which Long and Kalin (1992) attributed to contamination of the lithium reaction vessel surfaces.

McCormac et al. (1993) demonstrated that spectrophotometric benzene pipetted into counting vials produced lower background count rates than those obtained from benzene synthesized from an ancient carbon source. They combusted spectrophotometric benzene and reconverted the resulting  $\text{CO}_2$  back to benzene and compared the activities of the initial benzene with the reconverted benzene. Higher  $^{14}\text{C}$  levels were found in the reconstituted benzene, and so McCormac et al. (1993)

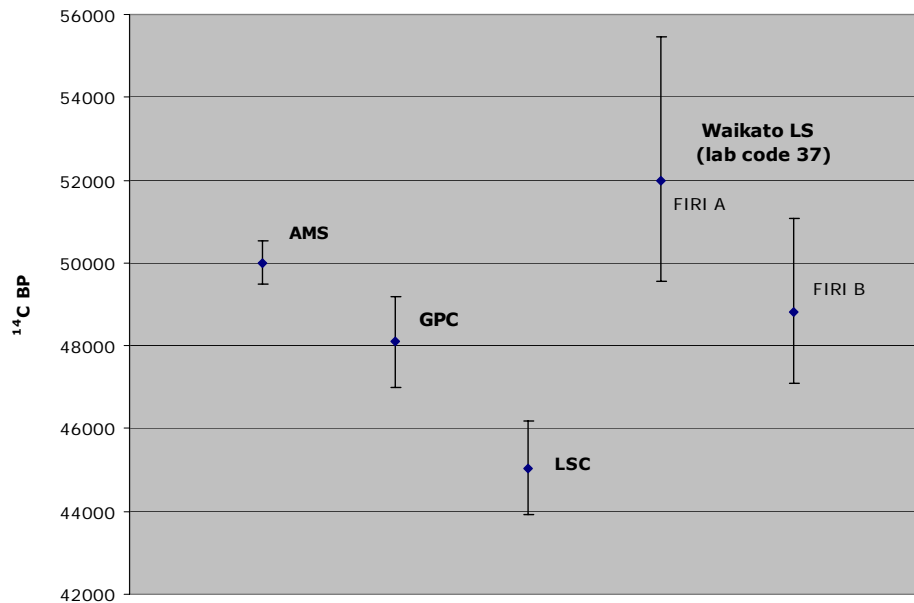


Figure 1 Mean  $^{14}\text{C}$  ages obtained by different laboratory types for the FIRI Kauri standards A and B, showing that some LS laboratories have seriously underestimated the ages. The Waikato LS results are given for comparison.

concluded that  $^{14}\text{C}$  was added to the reconverted benzene during combustion and synthesis. They suggested that most of the modern contamination was derived from C associated with either the lithium metal or from the reaction vessel walls.

Other possible sources of contamination during benzene synthesis include the following:

- Cross-contamination during combustion from either CuO used in furnaces or chemicals used to cleanse the  $\text{CO}_2$  gas;
- Cross-contamination from the catalyst used in the catalytic trimerization of acetylene to benzene, where the catalyst is regenerated between samples;
- Elevation of sample activity by contamination with radon gas derived from either the ancient wood samples or from the zeolite-based vanadium-activated catalyst.

The larger numbers of LS laboratories reporting younger ages for the near-background FIRI samples indicates that some laboratories are unaware of these possible sources of contamination during benzene synthesis. Therefore, it is essential that all LS laboratories utilizing spectrophotometric benzene to establish LS vial background levels routinely analyze  $^{14}\text{C}$ -dead background samples to provide a background correction for the contaminating  $^{14}\text{C}$  added during benzene synthesis.

Ancient wood standards have been run at monthly intervals in the Waikato laboratory over the last 2 yr to provide accurate background levels for routine analysis. This paper is a preliminary assessment of this data undertaken to demonstrate how necessary blank determination is and the effectiveness of the LS method for dating near-background samples. It also attempts to verify the suggestion of McCormac et al. (1993) that the carbide reaction is the predominant source of contamination and highlights steps undertaken in the Waikato laboratory to achieve lower and more stable background levels, both for research samples and routine dating applications.

### THE AIREDALE REEF ANCIENT WOOD (ARAW) STANDARD

Well-preserved, subfossil wood samples were collected by Dr B V Alloway from Airedale Reef, a coastal section in North Taranaki, New Zealand. The samples are from trees in growth position beneath a 4-m-thick debris avalanche deposit. Palynological and tephrochronological evidence show that the debris avalanche (and forest inundation) occurred during Marine Oxygen Isotope Stage 5c at about 110 ka (Newnham and Alloway 2001).

Wood samples were pretreated to  $\alpha$ -cellulose (Hoper et al. 1997) to remove mobile fractions and  $\Delta^{14}\text{C}$  measured by LS counting of benzene (Hogg et al. 1987) in Wallac 1220 Quantulus spectrometers (7.5-g benzene samples counted for 10k min per sample). The  $\alpha$ -cellulose extraction procedure outlined by Hoper et al. (1997) was modified for the near-background samples by utilizing acetone (derived from a petrochemical source) as a solvent in place of ethanol (some of which may be derived from modern wood).

We also analyzed untreated wood and the Kapuni  $\text{CO}_2$  gas standard (KCOG) for comparison. The KCOG standard is  $^{14}\text{C}$ -dead, high-purity  $\text{CO}_2$ , about 45 Ma in age, derived from the Kapuni Gas Field near New Plymouth, New Zealand. It is a useful standard for measuring memory effects in the lithium carbide and catalytic trimerization reactions but of course cannot be used to monitor the combustion of organic carbon. We “preconditioned” the vacuum lines before synthesizing the ARAW standard benzene samples by initial processing of 3 near-background subfossil wood samples.

We obtained statistically-identical ages on ARAW (untreated), ARAW ( $\alpha$ -cellulose), and KCOG standards of about 60 ka BP (Figure 2).

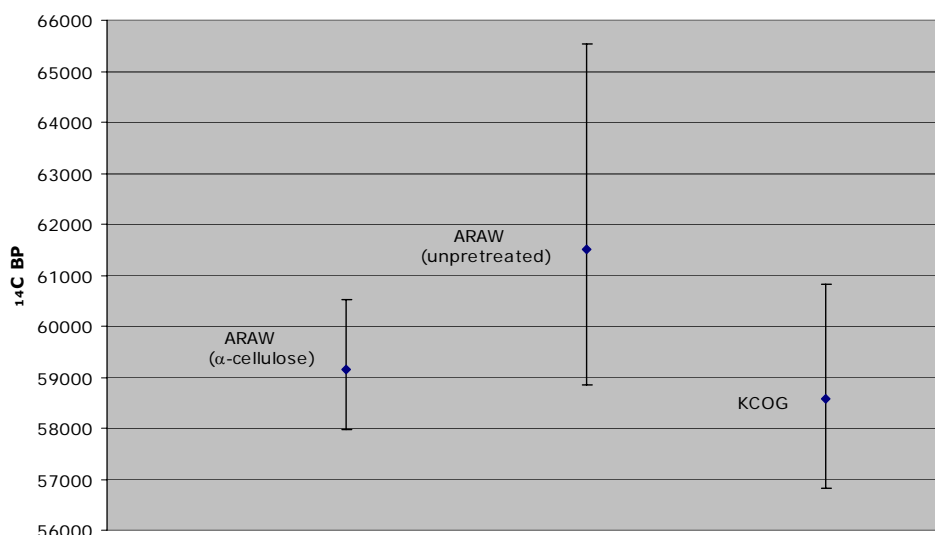


Figure 2  $^{14}\text{C}$  ages of the ARAW standard. The Kapuni  $\text{CO}_2$  Gas Standard (KCOG) is given for comparison (backgrounds based upon spectrophotometric benzene—no correction for memory effects). ARAW( $\alpha$ -cellulose) data, mean of 5 measurements; ARAW(untreated) data, mean of 2 measurements; KCOG data, mean of 2 measurements.

### METHODOLOGY EMPLOYED FOR NEAR-BACKGROUND RESEARCH SAMPLES

If known-age near-background research samples are being analyzed, we follow the procedures of Long and Kalin (1992) and McCormac et al. (1993) to reduce  $^{14}\text{C}$  activities in the vacuum lines by

initially processing a minimum of 2 near-background standards and by processing the samples in a batch. We have found a similar pattern to that obtained by Long and Kalin (1992) and McCormac et al. (1993) with background activities diminishing with successive standards (Figure 3). Near-background research samples in the Waikato laboratory utilize 7.5 g of benzene counted for 10 k min in Wallac 1220 Quantulus spectrometers. Benzene samples are counted in Waikato 10-mL synthetic silica liquid scintillation vials (Hogg 1993). At least 2  $^{14}\text{C}$ -dead standards are also included in the batch to provide an accurate blank for the samples.

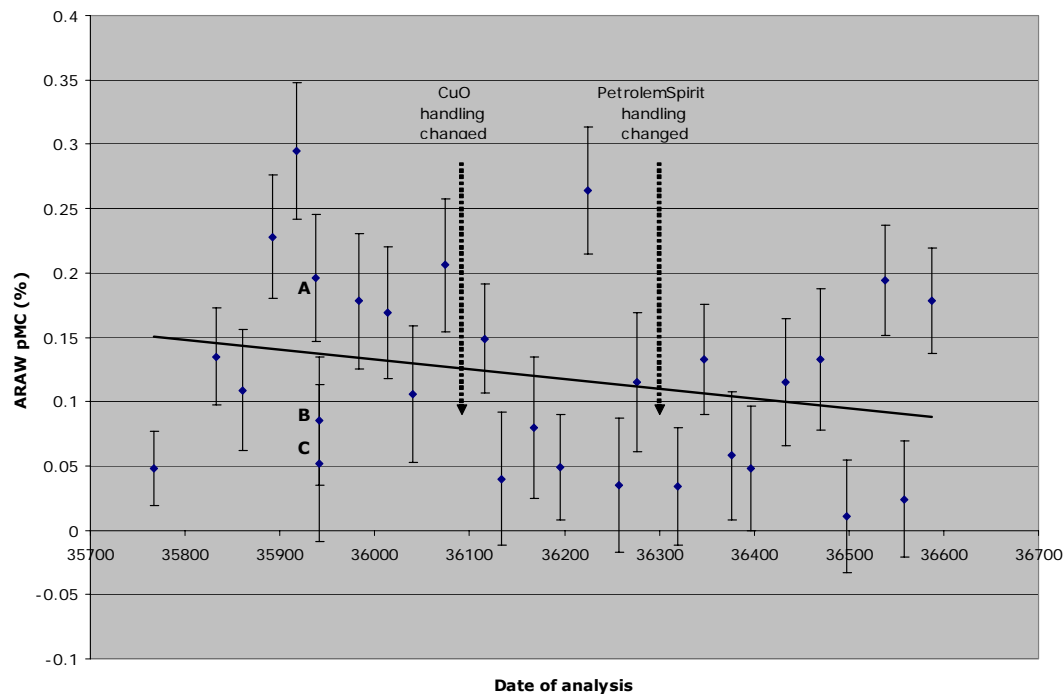


Figure 3  $^{14}\text{C}$  levels for routine analysis ARAW standards determined over a 24-month period at the Waikato laboratory. Backgrounds based upon spectrophotometric benzene—no blank correction. Benzene weight = 2.64 g; count time = 3 k min. Samples A, B, and C were run on successive days through the same vacuum line pathways and show decreasing activity.

#### METHODOLOGY EMPLOYED FOR ROUTINE DATING OF UNKNOWN-AGE SAMPLES

Low and reproducible background count rates can be readily achieved for research projects dating old material by preconditioning vacuum lines with  $^{14}\text{C}$ -dead standards before the samples are processed, as discussed above. This procedure cannot be followed for routine dating of unknown activity samples. Routine analysis in the Waikato laboratory utilizes 2.64 g of benzene counted for 3 k min, also in Wallac 1220 Quantulus spectrometers. Benzene samples are counted in Waikato 3-mL synthetic silica liquid scintillation vials (Hogg 1993).

ARAW blank standards are analyzed at monthly intervals (Figure 3 and Table 1). The order of processing of the ARAW standards is random and no attempt is made to deliberately process any particular ARAW standard after samples known to have low activity, although they do not follow high-activity modern standards such as OXII or ANU sucrose.

Table 1 ARAW standard data accumulated in the Waikato lab over a 24-month period. The count rates (cpm) of the samples that preceded the standard, through the combustion (A), carbide reaction (B) and the catalyst trimerization (C) are also given. ARAW standard activity is given as pMC (%)  $\pm 1$  standard error ( $\sigma$ ).

Lab nr (Wk)	pMC (%)	$\sigma$	cpm of the sample preceding the ARAW standard in:		
			A	B	C
			Combustion	Carbide reactor	Catalytic trimerization
10301	0.048	0.03	5.8	5.8	6.7
10302	0.135	0.04	19.8	5.4	15.9
10303	0.109	0.05	2.6	27.5	10.9
10858	0.228	0.05	28.5	26.1	7.2
10859	0.295	0.05	25.0	25.9	7.2
8790-4	0.196	0.05	20.8	6.7	6.7
8790-5	0.085	0.05	0.4	0.4	0.4
10860	0.052	0.06	0.4	0.4	0.4
10861	0.178	0.05	20.5	6.3	16.7
10862	0.169	0.05	1.6	15.6	8.7
10863	0.106	0.05	1.7	6.2	1.7
10864	0.206	0.05	23.2	16.9	12.6
10865	0.149	0.04	19.6	19.6	12.3
11926	0.04	0.05	21.9	13.8	3
11927	0.08	0.06	0.37	0.37	0.37
11928	0.05	0.04	0.3	0.3	3.4
12481	0.264	0.05	17.6	17.6	5.9
12482	0.035	0.05	5.5	5.5	2.7
12483	0.115	0.05	18.0	3.1	3.1
12484	0.034	0.05	13.4	4.4	10.6
12485	0.133	0.04	6.7	0.4	0.4
12486	0.058	0.05	23.1	3.7	3.7
12487	0.048	0.05	5.1	1.9	0.37
12488	0.115	0.05	21.1	9.5	0.6
13853	0.133	0.06	20.5	4.6	10.8
13854	0.011	0.04	0.5	0.5	0.5
13855	0.194	0.04	22.5	18.3	8.2
13856	0.024	0.05	6.3	2.4	0.4
13857	0.178	0.04	22.3	22.3	6.6

A line of best fit through the data of Figure 3 shows that background levels decreased over the 2-yr period. This may be due to the cumulative effect of numerous small improvements in laboratory practice, which in isolation are unlikely to significantly influence mean background levels. Two examples are given in Figure 3, the handling of CuO and petroleum spirit. The CuO, contained in combustion line furnaces, is now baked at 600 °C for 6 hr after each sample-combustion to ensure residual carbon is removed. Petroleum spirit, under which lithium metal is stored, is now changed frequently, at monthly intervals. Plotting the calendar dates on a graph (such as Figure 3) is a useful tool to evaluate the affect small changes in benzene laboratory synthesis procedures have on mean background levels.

The Waikato laboratory utilizes a mean blank correction for organic carbon samples calculated from the mean of the 10 most recent ARAW standard values. The mean ARAW activity of all measurements =  $0.11 \pm 0.08$  pMC (54 ka BP), ranging from a high of 0.295 pMC (47 ka BP) to a low of 0.024 pMC (67 ka BP). The data for the 10 most recent measurements are significantly lower: mean =  $0.095 \pm 0.07$  pMC (56 ka BP), with a high of 0.194 pMC (50.2 ka BP) and a low of 0.024 pMC (67 ka BP). A mean background level of less than 0.1 pMC compares favorably with AMS backgrounds, which are rarely better than 0.15 pMC (Bronk Ramsey et al., these proceedings). The low and reproducible background levels highlight the effectiveness of the LS method in the  $^{14}\text{C}$  dating of near-background samples.

Figure 4 shows the impact of the Waikato blank correction of 0.095 pMC and demonstrates how errors increase for near-background samples if no correction is applied. In the 2003 FIRI report, 26 laboratories produced Kauri A and B ages of less than 40 ka (Scott et al. 2003). Such underestimations of age imply that a large blank correction of at least 0.4 pMC must be applied to correct them (assuming a mean Kauri age of 47,634 BP: Scott et al. 2003). The influence of the blank correction of 0.4 pMC is also shown in Figure 4. Long and Kalin's (1992) contention that differences in  $^{14}\text{C}$  activity between spectrophotometric benzene and anthracite are "statistically invisible" implies that they can, therefore, be ignored. While the correction for memory effects may be insignificant for full-sized young samples, it can have a much larger impact upon gas-diluted, small or old samples, as is shown in Figure 4. Systematic errors are cumulative and they should, therefore, be corrected.

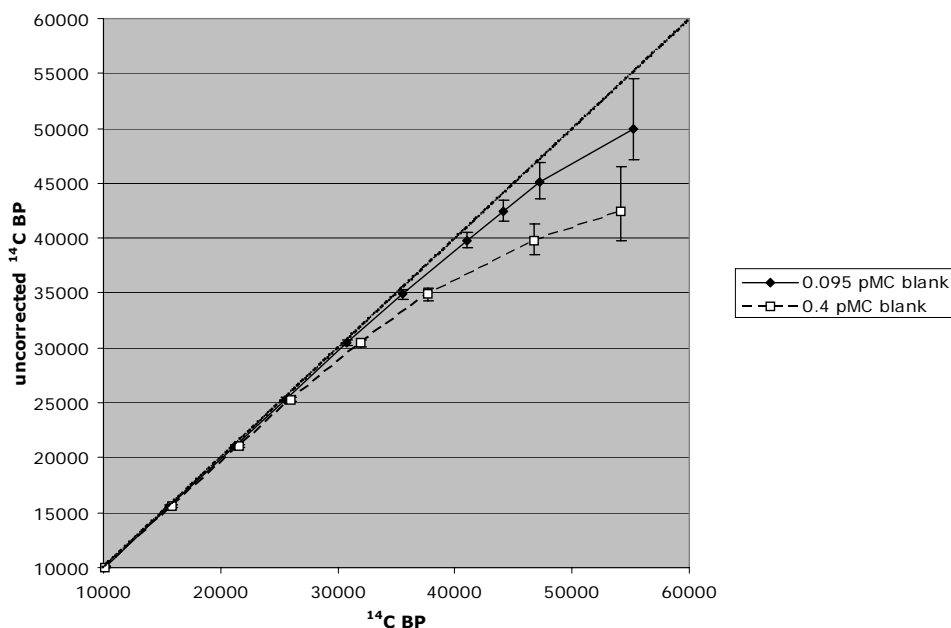


Figure 4 The influence of uncorrected  $^{14}\text{C}$  dates on dating accuracy (blank corrections of 0.095 and 0.4 pMC shown). The dotted line represents a zero blank correction.

#### ANALYSIS OF ARAW STANDARD DATA

It is clear from Figure 3 that activity from 1 sample (e.g. samples A–C) can contaminate the next (memory effects). The ARAW standard activities should, therefore, show a positive correlation between previous sample activity and ARAW standard activity. The ARAW standard data may also

be able to identify which benzene synthesis reaction (i.e. combustion, lithium carbide synthesis, or catalytic trimerization) is the most likely source of contamination, and also potentially provide a means for correcting this error.

### **CO<sub>2</sub> Generation (Combustion) as a Source of Contamination**

The potential for 1 sample combustion to contaminate the next is complicated by sample-size issues. Large samples may contaminate the combustion vacuum lines more than smaller samples. Unfortunately, many of the samples combusted prior to the ARAW standard combustions were undersized, obscuring any potential correlations. Therefore, all future ARAW standards will follow full-sized sample combustions to help clarify the contribution of sample combustion to memory effects.

### **C<sub>2</sub>H<sub>2</sub> and C<sub>6</sub>H<sub>6</sub> Generation-Reactions as Sources of Contamination**

The Waikato benzene synthesis procedure involves gas dilution of undersized samples with dead CO<sub>2</sub> to ensure a constant stoichiometry between the CO<sub>2</sub> and lithium (also recommended by McCormac et al. 1993). The samples preceding the ARAW standards through the carbide reactors and catalyst columns are, therefore, unaffected by sample size and may provide more reliable data than the combustion data to investigate the correlation between ARAW standard levels and previous sample activity.

The ARAW standard data are given in Table 1. Also included are the count rates (in cpm) of the samples that immediately preceded the ARAW standards through the reactions involved in the synthesis of benzene:

- cpm of the sample preceding the ARAW standard in the combustion system (reaction A—oxidation of sample C to CO<sub>2</sub>);
- cpm of the sample preceding the ARAW standard in the lithium carbide reactor (reaction B—conversion of CO<sub>2</sub> to C<sub>2</sub>H<sub>2</sub>);
- cpm of the sample preceding the ARAW standard on the catalyst column (reaction C—catalytic trimerization of C<sub>2</sub>H<sub>2</sub> to C<sub>6</sub>H<sub>6</sub>).

Other relevant data collected, but not given in Table 1, included the number of days the benzene was stored before counting. This storage time was measured to determine if activity derived from radon gas (from either the ancient wood standard or from the catalyst column) was present. There was no significant correlation between ARAW activity and duration of benzene storage before counting, which indicates that radon does not contribute significantly to the background activity.

The ARAW standard activity was plotted against the activities of the preceding samples, for the reactions A, B, and C as outlined above (Figure 5). Correlation coefficients (R<sup>2</sup>) were calculated from plots of the ARAW standard activity against the activities of the individual samples that preceded the standard through the various synthesis lines (Table 2). The correlation coefficient is highest for the carbide reaction (0.4712) with lower values for the combustion reaction (0.3733) and trimerization reaction (0.2265).

It is evident that there is a strong correlation between the ARAW standard activities and the sample activities that preceded them, especially for samples processed through the carbide reactor. This finding confirms those of Long and Kalin (1992) and McCormac et al. (1993). The outliers show that other memory effects are present and that they are unlikely to be derived from a primary source only (Figure 5). One explanation is that they may result from secondary effects where 2 samples have influenced a third. These results, and those of Long and Kalin (1992) and McCormac et al. (1993), suggests this is likely. There are insufficient data available at present to fully answer these questions.

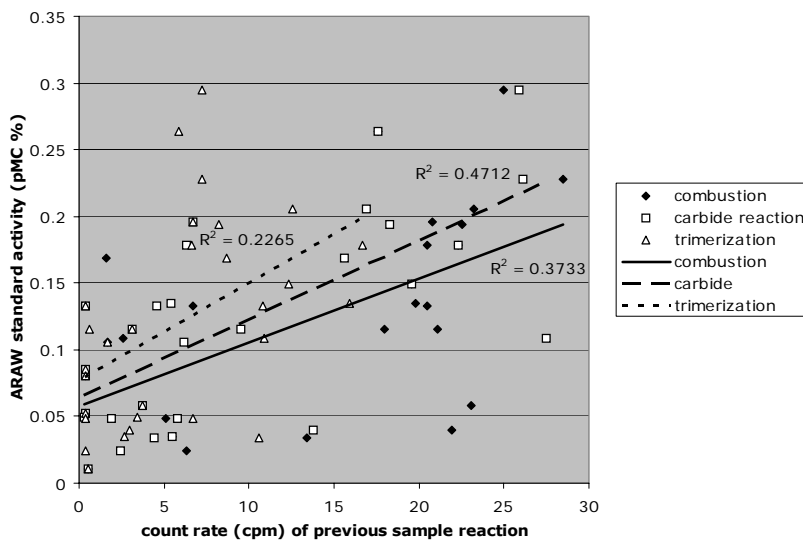


Figure 5 Dependence of ARAW activities on the count rates of the samples that preceded the combustion (A), carbide reaction (B), and the catalyst trimerization (C). The correlation coefficients ( $R^2$ ) are also given.

Table 2 The correlation coefficients ( $R^2$ ) for plots between ARAW standard activity and the activity of the samples preceding the ARAW standards, in reactions A (combustion), B (lithium carbide reaction), and C (catalytic trimerization). The probabilities for no correlation (calculated after Bevington 1969:124–125) are also given.

Reaction	Correlation coefficient ( $R^2$ )	Probability for no correlation
A – combustion	0.3733	0.0004
B – Li carbide synthesis	0.4712	0.0000
C – catalytic trimerization	0.2265	0.0091

## FUTURE WORK

This paper highlights the importance of the routine analysis of  $^{14}\text{C}$ -dead blanks to ensure that sources of contamination can be detected and eliminated. This process is on-going in the Waikato laboratory, with benzene synthesis procedures and their effect on the ARAW standard activities under continual review.

Future ARAW standards will be synthesized after at least 2 full-sized samples only, so that combustions and secondary effects can be seen more clearly.

The mathematical relationship between ARAW standard activity and preceding carbide sample activities could potentially be used to assign a unique background blank correction to every sample. A study is presently being conducted to test this hypothesis.

## CONCLUSIONS

- $^{14}\text{C}$ -dead standards should be routinely analyzed so that sources of contamination can be detected and eliminated.
- LS labs which use spectrophotometric benzene measurements alone to calculate background levels are very likely to report  $^{14}\text{C}$  ages that are too young, especially for near-background samples.



3. Research samples of near-background age can be processed in a batch through vacuum lines “pre-conditioned” by the initial processing of at least 2 low-activity samples.  $^{14}\text{C}$ -dead standards must be included to provide an accurate blank for the samples.
4. By repeatedly analyzing at regular intervals a new  $^{14}\text{C}$ -inert standard (ARAW), we have been able to obtain an accurate background correction for organic carbon samples routinely dated in the Waikato laboratory.
5. Analysis of the ARAW standard data shows that the activity of each sample processed through the vacuum lines is related to that of the sample preceding it. This relationship may provide a means to further improve background corrections, and hence the accuracy of  $^{14}\text{C}$  ages, especially for near-background samples.
6. The carbide synthesis reaction is a likely source of contamination in the Waikato LS laboratory. Future research will be needed to determine if secondary contributions are also significant.
7. This work suggests that reproducible background levels for routine dating of less than 0.1 pMC (55 ka  $^{14}\text{C}$  yr) are achievable. This is presently lower than backgrounds currently obtainable in routine AMS dating and highlights the benefits of LS spectrometry for near-background samples.

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