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Validation of carbonization as a part of benzene synthesis for radiocarbon measurement

Ines Krajcar Bronić*, Andreja Sironić, Jadranka Barešić

Ruđer Bošković Institute, Zagreb, Croatia

Abstract

Carbonization, i.e., turning organic sample to carbon, was validated for the benzene synthesis for the radiocarbon liquid scintillation measurement. Tests of sample preparation by combustion, carbonization followed by combustion and carbonization followed by a direct reaction with lithium were performed. Wood and charcoal samples were good for carbonization followed by direct reaction with lithium, while collagen obtained from bones had to be combusted. Direct reaction of carbonized sample with lithium required three times less amount of lithium than the combusted sample.

Keywords: liquid scintillation counting, radiocarbon measurement, benzene synthesis, carbonization

Corresponding author:

Ines Krajcar Bronić

krajcar@irb.hr

Department of Experimental Physics
Rudjer Bošković Institute
Bijenička cesta 5
10000 Zagreb
Croatia

ORCID numbers

Ines Krajcar Bronić	0000-0002-6534-4125
Andreja Sironić	0000-0001-7256-206X
Jadranka Barešić	0000-0003-4634-5859

Introduction

Radiocarbon can be measured by liquid scintillation counting (LSC) [1-3] or accelerator mass spectrometry (AMS) [3,4]. Although AMS technique is prevailing nowadays in archaeological research, there are still many LSC laboratories that offer their services [2,5]. In the Zagreb Radiocarbon Laboratory, we perform LSC analyses of samples, such as environmental, that can be supplied in the required amount to obtain 4 g of benzene as this is the measurement geometry established in our laboratory [6]. AMS analyses are performed for archaeological, geological and forensic applications [5,7] and all others where the amount of sample is not enough for LSC analysis.

In LSC technique, it is distinguished between benzene synthesis [2] and absorption of CO_2 in an absorption-scintillation mixture [8]. We have been applying both methods, absorption of CO_2 in a mixture of Carbosorb and Permafluor (LSC-A) and benzene synthesis (LSC-B) [6]. The LSC-A method always requires production of CO_2, while there are more possibilities for LSC-B method. Normal procedure of sample treatment includes combustion (of organic sample) to CO_2 and the reactions with lithium and H_2O to obtain C_2H_2 that is trimerized to C_6H_6 [2]. For such procedure of a sample, we need 20 - 24 g of lithium to finally obtain 4 g of benzene.

Here we present the validation of the carbonization procedure as a part of the benzene synthesis method. By carbonization we understand pyrolysis, i.e., heating of organic sample without the presence of oxygen. Carbonized samples can be further prepared by direct reaction with lithium making the preparation process faster and less expensive, since the direct reaction of sample with lithium, without combustion, requires only 7 - 9 g of lithium. Carbonized samples can also be combusted to CO_2, making the combustion procedure easier, since the high-volatile components of the sample, which can cause clogging in the combustion system, are removed during the carbonization process.

^{14}C sample procedure

Organic samples are mechanically cleaned and dried, and pre-treated by the acid-base-acid method [5,6,9]. All experiments were performed on a combustion system manufactured in our laboratory [10], which was regularly maintained and occasionally improved [6]. Benzene synthesis line following the procedure described in [2] was also developed and constructed in our laboratory [6].

Benzene was prepared from all samples for LSC-B technique. Measurements were performed in 7-ml pico vials in the Ultra low-level liquid scintillation counter Quantulus 1220 (Walac Oy, PerkinElmer Life Sciences) [6,9]. We used 4-g geometry and 15 mg butyl-PBD was added per gram of benzene. A counting run consisted of a background sample, a reference material sample, a control sample and a certain number of unknown samples. We used anthracite as the background sample, Oxalic Acid II (SRM 4990C) as the reference material, and ANU Sucrose (150.6 pMC) as the control sample.

In order to simplify the treatment procedure for organic samples for LSC-B, we performed a series of analysis that include carbonization and direct reaction with lithium. Several

preparations of the same sample were performed: combustion of pre-treated sample (reaction type 1), carbonization with combustion (reaction type 2), or carbonization with direct reaction with lithium (reaction type 3) (Figure 1). Certain types of samples (charcoal) are good samples for direct reaction with lithium without carbonization (reaction type 4) provided that they are "pure charcoal" without many impurities.

Carbonization is performed in an oven at 600 ^{o}C for 15 minutes. About 50 g of chemically pre-treated and dried sample is taken for carbonization, after which about 14 g of carbonized sample is obtained. Carbonized organic samples is then combusted in a stream of pure oxygen or is ready for direct reaction with lithium.

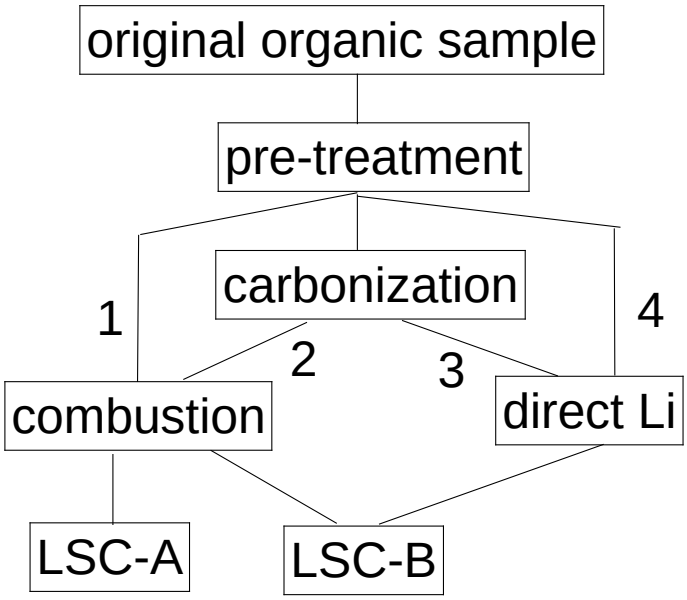

Figure 1. Schematic presentation of organic sample treatment for LSC technique. Reaction types: 1 – combustion, 2 – carbonization and combustion, 3 – carbonization and direct reaction with lithium, 4 – direct reaction with lithium without carbonization.

Results

As first stage in any comparison, background samples had to be prepared. We compared the mean count rates of anthracite prepared by combustion (1) and by carbonization followed by direct reaction with lithium (3) (Figure 2). The mean values were the same, although carbonization gives somewhat wider distribution.

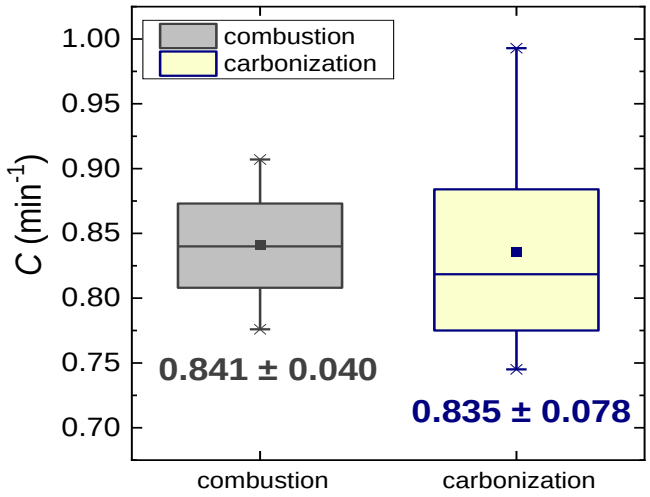

Figure 2. Comparison of count rate of background samples (anthracite) prepared by combustion and by carbonization followed by direct reaction with lithium.

List of samples prepared by various treatment strategies is shown in Table 1 and the results in Table 1 and Figure 3.

Wood samples Z-3523 and Z-6281 were treated by three different strategies, reaction types 1, 2 and 3. All three results were in very good agreement. Charcoal sample Z-3751 was a very pure charcoal sample and it was possible to apply direct reaction with lithium with (reaction type 3) and without (type 4) carbonization. ^{14}C results of both strategies show also very good agreement.

Charcoal Z-5337 was prepared by combustion (1) and by carbonization followed by direct reaction with lithium (3). The weight of carbonized sample was lower than the amount for 4-g geometry, and it had to be diluted with the background what inserts larger measurement uncertainty. Although the difference between the results was somewhat larger than in the previous cases, the agreement was satisfactory.

Bone sample Z-3591 was prepared by collagen extraction procedure [11,12]. Combustion of collagen can be difficult, so collagen was carbonized and the following combustion was much easier. However, direct reaction of collagen with lithium was very fast and violent, and the corresponding benzene was not synthetized.

Table 1. Comparison of measurement results of organic samples prepared by combustion (1), carbonization followed by combustion (2), carbonization followed by direct reaction with lithium (3) and direct reaction with lithium (4). Shaded squares represent treatment procedures for each sample.

Sample	Preparation number	Type	Carbo-nization	Direct reaction	Combu-stion	$a^{14}C$ pMC
Z-3523 wood	B147	1			■	96.35 ± 0.58
	B150	2	■		■	96.41 ± 0.58
	B193	3	■	■		96.61 ± 0.65
					Mean value	*96.46 ± 0.52*
Z-6281 wood	B1494	1			■	92.41 ± 0.82
	B1502	2	■		■	92.29 ± 0.59
	B1500	3	■	■		91.77 ± 0.70
					Mean value	*92.16 ± 0.61*
Z-3751 charcoal	B254	4		■		47.92 ± 0.66
	B255	3	■	■		47.59 ± 0.40
					Mean value	*47.76 ± 0.39*
Z-5337 charcoal	B1110	3	■	■		98.6 ± 1.1
	B1115	1			■	97.41 ± 0.69
					Mean value	*98.03 ± 0.66*
Z-3591 collagen	B212	1			■	81.78 ± 0.54
	B218	2	■		■	80.7 ± 1.1
		3	■	■		Not measured
					Mean value	*81.25 ± 0.61*

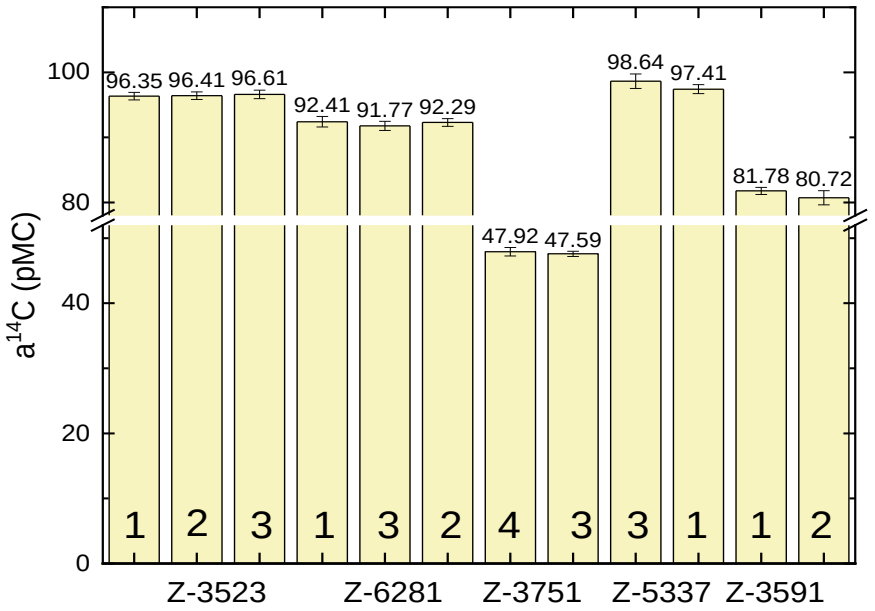

Figure 3. Comparison of results of measurements of samples prepared by different strategies: 1 – combustion, 2 – carbonization and combustion, 3 - carbonation and direct reaction with lithium, 4 – direct reaction with lithium without carbonization.

Conclusion

Carbonization is a procedure of turning (organic) samples to carbon by pyrolysis. Wood and charcoal samples are good candidates for carbonization. Carbonization leads to (almost) pure carbon and such samples are easier to combust or can be prepared directly with lithium. Direct reaction requires less amount of lithium (about three times) and thus sample preparation is less expensive. Tests of combusted sample, carbonized and combusted, and carbonized with direct reaction with lithium gave comparable results. Sample preparation for benzene synthesis is therefore easier and less expensive. However, collagen sample is not good for direct reaction with lithium, since it reacts very violently, and it is better to purify carbonized collagen by combustion.

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Author roles:

Ines Krajcar Bronić – conceptualization, supervision, visualization, writing – original draft, writing – review and editing

Andreja Sironić – investigation, writing – review and editing

Jadranka Barešić – data curation, investigation, methodology, writing – review and editing

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