# SET-UP, OPTIMIZATION AND FIRST SET OF SAMPLES AT THE RADIOCARBON LABORATORY IN LEBANON

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**Abstract:** A new radiocarbon laboratory has been established recently at the Lebanese Atomic Energy Commission. This laboratory consists of benzene synthesis line and a low background liquid scintillation counter, Tri-Carb 3180 TR/SL for measurements with Bismuth Germanate (BGO) guard detector. The effectiveness of the benzene line was tested firstly by preparing benzene from a wood sample after carbide and acetylene receiving. Normalization and standardization of the liquid scintillation counter was carried out, as well as the Factor of Merit (E2/B) was determined for three different counting regions. To assure accuracy and reliability of results, reference materials were used. Based on z-score and u-score evaluation, as well as Student's t-test, acceptable data were obtained from travertine and wood samples available through the International Atomic Energy Agency (IAEA-C2 and IAEA-C5), and humic acid (U) and murex shell (R) from the Fifth International Radiocarbon Intercomparison (VIRI). After that, a preliminary study was done, which is the base for future research in order to assess the anthropogenic impact and degree of environmental pollution in terms of radiocarbon isotope ratio ($\Delta^{14}C$) deduced from the Percent Modern Carbon or PMC. This work represents the results of four reference materials and those of five green grass samples. The $\Delta^{14}C$ of green grass samples collected from two different clean zones were found to be 50‰ and 52‰, while the values of those collected from different polluted zones were 23‰, 7‰ and 15‰.

**Keywords:** radiocarbon, Tri-Carb 3180, z-score, u-score, percent modern carbon, radiocarbon isotope ratio.

## 1. INTRODUCTION

Radiocarbon or $^{14}C$ is a radioactive isotope of carbon with a half-life 5730 years; it is a cosmogenic radionuclide, produced in the upper layer of atmosphere by the reaction of energetic neutrons from cosmic rays with nitrogen ($^{14}N$) nuclei (Svetlik *et al.*, 2010; Kulkova *et al.*, 2011). Together with other isotopes ($^{13}C$ and $^{12}C$), it enters the biological and geochemical carbon cycles, and is assimilated by all living organisms, in which equilibrium between decay and its replenishment is established

(Bronić *et al.*, 2010). After death, the exchange between atmosphere and organisms stops and the $^{14}C$ content decreases due to radioactive decay or disintegration. This is the basis of dating using radiocarbon for chronological studies. The radiocarbon method gained a great interest during the last decades, due to its wide applications, such as archaeology (Olsen *et al.*, 2013), forensic studies (Marzaioli *et al.*, 2011), hydrology (Hoque and Burgess, 2012; Nakata *et al.*, 2013) geology and recently ecology and environmental studies (Molnar *et al.*, 2007; Battipaglia *et al.*, 2010; Rakowski *et al.*, 2013). Hence, it was important and useful for Lebanon to create a radiocarbon laboratory dedicated to undergo related research.

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The first Radiocarbon Laboratory in Lebanon was established at the Lebanese Atomic Energy Commission (LAEC) in December 2010, in order to strengthen the infrastructure of the Environmental Radiation Control Department, which is dedicated for radionuclide analyses and their applications in environmental studies and other research related to the use of nuclear techniques.

The Environmental Radiation Control Department already incorporated two liquid scintillation counters; Tri-Carb 2300 TR and low level Tri-Carb 3180 TR/SL with Bismuth Germanate (BGO) guard detector. The benzene synthesis line was purchased from Atom Komplex Prylad — Ukraine under a National Technical Cooperation Project with the International Atomic Energy Agency (IAEA).

It is well known that analytical laboratories should test the performance through the application of a quality assurance program (Thompson et al., 2006), including regular analysis of reference materials and participation in intercomparison exercises (Beramandi-Orosco et al., 2006), in order to assure reliability, consistency and accuracy of results. For this reason, benzene was first synthesized from reference materials available through the International Atomic Energy Agency (IAEA) and from the Fifth International Radiocarbon Intercomparison (VIRI). The results were evaluated according to z-score and u-score (Scott et al., 2010; Sironić et al., 2013).

As the laboratory planned to undergo researches related to the anthropogenic impact of technologies on the ecosystem using radiocarbon as a biomarker (Pataki et al., 2010), preliminary study was carried out to determine the radiocarbon isotopic ratio ($\Delta^{14}C$) in selected clean zones and polluted zones. First data are reported in this work.

## 2. METHODS

### Samples

As quality control samples, two reference materials travertine IAEA-C2 and wood IAEA-C5 (Różanski et al., 1992) were bought from the International Atomic Energy Agency (IAEA). Also, two intercomparison samples, humic acid (U) and murex shell (R), from the Fifth International Radiocarbon Intercomparison (VIRI) (Scott et al., 2010) were analysed. For the preliminary data of the anthropogenic impact on the radiocarbon isotope ratio, green grass samples were collected from two different clean zones at altitudes of 1000 m and 1200 m, two samples were collected near an electrical power plant based on fuel combustion and one sample in the vicinity of a cement factory.

### Samples pretreatment

Reference materials and intercomparison samples were dried at 105°C without any previous chemical treatment (Sironić et al., 2013). While the green grass samples were treated by standard acid-alkali-acid (AAA) method to remove any possible contaminants containing other modern radiocarbon (Muraki et al., 2001; Bronić et al., 2009), then dried at 105°C for 12 hours (Kulkova et al., 2011).

### Benzene synthesis

Conventional method for benzene synthesis was used (Beramendi-Orosco et al., 2006; Mazeika et al., 2008). The line was purchased from Atom Komplex Prylad — Ukraine and installed at the LAEC by the developer Vadim Skripkin. The method consists of four essential steps: 1) carbonization, 2) lithium carbide production, 3) acetylene production, 4) trimerization of acetylene to transform it to benzene. Carbonization was done using a direct fusing method for green grass samples, i.e. the samples were charred in a closed crucible at temperature 700–800°C such that they were converted to charcoal. The coal was transferred into a stainless steel reactor containing adequate quantity of metallic lithium (1 g lithium per 1 g carbonized sample); the reactor was then heated under vacuum at a temperature of 750°C in order to produce lithium carbide. While for reference materials and intercomparison samples, vacuum pyrolysis was performed. A titanium liner containing the sample was inserted into a stainless steel reactor containing lithium metal. The reactor was then closed, evacuated, and heated in an electrical furnace at 750°C (**Fig. 1**). This technique allows the degradation of organic sample and chemical absorption of gaseous products by melted lithium (Skripkin and Kovaliukh, 1998). The obtained lithium carbide was then converted to acetylene ($C_2H_2$) by vacuum hydrolysis, purified by passing through a chromic acid solution and captured in a vial no. I. The produced ($C_2H_2$) was unfrozen in vial no. I and transferred to vial no. II, then transformed to benzene ($C_6H_6$) using a vanadium catalyst regenerated previously at 300–400°C. After that the benzene is retrieved to vial no. II. The whole process and the synthesis line are illustrated in **Fig. 2**. The ben-
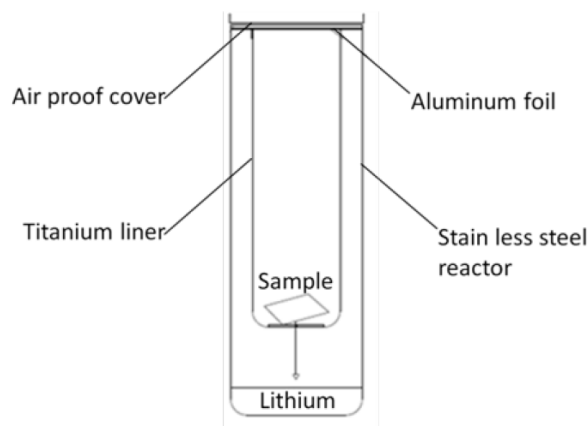


**Fig. 1.** *Vacuum pyrolysis.*

**Table 1.** *Counting region optimization data.*

| Counting region | Background (cpm) | Oxalic Acid II standard (cpm) | Efficiency (%) | *FOM* ($E^2/B$) |
|---|---|---|---|---|
| 20–85 | 0.17 ± 0.02 | 135.5 ± 0.4 | 41 | 9767 |
| 15–105 | 0.27 ± 0.03 | 170.4 ± 0.2 | 51 | 9846 |
| 10–95 | 0.33 ± 0.03 | 208.0 ± 0.5 | 62 | 11972 |

zene was purified by sulphuric acid followed by sublimation (Muraki *et al.,* 2001). Butyl-PBD was used as scintillator in proportion of 10 mg per 1 g of benzene.

## Measurement techniques

Low level liquid scintillation counter, Tri-Carb 3180 TR/SL was used for the radiocarbon measurement; the counting system is composed of two photomultiplier tubes (PMT), amplifier, analogue to digital convertor (ADC), multichannel analyzer (MCA), a PC to display spectra via Quanta Smart program. All electronic components are surrounded by a lead shield. The Tri-Carb 3180 incorporates a programmable time resolved electronics that, in addition to the incorporated bismuth germanate detector ($Bi_4Ge_3O_{12}$) and the pulse shape analyzer (PSA), reduces to a minimum the background interference and discriminate the true beta events. The tested samples were counted in 6 cycles for 300 minutes resulting in total of 1800 minutes per sample. The results were reported as PMC (%) which was obtained from the ratio of specific activity of sample to that of standard oxalic acid used, for the reference materials and intercomparison samples, and as $\Delta^{14}C$ per mil (‰) for green grass samples.
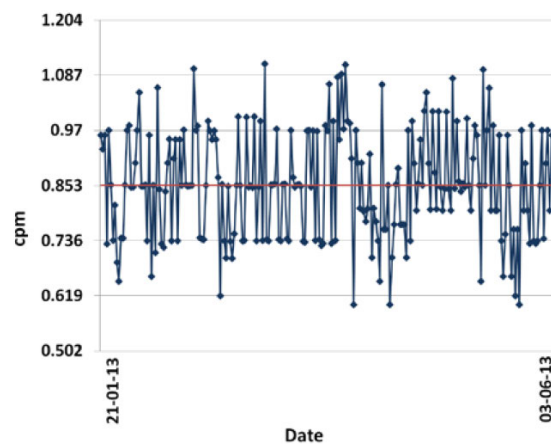
## Calibration of Tri-Carb for radiocarbon measurements

Normalization was carried out monthly to check the stability of the counting system, through the measurement of background, C-14 and H-3 standards provided by Perkin Elmer. **Fig. 3** shows the detector background results over time. Teflon vials of a volume of 7 ml were used. The counting region optimization was carried out to maximize factor of merit ($FOM = E^2/B$) which was calculated at three counting windows, where $E$ is the efficiency
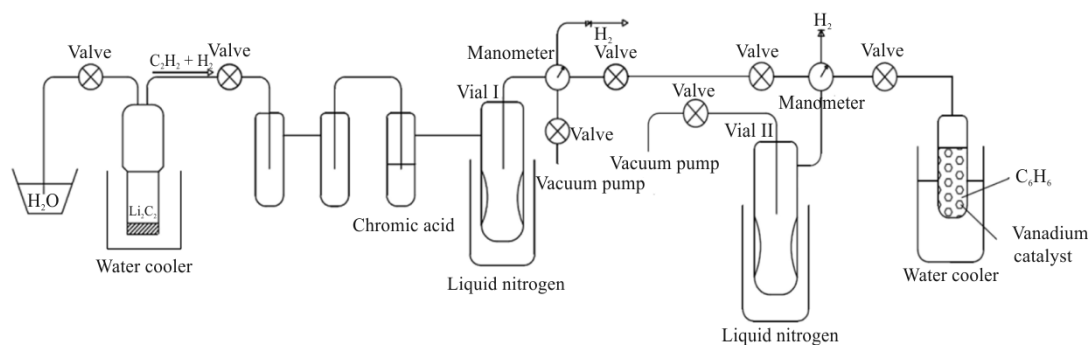
and $B$ is the background count rate (L'Annunziata, 2003; Bronić *et al.*, 2009; Knoll, 2010). For this purpose, blank sample containing commercial dead benzene purchased from Sigma-Aldrich, and a standard sample Oxalic Acid II from NIST-SRM 4990C were prepared and measured in the adopted counting geometry. **Table 1** represents the related data. For standardization, a set of standard oxalic acid II samples with different quenching degree were measured. The measurement results were presented in **Table 2** as well as the obtained quenching curve representing efficiency function of Spectral Index of the Sample (SIS) was illustrated in **Fig. 4**. In addition, these standards were measured routinely for stability check. Their specific activities were deduced and represented in **Fig. 5**.

## 3. RESULTS AND DISCUSSION

Measurement results of reference materials and intercomparison samples were analysed statistically using z-score and u-score calculated as follow:



**Fig. 3.** *Detector background results over time. These data are obtained from weekly measurements made on the same weekday over the period of six months.*



**Fig. 2.** *Benzene synthesis line.*

$$z\text{-}score = \frac{Lab\ value - Target\ value}{\sigma_{Lab}} \qquad (3.1)$$

$$u\text{-}score = \frac{|Lab\ value - Target\ value|}{\sqrt{\sigma_{Lab}^2 + \sigma_{Target}^2}} \qquad (3.2)$$

where $\sigma_{Lab}$ is the laboratory error and $\sigma_{Target}$ is the standard deviation of the target value.

For complying with fitness for purpose, z-score should be between –2 and +2; while for values between –3 and +3, further investigation is needed (Scott *et al.,* 2010; Sironić *et al.*, 2013). The u-score values were compared to critical ones listed in t-statistic tables; we choose 99% confidence interval for which a measurement result is acceptable if u-score is < 2.58 (Sironić *et al.*, 2013). **Table 3** lists the obtained z-score and u-score values.

The data obtained were acceptable, as z-score values were found to lie between –1.28 and 1.66, and u-score values were below the predefined acceptability limit of 2.58. The u-score values were close to the absolute values of z-score due to the fact that the error of target value ($\sigma_{Target}$) is much lower than lab error ($\sigma_{Lab}$).

Student's t-test applied to paired sets of data was also used to evaluate our results giving $p = 0.33$, a value > 0.05 which means that the compared sets of data are not different. Comparison between our values and target values is shown in **Fig. 6**.

The correlation coefficient ($R$) was found to be 0.997, showing a good correlation and agreement between lab results and target values.

The green grass samples results were reported as $\Delta^{14}C$ per mil (‰) deviation from standard (Oxalic acid II). The

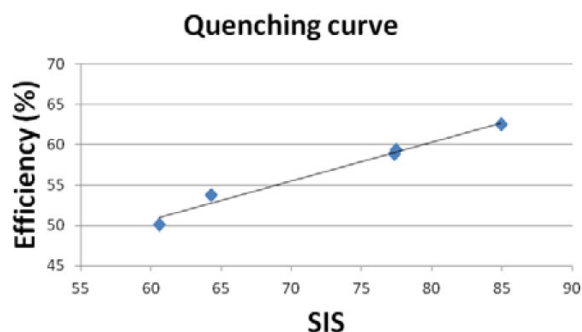**Table 2.** *Measurement results of standards with different quenching degree, efficiency and SIS values.*

| Standard | (cpm) | Efficiency (%) | SIS |
|---|---|---|---|
| 1 | 36.0 ± 0.5 | 50.11 | 60.56 |
| 2 | 36.2 ± 0.9 | 53.81 | 64.28 |
| 3 | 182.0 ± 0.2 | 58.83 | 77.34 |
| 4 | 190.7 ± 0.2 | 59.43 | 77.47 |
| 5 | 233.7 ± 0.6 | 62.54 | 84.93 |

measured activities of background and standard used for the calculation of percent modern carbon (*PMC*) were 0.25 cpm and 180.23 cpm, respectively, corresponding to specific activities of 0.06 cpm/g and 40.47 cpm/g. Formulae presented in literature (Stuiver and Polach, 1977; Battibaglia *et al.,* 2010; Pataki *et al.,* 2010) were used to calculate $\delta^{14}C$. No correction for isotope fractionation was done, as $\delta^{13}C$ values in grass range from –25‰ to –29‰ relative to PDB standard (Stuiver Polach, 1977); we assumed $\delta^{13}C$ in grass is –25‰ (Muraki *et al.,* 2001), and hence we used $\delta^{14}$ as $\Delta^{14}C$. $\delta^{13}C$ values could be determined for more accurate calculations and discussions. Difference in radiocarbon content in grass samples could be attributed to anthropogenic effect on isotopic ratio. Higher values were found in clean mountain air characterized by the absence of traffic and industries, while lower concentrations were present in the samples collected from the vicinity of an electrical power plant (7‰ and 15‰). Samples collected from the campus of a cement industry showed very low $\Delta^{14}C$ (–23‰). The depletion in radiocarbon content is attributed to the fossil fuel combustion that dilutes the natural radiocarbon by non-radioactive or dead carbon.
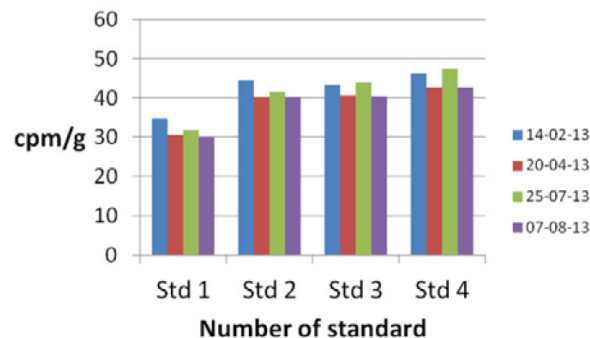


**Fig. 4.** *Quenching curve.*



**Fig. 5.** *Stability testing of standards.*

**Table 3.** *VIRI and IAEA values, lab error, z-score and u-score.*

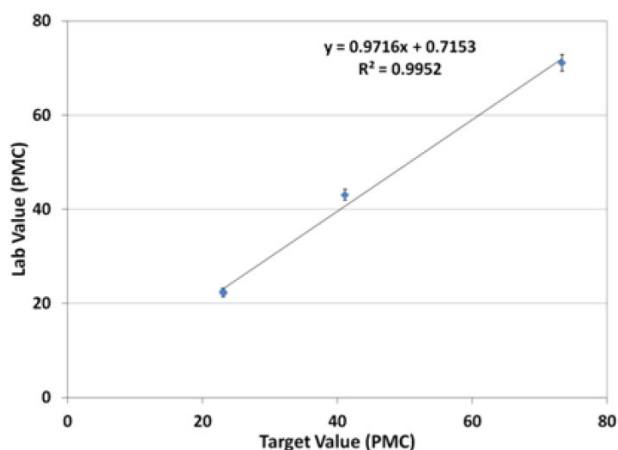| Sample Code | Sample type | Consensus value (PMC) | $\sigma_{Target}$ | Lab Value (PMC) | $\sigma_{Lab}$ | z-score | u-score |
|---|---|---|---|---|---|---|---|
| U | Humic acid | 23.079 | 0.0155 | 22.20 | 0.80 | -1.09 | 1.10 |
| R | Murex shell | 73.338 | 0.0368 | 71.11 | 1.74 | -1.28 | 1.28 |
| IAEA-C2 | Travertine | 41.14 | 0.03 | 43.07 | 1.16 | 1.66 | 1.66 |
| IAEA-C5 | Wood | 23.05 | 0.02 | 22.52 | 0.68 | -0.78 | 0.80 |

**Fig. 6.** *Comparison between lab values and target values.*

## 4. CONCLUSION

The results of reference materials and intercomparison samples are in good agreement with the target values, and hence the radiocarbon laboratory at the Lebanese Atomic Energy Commission is ready to undergo routine measurement of radiocarbon activity in different matrices and providing reliable results using conventional method. The measurement of $\Delta^{14}C$ in green grass samples is a sensitive and innovative tool to study anthropogenic impact on natural radiocarbon content. Based on these data, further advanced ecological studies will be implemented.

## ACKNOWLEDMENT

## REFERENCES

Battipaglia G, Marzaioli F, Lubritto C, Altieri S, Strumia S, Cherubini P and Cotrufo MF, 2010. Traffic pollution affects tree-ring width and isotopic composition of Pinus pinea. *Science of the Total Environment* 408(3): 586–593, DOI 10.1016/j.scitotenv.2009.09.036.

Beramendi-Orosco LE, Gonzalez-Hernandez G, Urrutia-Fucugauchi J and Morton-Bermea O, 2006. Radiocarbon Laboratory at the National Autonomous University of Mexico: First set of samples and new $^{14}C$ internal reference material. *Radiocarbon* 48(3): 485–491.

Bronić IK, Horvatinčić N, Barešić J and Obelić B, 2009. Measurement of $^{14}C$ activity by liquid scintillation counting. *Applied Radiation and Isotopes* 67(5): 800–804, DOI 10.1016/j.apradiso.2009.01.071.

Bronić IK, Obelić B, Horvatinčić N, Barešić J, Sironić A and Minichreiter K, 2010. Radiocarbon application in environmental science and archaeology in Croatia. *Nuclear Instruments and Meth-*

*ods in Physics Research A* 619(1–3): 491–496, DOI 10.1016/j.nima.2009.11.032.

Hoque MA and Burgess WG, 2012. $^{14}C$ dating of deep groundwater in the Bengal Aquifer System, Bangladesh: Implications for aquifer anisotropy, recharge sources and sustainability. *Journal of Hydrology* 444–445: 209–220, DOI 10.1016/j.jhydrol.2012.04.022.

Knoll GF, 2010. Radiation detection and measurement, fourth edition, USA.

Kulkova M, Chadov F and Davidochkina A, 2011. Radiocarbon in vegetation of coastal zone of Finnish Bay (Russia). *Procedia Environmental Sciences* 8: 375–381.

L'Annunziata MF, 2003. Handbook of radioactivity analysis, second edition, vol.2, Elsevier, USA.

Marzaioli F, Fiumano V, Capano M, Passariello I, Cesare NDe and Terrasi F, 2011. Forensic applications of $^{14}C$ at CIRCE. *Nuclear Instruments and Methods in Physics Research B* 269: 3171–3175, DOI 10.1016/j.nimb.2011.04.025.

Mazeika J, Petrosius R and Pukiene R, 2008. Carbon-14 in tree rings and other terrestrial samples in the vicinity of Ignalina Nuclear Power Plant, Lithuania. *Journal of Environmental Radioactivity* 99(2): 238–247, DOI 10.1016/j.jenvrad.2007.07.011.

Molnar M, Bujtas T, Svingor E and Fluto I, 2007. Monitoring of atmospheric excess $^{14}C$ around Paks nuclear power plant, Hungary. *Radiocarbon* 49(2): 1031–1043.

Muraki Y, Masua K, Arslanov, Toyoizumi H, Kato M, Naruse Y, Murata T and Nishiyama T, 2001. Measurement of radiocarbon content in leaves from some Japanese sites. *Radiocarbon* 43(2B): 695–701.

Nakata K, Kodama H, Hasegawa T, Hama K, Lwatsuki T and Miyajima T, 2013. Groundwater dating using radiocarbon in fulvic acid in groundwater containing fuorescein. *Journal of Hydrology* 489: 189–200, DOI 10.1016/j.jhydrol.2013.03.012.

Olsen J, Heinemeier J, Hornstrup KM, Bennike P and Thrane H, 2013. "Old wood" effect in radiocarbon dating of prehistoric cremated bones? *Journal of Archaeological Science* 40(1): 30–34, DOI 10.1016/j.jas.2012.05.034.

Pataki DE, Randerson JT, Wang W, Herzenach MK and Grulke NE, 2010. The carbon isotope composition of plants and soils as biomarkers of pollution. *West et al. (eds), Isoscapes: Understanding Movement, Pattern and Process on Earth Through isotope Mapping,* Springer: 407–423, DOI 10.1007/978-90-481-3354-3.

Rakowski AZ, Nadeau MJ, Nakamura T, Pazdur A, Pawelczyk S and Piotrowska N, 2013. Radiocarbon method in environmental monitoring $CO_2$ emission. *Nuclear Instruments and Methods in Physics Research B* 294: 503–507, DOI 10.1016/j.nimb.2012.07.017.

Rozanski K, Stichler W, Gonfianti R, Scott EM, Beukens RP, Kromer B and Vander Plitch J, 1992. The IAEA $^{14}C$ intercomparison exercise 1990. *Radiocarbon* 34(3): 506–519.

Scott EM, Cook GT and Naysmith P, 2010. The Fifth International Radiocarbon Intercomparison (VIRI): An assessment of laboratory performance in stage 3. *Radiocarbon* 52(2–3): 859–865.

Sironić A., Bronić IK, Horvatinčić N, Barešić J, Obelić B and Felja I, 2013. Statud report on Zagreb Radiocarbon Laboratory- AMS and LSC results. *Nuclear Instruments and Methods in Physics Research B* 294: 185–188, DOI 10.1016/j.nimb.2012.01.048.

Skripkin V and Kovaliukh N, 1998. Recent developments in the procedures used at the SSCER laboratory for the routine preparation of lithium carbide. *Radiocarbon* 49(1): 211–214.

Stuiver M and Polach HA, 1977. Discussion: Reporting of $^{14}C$ data. *Radiocarbon* 19(3): 355–363.

Svetlik I, Povinec PP, Molnar M, Meinhardt F, Michalek V, Simon J and Svingor E, 2010. Estimation of long-term trends in the tropospheric $^{14}CO_2$ activity concentration. *Radiocarbon* 52(2–3): 815–822.

Thompson M, Ellison SLR and Wood R, 2006. The international harmonized protocol for the proficiency testing of analytical chemistry laboratories. IUPAC Technical Report. *Pure and Applied Chemistry* 78(1): 145–196, DOI 10.1351/pac200678010145.