

PACS: 78.60.Kn

RADIOCARBON DATING OF ARCHEOLOGICAL MONUMENTS IN AZERBAIJAN

A.S. Ahadova, M.A. Gurbanov, S.G. Mammadov, A.B. Ahadov, A.Z. Abishov

Institute of Radiation Problems, MSE AR

a.ahadova@irp.science.az

Abstract: This study aims to enhance the accuracy of C-14 dating of archaeological monuments in the Republic of Azerbaijan. Charcoal samples were collected from various sites (Polutepe, Shomutepe, Goytepe, Pashatepe, Boyukdash-Anazaga, Burugtepe, Alkhantepe, Gebele-Selbir, Uzun Reme) for C-14 measurements. The counting vial was placed into a Tri-Carb 3100TR liquid scintillation analyzer and allowed to count for a period of 300 to 1000 minutes depending on the size, age, and precision requirements. As a scintillation solution, 1 ml of commercially available SIGMA-ALDRICH liquid scintillation mixture PPO/POPOP in toluene was used. In this study the radiocarbon dating method was employed to determine the age of charcoal samples from archeological monuments in Azerbaijan. Calibration results were calculated with a 68% and 95% probability ($t = 1950$).

Keywords: dating, radiocarbon, Azerbaijan, archeology.

1. Introduction

Radiocarbon (^{14}C) dating is a fundamental technique for determining the age of carbon-bearing materials up to approximately 40,000-50,000 years [1]. However, its application to oil – a substance derived from ancient organic material millions of years old – presents unique challenges and opportunities [2–10]. This paper explores the applications of ^{14}C dating in analyzing samples that absorbed carbon during various periods in Azerbaijan. We collected samples from several monuments, including Polutepe, Shomutepe, Goytepe, Pashatepe, Boyukdash-Anazaga, Burugtepe, Alkhantepe, Gebele-Selbir, Uzun Reme in Azerbaijan.

2. Methodology

The benzene synthesis line for radiocarbon dating from the sample's original state to benzene is schematically described [11–16]. Like many laboratories, we also utilize silica-alumina catalysts for the cyclization of acetylene into benzene. The catalyst can be easily reactivated by heating in air at 570 °C, which causes the oxidation of the Cr(III) and Cr(IV) to Cr(VI).

In carbon-14 dating, the assumption is that the sample has only undergone radioactive decay within the years, since it ceased interacting with the biosphere. However, the archaeological artifacts and geological specimens are often found embedded in or contaminated by other carbon-bearing materials, which can influence the carbon-14 content of samples. The reliability of the dating ancient charcoal samples depends on the chemical treatment to remove any external ^{14}C while preserving reliable fractions for analysis. Charcoal samples, weighing 25 grams were treated using an acid-alkali-acid (AAA) method [17–21] after the removal of visible contaminants. The concentration of the acid (HCl) and alkali (NaOH) were 0.5%.

Benzene production was achieved through the following reactions:

- a) $2\text{C} + 2\text{Li} = \text{Li}_2\text{C}_2$
- b) $\text{Li}_2\text{C}_2 + \text{H}_2\text{O} = \text{C}_2\text{H}_2 + \text{Li}_2\text{O}$
- c) $3\text{C}_2\text{H}_2 = \text{C}_6\text{H}_6$

To eliminate potential ammonia compounds, acetylene is passed through phosphoric acid. A chromium-activated alumina-silica catalyst was employed for the conversion of acetylene to benzene at room temperature. The benzene was subsequently evaporated from the catalyst at 120 °C and collected under vacuum at liquid nitrogen temperature. The synthesized benzene [22–26] was transferred into 20 ml low-potassium glass counting vials and brought to a final volume of 3 ml by adding petroleum-derived benzene. As a scintillation solution, 1 ml of commercially available SIGMA-ALDRICH liquid scintillation mixture PPO/POPOP in toluene was added. The counting vial was then transferred into the liquid scintillation analyzer Tri-Carb 3100TR and allowed to count for a period of 300 to 1000 minutes depending on the size, age, and precision requirements. Radiocarbon dating using the Tri-Carb 3100TR is a well-established absolute dating technique widely applied in various fields of research for analyzing a broad range of organic materials. Precision levels on the order of 0.2–0.3% in the measured age have been achieved, and several international intercomparison exercises have demonstrated the high degree of reproducibility of the results.

Figure 1 The following diagram illustrates the configuration of the vacuum line employed in the synthesis of benzene. The benzene synthesis proceeds from left to right.

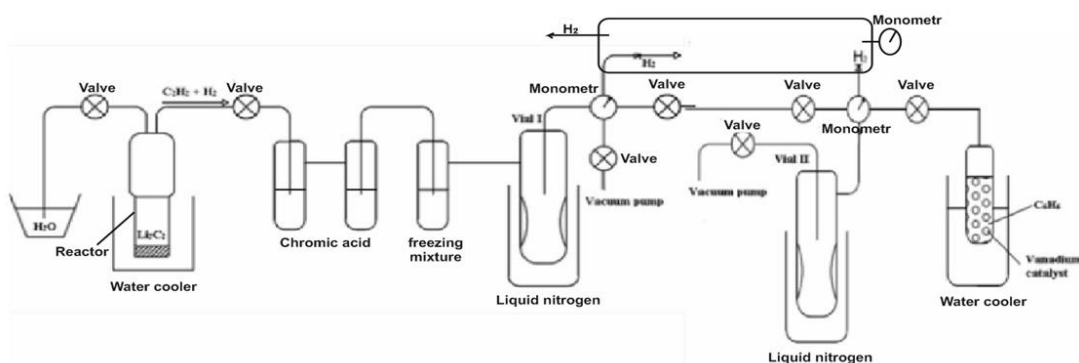


Fig. 1. Vacuum line employed in the synthesis of benzene.

The charcoal was converted to carbide with 95% efficiency through reaction (a) in the reactor. The reaction proceeded readily at 700 °C for 15 minutes, after which the temperature was raised to 900 °C. At this final temperature, the production of carbide [27–32] was completed. Subsequently, the hydrolysis of the lithium carbide was conducted in the water-cooled reactor by introducing distilled water at a rate of approximately 100 ml/min. This process proceeded with a quantitative yield according to reaction (b). The excess lithium reacts with the evolved hydrogen gas, which is not required in our procedure.

The gases produced from the hydrolysis reaction pass through a series of traps. The first of the two traps, located on the right side of the reactor and containing chromic acid, is designed to capture excess gases. In the third trap, which is cooled with a freezing mixture of acetone and dry ice, the gases are almost completely dried. After passing through these three traps, the acetylene is effectively dried and can be condensed in the subsequent “cold finger”, which is cooled with

liquid nitrogen. At this point, the hydrogen gas, which cannot freeze at the temperature of the “cold finger”, is removed using vacuum pump [33–35].

3. Results and Conclusion

Table 1 shows the results of the C-14 measurements of the monuments in Azerbaijan. Calibration results were calculated with a 68% and 95% probability (0 = 1950).

Table 1

Ages of various monuments in Azerbaijan.

Sample name	14C age (BP)	± error	Cal BC(68%) 1-sigma	CalBC(95%) 2-sigma	Material
Polutepe (sample 1)	6220	85	5303–5052	5364–4951	charcoal
Polutepe (sample 2)	6380	99	5473–5224	5531–5069	charcoal
Shomutepe	5801	96	4783–4542	4901–4446	charcoal
Goytepe	7746	88	6646–6476	6906–6422	charcoal
Pashatepe	6704	88	5713–5556	5749–5477	charcoal
Boyukdash-Anazaga	12644	210	13413–12514	13681–12210	charcoal
Burugtepe	6888	31	5796–5726	5877–5714	charcoal
Alkhantepe	5079	29	3952–3805	3959–3796	charcoal
Gebele-Selbir	1105	11	899–988	893–993	charcoal
Uzun Reme	3390	26	1732–1631	1750–1613	charcoal

References

1. S. Mammadov, M. Gurbanov, A. Ahadova, A. Abishov, Characterization of ancient ceramic shreds: Insights into firing conditions and manufacturing technology, *Recent Res. Sci. Technol.*, Sep. 2023, Vol. 15, pp. 12–17, <https://doi.org/10.25081/rrst.2023.15.8501>
2. S. Mammadov, A. Ahadova, Comprehensive Investigation of Neolithic Ceramic Samples: Firing Technology and Age Insights, *East Eur. J. Phys.*, 2023, Vol. 2023, No. 3, pp. 531–534, <https://doi.org/10.26565/2312-4334-2023-3-61>
3. S. Mammadov, A. Ahadova, A. Abishov, A. Ahadov, The Thermoluminescence Parameters of Irradiated K-Feldspar, *East Eur. J. Phys.*, Jun. 2023, Vol. 2023, No. 2, pp. 182–186, <https://doi.org/10.26565/2312-4334-2023-2-18>
4. S. Mammadov, M. Gurbanov, A. Ahadova, M. Bayramov, A. Ahmadov, Z. Dadashov, Electron Spin Resonance Dating of Fossil Tooth Enamel, *J. Radiat. Res.*, 2018, Vol. 5, No. 2, pp. 435–438, Available at: [Issue page](#), [PDF](#)
5. S. Mammadov, M. Bayramov, A. Abishov, A. Ahadova, Isothermal decay of the thermoluminescence (TL) glow curves in feldspar at an ambient temperature, *J. Radiat. Res.*, 2019, Vol. 6, No. 2, pp. 80–88, Available at: [Issue page](#), [PDF](#)
6. S. Mammadov, M. Bayramov, A. Abishov, A. Ahadova, Numerical Simulation of Thermoluminescence Dose Response of Quartz, *J. Radiat. Res.*, 2020, Vol. 7, No. 1, pp. 63–68, Available at: [Issue page](#), [PDF](#)
7. S. Mammadov, O. Samedov, M. Gurbanov, M. Bayramov, A. Abishov, A. Ahadova, Thermoluminescence Properties of Irradiated Quartz and Feldspar at Different Dose Rates, *J. Radiat. Res.*, 2020, Vol. 7, No. 2, pp. 70–75, Available at: [Issue page](#), [PDF](#)

8. S. Mammadov, A. Ahadova, Insights into ancient ceramic technology: a comprehensive analysis of mineralogy, chemistry and firing conditions, *Recent Res. Sci. Technol.*, 2024, Vol. 16, pp. 1–7, <https://doi.org/10.25081/rrst.2024.16.8758>
9. S. Mammadov, M. Bayramov, A. Abishov, A. Ahadova, Thermoluminescence parameters of quartz extracted from beach sand, *J. Radiat. Res.*, 2019, Vol. 6, No. 1, pp. 81–88, Available at: [Issue page](#), [PDF](#)
10. A.S. Ahadova, S.G. Mammadov, M.A. Bayramov, Spectral Deconvolution of Fossil Tooth Enamel Electron Paramagnetic Resonance Spectrum, *World Sci. Res.*, Sep. 2019, Vol. 6, No. 1, pp. 1–4, <https://doi.org/10.20448/journal.510.2019.61.1.4>
11. S.G. Mammadov, Z.Kh. Dadashov, A.B. Ahadov, A.S. Ahadova, M.A. Bayramov, F.Y. Humbatov, Thermo Luminescence Dating of Pottery Sample from Chukhur Gabala Archaeological Site in Gabala District of Azerbaijan, *Int. Rev. Appl. Sci.*, 2018, Vol. 4, No. 1, pp. 1–5, <https://doi.org/10.20448/journal.513.2018.41.1.5>
12. S.G. Mammadov, M.A. Bayramov, A.Z. Abishov, A.S. Ahadova, Anisotropy of the EPR spectra of fossil tooth enamel plates, *J. Radiat. Res.*, 2021, Vol. 8, No. 2, pp. 5–9, Available at: [Issue page](#), [PDF](#)
13. T.I. Akhundov, S.G. Mammadov, A.A. Ahadova, A.N. Abdullayev, Dating of Charcoal Samples from the Polutepe Archeological Site in Azerbaijan, *Asian J. Humanit. Soc. Stud.*, Sep. 2018, Vol. 6, No. 4, pp. 147–151, <https://doi.org/10.24203/ajhss.v6i4.5459>
14. S. Mammadov, M. Bayramov, A. Abishov, A. Ahadova, EPR Study of the Modern Tooth Enamel, *J. Radiat. Res.*, 2020, Vol. 8, No. 1, pp. 30–35, Available at: [Issue page](#), [PDF](#)
15. S. Mammadov, A. Ahadov, Kinetic parameters of Thermoluminescence in nano α -Al₂O₃: A Heating Rate Study, *J. Radiat. Res.*, 2023, Vol. 10, No. 2, pp. 44–50, Available at: [Issue page](#), [PDF](#)
16. A.R. Millard, Conventions for Reporting Radiocarbon Determinations, *Radiocarbon*, 2014, Vol. 56, No. 2, pp. 555–559, <https://doi.org/10.2458/56.17455>
17. G. Belluomini, A. Delfino, L. Manfra, V. Petrone, Benzene synthesis for radiocarbon dating and study of the catalyst used for acetylen trimerization, *Int. J. Appl. Radiat. Isot.*, 1978, Vol. 29, No. 7, pp. 453–459, [https://doi.org/10.1016/0020-708X\(78\)90083-2](https://doi.org/10.1016/0020-708X(78)90083-2)
18. C.J. Heusser, Radiocarbon Dates of Peats from North Pacific North America, *Radiocarbon*, 1959, Vol. 1, pp. 29–34, <https://doi.org/10.1017/s0033822200020336>
19. M. Stuiver, H.A. Polach, Discussion: Reporting of ¹⁴C Data, *Radiocarbon*, 1977, Vol. 19, No. 3, pp. 355–363, <https://doi.org/10.1017/S0033822200003672>
20. P. Guibert, C. Ney, F. Bechtel, M. Schvoerer, F. Geus, TL and radiocarbon dating of neolithic sepultures from Sudan: Intercomparison of results, *Radiat. Meas.*, Apr. 1994, Vol. 23, No. 2–3, pp. 393–398, [https://doi.org/10.1016/1350-4487\(94\)90069-8](https://doi.org/10.1016/1350-4487(94)90069-8)
21. Y.T. Handayani, W. Soemadi, K. Isogaf, Radiocarbon Dating Using LSC, *Widyanuklida*, 2004, Vol. 5, No. 2, pp. 1–9.
22. H. Oeschger, T. Riesen, Bern Radiocarbon Dates IV, *Radiocarbon*, 1965, Vol. 7, pp. 1–9, <https://doi.org/10.1017/s0033822200037048>
23. C.M. Wurster, M.I. Bird, I. Bull, C. Bryant, P. Ascough, A protocol for radiocarbon dating tropical subfossil cave guano, *Radiocarbon*, 2009, Vol. 51, No. 3, pp. 977–986, <https://doi.org/10.1017/S0033822200034056>
24. J.A. Lowdon, Carbon-Isotope Fractionation During Dry Combustion of Oxalic Acid, *Radiocarbon*, 1970, Vol. 12, No. 2, pp. 347–349, <https://doi.org/10.1017/S0033822200008110>
25. M.L.T.G. Mendonça, J.M. Godoy, R.P. da Cruz, R.A.R. Perez, Radiocarbon dating of archaeological samples (sambaqui) using CO₂ absorption and liquid scintillation spectrometry

- of low background radiation, *J. Environ. Radioact.*, 2006, Vol. 88, No. 3, pp. 205–214, <https://doi.org/10.1016/j.jenvrad.2005.12.011>
26. M.I. Bird, Radiocarbon Dating | Charcoal, *Encyclopedia of Quaternary Science*, 2013, pp. 353–360, <https://doi.org/10.1016/b978-0-444-53643-3.00047-9>
27. G.M. Santos et al. Radiocarbon dating of wood using different pretreatment procedures: application to the chronology of Rotoehu Ash, New Zealand, *Radiocarbon*, 2001, Vol. 43, No. 2A, pp. 239–248, <https://doi.org/10.1017/S0033822200038066>
28. G. Zaitseva, V. Skripkin, N. Kovaliukh, G. Possnert, P. Dolukhanov, A. Vybornov, Radiocarbon dating of neolithic pottery, *Radiocarbon*, 2009, pp. 795–801, <https://doi.org/10.1017/S0033822200056101>
29. Y. Nazoki, Yale University geology and geophysics radiocarbon dates I, *Radiocarbon*, 1977, Vol. 19, No. 1, pp. 138–141, <https://doi.org/10.1017/S0033822200003416>
30. S.W. Manning, Problems of Dating Spread on Radiocarbon Calibration Curve Plateaus: The 1620–1540 BC Example and the Dating of the Therasia Olive Shrub Samples and Thera Volcanic Eruption, *Radiocarbon*, 2024, Vol. 66, No. 2, pp. 341–370, <https://doi.org/10.1017/rdc.2024.44>
31. R.E. Taylor, Radiocarbon Dating of Bone: To Collagen and Beyond, *Radiocarbon After Four Decades*, 2013, pp. 375–402, https://doi.org/10.1007/978-1-4757-4249-7_25
32. R. Switsur, J.S. Waterhouse, Benzene purity in radiocarbon dating samples, *Radiocarbon*, 1989, Vol. 31, No. 3, pp. 260–263, <https://doi.org/10.1017/S0033822200011772>
33. A. Ahadova, A. Ahadov, A. Abishov, M. Gurbanov, S. Mammadov, Temperature effect on thermoluminescence kinetic parameters of nano-alumina, *Adv. Phys. Res.*, 2024, Vol. 6, No. 3, pp. 239–246, <https://doi.org/10.62476/apr63239>
34. I.I. Mustafayev, H.M. Hajiyevev. Low-carbon radiation-thermal pyrolysis of lignites. *J. Radiat. Res.*, 2022, Vol. 9, No. 2, pp. 5–13. Available at: [Issue page](#), [PDF](#)
35. T.N. Aghayev, S.Z. Malikova. Study of Radiation-catalytic activity of n-ZnO₂ during the decomposition of hexane and hexane-water solutions. *J. Radiat. Res.*, 2023, Vol. 10, No. 2, pp. 1–6, Available at: [Issue page](#), [PDF](#)

РАДИОУГЛЕРОДНОЕ ДАТИРОВАНИЕ АРХЕОЛОГИЧЕСКИХ ПАМЯТНИКОВ АЗЕРБАЙДЖАНА

А.С. Ахадова, М.А. Гурбанов, С.Г. Мамедов, А.Б. Ахадов, А.З. Абишов

Резюме: Представленная работа была попыткой повысить точность датирования археологических памятников Азербайджанской Республики по методу С-14. Образцы древесного угля были собраны из различных мест (Полутепе, Шомутепе, Гейтепе, Пахсатепе, Беюкдаш-Аназага, Буругтепе, Алхантепе, Гебеле-Сельбир, Узун Реме) для измерений С-14. Счетный флакон был помещен в жидкостный сцинтилляционный анализатор Tri-Carb 3100TR и оставлен для подсчета в течение периода от 300 до 1000 минут в зависимости от размера, возраста и требований к точности. В качестве сцинтилляционного раствора был добавлен 1 мл коммерчески доступной жидкостной сцинтилляционной смеси SIGMA-ALDRICH PPO/ПОРОП в толуоле. В этом исследовании метод радиоуглеродного датирования был использован для датирования возраста образцов древесного угля из археологических памятников Азербайджана. Результаты калибровки были рассчитаны с вероятностью 68% и 95% (0 = 1950).

Ключевые слова: датировка, радиоуглеродный, Азербайджан, археология.

AZƏRBAYCAN ƏRAZİSİNDƏ YERLƏŞƏN ARXEOLoji ABİDƏLƏRİN RADIOKARBON TARİXLƏNDİRİLMƏSİ

A.S. Əhədova, M. Ə. Qurbanov, S.Q. Məmmədov , Ə.B. Əhədov, A.Z. Abışov

Xülasə: Təqdim olunan iş Azərbaycan Respublikası ərazisində yerləşən arxeoloji abidələrin C-14 metodu ilə mütləq tarixləndirilməsinə əsaslanır. C-14 ölçmələri üçün müxtəlif ərazilərdən (Polutəpə, Şomutəpə, Göytəpə, Pəhsətəpə, Böyükdaş-Anazağa, Buruqtəpə, Alxantəpə, Qəbələ Səlbir, Uzun Rəmə kömür nümunələri toplanmışdır. Hesablayıcı flakon Tri-Carb 3100TR Maye Sintilyasiya Analizatoruna yerləşdirildi və ölçüdə və dəqiqlik tələblərindən asılı olaraq 300 ilə 1000 dəqiqə arasında dəyişən müddət ərzində hesablandı. Toluolda 1 ml SIGMA-ALDRICH PPO/POPOP maye sintillyasiya qarışığı(kokteyl) sintilasiya məhlulu kimi əlavə edildi. Bu tədqiqatda Azərbaycanda arxeoloji ərazilərdən alınan kömür nümunələrinin yaşını təyin etmək üçün radiokarbon tarixləndirmə üsulundan istifadə edilmişdir. Kalibrlemə nəticələri 68% və 95% (0 = 1950) ehtimalı ilə hesablanmışdır.

Açar sözlər: tarixləndirmə, radiokarbon, Azərbaycan, arxeologiya.