REPUBLIC OF AZERBAIJAN

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ABSTRACT

of the dissertation for the degree of Doctor of Philosophy

COMPARATIVE DATING OF NEOLITHIC PERIOD ARCHAEOLOGICAL SITES IN AZERBAIJAN USING RADIOCARBON, EPR, AND THERMOLUMINESCENT METHODS

Speciality: 2225.01 - Radiation Materials Science

Field of science: Chemistry

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GENERAL CHARACTERISTICS OF THE WORK

Relevance of the topic and degree of development.

In recent years, the analysis of materials discovered during the investigation of archaeological monuments using modern scientific methods has become an integral part of scholarly research. Although a small number of Neolithic period samples from Azerbaijani archaeology have been dated in foreign laboratories using only the Radiocarbon (^{14}C) method within a limited framework[1,2], no attempts have been made to apply Electron Paramagnetic Resonance (EPR) or Thermoluminescent (TL) dating techniques. Furthermore, a review of the protocols for the Radiocarbon analyses available in the literature reveals that the physical and chemical characteristics of the analyzed samples, as well as the values of ^{14}C activity within them, are not provided - only the age estimates of the samples are reported. Considering the theoretical advantages offered by direct dating techniques, it is evident that a comprehensive application of the ^{14}C, EPR, and TL methods based on the physico-chemical properties of materials has yet to gain a proper foothold in Azerbaijani archaeology. The ages of many Neolithic sites in Azerbaijan have primarily been determined using traditional or stratigraphic methods (based on the depth at which the material was found and other theoretical approaches), which can sometimes result in inaccurate conclusions. Recent advances in understanding the physical and chemical processes underlying the methods used in this dissertation have turned them into more reliable tools for archaeological dating.

On the other hand, unlike the Neolithic period, there is a sufficient number of archaeological artifacts (such as buildings, various weapons, coin specimens, certain inscribed monuments, etc.) available

[1] Butomo S.V. Radiocarbon Dating in the Soviet Union // Radiocarbon - 1965. vol. 7, doi: 10.1017/s003382220003722x., P. 223–228

[2] Nishiaki Y. Investigating Cultural and Socioeconomic Change at the Beginning of the Pottery Neolithic in the Southern Caucasus: The 2013 Excavations at Hacı Elamxanlı Tepe, Azerbaijan / F.Guliyev, S.Kadowaki, V.Alakbarov [et.al] // Bull. Am. Sch. Orient. Res. - 2015. Nov. vol. 374, doi: 10.5615/bullamerschoorie.374.0001. , P. 1–28.

to clarify the chronology of monuments from more recent historical periods. However, for Neolithic-era monuments, no such data are accessible anywhere. The methods proposed in this dissertation allow for the dating of materials with an accuracy of approximately 85–90%.

In the field of radiation materials science, thermoluminescent studies serve as a valuable tool for examining dielectrics, particularly the quartz components found in ancient ceramics. Investigating the thermoluminescent properties of natural quartz enables a better understanding of the radiation dose absorbed by these materials and contributes to the improvement of radiation measurement techniques. Developing methodological foundations in this area of materials science is of critical relevance today.

The application of these methods will contribute not only to the modernization of archaeological research in Azerbaijan but also across the entire Caucasus region. This, in turn, will help ensure that national science aligns with international standards.

Object and subject of the research.

As research objects, various archaeological materials uncovered during excavations - such as tooth samples, ceramics, charcoal, and others - were selected. The subject of the dissertation is the extraction of enamel, quartz, and carbon materials from these samples, the investigation of changes occurring in them under the influence of natural radiation, and their chronological dating through the study of their physic - chemical characteristics using Radiocarbon, Thermoluminescent, and Electron Paramagnetic Resonance methods.

Goals and objectives of the dissertation work.

The aim of this research is to investigate the physico-chemical parameters of materials used for the dating of Neolithic period monuments in Azerbaijan and to explore the applicability of Radiocarbon, EPR, and Thermoluminescent methods for this purpose.

In order to achieve the goal of the dissertation work was planned to implement the following:

- Convert organic archaeological artifacts and modern standard samples uncovered during excavations into benzene through chemical transformation, and determine their activity using a scintillation counter.

- Determine the age of organic archaeological finds and modern standards using the Radiocarbon method based on their measured activity levels, and calibrate the obtained radiocarbon ages in accordance with international standards.

- Isolate quartz material from ceramics following international protocols and study their thermoluminescent properties.

- Investigate the dose dependence of the thermoluminescent signal of quartz and, based on this relationship, determine the historically absorbed dose and the equivalent dose (D_e) of the ceramic samples.

- Collect soil samples from the immediate vicinity of the archaeological site and determine the activity of isotopes in the Uranium, Thorium, and Potassium decay chains within these samples using gamma-spectroscopy.

- Determine the age of Neolithic ceramics in accordance with international protocols based on results obtained from thermoluminescent and gamma-spectroscopy methods.

- Measure the thermogravimetric parameters and X-ray phase spectra of the studied ceramic materials in order to estimate their firing temperatures.

- Investigate the paramagnetic properties of tooth enamel using the EPR method and calculate the equivalent dose historically absorbed by the tooth sample based on this data. Estimate the age of the archaeological object by determining both the equivalent dose and the annual dose rate provided by the surrounding soil in which the fossil tooth was found.

Research methods.

In the course of this research, the scintillation method based on benzene synthesis was employed for age determination using the Radiocarbon method. Benzene was obtained from the sample, which had undergone special purification stages (Acid-Alkali-Acid treatment and drying), following this sequence: synthesis of lithium carbide using lithium metal melted at a minimum of 700°C, hydrolysis of lithium carbide in an oxygen-free environment to produce acetylene, and catalytic trimerization of acetylene to yield benzene. As the scintillation cocktail, a commercially available liquid scintillation mixture

(PPO/POPOP) dissolved in toluene and produced by SIGMA-ALDRICH was used. For age determination based on radiocarbon decay, three key parameters were identified: the specific activity of the sample, the activity of a standard sample, and the background level (environmental radioactivity). For the measurement of background radiation, "dead" benzene derived from petroleum was used. Prepared samples were placed into a “Tri-Carb 3100TR” liquid scintillation analyzer manufactured by PERKIN ELMER, and the number of radioactive decay events was recorded over 300–1000 minutes, depending on the required precision, the amount of benzene, and the estimated age range. Key technical specifications of the device include: an energy range of 0–2000 keV; a background level of ~16 CPM for ^{14}C; a measurement chamber temperature controlled with a precision of ±0.5°C (within an approximate range of 5–35°C); and an internal control system operated via a dedicated computer and proprietary “LSC” software developed by “PerkinElmer”.

For thermoluminescent measurements, quartz material was chemically extracted from the ceramic matrix using a series of treatments involving hydrochloric acid, hydrogen peroxide, hydrofluoric acid, and sodium polytungstate (with a specific gravity of 2.5–3 g/cm³). The resulting samples were then mounted onto discs approximately 0.5 cm in diameter, and these discs were placed in the device to record their TL spectra. The optimal sample mass for TL analysis is typically between 5–10 mg. TL measurements were conducted using a “Harshaw TLD 3500 Manual Reader.” The heating range of this instrument extends from room temperature up to 400°C, and the heating rate can be adjusted from 1°C/sec to 40°C/sec. Irradiation of the quartz grains was performed using cobalt-60 (^{60}Co) gamma-ray sources, specifically the “MRX-ɤ25” and “RXUND-20000” models located at the High Technologies Park of the Azerbaijan National Academy of Sciences. The dose rate of the ^{60}Co gamma source was measured using a “Magnette Miniscope MS400 EPR” spectrometer in combination with BioMax alanine dosimeter films manufactured by “Eastman Kodak”.

As additional methods for the dating of ceramics, X-ray fluorescence (XRF) spectroscopy was employed. This technique is

used to non-destructively determine the elemental composition of a material. XRF analysis enables accurate quantification of the primary chemical components in ceramic samples. The device's radiation source consists primarily of an X-ray tube with a Rhodium (Rh), Molybdenum (Mo), or Silver (Ag) anode. Its energy range can be adjusted between 1–40 keV. The detector is based on a lithium-drifted silicon (Si(Li)) crystal. To assess mass loss and thermal stability, thermogravimetric analysis (TG) was used. Differential thermal analysis (DTA) was employed to detect exothermic and endothermic reactions (e.g., dehydration, crystallization), and X-ray fluorescence (XRF) was utilized to determine the crystalline structure.

Thermogravimetric (TG) and differential thermal analyses (DTA) of ceramic powders were conducted using a "Perkin Elmer STA6000 Simultaneous Thermal Analyzer" under the following conditions: heating temperature from ambient temperature up to 950°C, heating rate of 5°C per minute, balance sensitivity of 0.1 µg, and a nitrogen gas flow rate of 20 ml/min. Powder X-ray diffraction (PXRD) analysis of the samples was performed using a "Bruker D2 Phaser" diffractometer. CuKα radiation (λ = 1.5406 Å) was employed during the analysis, and the samples were randomly oriented. The scanning was carried out over the angular range of $5° \leq 2\theta \leq 75°$ at a rate of 1.2° per minute.

For EPR measurements, the crushed and cleaned enamel layer of the tooth sample (typically less than 2 g) was divided into several fractions to be irradiated with increasing doses under identical conditions using a ^{60}Co radiation source. Subsequently, each fraction was irradiated under laboratory conditions. The EPR spectrum of the irradiated samples was measured, and a dose-response curve was constructed by plotting the spectral intensity against the absorbed dose. Quantitative measurements were generally performed using an X-band EPR spectrometer. The typical parameters of the EPR spectrometer used for measuring the paramagnetic properties of tooth enamel were as follows: center of the magnetic field range at 3500 G; magnetic field sweep width of 60 G; microwave frequency of 9.8 GHz; microwave power of 2.15 mW; modulation frequency of 100 kHz; modulation

amplitude of 3.26 G; conversion time of 80 ms; and time constant of 160 ms.

Basic provisions for protection.

- Organic-origin artifacts uncovered during archaeological excavations, as well as samples taken as standards, were chemically converted into benzene. The specific activity of ^{14}C activity in the benzene obtained from each sample was measured using a liquid scintillation device. The applied protocol allows the determinate the sample's age.

- Thermogravimetric (TG) analysis showed that raw ceramics generally exhibit a greater mass loss during hydroxylation and dehydration processes compared to ancient ceramic fragments. The older the ceramic, the more it tends to lose mass during hydroxylation. These findings can be used to distinguish newly fired ceramics from ancient ones.

- For age determination using the Thermoluminescent method, the intensity of the peak within the temperature range of 250°C to 400°C was utilized. The dependence of the TL glow curve peak intensity above 250°C on the historically absorbed dose was evaluated.

- Investigation of the Paramagnetic Properties of the CO_2^-- radical (g = 2.018) for age determination of archaeological tooth enamel using the EPR method; Calculation of the annual radiation dose for TL and EPR dating based on the concentration of radionuclides in soil samples taken from the surrounding environment of the specimen.

Scientific novelty of the research.

- For the first time in the history of Azerbaijani archaeology, comprehensive physico-chemical dating was carried out. The application of Radiocarbon, EPR, and TL methods enabled the absolute dating of numerous Neolithic period sites.

- For the first time, a comprehensive characterization of ancient Neolithic ceramics from Azerbaijan was performed using an inter-method approach involving thermogravimetric, thermoluminescent, and X-ray phase diffraction techniques. Their mineralogical, chemical, and thermal properties were described, and the firing temperature of the ceramics was determined.

- To determine whether local raw materials were used in ceramic production, comparative X-ray phase analysis (XRD) was performed between modern raw ceramic paste and ancient ceramics to evaluate their mineral compositions.

- Based on the physico-chemical parameters of materials obtained from the same archaeological site, their absolute ages were comparatively determined using all three methods.

- The dependence of the EPR signal intensity of the paramagnetic center identified in the enamel layer of a fossil tooth—considered suitable for dating—on the historically absorbed dose was evaluated. Based on the calculated g-factor of the main dosimetric signal, the type of radical corresponding to this center was identified.

Theoretical and practical significance of the research.

The application of modern dating methods in Azerbaijani archaeology represents a significant advancement in the field and offers numerous material and socio-cultural benefits to the country by enabling local specialists to determine the age of artifacts and historical monuments with greater accuracy and reliability. Alongside these methods, conducting complementary analyses such as TG, DTG, DTA, and X-ray phase analysis (RFA) allows for a better understanding of the production technologies employed by ancient peoples of that era. Modern dating techniques like Radiocarbon, TL and EPR provide higher precision and reliability compared to traditional dating methods. This, in turn, facilitates the establishment of robust chronological sequences and enhances comprehension of the archaeological context of findings.

Moreover, contemporary physico-chemical dating techniques contribute to the study of environmental and climatic changes. Dating geological formations and archaeological layers enables the correlation of ancient human activities with environmental transformations, enriching our knowledge of how past societies adapted to or impacted their surroundings. The comprehensive physico-chemical characterization of Neolithic materials will more reliably align Azerbaijani science with contemporary international standards.

Modern dating tools also foster interdisciplinary collaboration among researchers from chemistry, physics, history, geology, and other

scientific fields. This interdisciplinary approach will enhance the reliability of archaeological interpretations and methodologies, allowing for a more detailed and holistic examination of cultural heritage artifacts and their physico-chemical properties. In conclusion, the implementation of modern dating techniques in archaeology, by increasing the precision of chronological data, has the potential to position the Republic of Azerbaijan as a leading center for archaeological research across the entire Caucasus region.

Approval and implementation of work.

The main results of this work have been presented and discussed at conferences organized by the Institute of Radiation Problems of the Ministry of Science and Education of the Republic of Azerbaijan, as well as at other local and international scientific conferences, and have been published in the proceedings of these events:

- Radiation and chemical safety problems, International Scientific –Practical Conference, 5-6 November 2019, Baku.
- Second International Scientific Conference of Young Scientists and Specialists, 3-6 March 2020, Baku
- LXX international conference "Nucleus-2020: "Nuclear Physics and Elementary Particle Physics.Nuclear Physics Technologies", 11-17 October 2020, Sankt-Petersburg University, Russia
- "3rd International Conference Radiocarbon in The Environment". Institute of Physics – Center For Science And Education, Silesian University of Technology, 5-9 July 2021. Gliwice, Poland.
- IV International Scientific Forum "NUCLEAR SCIENCE AND TECHNOLOGIES" Dedicated to the 65th Anniversary of the Institute of Nuclear Physics, 26-30 September 2022, Almaty, Republic of Kazakhstan
- Scientific and Technical Conference on Radiological and Chemical Risks in the Territories of Karabakh Liberated from Occupation, October 28-29, 2022, Baku
- Republic Scientific and Technical Conference on "Radiation Technologies and Their Applications," dedicated to the 100th anniversary of the birth of the Great Leader H. Aliyev, 2023, Baku/

- Scientific and Technical Conference on Radiation Safety Issues: Regional Aspects, dedicated to the 75th anniversary of Academician Mahmud Karimov, October 18–19, 2023, Baku.

- International Scientific Conference on "Karabakh and Zangezur's Cultural Heritage in Archaeological and Ethnographic Studies," dedicated to the 90th anniversary of Professor Qudrat Ismayilzade, November 5–6, 2024, Baku State University, Azerbaijan.

- V International Scientific Forum "Nuclear Science And Technologies", 7-11 October 2024, Almaty, Kazakhstan

Publications. The results of the research have been reflected in **25 scientific publications—**including **13 articles and 12 conference abstracts**—published in international and national scientific journals and conference proceedings. Four of the articles have been published in journals indexed by the international scientometric databases '**SCOPUS'** and '**Web of Science'**, while five have appeared in journals recognized by the **'Chemical Abstracts Service (CAS)**' database.

Name of the organization the dissertation work was performed.

The dissertation research was conducted from 2019 to 2025 at the "Radiation Chemistry of the Environment" laboratory of the Institute of Radiation Problems under the Ministry of Science and Education of the Republic of Azerbaijan.

Structure and scope of work.

The submitted dissertation consists of an introduction (35336 characters), five chapters (Chapter I – 38257 characters, Chapter II – 47267 characters, Chapter III – 23376 characters, Chapter IV – 29793 characters, Chapter V – 32058 characters), and conclusions (3304 characters), totaling 213344 characters (excluding tables, figures, and bibliography). The dissertation comprises 208 pages, including 127 pages of text, 87 figures and graphs, 50 tables. 181 scientific literature sources were referenced in the dissertation.

Author's personal contribution includes: conducting a literature review and analysis on the research topic; planning the research; collecting samples from archaeological sites; preparing samples for analysis; synthesizing benzene from organic-origin artifacts as well as from materials used as standards; determining the benzene

activity using a scintillation counter; isolating quartz from ceramic samples; irradiating the samples; performing thermoluminescent measurements and analyzing the results; preparing tooth enamel for experimental study; and actively participating in writing and preparing manuscripts for publication.

MAIN CONTENT OF THE RESEARCH

The introduction substantiates the relevance of the research topic and the applied methodological approach, highlights the scientific novelty and practical significance of the study, and provides information on the objectives, structure, and content of the work. Additionally, the main statements submitted for defense and the approval (validation) of the research are presented.

Chapter I of the dissertation presents a brief summary of Neolithic period sites in Azerbaijan. It also examines the radiometric and spectroscopic dating methods and their application within the context of Azerbaijani archaeology. It is demonstrated that the Neolithic era is primarily characterized by the large-scale production of polished stone and bone tools, as well as ceramic artifacts, by hunter-gatherer communities. The first genuine Neolithic site within the modern territory of Azerbaijan was discovered in the 1950s by O. Habibullayev during his research at the Kultepe site in Nakhchivan. This site represents the first archaeological location in Azerbaijan dated using the radiocarbon method. In the subsequent years, there was a prolonged hiatus in the application of the radiocarbon technique for dating archaeological sites. Its limited use was revived only in the years following Azerbaijan's independence, primarily through sending samples abroad for analysis. In recent years, approximately fifteen archaeological sites have been dated using the radiocarbon method; however, this process lacks systematic organization and mainly encompasses sites located along the Baku-Tbilisi-Jeyhan oil and gas

pipeline corridor. A review of the literature reveals that [3], within the territory of the Republic of Azerbaijan, modern physicochemical dating methods - especially those involving the investigation of the physicochemical properties of materials, such as TL and EPR - have yet to be implemented in archaeological research. This indicates a significant scientific gap in refining the chronology of ancient sites in the country.

Chapter II of the dissertation provides specific information regarding the research methodologies employed and the instruments utilized.

Radiocarbon Method. The chemical element carbon consists of three isotopes. Two of these - ^{12}C and ^{13}C - are stable, while the third isotope, ^{14}C, also known as radiocarbon, is radioactive. The ^{14}C isotope is continuously produced artificially in the Earth's stratosphere as a result of the bombardment of nitrogen atoms by neutrons, which are components of cosmic rays. Newly synthesized ^{14}C isotopes enter the Earth's carbon cycle together with ^{12}C and ^{13}C isotopes in the atmosphere, biosphere, and hydrosphere over a period of several years.

While an organism is metabolically exchanging substances with its environment (for example, when a tree absorbs carbon in the form of carbon dioxide from the atmosphere through photosynthesis), the quantity of ^{14}C within its structure remains constant, maintaining equilibrium with the radiocarbon concentration in the atmosphere. Upon cessation of this exchange with the environment - such as when a living organism dies - the intake of "fresh" ^{14}C from outside stops, and the amount of radioactive isotope begins to decline, since metabolic processes have ended. The radioactive decay of any element proceeds at a constant rate that can be precisely determined. The half-life of the ^{14}C isotope has been established to be approximately 5,730 years.

Thus, by knowing the amount of ^{14}C both during equilibrium (when the organism was alive) and in fossil remains, it is possible to

[3] Y. Nishiaki. The Mesolithic-Neolithic interface in the Southern Caucasus : 2016 – 2017 excavations at Damjili Cave, West Azerbaijan / Zeynalov A., Mansrov M., Akashi C. [et. al] // Archaeol. Res. Asia - 2019. vol.19, P.1–16

determine how much time has passed since the death of a carbon-based organism or plant. However, this requires that the remains have not participated in any carbon exchange with the external environment during the subsequent preservation period. For some samples, this condition can be readily fulfilled. Examples include biological remains preserved in permanent ice, as well as artifacts and objects that have been protected from external influences and stored under favorable conditions.

There are several methods for determining the amount of radiocarbon. In the course of this dissertation research, the benzene synthesis method was employed. After an initial purification, the sample under investigation is converted into benzene through a series of chemical procedures. The resulting benzene is then analyzed using a Tri-Carb 3100TR scintillation counter. In the scintillation apparatus, the number of disintegrations per unit time of the carbon atoms in the benzene is measured and compared with a standard sample. Based on the results of these measurements, the age of the artifact is determined.

Thermoluminescent Method. In an ideal crystal, atoms are arranged in a perfectly periodic structure. However, in reality, crystals always contain certain defects. These defects play a crucial role in the generation of thermoluminescent signals. Due to atomic vacancies, dislocations, or the presence of impurities (for example, when aluminum ions enter the quartz crystal lattice and replace Si^{4+} ions), the charge balance within the crystal can be disrupted. As a result, in order to compensate for this imbalance, electron traps or oxygen vacancies are formed. These traps are essential for the formation of thermoluminescent signals—electrons become "trapped" in these defects as a result of radiation exposure, and upon heating, they are released and emit light. This phenomenon of light emission is known as thermoluminescent.

TL age of ceramic vessels indicates the time elapsed since they were last fired. During the initial firing, any energy accumulated in the crystal structures of the ceramics due to natural radiation is reset to zero. As the minerals within the ceramic remain buried in the soil over time, they begin to absorb radiation once again. When the sample is later heated in a TL device, this reabsorbed energy is released in the

form of light emission.

Thermoluminescent dating consists of four main stages: 1) Sample preparation; 2) Determination of the equivalent dose; 3) Determination of the annual dose rate; 4) Calculation of the TL age.

Ceramic vessels discovered during archaeological excavations typically contain quartz and feldspar crystal particles. These crystals originate from the raw material-clay-used in the production of the ceramics. During the investigation, quartz from the ceramic is isolated and purified using specific methods, and the total absorbed dose accumulated over time is determined using the thermoluminescent technique. This method is known as the "quartz inclusion" method. The primary aim of TL measurements in age determination studies is to quantify the amount of energy absorbed by the mineral particles. The absorbed energy is determined by heating the sample to stimulate it and measuring the amount of emitted light. To determine the equivalent dose, the purified sample is divided into 6–7 aliquots and irradiated. One portion of the sample is kept aside without any thermal treatment in order to measure the absorbed dose resulting solely from natural radiation exposure. In this dissertation, the irradiation of samples was conducted using a ^{60}Co gamma-ray source. The dose rate of the ^{60}Co gamma source was measured with the use of alanine dosimeters via the “Magnette Miniscope MS400” EPR spectrometer. The spectrometer, equipped with a 15 cm lead shielding and a high-purity germanium (GeHP) detector, is capable of detecting gamma rays with an energy of 661.6 keV at an efficiency of 43.5%.

For the luminescence measurements of irradiated samples, a TLD3500 Manual Reader device was used. The luminescence signal emitted from the sample passes through optical filters and is subsequently detected by a photomultiplier tube. The resulting pulses are then amplified, and the output current is presented as photon counts, which represent the luminescence signal. TL devices allow the sample to be heated at various rates. After measuring the TL spectra of both irradiated and unirradiated samples, a dose-response curve is constructed based on the intensity of the signal as a function of radiation dose. The equivalent dose, or the total dose

absorbed over time, is then estimated by extrapolating this dependency to the dose axis (abscissa). This method of determining the equivalent dose is known as the "added dose method".

To calculate the luminescence age, the total dose absorbed by the sample over time (equivalent dose, or paleodose) must be divided by the rate at which energy has accumulated (dose rate). In natural conditions, the accumulation of luminescence energy is primarily driven by isotopes from the decay chains of uranium and thorium, as well as the radioactive isotopes of potassium and rubidium, in addition to cosmic radiation. To determine the concentrations of these elements, approximately 500 grams of soil was collected for each ceramic sample from the locations where they were excavated. The samples were then dried, and a portion of each soil sample was sealed in specialized compact containers and stored for 15-20 days. This process helps prevent radon loss from the uranium and thorium decay chains and allows the establishment of secular equilibrium between decay products. In the next stage, the concentrations of the aforementioned elements in the soil were measured using a "Canberra GR4520" gamma spectrometer. Using specific conversion factors, the dose rates from these elements were calculated. For this purpose, specialized computer software programs have been developed. In this study, one such program, "DRAC (Dose Rate and Age Calculator)," was widely employed. The DRAC software also accounts for the contribution of cosmic radiation to the total dose rate. Additionally, it is worth noting that in TL dating, signal intensity in some materials can be enhanced through the use of nano-aluminum (nano-sized Al_2O_3 or Al particles). For example, nano-forms of aluminum can act as dopants to improve signal strength. While such particles are not yet directly used in routine TL dating procedures, experimental and technological research in this direction is ongoing.

Electron Paramagnetic Resonance Method. The estimation of EPR age is the result of a comprehensive analytical process that combines fieldwork and laboratory procedures. This process consists of five main stages: (1) sample collection and in-situ measurements, (2) sample preparation, (3) EPR dosimetry, (4) assessment of the

natural radioactivity of the sample and its surrounding environment (5) calculation of the EPR age.

In the initial stage, fossil teeth are typically selected either from archaeological sites or from museum collections and archives. Preference is usually given to the teeth of large mammals, especially herbivores, because their enamel layer tends to be thicker. Subsequently, at or near the excavation site where the sample was found-preferably as close as possible-measurements of natural radioactivity are conducted to calculate the gamma dose rate. Traditionally, various methods can be employed for this purpose, such as burying synthetic thermoluminescent dosimeters (e.g., $CaSO_4$:Dy, Al_2O_3:C) at the site and retrieving them after several months to determine the total gamma dose rate.

In the second stage, the different tissues of the fossil tooth (enamel, dentin, cementum) are mechanically separated in the laboratory. The enamel layer is then ground into finer fractions. This step is critical because the EPR signal of tooth enamel is angle-dependent within the resonator; failure to properly prepare the enamel can significantly distort the results. Since historical artifacts (such as teeth and bones) are crushed and ground during the analysis, EPR is regarded as a "destructive dating method".

For EPR dosimetry analysis, the ground enamel layer (typically less than 2 grams) is divided into several aliquots to be irradiated under identical conditions with increasing doses using a gamma radiation source. Subsequently, each aliquot is irradiated under controlled laboratory conditions. The EPR spectra of the irradiated samples are then measured, and a dose-response curve illustrating the dependence of the spectral intensity on the administered dose is constructed.

Quantitative measurements are typically performed using X-band EPR spectroscopy. To minimize any uncertainties that could affect the measurements, the analyses are conducted under controlled experimental conditions following standardized analytical protocols.

In the next stage, the natural radioactivity of both the sample itself and its surrounding environment is assessed. The dose rate in

the environment surrounding the tooth is determined by considering the tooth and its immediate vicinity (approximately a 30 cm radius). The concentrations of radioactive elements are then used to calculate the dose rates, taking into account several parameters such as the moisture content of the sample and soil, the thickness and density of the tooth tissues, and the alpha efficiency. If the burial depth of the sample is less than approximately 20 meters, the contribution of cosmic dose rate is also evaluated. This assessment is carried out using established tables, with calculations adjusted based on the sample's depth, soil density, geographic latitude, and altitude of the site. Finally, the EPR age is calculated as the ratio of the equivalent dose to the annual dose rate.

In Chapter III of the dissertation, the dating of a series of archaeological findings using the Radiocarbon method has been investigated:

Coal sample recovered from the Polutepe monument. The radiocarbon dating of this sample was carried out through the following stages: Approximately 50 grams of wood charcoal fragments were carefully collected and then cleaned of surrounding soil and other contaminants using mechanical and chemical methods. To remove impurities from the charcoal, the sample was sequentially washed in acid (0.5% HCl), alkali (5% NaOH), and again in acid (0.5% HCl). After undergoing this acid-alkali-acid treatment (AAA procedure), the samples experienced a weight loss of approximately 20%. This is a standard procedure, and all other samples underwent the same cleaning process. In the next stage, benzene was extracted from the purified charcoal. During the benzene extraction process, the charcoal reacted with lithium metal to form lithium carbide, which was then hydrolyzed to produce acetylene. Finally, acetylene was converted to benzene in the presence of an aluminosilicate catalyst. An identical procedure was applied to the standard reference material. The experiment yielded the following results:

Mass of benzene extracted from the sample, m_1= 1.761 gr,
Mass of benzene extracted from the standard, m_2= 2.431 gr,
Mass of benzene taken as background, m_3= 8.786 gr (10 ml)

Figures 1, 2, and 3 illustrate the specific activities of the background, standard, and sample measured using the Tri-Carb 3100TR scintillation counter, expressed as counts per minute (CPM) of Carbon-14 isotope decays.

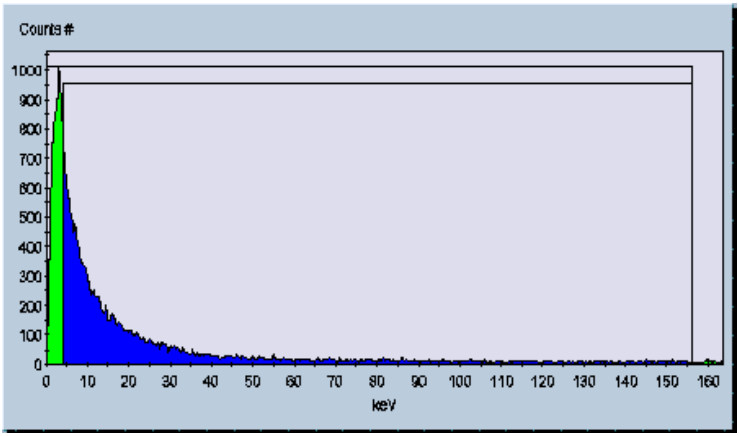

Figure 1. Dependence of the natural background specific activity measured by the Tri-Carb 3100TR scintillation counter on the energy of electrons produced by radioactive decay.

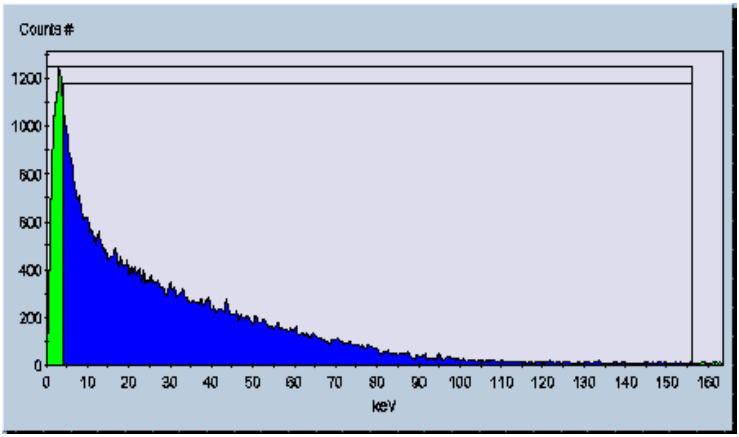

Figure 2. Dependence of the activity of benzene taken as a standard, measured by the Tri-Carb 3100TR scintillation counter, on the energy of electrons produced by radioactive decay.

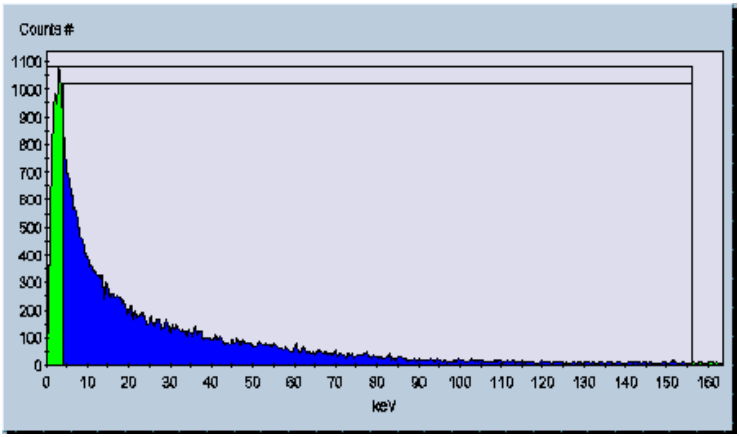

Figure 3. Dependence of the activity of benzene extracted from coal found in the Polutepe area, measured by the Tri-Carb 3100TR scintillation counter, on the energy of electrons produced by radioactive decay.

Based on these graphs, the values of specific activity were calculated. The number of radioactive decay counts per minute for the ancient coal sample, the standard sample, and the background (denoted as C_{sample} , $C_{standart}$, and $C_{background}$, respectively) were counted within the window from channel 157 to 511, and the resulting values are as follows:

For the sample n C_{sample}=9.9651±0.15 cpm,

For the background $C_{background}$ =20.4799±0.19 cpm,

For the standard sample $C_{standart}$=39.3593±0.17 cpm.

For the isotope ratios, the value of $^{13}C/^{12}C$= -25‰ was assumed, and the half-life of radiocarbon was taken as 5568 years. The following formula was used to calculate the radiocarbon age (t):

$$t = 8033 \cdot \ln (A_{standart}/A_{sample})$$

The results of the analysis of the coal sample found in the Polutəpə area are as follows:

The percentage of modern carbon (pMC) = 46.101±1.20%

Modern carbon fraction: 0.4610±0.012

Calculated radiocarbon age: 6220±85 BP years (0=1950). The "OxCal version 2020" software was used to obtain the calibrated age graph (https://c14.arch.ox.ac.uk/oxcal/OxCal.html#).

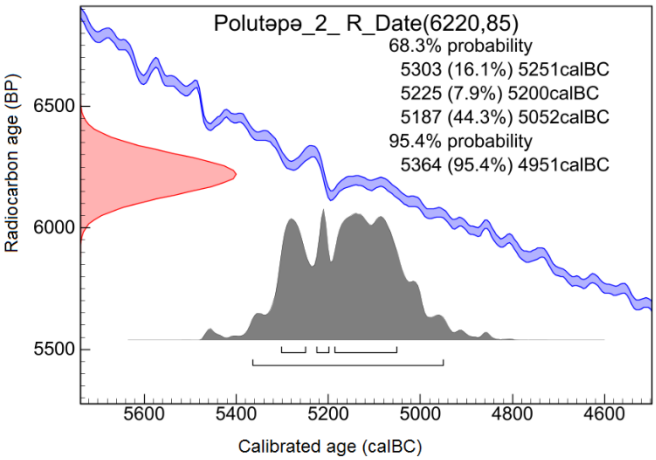

Figure 4. The radiocarbon and calibrated age chart of charcoal samples obtained from the Polutepe monument.

The calibrated age of the sample has been determined to be 5303–5052 BC with 68.3% confidence and 5364–4951 BC with 95.4% confidence (Figure 4). Charcoal samples found in other areas were also subjected to the aforementioned procedures, and the resulting determinations are presented below:

Table 1.
List of archaeological monuments with absolute ages determined by the Radiocarbon method

Sample name	*Material*	*Modern Carbon Percentage "pMC" , %*	*Calculated radiocarbon age, year (BP) (0=1950)*	*Calibrated age, year (BC)*	
				68.3% (1-sigma)	*95.4% (2-sigma)*
Polutepe	I. charcoal II.charcoal	46.10±1.20 45.19±1.10	6220±85 6380±99	5303-5052 5473-5224	5364-4951 5531-5069
Shomutepe	charcoal	48.56± 0.44	5801±96	4783-4542	4901-4446

Continuation of Table 1					
Göytepe	charcoal	38.13±1.10	7746±88	6646-6476	6906-6422
Paşatepe	charcoal	43.41±1.20	6704±88	5713-5556	5749-5477
Boyukdsh-Anazaga	charcoal	20.72±1.13	12644±210	13413-12514	13681-12210
Alkhantepe	charcoal	53.14±1.18	5079±29	3952-3805	3959-3796
Burugtepe	charcoal	42.42±0.48	6888±31	5796-5726	5877-5714
Selbir	charcoal	87.14±1.14	1105±11	899-988 (AD)	893-993 (AD)
Uzun Reme kurgan	charcoal	68.07±1.17	3090±22	1409-1305	1420-1286

As seen in Table 1, the conducted research encompasses not only the Neolithic period but also subsequent eras.

Chapter IV of the dissertation is dedicated to the age determination of ancient archaeological findings using the TL method, as well as to the TG and XRF analyses of ceramic samples.

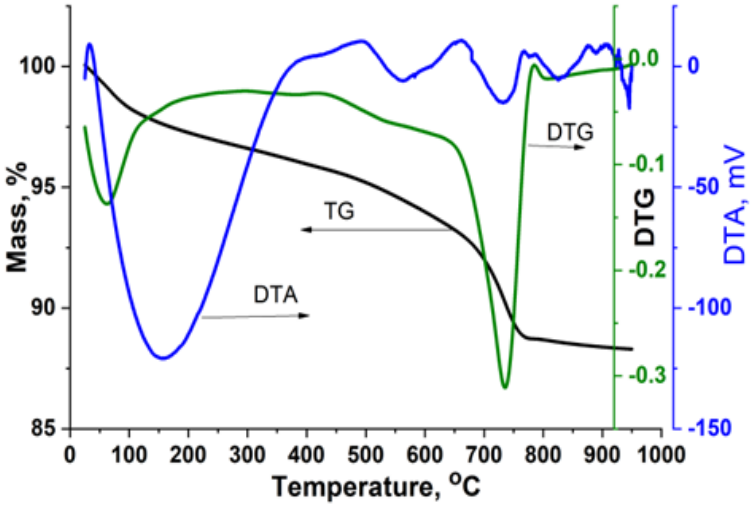

Figure 5. TG/DTG and DTA Curves of Ceramic Samples Collected from Polutepe.

Ceramics represent one of the most significant attributes for characterizing the Neolithic period, and the comprehensive description of ancient pottery often includes the characterization of

its mineralogical, chemical, and thermal properties. The analytical results obtained through these methods can yield critical insights in age determination studies and in establishing the chronology of technological developments in antiquity. In the dissertation, thermal analysis methods - such as TG, DTA, and Thermoluminescent - were extensively applied in various combinations for the study of ancient ceramics. X-ray phase analysis, in turn, enabled the identification of the mineral composition of the ceramics. The results of the TG/DTG and DTA analyses of ceramic fragments from Polutepe are presented in Figure 5.

TG and DTA analyses were conducted on 14 ceramic samples obtained from various locations (Table 2). For comparative purposes, an analysis was also carried out on an unfired ceramic paste. The results of the TG/DTG experiments performed on the raw ceramic sample indicate that the mass loss during dehydration was 8.06%, while the loss associated with the decomposition of hydroxyl groups was 3.16%. Dehydration and dehydroxylation occurred within the temperature ranges of 50°C–350°C and 350°C–600°C, respectively. These findings suggest that the examined material underwent only two distinct stages of mass loss and that the composition of the sample does not include calcite.

Table 2

Mass loss of ancient ceramic samples and raw ceramic pastes within the temperature range

№	Name of sample	Kütlə itkisi, %			m1, % ≤350°C	m2, % 300-650 °C	m3, % 650-850 °C	Cəm itki, %
		≤350 °C	≤600 °C	≤850 °C				
1.	Leletepe	98.70	97.90	96.32	1.30	0.80	1.58	3.68
2.	Leletepe	96.47	94.4	91.72	3.53	2.07	2.68	8.28
3.	Leletepe	97.33	95.59	94.64	2.67	1.74	0.95	5.36
4.	Leletepe	97.98	96.56	94.75	2.02	1.42	1.81	5.25
5.	Shomutepe	96.93	95.31	92.10	3.07	1.61	3.21	7.90

								Continuation of Table 2
6.	Menteshtepe	98.48	97.52	97.11	1.52	0.96	0.41	2.89
7.	Polutepe	96.30	93.98	88.51	3.70	2.32	5.47	11.49
8.	Ismailtepe	95.57	92.82	88.33	4.43	2.75	4.49	11.67
9.	Hasansu	97.29	96.26	95.82	2.71	1.03	0.44	4.23
10.	HajiElimkhanli	96.76	96.52	95.26	3.24	0.24	1.26	4.74
11.	Goytepe	98.16	96.68	95.44	1.84	1.48	1.24	4.56
12.	Lenkeran	97.99	96.87	96.26	2.01	0.62	0.61	3.74
13.	Raw ceramic paste	91.94	88.78	87.68	8.06	3.16	1.1	12.32
14.	Raw ceramic paste	85	79.55	78.61	15	5.45	0.94	21.39

The mass loss of the 14 analyzed ceramic samples has been summarized according to three temperature intervals: below 350°C (m_1 – dehydration), 350–600°C (m_2 – dehydroxylation), and 600–850°C (m_3 – decomposition of carbonates, micas, etc.). While each of these samples exhibits distinctive characteristics in their thermal analyses, they also share common features. The results indicate that the DTG curves of the samples display three distinct peaks. Two of these peaks are situated in the lower temperature range and correspond to dehydration and dehydroxylation processes. Consequently, these two processes also occur during the firing of ancient pottery. The third peak is generally associated with the decomposition of calcite. The DTA curves reveal four distinct endothermic events. Three of these correspond with the processes identified in the DTG analysis, namely dehydration, dehydroxylation, and calcite decomposition, thus supporting and reinforcing the interpretations derived from the TG/DTG results.

X-ray phase analysis was conducted on 15 different samples, including raw ceramic material. The results of the X-ray phase analysis for a ceramic sample recovered from the Polutəpə site are presented in Figure 6.

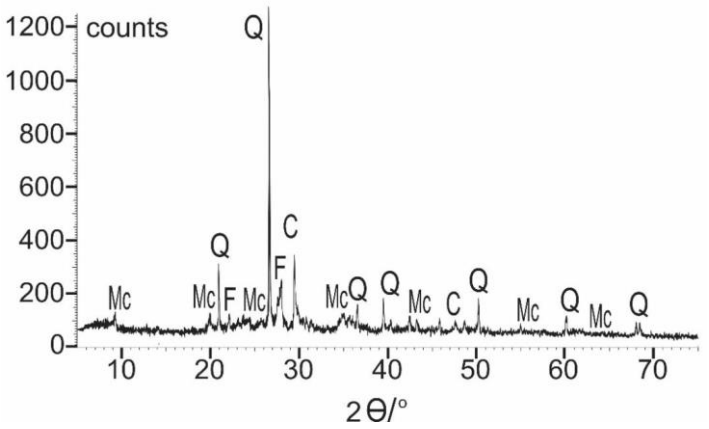

Figure 6. XRD patterns of ceramic fragments recovered from Polutepe: Mc – Muscovite; Q – Quartz; F – Feldspar (Albite); C – Calcite.

The X-ray phase analysis of the ceramic fragments indicates that all examined samples contain quartz, feldspar, clay minerals, and other components. The presence of calcite in the samples suggests that the firing temperature was around 700°C, as calcite typically decomposes at approximately this temperature. The existence of calcite in the ceramic matrix is also confirmed by the X-ray phase analysis conducted on a sample boiled in hydrochloric acid for one hour, during which the calcite content decreased from 10.9% to 0.2% (Table 3). If calcite is absent in a sample, this implies that the firing was conducted at a temperature range of 800–900°C—above the decomposition threshold of calcite. The results of the X-ray phase analysis indicate that the firing temperature of the Neolithic ceramics studied in this research was approximately 700°C. The specific results of the X-ray phase analysis for the sample from the Polutəpə site are presented in Table 3.

Table 3
Mineralogical composition of the ceramic sample recovered from the Polutepe site.

Sample	*Quartz, %*	*Feldspar və Albite, %*	*Muscovite, %*	*Calcite, %*
Polutepe (natural)	33.8	21.7	33.6	10.9
Polutepe (sample+ HCl)	37.7	24.4	37.7	0.2

Although there have been various attempts to investigate the firing temperature of ceramics using the TL method, these efforts have not yielded successful results. However, the TL method is highly effective for determining the age of ceramics. The following example outlines the age determination procedure applied to a ceramic sample recovered from the Polutepe site.

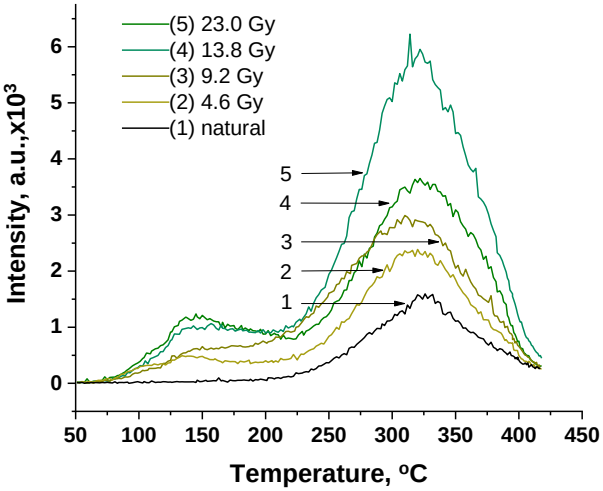

Figure 7. TL glow curve of quartz extracted from ancient pottery under various laboratory-induced radiation doses.

Quartz samples extracted and purified from ceramic fragments were irradiated with a ^{60}Co gamma source, and their TL glow curves were measured two days after irradiation. Analysis of the TL spectra

revealed that the glow curve consists of several peaks, each corresponding to different electron traps. Visually, two distinct peaks can be identified at approximately 150°C and 325°C, with peak widths of about 50°C. The peaks used for age determination are typically located in the temperature range above 250°C. To accurately identify this stable temperature region, a "plateau test" was employed.

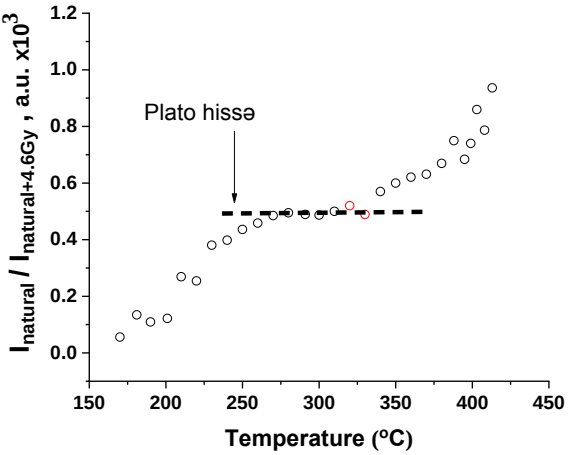

Figure 8. Plateau test conducted using the ratio of the natural TL intensity ($I_{natural}$) of the quartz sample extracted from the specimen to the TL intensity obtained after additional laboratory irradiation ($I_{natural}$+4.6 Gy).

To perform the plateau test, the TL intensity of the naturally irradiated material must be compared to the TL intensity measured after the material has been additionally irradiated under laboratory conditions (Figure 8). For age determination, the intensity of the peak at 325°C was used. The dependence of the TL peak intensity at 325°C on the absorbed dose was established, and by extrapolating to the dose axis, the paleodose (equivalent dose) was calculated to be 22.19 ± 1.36 Gy (Figure 9).

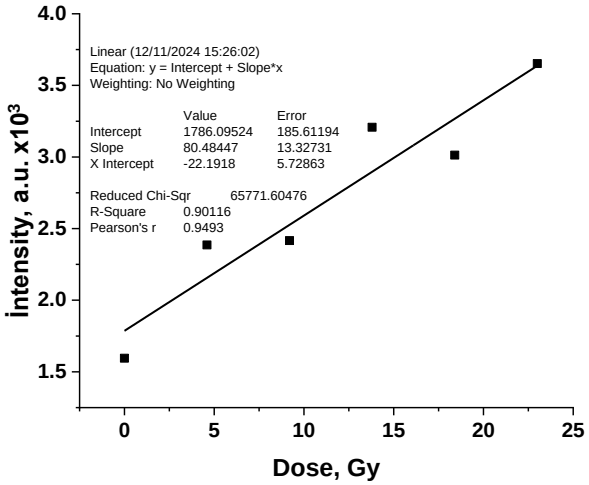

Figure 9. Dose dependence of the glow curve peak intensity at the 325°C temperature region.

Table 4 presents the calculated values of the absorbed dose in quartz extracted from ceramics, based on the quantities of uranium, thorium, and potassium decay chain isotopes in the soil samples taken from the locations where the ceramics were found at the Polutepe site.

Table 4.
Calculated age estimates for the ceramic sample recovered from the polutəpə archaeological site.

Radionuclides	*Quantity*	*Dose Rate*		
		Alpha (Gy/1000il)	*Beta (Gy/1000il)*	*Gamma (Gy/1000il)*
^{238}U (ppm)	2.24±0.02ppm	6.261±0.56	0.326±0.029	0.250±0.022
^{232}Th (ppm)	8.31±0.80ppm	6.129±0.59	0.230±0.023	0.398±0.038
^{40}K (mass, %)	2.39±0.23 %	0	1.908±0.184	0.595±0.058
After 20 minutes of etching with 40% HF				
^{238}U (ppm)		0.791±0.163	0.29±0.026	0.25±0.022
^{232}Th (ppm)		0.896±0.227	0.195±0.02	0.398±0.038

			Continuation of Table 4
^{40}K (mass, %)	0	1.816±0.177	0.595±0.058
Total	1.687±0.164	2.314±0.18	1.243±0.039
Taking into account the 5% water content in the sample	0	2.178±0.177	1.176±0.074
Estimated value of the sample's accumulated dose and thermoluminescent age			
Equivalent dose	22.19 ± 1.36 Gy		
TL age of the ceramic, years	6400±530 BP		

Based on the quantities of Uranium, Thorium, and Potassium decay chain isotopes in the soil taken from the location where the ceramics were found at the Polutəpə site, the calculated absorbed dose rate in quartz extracted from the ceramics was determined to be 3.354 mGy/year. Correspondingly, the age of the ancient ceramic sample was estimated to be 6400 ± 530 years.

The above protocol can be considered a standard functional procedure for Thermoluminescent dating and has been applied to other ceramic artifacts as well. The determined ages of ceramic samples found in other areas are as follows:

Table 5.

List of historical monuments with absolute ages determined by the Thermoluminescent method

Name of the sampled area	*Material*	*Equivalent dose (D_e), Gy*	*TL age, year (BP)*
Jalilabad-Polutepe	Pottery	22.19 ± 1.36	6400±530
Fuzuli-Lələtepe	Pottery	26.1 ± 0.45	7919 ± 455
İsmailbeytepe	Pottery	25 ± 1.36	6908 ± 117
Akhstafa-Hasansu	Pottery	9.73 ± 0.48	7913 ± 324
Barda-Amirli 3	Pottery	19.8 ± 1.35	8189 ± 850
Jalilabad-Pashatepe	Pottery	12.16 ± 0.6	7826 ± 513
Gobustan-Anazaga	Fried soil	35.2 ± 1.37	15013 ± 1324
Gobustan-Boyukdash	Pottery	23.8 ± 0.2	6835 ± 383
Gobustan-Kichikdash	Pottery	18 ± 0.2	5655 ± 233
Jalilabad-Khudutepe	Pottery	13.6 ± 0.6	7116 ± 343
Chukhur Gabala	Pottery	6.12 ± 1.36	2230±110

The TL method enables age determination based on quartz extracted from burnt soil collected from ancient hearths. Using this technique, the age of a hearth at the Ana-Zaga ancient settlement in the Gobustan National Historical-Artistic Reserve has been estimated (Table 5).

Chapter V of the dissertation is dedicated to the dating of archaeological findings using the EPR method and to the study of radiation-induced changes in tooth enamel employed for this purpose.

Approximately 95% of tooth enamel consists of hydroxyapatite, while the remaining portion comprises water and/or organic matter. The carbonate substitution in hydroxyapatite replaces a fraction of phosphate and/or hydroxyl anions within its crystal lattice. Ionizing radiation generates various types of radicals trapped in the crystal lattice, such as CO_2^-, CO_3^{3-}, CO^- , O^-, which are located at positions close to g ≈ 2. These radicals have been studied by electron paramagnetic resonance (EPR) spectroscopy in both ancient and modern dental enamel samples. The stable CO_2^- radical formed as a result of radiation exposure in tooth enamel or bone serves as the primary signal for age determination. In fossil tooth enamel, the EPR signal manifests as an asymmetric signal characterized by three peaks at g = 2.0043, g = 2.0013, and g = 1.9985. Figure 10 presents the EPR spectrum of the enamel layer of a tooth sample found in the Mingachevir region of Azerbaijan, which was subjected solely to natural radiation.

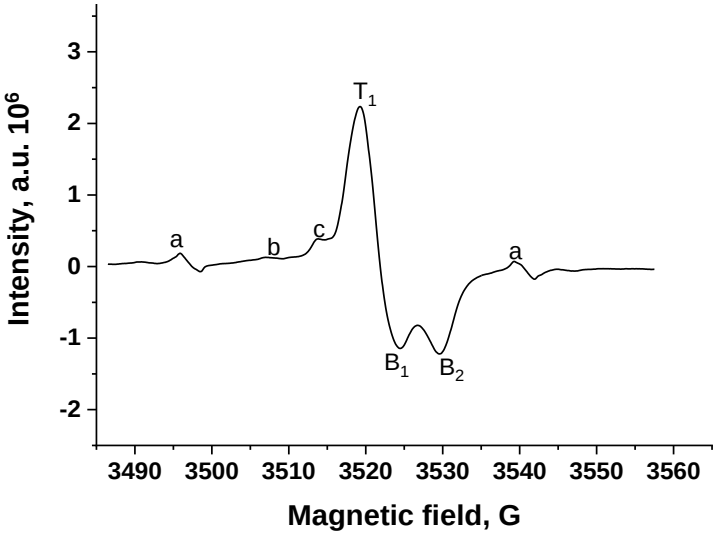

Figure 10. The EPR spectrum of the enamel layer of a tooth sample found in the Mingachevir region of Azerbaijan, which was exposed only to natural radiation.

The points characterizing the EPR signal have been assigned according to the conventions accepted in the literature of this field: the signal marked as "a" is a septet signal centered at g = 2.0043 (only three lines are visible in this magnetic field range) and is attributed to the free dimethyl radical; the isotropic line marked as "b" is an isotropic signal centered at g = 2.0114 and is attributed to the CO_3^- - radical; the signal marked as "c" is an isotropic signal centered at g = 2.0075 and may be assigned to the SO_2^- - free radical. The main dosimetric signal, marked as T1, B1, and B2, is attributed to the CO_2^- - radical. During laboratory irradiation, an increase in the EPR signal was observed depending on the dose, and this increase occurred mainly in the central part of the spectra, while the peaks related to isopropyl radicals remained unchanged. The same samples were evaluated again after six months, showing a slight decrease in the intensity of the central signal.

In the non-irradiated modern tooth sample, the EPR signal was extremely weak; however, it was observed that the nature of the radicals formed during subsequent irradiation is the same as those found in fossil tooth enamel.

Figure 11. Description of the human skull discovered at the Polutepe site and the tooth sample extracted from it for analysis.

This section also describes the results of applying the EPR method to determine the age of tooth enamel discovered at the Polutepe site. The sample preparation and EPR measurement procedures were carried out using standard methods. Figure 11 depicts a tooth extracted from a human skull found in the Polutepe area.

After the dental enamel was cleaned and separated, it was irradiated, and the EPR spectra of the enamel irradiated at various doses were recorded (Figure 12).

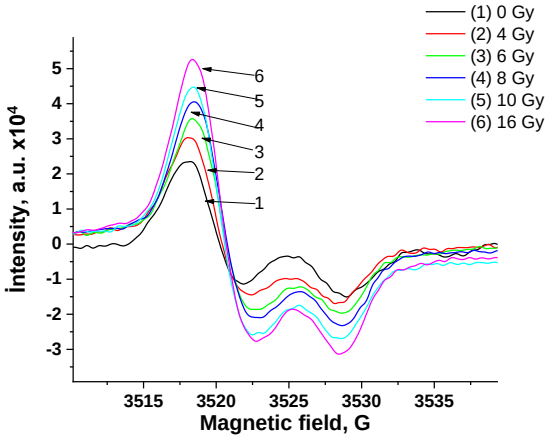

Figure 12. The natural EPR spectrum of the tooth enamel from the Polutepe site (1) and the spectra of the tooth enamel irradiated in the laboratory (2)–(6).

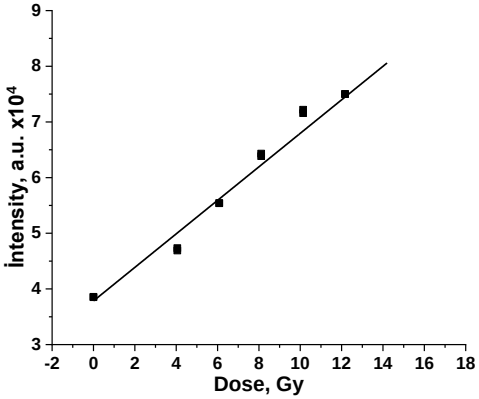

Figure 13. Dependence of the intensity of the EPR spectrum of tooth enamel on the dose (tooth sample found in Polutepe in 2015).

Irradiation was conducted at dose levels of 4 Gy, 6 Gy, 8 Gy, 10 Gy, and 16 Gy. The graphical representation of the experimental results was fitted using the 'Single Saturating Exponential' (SSE)

function. Figure 13 illustrates the dose–response curve of the enamel EPR signal intensity for a tooth sample discovered in 2015 at Polutapa. Based on extrapolation to the ordinate axis, the equivalent dose was determined to be 12.57 Gy.

Table 6 presents the dose rate values and the corresponding absorbed equivalent doses calculated based on the amounts of isotopes from the uranium, thorium, and potassium decay chains found in the soil surrounding the tooth sample. The age of the sample was determined using the DRAC calculator.

Table 6.
Final age estimation of the tooth sample found at the Polutepe site in 2015.

Calculated equivalent dose		12.57±0.25 Gy		
Radionuclides	Matrix	Cementum	Enamel	Dentin
^{238}U (ppm)	2.20±0.1	2.20±0.1	2.15±0.2	1.31±0.05
^{232}Th (ppm)	8.30±0.5	8.30±0.5	8.31±0.4	1.30±0.12
^{40}K (mass, %)	2.39±0.3	2.39±0.3	2.36±0.2	1.25±0.02
Density	2.7	3.1	4.0	3.0
Water (mass,%)	11	4.7	1.4	4.1

Distribution of the dose rate calculated according to the uranium early adsorption model by type of irradiation (mGy/a)

	Alpha	Beta	Gamma	Cosmic	Cosmic+ Gamma
Dentin	0.1	0.1	-	-	-
Enamel	0.2	0.1	-	-	-
Cementum	0.2	0.2	-	-	-
Matrix	4.33	321.79	1098.16	-	-
^{238}U (ppm)	1.86	43.76	222.96	-	-
^{232}Th (ppm)	2.47	29.04	354.33	-	-
^{40}K(mass,%)	-	248.99	520.87	-	-
Total	4.33	321.79	1098.16	145.96	1244.13

Depth= 4.5 m
(alpha+beta) dose rate = 326.13 microGy/a
Annual dose rate = 1570.25 microGy/a
Calculated effective dose = 12.5 Gy
Age calculated according to the UEA model = 7960±146BP year

The age determination results of tooth samples found in other areas are as follows:

Table 7.

List of historical monuments with absolute ages determined by the EPR method

Name of the sampled area	*Material*	*Equivalent dose (D_e), Gy*	*EPR age, year (BP)*
Jalilabad- Polutepe (A dental specimen discovered in 2009)	Animal tooth	11.4±0.2	7421±130
Jalilabad- Polutepe (A dental specimen discovered in 2014)	Animal tooth	12±0.2	7774±129
Jalilabad- Polutepe (A dental specimen discovered in 2015)	Human tooth	12.57±0.25	7960±146
Akhstafa-Hasansu	Animal tooth	9.73±0.67	8432±416
Barda-Amirli 3	Animal tooth	9.2±0.3	7937±258
Gobustan-Boyukdash	Animal tooth	2.55±0.4	1894±97
Gobustan-Boyukdash	Snail shell	22±0.9	14402±267
Gobustan-Kichikdash	Animal tooth	3.9±0.6	2620±304
Gobustan-Kichikdash	Deer antler	9.72±0.47	4233±364
Jalilabad-Khudutepe	Animal tooth	15.51±0.23	8225±123
Chukhur-Gabala	Animal tooth	2.7±0.15	2550 ± 200
Mingechevir	Animal tooth	514±20	275800 ± 10390
Jalilabad - Alikomaktepe (sample-1)	Animal tooth	9.27±0.8	5959+122
Jalilabad - Alikomaktepe (sample-2)	Animal tooth	9.1±0.3	5782+118
Gabala-Galayeri	Animal tooth	8.49±0.5	5514±124
Yardimli-Komani	Human tooth	7.34±0.1	4775±664
Yardimli-Sarıbulag	Human tooth	9.85±0.28	5356±199

The data obtained using all three age determination methods were comparatively analyzed (Table 8). It has been demonstrated that the values obtained through these methods are consistent with each other, as well as with the stratigraphic data reported in the literature.

Table 8.
A list of historical monuments for which absolute ages have been determined using ^{14}C, EPR və TL dating methods

Name of the sampled area	*Calculated radiocarbon age, year (BP) (0=1950)*	*TL age, year (BP)*	*EPR age, year (BP)*
Polutepe	6220±85 6380±99	6400±530	7421±130 7774±129 7960±146
Shomutepe	5801±96	-	-
Goytepe	7746±88	-	-
Pashatepe	6704±88	7826 ± 513	-
Boyukdash	12644±210	15013 ± 1324 6835 ± 383	14402±267 1894±97
Kichikdash	-	5655 ± 233	2620±304 4233±364
Alkhantepe	5079±29	-	-
Burugtepe	6888±31	-	-
Selbir	1105±11	2230±510	2550 ± 200
Uzun Reme kurgan	3090±22	-	-
Leletepe	-	7919 ± 455	-
İsmailbeytepe	-	6908 ± 117	-
Hesensu	-	7913 ± 324	8432±416
Amirli-3	-	8189 ± 850	7937±258
Khudutepe	-	7116 ± 343	8225±123
Mingechevir	-	-	275800 ± 10390
Alikomektepe	-	-	5959+122 5782+118
Galayeri	-	-	5514±124
Komani	-	-	4775±664
Saribulag	-	-	5356±199

MAIN CONCLUSION

1. Charcoal, wood, and other materials uncovered during archaeological excavations were chemically converted into benzene, with the trimerization of acetylene yielding benzene at an average efficiency of 98–99%. The radioactivity of the resulting samples was measured using a scintillation counter, enabling the determination of the age of the artifacts [2,22].

2. The specific activity of the ^{14}C isotope present in the materials recovered during archaeological excavations was calculated based on the number of disintegrations per minute. A tree-ring sample felled in 1937 was used as a reference standard. This standard material was converted into benzene, and its radioactivity was measured. The radiocarbon age obtained via the radiocarbon method was calibrated in accordance with international standards. Based on the ^{14}C activity in some of the analyzed samples, it was revealed that these specimens do not belong to the Neolithic period. The results obtained were found to be in complete agreement with the stratigraphic data available in the literature [1].

3. Quartz minerals were extracted from the studied materials using physicochemical methods, and their thermoluminescent properties were investigated. Through the application of the 'plateau test', it was determined that the intensity of the TL signal peak at 325 °C varies linearly with dose, enabling the calculation of the equivalent dose. Additionally, for each sample, the activity of isotopes from the decay chains of uranium, thorium, and potassium was measured, and the corresponding annual dose rate was calculated based on the obtained data. The results revealed that although the majority of the materials date back to the Neolithic period, several samples belong to other archaeological periods [3,4,6,21,25].

4. TG, DTG, and DTA results demonstrated that mass loss in Neolithic ceramics occurs within three principal temperature intervals. The dehydration process takes place between 50°C and 350°C, while dehydroxylation occurs between 350°C and 600°C. At temperatures exceeding 600°C, thermal decomposition of calcite and

other minerals was observed. The mass loss identified in the TG analysis of ancient ceramics is attributed to the absorption of moisture from the surrounding environment over time, and the recombination of OH^- groups to form additional water, which then evaporates. In contrast, no significant mass loss was recorded in modern ceramic samples. Consequently, TG analysis has proven to be a reliable method for distinguishing between ancient and contemporary ceramics [7,8,10,11,12].

5. XRD analysis was performed on ceramic samples unearthed during archaeological excavations. The results revealed that the examined ceramics predominantly share a similar mineral composition, including quartz, feldspars (albite, microcline, anorthite, calcite), and clay minerals (muscovite, montmorillonite, diopside, maghemite, brucite, zeolite). For comparison, a raw ceramic paste sample collected from the same region was also analyzed using the same method. The comparison of analytical results indicated that Neolithic ceramic artifacts were produced exclusively from locally sourced materials. This also suggests that carbonates did not fully decompose during firing, thereby confirming that the firing temperature of Neolithic ceramics was approximately 700°C [5,9,13,14,15,16].

6. The enamel layer of a fossil tooth was analyzed using the Electron Paramagnetic Resonance (EPR) method. It was established that the primary dosimetric signal arises from the radiation-induced CO_2^- radical, whose EPR spectrum is characterized by three asymmetric peaks at g-values of 2.0043, 2.0013, and 1.9985. The dose dependence of the EPR signal intensity was investigated, revealing that the intensity of the paramagnetic center's EPR signal exhibits a linear relationship with the absorbed dose. Utilizing the additive dose method, the historically absorbed dose and the age of the fossil tooth were determined. The obtained values confirm that the majority of the materials belong to the Neolithic period and show strong consistency with stratigraphic data reported in the literature [17,18,19,20,23,24].

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