Technical Physics Letters, 2025, Vol. 51, No. 8

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Assessing the ^{14}C on the surface of the detectors to evaluate contribution in low-background experiments using oxythermography

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Received December 27, 2024
Revised June 5, 2025
Accepted June 5, 2025

The method for assessing of radiocarbon on surfaces of solids materials used in low-background experiments is proposed. At the heart of this method is detection of the amount of carbon-containing substances on the surface of the materials using oxythermography. The method evaluates the amount of radiocarbon on the surface based on its percentage content in the total carbon. The method has been tested in laboratory rooms of two different institutions - JINR and „Dubna"University.

Keywords: oxythermography, assessing radiocarbon on surfaces of solid materials, low-background experiments.

DOI: 10.61011/TPL.2025.08.61552.20240

Radioactive contaminants on the surface of materials pose a problem for low-background experiments. In certain cases, it becomes especially difficult to estimate low ^{14}C activities on the surface.

The accumulation of this radionuclide has both natural and anthropogenic causes. Radiocarbon (^{14}C) forms continuously in the upper layers of the atmosphere (at an altitude of 8–18 km) as neutrons of cosmic origin interact with nitrogen nuclei in reaction ^{14}N $(n, p)^{14}$C. A large amount of ^{14}C was formed during nuclear weapons tests in 1945–1980 (a total of $2.2 \cdot 10^8$ GBq ^{14}C), which led to a significant increase in its concentration in the atmosphere (the indicated value is 1.6 times higher than the equilibrium activity) [1]. However, the current concentration of ^{14}C has almost reverted to pre-1945 levels [2] due to self-purification of the atmosphere, intense mass exchange with the world ocean, and dilution of CO_2 contained in the atmosphere with carbon dioxide formed during the combustion of fossil fuels (coal, oil, gas, etc.), where radioactive ^{14}C has decayed almost completely.

Similar to ordinary carbon, radiocarbon oxidizes in air, producing radioactive carbon dioxide. Winds drive constant mixing of the atmosphere, and radioactive carbon dioxide formed under the influence of cosmic rays eventually gets distributed uniformly in atmospheric carbon dioxide. However, the relative content of ^{14}C in the atmosphere remains extremely low: about 10^{-12} g per 1 g of ordinary carbon (^{12}C), which corresponds to 230 Bq/kg [2]. This ratio in oil is four to six orders of magnitude smaller [3]. In a living organism, the concentration of ^{14}C is always maintained at the level of its natural concentration in the atmosphere due to metabolism.

Even a thin layer (1.5–4 nm) of organic compounds on surfaces may produce a significant contribution to the background conditions of an experiment aimed at searching for rare events [4]. It is known that organic matter is the most probable carrier of this radionuclide on surfaces. In view of this, it may turn out that the only way to determine the concentration of ^{14}C is to examine organic matter on the surface. The contribution of ^{14}C is evaluated based on the natural ratio of $[^{14}\mathrm{C}]/[^{12}\mathrm{C}] = 230\,\mathrm{mBq/g} = 10^{-12}\,\mathrm{g}/1\,\mathrm{g}$ with account for the average ^{14}C content in organic matter and the total content of organic matter on the studied surfaces [2].

More than a hundred methods for analyzing surface contamination, which offer different scenarios of exposure and detection of the secondary signal, are available at present. The most widely used of them include various types of mass spectrometry, IR spectroscopy, scanning electron microscopy, and low-energy electron spectroscopy with radioactive sources, which allow one to obtain local data on the analyzed substances on the surface of examined materials. These methods and approaches are often time-consuming, provide no data on the overall contamination of the object under study, and require a relatively large free space to install the needed equipment, highly qualified personnel of specialized training, and, accordingly, significant capital investments. In addition, surface analysis is carried out in vacuum, which translates into a significant deviation from the surface concentration of organic substances in air of the research environment.

The mentioned issues pose new challenges for researchers in developing and improving the methods and approaches to

Content (μg/cm^2) of adsorbed carbon on the surface of solids in the laboratory premises at the Dubna State University and the Joint Institute for Nuclear Research (italics) obtained by oxythermography

Sample	Adsorption time									
	10 min	1 h	3 h	1 day	2 days	3 days	5 days	7 days	14 days	34 days
Quartz	< DL	< DL	< DL	< DL	< DL	< DL	0.4 ± 0.1	0.4 ± 0.1	0.4 ± 0.1	0.4 ± 0.1
Platinum	< DL	19 ± 2	20 ± 2	55 ± 8	79 ± 9	100 ± 9		272 ± 14	516 ± 16	517 ± 17
	< DL	*< DL*	*< DL*	*< DL*	*< DL*	*< DL*		*14 ± 1*	*35 ± 3*	*78 ± 8*
Palladium	< DL	< DL	< DL	< DL	< DL	< DL	9 ± 1	13 ± 2	28 ± 3	80 ± 7
	< DL	*< DL*	*< DL*	*< DL*	*< DL*	*< DL*		*< DL*	*< DL*	*24 ± 3*

Note. DL — detection limit.

assessing surface concentrations of ^{14}C in low-background experiments.

In the present study, we propose a new oxythermographic approach to assessing the ^{14}C content on the surface of materials used in low-background experiments. The classical oxythermography method has been developed for the purpose of determination of organic matter in water bodies [5]. The essence of this method is the determination of concentration of oxygen and other gases in a flow of a binary mixture (inert gas−oxygen) or atmospheric air downstream of a thermal chamber with the analyzed sample. Further development of the oxythermography method was discussed in [6–8]. The applicability of this method to evaluation of ^{14}C content was demonstrated using the example of passive adsorption of carbon-containing compounds on the surface of quartz, platinum, and palladium. The surface area of samples was 2 cm^2, and their thickness was 0.23 mm. The proposed approach was implemented in two different laboratory settings. Tests were carried out as follows: the analyzed sample was annealed in a furnace (750 °C) prior to exposure in the laboratory environment. Following a certain period of exposure to air (from several minutes to several days), it is fed into a high-temperature reactor through which a gas mixture with a predetermined partial pressure of oxygen (in the present case, clean atmospheric air from a clean air generator) is pumped. When the sample is introduced into the chosen high-temperature reactor zone, organic compounds on its surface are oxidized in a flow of oxygen. Highly sensitive oxygen (diffusion-potentiometric O_2 sensor (Bosch) with a sensitivity range from 0 to 1000 ppm and an accuracy of ±10 ppm) and carbon dioxide (Smartgas CO_2 sensor with a sensitivity range from 0 to 5000 ppm and an accuracy of ±50 ppm) sensors mounted at the outlet monitor continuously the oxygen and carbon dioxide content in the gas flow leaving the reactor. This tandem of sensors provides an opportunity to determine not only organic carbon, but also carbon contained in carbonates. The analytical signal is the magnitude of the positive peak of formed carbon dioxide and the negative peak of oxygen consumption due to the proceeding reactions. The results are obtained in the form of kinetic curves (oxythermogram, which is the dependence of carbon dioxide formation and oxygen consumption on the time of a temperature-programmed process). The amount of organic matter is determined with the use of a calibration curve based on the measured magnitude of the carbon dioxide emission peak and the corresponding magnitude of the oxygen consumption peak. The calibration curve characterizes the relation between the peak area in standard units and the amount of carbon/oxygen in milligrams. If the surface area of a solid is known, one may determine the surface concentration of adsorbed organic matter. The obtained amount of organic matter may be converted into the amount of carbon adsorbed on the surface of the analyzed solid material.

Using the 3σ criterion and the slope of the calibration curve, we determined the minimum mass of carbon that can be detected within a time interval corresponding to the extent of the peak. It was $3 \cdot 10^{-6}$ g.

The results of our experiments are listed in the table.

The surface of platinum and palladium plates was analyzed with a Mira 3 scanning electron microscope with an energy-dispersive microanalyzer (Tescan, Czech Republic). It was found that the platinum plate had a multi-domain surface structure and individual islands of porosity, while the palladium plate, on the contrary, had a homogeneous surface structure without any significant defects. Moreover, platinum features strong catalytic properties and, if one takes the differences in crystal lattice structure into account, a significantly greater number of active centers than palladium. The observed effects will be studied in detail and characterized in future studies.

The oxythermographic approach was used to demonstrate that the surface structure and state have a significant impact on sorption processes. The use of ambient oxygen from a research room as an oxidizing environment makes it possible to analyze the surface of materials *in situ* without the loss of a certain fraction of sorbed organic substances or contamination of the sample with new compounds.

The amount of organic compounds determinable within a surface area of 1 cm^2 is 60−70 monolayers, which corresponds to an organic layer thickness of 6−8 nm (based on the average size of an organic molecule and the lengths of C−C and C−H bonds). With the natural ratio of $[^{14}\mathrm{C}]/[^{12}\mathrm{C}] = 230\,\mathrm{mBq/g} = 10^{-12}\,\mathrm{g/1\,g}$ and the upper limit of determination of the total organic matter content by oxythermography taken into account, we found that the evaluable amount of ^{14}C is $2 \cdot 10^{-6}$ Bq/cm^2.

Funding

This study was financed from budget funds of the Joint Institute for Nuclear Research and the Vernadsky Institute of Geochemistry and Analytical Chemistry of the Russian Academy of Sciences. No additional grants for conducting or supervising this research were received.

Conflict of interest

The authors declare that they have no conflict of interest.

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Translated by D.Safin