AZERBAIJAN REPUBLIC

On the right of manuscript

ABSTRACT

of the dissertation for the degree of Doctor of Science

DEVELOPMENT OF SCIENTIFIC BASIS OF RADIOLYSIS AND PHOTOLYSIS PROCESSES OF CHLORINED ORGANIC COMPOUNDS IN LIQUID SYSTEMS

Specialty:	2305.01 – Nuclear chemistry
Field of science:	Chemistry
Applicant:	**Zenfıra Iskandar gızı Iskandarova**

Baku – 2024

The dissertation work was carried out at the Institute of Radiation Problems of the Ministry of Science and Education of Azerbaijan Republic.

Scientific adviser: **Muslum Ahmad Gurbanov**
Doctor of chemical sciences, professor

Official opponents: Doctor of chemical sciences, professor
Full member of ANAS, academician
Adil Abdukhalig Garibov

Doctor of chemical sciences, professor
Sevinj Rafig Hajiyeva

Doctor of chemical sciences, professor
Najaf Tofig Gahramanov

Doctor of chemical sciences, professor
Akif Shikhan Aliyev

Dissertation Council BED 1.22 of the Supreme Attestation Commission under the President of the Republic of Azerbaijan operating at the Institute of Radiation Problems of Ministry of Science and Education of Azerbaijani Republic.

Chairman of the Dissertation Council: Doctor of chemical sciences, professor,
Corresponding member of ANAS
Islam Israfil Mustafayev

Scientific Secretary of the Dissertation Council: Doctor of phylosophy in chemistry
Ulviya Aydin Guliyeva

Chairman of the scientific seminar: Doctor of chemical sciences,
Associate professor
Khagani Farzulla Mammadov

GENERAL CHARACTERISTICS OF THE WORK

The relevance of the subject: The application of ionizing and UV radiation sources to the solution of environmental problems includes research areas of scientific disciplines such as high energy chemistry, radiation and photochemistry, nuclear chemistry, environmental chemistry. Radiation and photochemistry of organochlorides are important in this direction. Many of these compounds are chemically and thermally resistant to the environment, have the ability to spread over long distances, and are considered global pollutants. Some of these compounds enter the human body through the food chain and pose serious health hazards.

Given the serious environmental impact of organochlorine compounds, the United Nations has adopted the Stockholm Convention on Persistent Organic Pollutants, which includes chlorinated biphenyls, chlorinated pesticides, hexachlorane, etc., currently a total of about 20 chemical compounds. By the Law of the Republic of Azerbaijan dated December 9, 2003, the Republic of Azerbaijan acceded to the Stockholm Convention on “Persistent Organic Pollutants” dated May 22, 2001, It acceded to the Basel Convention of 22 March 1998 on the “Control of Transboundary Movements and Disposal of Hazardous Wastes” by the Act of 16 February 2001. At present, the Republic of Azerbaijan is on the point of acceding to the Rotterdam Convention on the Preliminary Approval of International Trade in “Certain Toxic Chemicals and Pesticides”.

According to the requirements of the Stockholm Convention, used PCB oils (with PCB concentration greater than 50 mg/kg) must be decommissioned and neutralized by 2028. In addition to that, national programs should be developed for the environmentally sound management of PCB-containing oils with a concentration of less than 50 mg/kg. In this case, research should be conducted on the degradation of oils in the environment, and new effective methods should be developed to clean up sources of pollution. Hence, vast considerable scope is created in the field of radiation technology in this area.

It should be noted that significant work is being done in

Azerbaijan to implement the requirements of the Stockholm Convention. With the financial support of the United Nations Industrial Development Organization, a Canadian-made low-temperature (with the use of alkali metals) PCB oil treatment plant was purchased and is currently being tested to neutralize oils containing more than 50 mg/kg of PCBs.

Chlorinated aromatic compounds are widely used in various industries. For instance, in agriculture, chlorinated biphenyls are applied in the energy sector (power transformers, capacitors, electrical switches, electrical equipment), paint production, etc. up to present day. Although chlorinated biphenyls (PCBs) are not produced in Azerbaijan, about 680 tons of transformer oil contaminated with PCBs and about 100 tons of pure PCB oil in capacitors have been found in current electrical equipment. Due to the fact that Sovtol-10 brand oil produced in the USSR and used in transformers contains 10% trichlorobenzene (TCB), the release of oils into the environment also has negative environmental effects associated with this chemical compound. A number of chlorinated compounds are formed during the treatment of drinking water with chlorine. They include more than 100 chlorinated hydrocarbons, including chlorine compounds with hydrocarbons (chlorinated compounds of methane and ethylene), chlorinated compounds of phenol and benzene. The application of radiation technologies for the purification of water from toxic compounds, provides its biological purification, along with improving its quality.

Areas contaminated with PCBs are widespread in Azerbaijan as a result of the extensive use of chlorinated biphenyls. The level of soil contamination with PCBs in Sumgayit is 0.26 mg/kg. PCBs contamination was observed in the Balakhani and Sabunchu oil areas, as well as in the sediments of the Caspian Sea and the Baku Gulf. More so in the bottom sediments of the Kura River amount of PCBs was found to be at the level of 28-30 ng/g.

Given the high environmental hazard of chlorinated aromatic compounds, the study of their transformation in the environment as a result of various physical effects is a pertinent scientific problem. The interest in radiolysis of PCBs is related to the need of study the radiation resistance of PCB-containing oils in order to purify contaminated oils from PCBs, convert PCB compounds in various media, especially aquatic media, and use biphenyls as a coolant and dielectric fluid in nuclear reactors. Although extensive research has been conducted on the radiation-chemical treatment of oils from PCB compounds, little has been studied about the above-mentioned problems - environmental degradation of PCBs and reuse of contaminated oils after decontamination and application of radiation technologies in order to decontaminate high-density PCB oils. Specifically kinetic modeling has not been performed to study the mechanism of dechlorination .

The following work was carried out in accordance with the research plan of the Institute of Radiation Problems (№0106 Az00725, 01114160, 01144013).

The purpose of the work: Determination of kinetic regularities and mechanisms of radiolytic conversion processes of chlorinated organic hydrocarbons (methane, benzene, biphenyls) in different solutions, analysis of the application possibilities of radiation technologies to these processes and the development of scientific foundations

Issues raised:

1. Study of the kinetic regularities of the conversion of chlorinated compounds of benzene and biphenyls (1,2,4-trichlorobenzene, polychlorinated biphenyls) under the influence of ionizing and UV radiation.
2. Investigation of kinetic regularities of radiolytic (indirect radiolysis) conversion of chloroform, 1,2,4-trichlorobenzene and polychlorinated biphenyl in aqueous medium.
3. Investigation of chemical transformations in the studied systems under the influence of gamma rays by UV and IR spectroscopy methods.
4. Investigation of kinetic regularities of radiolysis process of polychlorinated biphenyls in organic solvents (ethanol, hexane, isopropyl alcohol).
5. Study of the effect of polychlorinated biphenyls on the radiolysis process of transformer oil.

6. Kinetic modeling of radiolysis of chloroform and biphenyls in water and organic solvents, respectively.
7. Study of the radiolysis process of polychlorinated biphenyl-containing transformer oil and 1,2,4-trichlorobenzene in the presence of nano-γ-Al_2O_3 oxide.
8. Assessment of application possibilities of radiation-chemical technologies for neutralization of chlorinated organic compounds.

The scientific novelty of the work:

- For the first time, the decomposition process of 1,2,4-trichlorobenzene and Sovtol brand transformer oil containing PCB under the effect of γ-rays was studied. Radiation-chemical yields of products of conversion of high-chlorinated biphenyls to low-chlorinated biphenyls as a result of dechlorination decomposition reaction under the effect of ionizing radiation on PCB-containing oil were determined, kinetic properties of the products were determined.
- For the first time, the kinetics of changes in the physical properties (viscosity, electrical conductivity, density) of PVC-containing oils under the influence of ionizing radiation depending on the absorption dose were studied. For the first time, a kinetic model of the process of chain radiolysis of aqueous solutions of chloroform was created and mathematical modeling was carried out.
- For the first time, the kinetic parameters of the radiolysis process of 1,2,4-trichlorobenzene and PCB-containing oils in water were determined.
- The process of radiolysis in various organic solvents of PCB-containing oils was studied, the radiolysis process of the system was determined kinetically modeled, the parameters characterizing the conversion process were determined.
- For the first time, the kinetics of gaseous products formed during the radiolysis process of PCB and chlorobenzene in transformer oil were studied and the radiation-chemical yield of the products was determined.
- For the first time, the effect of nano-γ-Al_2O_3 oxide 1,2,4-

trichlorobenzene on the radiolysis process of PCB-containing oils was studied and the radiolytic processes occurring in these systems were analyzed.

Practical significance of the work:

- Radiation-chemical treatment of transformer oils contaminated with PCBs allows the reuse of purified oils depending on the amount of PCBs contained in the oil and the strength of the ionizing radiation sources used.
- The results obtained can be used to assess the risks of contact of chlorinated compounds with contaminated media.
- Kinetic approaches and models used in the research process for the dechlorination process can be applied to solve similar problems in chemical kinetics.

Protected provisions:

- Radiolysis of 1,2,4-trichlorobenzene and kinetic regularities of its radiolytic conversion processes in transformer oil;
- Regularities of kinetic transformation of chlorinated biphenyls under the influence of γ-rays and UV radiation;
- Kinetic regularities and mechanism of radiolysis of aqueous solutions of chloroform;
- Regularities of radiolysis of a solution of PCB-containing oils in organic solvents;
- Kinetic regularities and mechanism of radiolysis process of PCBs in alkaline environment and in the presence of organic solvents;
- The effect of nano-γ-Al_2O_3 oxide on the radiolytic decomposition of chlororomatic compounds;
- Results of the evaluation of the possibilites of applying radiation-chemical technology to neutralize chlorinated organic compounds.

Approbation of the work:

The results of the work were discussed at the following seminars and conferences:

Republican scientific conference dedicated to the 800th anniversary of Nasreddin Tusi (Baku, 2001); V International scientific conference "Ecology and Civil Defence" (Sumgayit, 2004); Scientific-theoretical conference on "Modern period and environmental policy in Azerbaijan" (Baku, 2007); Scientific-theoretical conference on “The impact of oil and gas production on the radioecological status of the Absheron Peninsula” (Baku, 2007); International conference dedicated to the 60th anniversary of Academician Mahmud Karimov (Baku, 2008); Scientific conference dedicated to the anniversary of academician M.F.Nagiyev (Baku, 2008); The Fifth Eurasion on Nuclear Science and its Application (Ankara, Turkey, 2008); VII Baku International Mamedaliyev Conference on Petrochemistry dedicated to the 80th anniversary of the Institute of Petrochemical Processes of the National Academy of Sciences of Azerbaijan (Baku, 2009); International conference dedicated to the 40th anniversary of the Institute of Radiation Problems of ANAS (Baku, 2009); International Conference "Peaceful Use of Nuclear Energy" dedicated to the 100th anniversary of M.M.Malikzade (Baku, 2010); Conference on "Radiation and Environment" dedicated to the 60th anniversary of the corresponding member of ANAS, honored scientist Adil Garibov (Baku, 2010); Republican Scientific Conference dedicated to the 85th anniversary of Academician T.Shakhtakhtinsky (Baku, 2011); IV International Conference on “Perspectives of Peaceful Use of Nuclear Energy” (Baku, 2011); V International Conference on “Perspectives of Peaceful Use of Nuclear Energy” (Baku, 2012); VIII Conference "Radiation Research and their practical aspects" dedicated to the 65th anniversary of academician M.K.Karimov (Baku, 2013); 7th Eurasian Conference on “Nuclear science and its application” (Baku, 2014); IV All-Russian Conference with international participation on "Actual issues of chemical technology and environmental protection" (Cheboksary, 2014); Scientific-practical conference on "Emergencies and safe life" dedicated to the 10th anniversary of the Ministry of Emergency Situations (Baku, 2015); The VIII International Scientific-Practical Conference on "Science in the Modern World" (Kiev, 2016); The 4th International Scientific-Practical Conference "Problems and Prospects of Modern Science" (Moscow, 2016); International Scientific Forum on Nuclear Science and Technologies dedicated to the 60th anniversary of the Institute of Nuclear physics, 11th International conference “Nucleus-2017”, 8th Eurasian Conference on

“Nuclear Science and its Application” (Almaty, 2017); 68 International Conference on "Fundamental Problems of Nuclear Physics, Atomic Energy and Nuclear Technology", Conference "Nucleus 2018" (Voronezh, 2018); IV International Conference on "Actual and scientific and scientific-technical problems of providing chemical safety" (ASTICS-2018); ISEF-2018 Conference (Baku, 2018); International scientific-practical conference on "Environmental, industrial and energy security-2018" (Sevastopol, 2018); International Scientific-Practical Conference on «Radiation and chemical safety problems» (Baku, 2019); Republican Scientific-Technical conference on “Radiological and Chemical Risks in the Territories Liberated From Occupation” (Baku, 2022); Scientific-Technical Conference dedicated to the 100th anniversary of the birth of Heydar Aliyev “Radiation Technologies and Their Application” (Baku, 2023).

Structure and scope of the dissertation. The dissertation consists of an introduction, 8 chapters, conclusions, a list of used literature and a list of abbreviations, and the total volume is _325_ pages.

The total volume of the dissertation with a sign indicating the volume of the structural sections of the dissertation separately. Dissertation title page - **1** page, table of contents - **4** pages (**5525** marks), introduction - **16** pages (**29494** marks), chapter 1 - **50** pages (**75847** marks), chapter 2 - **47** pages (**47731** marks), 3 - chapter **26** pages (**29095** marks), chapter 4 - **27** pages (**25826** marks), chapter 5 - **21** pages (**25469** marks), chapter 6 - **33** pages (**44546** marks), chapter 7 - **39** pages (**38793** mark), chapter 8 is **22** pages (**27887** marks) with main results - **4** pages (**4845** marks), 305 names cited bibliography - **43** pages (**69571** marks) and abbreviations and conventional marks - **1** page (**366** marks) it consists of **325** pages in total. The total number of marks available in the dissertation is **425403.** 305 references are cited in the dissertation work, of which _21_ are Azerbaijani, _126_ are Russian and _178_ are in English.

BRIEF SUMMARY OF THE WORK

In the first chapter, general information on chlorinated organic compounds is analyzed, along with information on traditional methods of neutralization of oils contaminated with chlorinated biphenyls and innovative technologies used for this purpose - radiation-chemical, photochemical, plasmachemical, electrochemical. Unlike conventional technologies, innovative technologies are characterized by purification processes at low temperatures, without addition of chemical reagents, and with minimal impact on the environment. The effect of various solvents on the efficiency of purification processes has been studied and it has been determined that the dechlorination of chlorinated biphenyls is more rapid in the presence of polar solvents, and dissolved oxygen has a negative effect on this process. The results show that chlorine depletion reactions occur as a result of the formation of chlorine atoms due to the effective reaction of chlorinated biphenyls with solvated electrons (Sherman mechanism). This chapter also analyzes the processes of decomposition of other chlorinated organic compounds under the effect of physical factors. These compounds include chlorinated pesticides and chlorbenzenes, as well as low-molecular-weight chlorine organic compounds. The results of research on the processes of radiolysis and photolysis of two-phase systems of chlorinated organic compounds in water have been studied and it has been shown that in both cases the effect of these physical factors leads to the decomposition of chlorinated compounds and, consequently, degradation processes.

Despite the extensive research on radiolysis and UV photolysis of chlorinated mixtures, the following issues have been little studied:

- radiation-chemical processes occurring during irradiation of chlorinated biphenyls and chlorinated compounds of benzene with ionizing radiation;
- radiation-chemical degradation processes of chlorinated compounds in environmentally important systems such as water and transformer oil;
- Radiation-chemical conversion processes of high-density PCB isomers in solvents;
- Changes in the electrophysical properties of oil during irradiation of transformer oils containing PCB;

- Modeling based on kinetic schemes and development of a possible mechanism.

In the second chapter, chromatographic, spectroscopic and chemical analysis methods were used to determine the kinetic regularities of decomposition, condensation and oxidation processes under the influence of γ-rays of 1,2,4-TCB, TCB transformer oil and pure transformer oil.

- The dependence of the concentration of H_2O_2 and H_2 on the absorbed dose in the radiolysis of 1,2,4-trichlorobenzene was studied and it was shown that the concentration of H_2O_2 increases up to ~4 kGy-dose, then decreases with increasing dose. The radiation-chemical yield of H_2O_2 is 0.76 molecules/ 100 eV. The concentration of H_2 increases with increasing dose and reaches a steady state at doses >60 kGy. The radiation-chemical yield of H_2 was 0.045 and is close to the radiation-chemical yield of H_2 in the radiolysis of benzene ~0.04.
- The splitting occurs as a result of the effective capture of electrons by 1,2,4-TCB molecules. As a result, HCl acid is formed, and this has been observed experimentally. It has been shown that increasing the dose causes a decrease in pH, while at a dose of 136.8 the pH decreases from 6.4 to 3.1.
- The results of the chromatographic study of radiolysis products of 1,2,4-TCB are given in Figure 1. TCB was analyzed with Agilent Technologies 7820 A chromatograph.

Figure 1 shows the dependence of the absorption dose of the concentration of products formed during radiolysis under the influence of gamma rays of TCB.

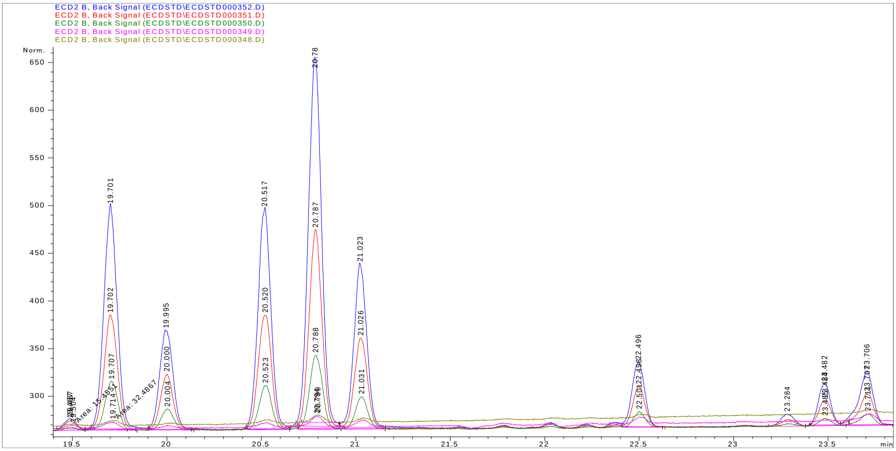


Figure 1. Chromatograms of 1,2,4-TCB samples irradiated at different doses (4.1; 27.4; 68.4; 136,.8 kGy).

Chromatographic analysis shows that the corresponding release time of the compounds formed during the radiolysis of 1,2,4-TCB is 6-7 times longer than the release time of the original 1,2,4-TCB. It can be assumed that, as in the radiolysis of benzene, the condensation reaction in the radiolysis of 1,2,4-TCB results in the formation of heavier benzene-containing compounds.

As can be seen, the intensity of all peaks increases with increasing dose.

Chemical changes during radiolysis of 1,2,4-trichlorobenzene were studied by IR spectroscopy. Figure 2 shows the IR spectra of irradiated 1,2,4-trichlorobenzene samples at different absorption doses up to 136.8 kGy.

Additional information on radiolysis products was obtained by UV spectroscopy. The spectra were taken on Varian 50 spectrophotometer. TCB samples were drawn on the wall surface of the tube and spectra were obtained after a stationary layer was obtained. Figure 3 shows the UV spectra of irradiated 1,2,4-trichlorobenzene samples at different absorption doses.

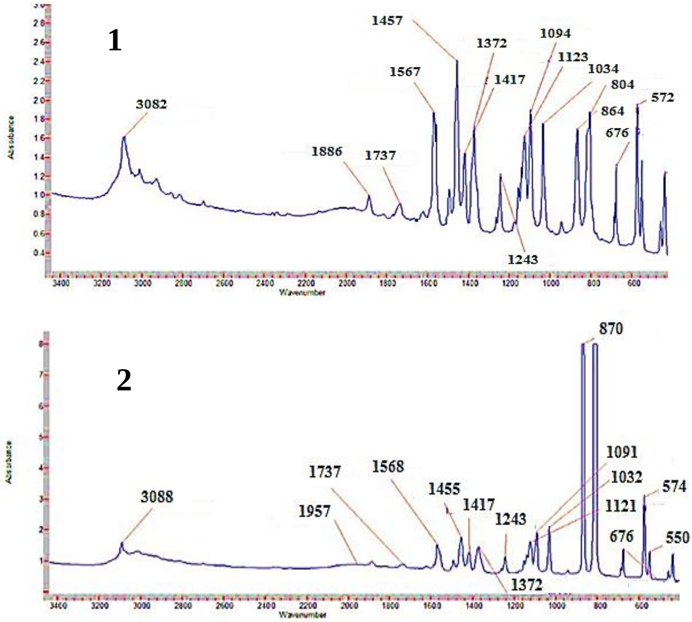


Figure 2. IR spectra of 1,2,4-trichlorobenzene samples (1 – D=0; 2 – D=136.8 kGy).

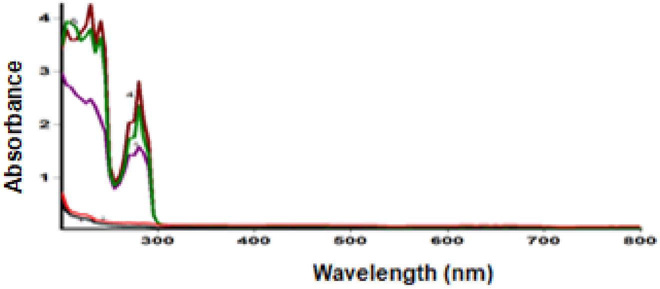


Figure 3. UV absorption spectra of radiolysis products of TCB at different radiation doses. 1 - Initial; 2 – 4.1 kGy; 3 –27.4 kGy; 4 – 68.4 kGy; 5 – 136.8 kGy.

As can be seen, the intensities of peaks observed in the region below 300 nm increase sharply as the absorption dose increases, proving that TCB undergoes chemical transformations during irradiation.

- During the radiolysis of transformer oil containing 5-40 mg /

kg of 1,2,4-trichlorobenzene, the concentration of CO_2, H_2O_2, which are oxidation products, and the pH of 1,2,4-trichlorobenzene-free transformer oil were studied.

Depending on the dose, the maximum dose of hydrogen peroxide was observed to be ~27 kGy. With subsequent increase in dose, the concentration of H_2O_2 decreases, which indicates its participation in secondary reactions. The maximum value of CO_2 concentration is observed at 27 kGy and the radiation-chemical yield is 0.18 molecules/100eV.

It has been shown that the radiation-chemical yields of both oxidation products (H_2O_2, CO_2) increase as the concentration of TCB in the oil increases and increases from 3.6 to 6 for H_2O_2 and from 0.18 to 1.8 for CO_2.

Along with the oxidation process, the molecules of the components of the transformer oil are decomposed under the influence of ionizing radiation. This leads to the formation of gas products. Hydrogen and hydrocarbon products such as CH_4, C_2H_4, C_2H_6, C_3H_8, C_4H_{10}, C_5H_{12} and C_6H_{14} have been identified.

Radiation-chemical yields of gas products at different concentrations of 1,2,4-TCB in transformer oil vary extremely depending on the concentration of TCB.

Thus, the consumption of gaseous products increases up to 15 mg/kg of the concentration of TCB, and a further increase in the concentration of TCB leads to a weak reduction in yields.The results of the study of the radiolysis process of transformer oil with different concentrations of TCB by IR spectroscopy are given in Figure 4.

As can be seen, significant changes in the spectrum are observed under the influence of γ-rays.

Power transformers are widely used in the energy sector, including nuclear power. Therefore, the study of radiation resistance of transformer oils is an important issue. Problems related to the radiation resistance of materials of electrical equipment resulting from various accidents, dedicated to the determination of the operability of units and various parts of nuclear power plants, have been studied in a number of studies. After the accident at the Chernobyl nuclear power plant in 1986, this issue became even more urgent.

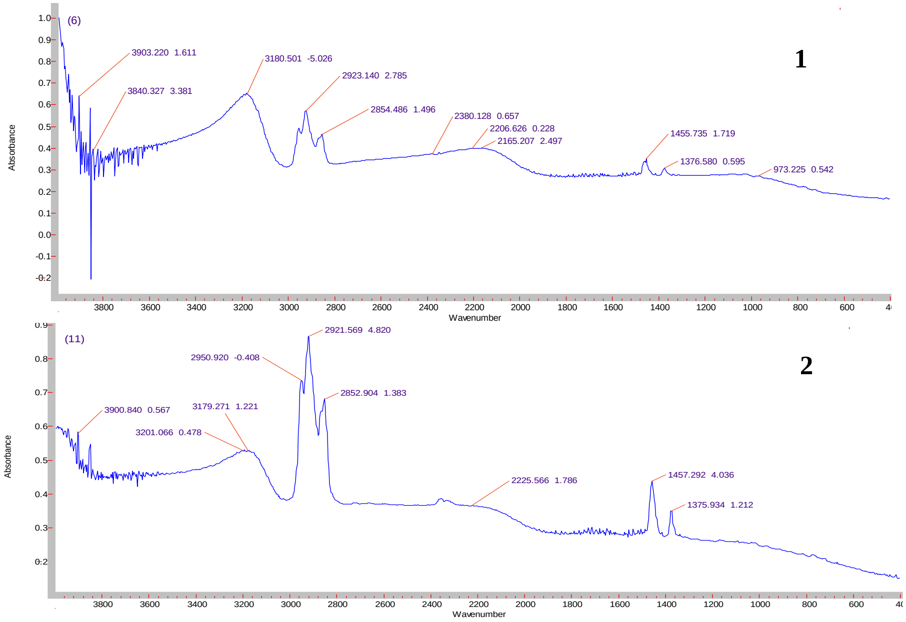


Figure 4. IR spectra of samples at different absorption doses (1 - D = 0; 2 - D = 68.4 kg) in the process of radiolysis of transformer oil containing TCB of different concentrations.

Problems related to the radiation resistance of electrical equipment in various emergency situations have been studied in many studies to determine the performance of various parts and units of nuclear power plants. In order to determine the possible reduction in reliability during accidental radiation, more functional components and electrical equipment such as - transformer oil and electrically insulated cardboard - were studied.

Study of radiation resistance of transformer oils under the influence of γ-rays and physico-chemical parameters, gas products, H_2, CH_4, C_2H_4, C_2H_6, C_3H_8, C_4H_{10}, C_5H_{12}, C_6H_{14}, density, viscosity and specific resistance (29.7-237.6) in the absorbed dose range of kGy variability has been studied. IR absorption spectra of the samples were also studied.

It is shown that all kinetic curves are characterized by an induction period when the absorbed dose is 60 kGy. An increase in the dose above 60 kGy leads to a sharp increase in the rate of formation of these products. The highest rate is observed in the formation of H_2. The sequence of rate values is: w (H_2) > w (CH_4) > w (C_2H_4) > w (C_2H_6).

The induction period is also observed during the formation of $\sum C_3$, $\sum C_4$ hydrocarbons. Heavy products such as C_5, C_6 are formed in high doses and are only identified at doses above 70 kGy. Thus, the rate of formation of hydrocarbon C_6 is higher than the rate of formation of C_5.

In addition to hydrocarbons, oxidation products such as hydrogen peroxide and carbon dioxide have been observed and their kinetics have been studied.

It has been shown that in both kinetic dependencies, the maximum concentration is observed at a dose of 20-30 kGy. Subsequent increase in dose leads to a decrease in its concentration. For hydrogen peroxide, the rate of formation and the maximum concentration are slightly higher (~5-6 times). The radiation-chemical yields of H_2O_2 and CO_2 are 3.6 and 0.18 molecules/100 eV, respectively. The results show the breakdown of transformer oil in the studied absorbed dose range, and as a result, this change affects other physicochemical quantities. Density and viscosity of irradiated transformer oil were determined in the dose range of 29.7-237.6 kGy. It was found that in the range of doses considered, the density of the oil varies in the range of 0.86-0.60 g/cm^3, and the viscosity varies in the range of 5.42-5.73 mm^2/sec. With increasing dose, there is a decrease in specific resistance and, accordingly, an increase in electrical conductivity, which is associated with the process of decomposition and oxidation products, the formation of relatively high mobility products.

Figure 5 shows the IR absorption spectra of transformed oil irradiated at different doses. From Figure 5, the IR-absorption spectrum is observed in the range $\Delta\lambda_1$=2800-3300 cm^{-1}, $\Delta\lambda_2$=2000 cm^{-1}, $\Delta\lambda_3$=1350-1450 cm^{-1} and $\Delta\lambda_4$=600-1200 cm^{-1}.

As can be seen, valence oscillations =C–H, plane deformation oscillations - C=C and non-plane oscillation oscillations - CH aromatic compounds are observed in the spectra. In addition, valence oscillations - C–H and deformation oscillations - are observed in C–CH_3 (asymmetric and symmetric) alkanes.

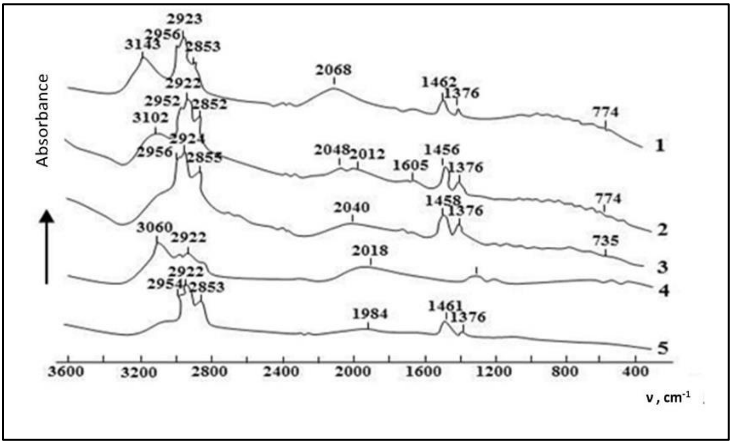


Figure 5. IR-absorption spectra of transformed oil irradiated at different doses: 1– primary; 2 - 4.1 kGy; 3 - 27.4 kGy; 4 - 68.4 kGy; 5 - 136.8 kGy

Figure 5 (2-5) shows the absorption spectra of irradiated samples at doses of 4.0-136.8 kGy. As can be seen, absorption is observed as the intensity of the bands changes with increasing dose.

It is shown that for strips λ_{max}=3143 cm^{-1}, 2068 cm^{-1} and 774 cm^{-1}, the value of J_{max}/J_0 decreases at the initial dose (up to 4 kGy), increasing with increasing dose to 68.4 kGy. Subsequent increase in dose reduces the value of J_{max}/J_0. As mentioned above, these absorption bands are characteristic of aromatic hydrocarbons.

Unlike aromatic hydrocarbons, the intensity of the bands characteristic of alkanes increases to a dose of 68.4 kGy, then decreases with increasing dose.

In the third chapter, the kinetic regularities of the conversion processes of Sovtol-10 transformer oil containing PCB under the influence of γ- and UV rays were studied, the dependence of oil density and electrophysical parameters, pH oxidation products (H_2O_2, CO_2) and hydrocarbon gases on radiation time was studied.

Identified isomers and homologues in Sovtol-10 oil are PCB 18 (2,2',5-trichlorobiphenyl), PCB 28+31 (2,4,4'-trichlorobiphenyl +

2,4',5-trichlorobiphenyl), PCB 52 (2,2',5,5'-tetrachlorobiphenyl), PCB 44 (2,2',3,5'-tetrachlorobiphenyl), PCB 101 (2,2',4,5,5'-pentachlor-biphenyl), PCB 118+149 (2,3',4,4',5-pentachlorobibenyl+2,2',3,4',5',6-hexachlorobiphenyl), PCB 153 (2,2',4,4',5,5'-hexachlorobiphenyl), PCB 138 (2,2',3,4,4',5'-hexachlorobiphenyl), PCB 180 (2,2',3,4,4',5,5'-heptachlorbiphenyl), PCB 194 (2,2',3,3',4,4',5,5'-octachlorobiphenyl). Radiation-chemical yields of the isomers identified from the kinetic curves are determined and given in Table 1.

Table 1

Radiation-chemical yields of decomposition of PCBs determined during radiolysis of Sovtol 10 type PCB-containing oil

PCBs	PCB -52	PCB -101	PCB -149+118	PCB -138	PCB -153	PCB -total
Radiation-chemical yields, G, molecules/100 eV	2.33	1.9	2.45	1.34	1.11	9.1

The results obtained can be explained by the capture of solvated electrons by these molecules during the radiolysis of PCB-containing oils. It was found that the values of the rate constants are equal to the di-, tetra- and decachlorobiphenyl molecules of the solvated electrons, respectively: $3.8\cdot10^{9}$ $M^{-1}s^{-1}$, $3\cdot109$ $M^{-1}s^{-1}$, $7\cdot10^{9}$ $M^{-1}s^{-1}$. The rate constants of the reaction of electrons with oxygen are also in the following order: $1.9\cdot10^{10}$ $M^{-1}s^{-1}$.

$$C_{12}H_{10-n}Cl_n \overset{\gamma}{\rightarrow} C_{12}H_{10-n}Cl_n^{+} + e^{-}$$

$$C_{12}H_{10-n}Cl_n \overset{\gamma}{\rightarrow} C^{\cdot}{}_{12}H_{10-n}Cl_{n-1} + Cl^{\cdot}$$

$$e^{-} + C_{12}H_{10-n}Cl_n \rightarrow C^{\cdot}{}_{12}H_{10-n}Cl_{n-1} + Cl^{-}$$

$$Cl^{\cdot} + C_{12}H_{10-n}Cl_n \rightarrow C^{\cdot}{}_{12}H_{10-n-1}Cl_n + HCl$$

$$e^{-} + C_{12}H_{10-n}Cl_n^{+} \overset{\gamma}{\rightarrow} C^{\cdot}{}_{12}H_{10-n}Cl_{n-1} + Cl^{\cdot}$$

$$e^{-} + O_2 \rightarrow O_2^{-}$$

Taking into account the above, we can write the following equations for describing the dependance of concentration of varying concentration of electrons, chlorine atoms and PCB molecules on time during the radiolysis of PCB oils:

$$\frac{\partial e}{\partial t} = G_e * J * 10^{-2} \text{-} k_1[e][ArCl^{+}] - k_2[e][ArCl] - k_3[e][O_2]$$

$$\text{-}\ \frac{\partial [ArCl]}{\partial t} = \omega_0 + k_2[e][ArCl] + k_4[Cl][ArCl]$$

$$\frac{\partial \mathrm{Cl}}{\partial \mathrm{t}} = \omega_{0-}\mathrm{k}_4\,[\mathrm{Cl}][\mathrm{ArCl}]$$

G_e - radiation-chemical yield of all electrons during radiolysis of PCB, molecule/100 eV; J-absorbed dose rate, kGy/sec; rate constants of the corresponding reactions, M^{-1} sec^{-1}; Ionization and decomposition rate of ω_0 – PCB molecule, M · sec^{-1}.

Compared to the PCB concentration, it can be assumed that at low values of O_2 concentration and dose rate ω_1 and $\omega_3 << \omega_2$. Then,

$$\frac{\partial \mathrm{e}}{\partial \mathrm{t}} = \mathrm{G_e} * \mathrm{J} * 10^{-2} - \mathrm{k}_2[\mathrm{e}][\mathrm{ArCl}]$$

In stationary case: $\frac{\partial \mathrm{Cl}}{\partial \mathrm{t}} = 0, \quad \frac{\partial \mathrm{e}}{\partial \mathrm{t}} = 0$

Then: $[\mathrm{e}]_s = \frac{\mathrm{G_e} * \mathrm{J} * 10^{-2}}{\mathrm{k}_2[\mathrm{ArCl}]}, \qquad [\mathrm{Cl}]_s = \frac{\omega_0}{\mathrm{k}_4\,[\mathrm{ArCl}]}$

For the maximum radiation-chemical yield of the decomposition of PCB molecules, we obtain the expression $\mathrm{G}_{[-\mathrm{ArCl}]} = 2\,\mathrm{G}_{\mathrm{ArCl}^+,\mathrm{Cl}} + \mathrm{G_e}$ Since the yield of electrons and ions during the radiolysis of organic matter is in the order of about 3 particles/100eV, $G_{[-ArCl]}$=8-9 molecules/100 eV is obtained. Exposure to UV light and γ-rays causes chemical transformations of transformer oil components.

Figure 6 shows the temperature dependence of the specific resistance of Sovtol-10 at different UV-irradiation periods.

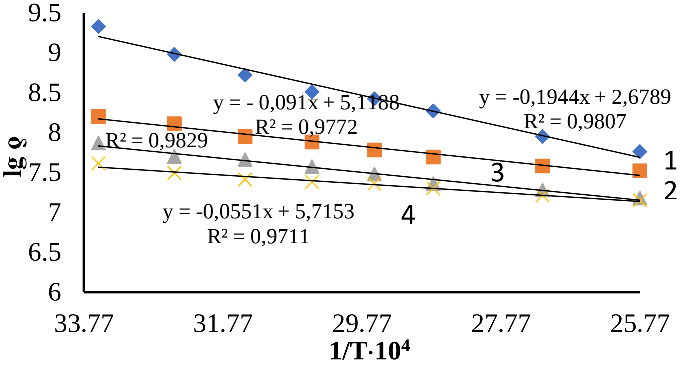


Figure 6. Temperature dependence of the specific resistance of Sovtol-10 at different UV-irradiation periods (I=2·10^{15} quantum/s).
(1 - initial sample; 2 - 1 hour; 3 - 2 s 30 min; 4 - 3 s 30 min).

Table 2

Activation energies of changes in electrical conductivity of Sovtol-10 transformer oil at different irradiation periods (0.1; 2.5 and 3.5 hours)

τ radiation, clock	0	1	2.5	3.5
E_{active}, kcal/mol	5.3	2.1	1.3	0.97

Used PCB oils are strong dielectrics with a specific resistance of 10^{11}-10^{12} $Ohm^{-1}m$The value of the specific resistance we analysed for used oils is 109 $Ohm^{-1}m$, which is lower than that of fresh oil at 25°C. This is because the PCB molecule breaks down under the influence of radiation. The conductivity of oils is due to the formation of weakly bound loads ($HCl \rightarrow H^{+} + Cl^{-}$) under the influence of radiation and the presence of metals in the processed oils. The conductivity of the oil mixture may also be due to the presence of the metals we have determined experimentally (Cr, Mn, Fe, Rb, Sr, Zr, Mo, Ba and Pb).

Under the influence of UV rays, a decrease in the viscosity of Sovtol 10 is observed, which increases the mobility of the oil. A similar dependency was obtained for used oils that do not contain PCBs. The absorption spectra of UV photolysis products of transformer oil containing 14 mg/kg PCB are shown below.

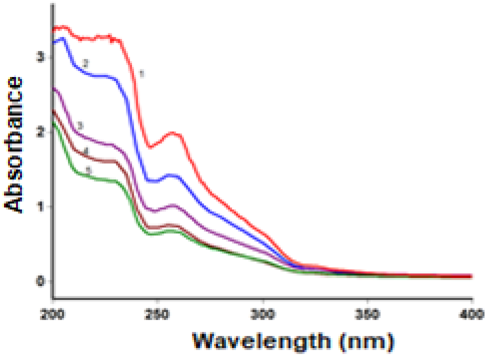


Figure 7. UB-absorption spectra of UV-photolysis products of transformer oil containing "Sovtol -10": 1 - primary; 2 - 10 minutes; 3 - 15 minutes; 4 - 20 minutes; Radiation for 5 - 40 minutes ($I=2\cdot10^{15}$ quantum/sec)

As can be seen, high level absorption occurs at a wavelength of λ <300 nm. The maximum of the observed absorption bands are λ_{max}=201.9 nm, 205.1 nm, 207.0 nm, 211.0 nm, 222.0 nm, 227.1 nm, 228.9 nm, 231.9 nm, 258.0 nm. It was found that the Abs (absorption) of the corresponding bands decreases with increasing radiation time.

The dependence of the oxidation products (H_2O_2, CO_2) and the decomposition of the components of the transformer oil as a result of radiolysis of transformer oil containing PCBs on the dose of gas (C_1-C_7) products, and the pH value on the PCB concentration in the oil were studied.

Figure 8 shows the dose dependence of the concentration of H_2O_2 in different amounts of PCBs in oil.

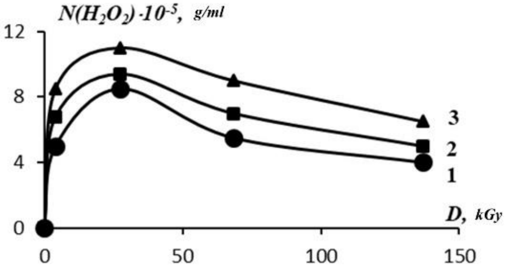


Figure 8. Dose dependence of the concentration of H_2O_2 in different amounts of PCBs in oil. 1) 5; 2) 15; 3) 40 mg/kg PCB.

As can be seen, the dose dependence of the concentration of H_2O_2 in the considered concentration range of PCB during radiolysis of PCB transformer oil is extreme. The maximum concentration of H_2O_2 is observed at a dose of ~27 kg. At high dose values, a decrease in the concentration of H_2O_2 is observed, which occurs as a result of the reaction of active particles formed during its radiolysis. Figure 9 shows the dose dependence of the carbon dioxide concentration at different values of the initial PCB concentration.

As the dose increases, the concentration of carbon dioxide increases and reaches a steady state at doses above 27 kGy. From the above kinetic curves, the values of different initial concentrations of PCBs were calculated and given below in the table 3.

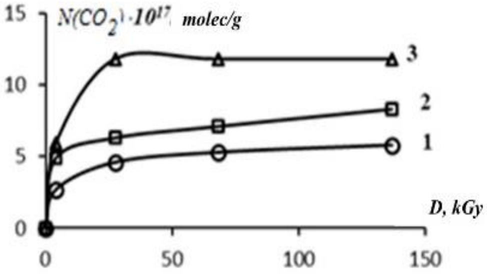


Figure 9. Dose dependence of carbon dioxide concentration at different values of initial concentration of PCB 1) 5, 2) 15, 3) 40 mg / kg PCB

Table 3
Radiation chemical yields of H_2O_2 and CO_2 during radiolysis of transformer oil containing 5-40 mg / kg PCB

C_{PCB}, mg / kg	G, molecules/100 eV	
	H_2O_2	CO_2
0	3.6	0.18
5	3.9	1.1
15	4.7	1.9
40	5.9	2.3

The obtained results show that during the radiolysis of the considered systems, the radiation chemical yield of H_2O_2 and CO_2 gases increases depending on the initial concentration of PCB.

During the radiolysis of the considered systems, the kinetics of the formation of H_2 and hydrocarbons CH_4, C_2H_4, C_2H_6, C_3H_8, C_4H_{10}, C_5H_{12}, C_6H_{14} as gaseous products in the initial concentrations of PCBs in oil were studied. have an induction period. After a dose of 68 kGy, the rate of formation of gases and radiation-chemical yields increases.

It has been shown that regardless of concentration the kinetic curves have an induction period. As can be seen from the table 4, the radiation-chemical yields of these gases vary slightly depending on the initial concentration of the PCBs.

The process of radiolytic dechlorination of PCBs in transformer oil is characterized by pH value. Figure 10 shows the dose-dependent variation of pH at different initial concentrations of PCBs.

Table 4

Radiation chemical yields of H_2, CH_4, C_2H_4, C_2H_6, C_3H_8 during radiolysis of transformer oil containing 5-40 mg / kg PCB

C_{PCB}, ppm	G, molecules/100 eV			
	H_2	CH_4	C_2H_4	C_2H_6
0	0.24	0.65	0.30	0.13
5	0.31	0.44	0.21	0.19
15	0.35	0.47	0.15	0.11
40	0.41	0.51	0.2	0.12

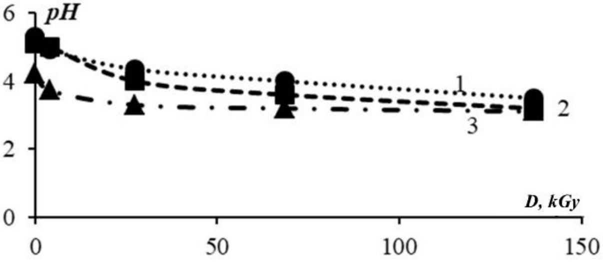


Figure 10. Dose dependence of pH at different initial concentrations of PCB: 1) 5; 2) 15; 3) 40 mg/kg PCB.

As can be seen, the value of the pH value decreases with increasing dose, which is due to the formation of acidic compounds as a result of dechlorination of PCBs.

In the fourth chapter the kinetic regularities of aqueous solution in different initial concentrations of chloroform were studied, chemical processes occurring during the radiolysis of the system were studied and based on the obtained results the parameters characterizing the decomposition rate of chloroform by the method of stationary concentrations (chloroform and dissolved oxygen) a connecting coherent expression was obtained. A kinetic model describing the observed chain reaction regime was developed and mathematically modeled. The results of the calculations were compared with the experimental results and it was determined that the kinetic model was adequate to the obtained results.

Radiolytic conversion of chloroform in aqueous solutions and kinetics of formation of chlorinated compounds.

Kinetic studies were conducted by 2 methods. a) In the first method (dynamic regime), the samples were irradiated by releasing air through a solution of chloroform in water at different speeds. b) In the second method (static regime), an aqueous solution of chloroform was irradiated at different doses under static conditions by keeping in contact with air.

During irradiation under static conditions, depending on the initial concentration of chloroform, the radiation-chemical yield of its decomposition process increases from 6.4 to 129 molecules/100 eV ($8.3 \cdot 10^{-2}$M). The results show that the radiolytic conversion of chloroform at values greater than $4.2 \cdot 10^{-2}$M occurs in chain reactions.

In the UV spectra of irradiated samples, the optical density increases from 0.4 to 1.2 at initial dose values, and an increase in absorption dose at values above 8.6 kGy leads to a decrease in optical densities. This dependence is due to the fact that the resulting products are subjected to large doses of radiolytic degradation.

Dichloromethane and tetrachloroethane have been identified as chlorinated compounds of chloroform in aqueous solution and it has been shown that their concentration reaches maximum values at a dose of 8.6 kGy, and subsequent increase in dose leads to a decrease in the concentration of these chlorinated compounds.

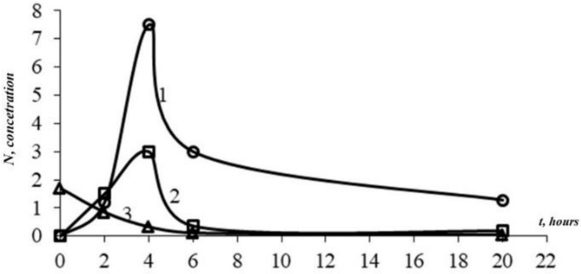


Figure 11. Dose dependence of the concentration of chloroform, dichloromethane and tetrachloroethane formed during the radiolysis of an aqueous solution of chloroform with a concentration of $1.7 \cdot 10^{-2}$M.
1) CH_2Cl_2, 10^{-5}M; 2) $C_2H_2Cl_4$, 10^{-3}M; 3) CHC^{l3}, 10^{-2}M (J = 0.6 Gy/s)

The kinetics of changes in pH and COD parameters of irradiated samples in the process of radiolysis of aqueous solution of chloroform is given in the following table:

Table 5

$4.2 \cdot 10^{-2}$ Dependence of COD and pH on the absorbed dose in the radiolysis of

aqueous solutions of chloroform with a concentration of $4.2 \cdot 10^{-2}$ M

D, kGy	0	4.3	8.6	13	43
pH	7	4.6	3.9	3.5	2.3
COD, mgO/L	170	153	120	105	53

As can be seen, as the dose increases, a decrease in COD and pH is observed, which indicates the decomposition of organic compounds and the formation of acids. These products can be formed as a result of hydrolysis of a number of products. For example, CCl_3 OOH in the hydrolysis reactions of phosgene

$$CCl_3OOH + H_2O \rightarrow 2HCl + HClO + CO_2 \; (3H^+ + ClO^- + 2Cl^- + CO_2)$$

$$COCl_2 + H_2O \rightarrow 2HCl + CO_2 \; (2H^+ + 2Cl^- + CO_2)$$

It was found that the pH and OCT decrease with increasing dose, which indicates the decomposition of organic compounds and the formation of acids. The radiation-chemical yield of chloroform decomposition depends on its initial concentration. Thus, when the concentration is $\geq 4.2 \cdot 10^{-2}$ M, the radiation-chemical yield is in the range of 52-245 molecules/100 eV.

The conversion of chloroform occurs due to the initial particles formed during the radiolysis of water - H atoms, OH radicals and hydrates. When there is oxygen in the solution, the chloroform breaks down in a chain.

$$CCl_3 + O_2 \rightarrow \acute{O}_2 CCl_3, \; \acute{O}_2 CCl_3 + CHCl_3 \rightarrow CCl_3OOH + CCl_3$$

Kinetics of changes in the concentrations of H_2O_2 and gaseous products formed during the radiolysis of aqueous solution of chloroform

The kinetics of changes in the concentrations of H_2O_2 and gaseous products formed during the radiolysis of an aqueous solution of chloroform are given below in the fig. 12.

As can be seen, the dose-dependent increase in H_2O_2 is initially observed, followed by a decrease after 14 kGy, and the radiation-chemical yield is 3 molecules/100 eV. The value obtained is higher than the radiation-chemical yield of hydrogen peroxide during radiolysis of water (0.7-0.8 molecules/100 eV). This indicates the additional formation of hydrogen peroxide in the process of radiolytic oxidation of chloroform solution. This indicates that the stages of H_2O_2 formation up to 14 kGy and decomposition reactions occur after

14 kGy.

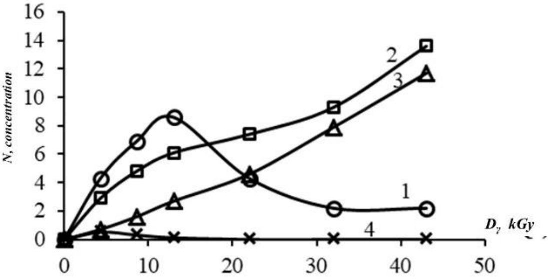


Figure 12. Dose dependence of the concentration of gaseous products (H_2O_2, CO_2, H_2, CO) formed during the radiolysis of aqueous solutions of chloroform with a concentration of 4.2·10-2M. 1) $N_{H_2O_2}$, 10-5g / ml, 2) N_{CO_2}, 10^{18}molec / q, 3) N_{H_2}, 10^{18}molec / g, 4) N_{CO}, 10^{18}molec / q (J = 0.6 Gy / s)

H_2O_2 formation reactions
$OH + OH \rightarrow H_2O_2,$ $k = 5{,}5 \cdot 10^9,\ M^{-1}s^{-1}$
$H + HO_2 \rightarrow H_2O_2,$ $k = 1{,}0 \cdot 10^{10}, M^{-1}s^{-1}$
$HO_2 + HO_2 \rightarrow H_2O_2 + O_2,$ $k = 8{,}3 \cdot 10^5,\ M^{-1}s^{-1}$
$H^+ + HO_2^- \rightarrow H_2O_2,$ $k = 2 \cdot 10^{10},\ M^{-1}s^{-1}$
H_2O_2 reactions
$OH + H_2O_2 \rightarrow HO_2 + H_2O,$ $k = 3{,}8 \cdot 10^7,\ M^{-1}s^{-1}$
$e_{aq}^- + H_2O_2 \rightarrow OH + OH^-,$ $k = 1{,}1 \cdot 10^{10},\ M^{-1}s^{-1}$
$H + H_2O_2 \rightarrow H_2O + OH,$ $k = 3{,}4 \cdot 10^7,\ M^{-1}s^{-1}$
$O^- + H_2O_2 \rightarrow O_2^- + H_2O,$ $k = 5{,}0 \cdot 10^8,\ M^{-1}s^{-1}$
$H_2O_2 \rightarrow H^+ + HO_2^-,$ $k = 3{,}6 \cdot 10^{-2}, s^{-1}$
$OH + H_2O_2 = HO_2 + H_2O,$ $k = 3{,}8 \cdot 10^7,\ M^{-1}s^{-1}$
$HO_2 + H_2O_2 = O_2 + OH + H_2O,$ $k = 3{,}7,\ M^{-1}s^{-1}$
$O_2^- + H_2O_2 = O_2 + OH^- + OH,$ $k = 16,\ M^{-1}s^{-1}$

As can be seen from the figure, the concentration of CO_2, H_2, which is a product of radiolysis, increases with increasing absorbed dose, and the concentration of carbon monoxide increases to 5 kg, and then decreases. Radiation-chemical yields of CO_2, CO, H_2 were calculated.

$$G_{CO_2} = 8{,}0\frac{\text{molec}}{100\text{eV}} \qquad G_{H_2} = 1{,}3\frac{\text{molec}}{100\text{eV}} \qquad G_{CO} = 1{,}2\frac{\text{molec}}{100\text{eV}}$$

Carbon dioxide is formed mainly in the process of hydrolysis and recombination of carboxyl radicals.

$$COCl_2 + H_2O = 2HCl + CO_2,$$
$$CCl_3OOH + H_2O = 2HCl + HClO + CO_2,$$
$$\dot{C}Cl_2O_2 + H_2O = 2HCl + CO_2,$$
$$2\dot{C}OOH = HCOOH + CO_2,$$
$$\dot{C}HCl_2O_2 + H_2O = OH + CO_2 + 2HCl$$

The radiation-chemical yield of molecular hydrogen is ~3 times higher than the yield of hydrogen that can be formed during the radiolysis of water. This indicates the presence of additional channels for the formation of hydrogen in the system:

$$H + CHCI_3 = H_2 + CCI_3,$$
$$H + C_2H_2CI_4 = CCI_3CHCI + H_2,$$
$$H + CH_2CI_2 = CHCI_2 + H_2,$$

Kinetic modeling of radiolysis of chloroform aqueous solutions.

The formal-kinetic scheme of the process is based on the values obtained during the γ-radiolysis of aqueous solutions of chloroform and the literature values of the rate constants of elementary reactions.

The formal-kinetic scheme includes elementary reactions involving primary particles of radiolysis of water (38 reactions) and their reaction with the products of conversion of chloroform molecules (24 reactions) as well as the formation of CO_2 and HCl and hydrolysis of chlorine containing products (intermediate and final 6 reactions). included.

$$CCl_3+2H_2O \rightarrow COOH+3HCl,\ CHCl_2+H_2O \rightarrow CHO+2HCl,$$
$$O_2CCl_3+2H_2O \rightarrow HO_2+CO_2+3HCl,\ O_2CHCl_2+H_2O \rightarrow OH+CO_2+2HCl$$

The probable reactions of the process of radiolytic conversion of chloroform in aqueous solutions are given below in the table 6.

The results of the calculation are given in Figure 13 (a, b, c, d). The variation of concentration of chloroform of various initial concentrations depending on the duration of irradiation.

Table 6.

Formal-kinetic scheme of radiolytic conversion processes in radiolysis of aqueous solution of chloroform

Elementary reactions		Reaction rate constants, 1/sec, l/mol·sec
1.	$OH + CHCI_3 = H_2O + CCI_3$	5e+06
2.	$H + CHCI_3 = H_2 + CCI_3$	7.8e+07
3.	$e^- + CHCI_3 = CHCI_2 + CI^-$	1e+10
4.	$OH + C_2H_2CI_4 = CCI_3CHCI + H_2O$	1e+06
5.	$H + C_2H_2CI_4 = CCI_3CHCI + H_2$	1e+07
6.	$e^- + C_2H_2CI_4 = C_2H_2CI_3 + CI^-$	1e+10
7.	$OH + CH_2CI_2 = CHCI_2 + H_2O$	9e+07
8.	$H + CH_2CI_2 = CHCI_2 + H_2$	4e+06
9.	$e^- + CH_2CI_2 = CH_2CI + CI^-$	6e+09
10.	$CCI_3 + O_2 = CCI_3O_2$	4.7e+09
11.	$CCI_3O_2 + CHCI_3 = CCI_3OOH + CCI_3$	1e+04
12.	$2CCI_3 = C_2CI_6$	3.7e+08
13.	$2CHCI_2 = C_2H_2CI_4$	1e+08
14.	$CHCI_2 + CHCI_3 = CH_2CI_2 + CCI_3$	1e+08
15.	$CHCI_2 + O_2 = HCIO + COCI$	4.7e+09
16.	$COCI + CHCI_3 = COCI_2 + CHCI_2$	1e+04
17.	$2CCI_3O_2 = C_2CI_6 + 2O_2$	1e+08
18.	$COCI_2 + H_2O = 2HCI + CO_2$	1e+05
19.	$CCI_3OOH + H_2O = 2HCI + HCIO + CO_2$	1e+06
20.	$H_3O^+ + CI^- = HCI$	1e+06
21.	$HCI = H_3O^+ + CI^-$	1e+10
22.	$CHCI_2 + H_2O = CHO + 2HCI$	1e-04
23.	$CHO + H_2O = HCOOH + H$	1e-04
24.	$CCI_3O_2 + H_2O = OH + PrA + HCI$	1e-05
25.	$CCI_2O_2 + H_2O = 2HCI + CO_2$	1e-05
26.	$CCI_3 + H_2O + H_2O = COOH + 3HCI$	1e-05
27.	$2COOH = HOOCCOOH$	1e-05
28.	$2COOH = HCOOH + CO_2$	5e+08
29.	$CHCI_2 + O_2 = CHCI_2O_2$	1e+07
30.	$CHCI_2O_2 + H_2O = OH + CO_2 + 2HCI$	1e+05

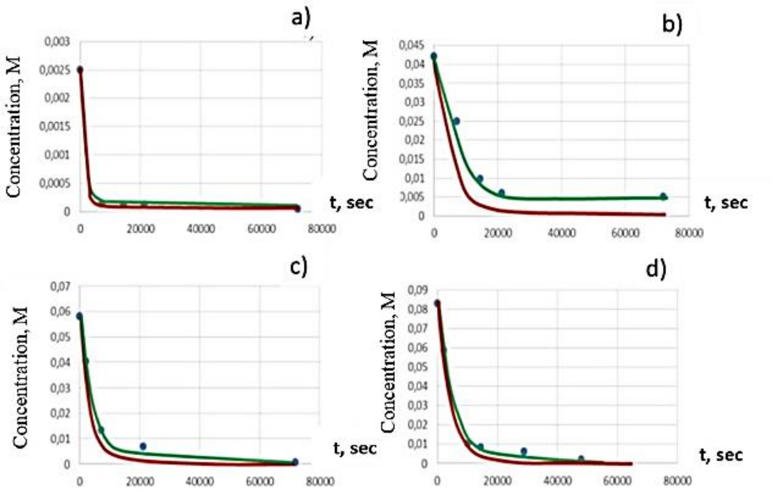


Figure 13. Dependence of the concentration of chloroform on the duration of irradiation during radiolysis at different initial concentrations.
1) $0.25\cdot10^{-2}$, 2) $4.2\cdot10^{-2}$, 3) $5.8\cdot10^{-2}$, 4) $8.3\cdot10^{-2}$ M curve, points are experimental values, J=0.6 Gy/sec, T= 300ºK.

Based on the initial parts of the kinetic curves, the radiation-chemical yield of chloroform decomposition was determined at different initial concentrations and is given in the table 7.

Table 7

Radiation-chemical yields of the decomposition process at different initial concentrations of chloroform

Radiation-chemical yields, molecule/100 eV		
Concentration, M	$G_{experience}$	$G_{theoretical}$
$2.5\cdot10^{-3}$	6,4	6.5
$4.2\cdot10^{-2}$	46	72.2
$5.8\cdot10^{-2}$	80	180
$8.3\cdot10^{-2}$	129	267.8

The comparison of the experimental and calculated values of the conversion process of chloroform in the table shows that the considered kinetic scheme is adequate to the chemical transformations taking place in the solution.

Chapter V examines the laws of kinetic transformation of transformer oil and transformer oil containing trichlorobenzene and chlorinated biphenyls in water under the influence of γ-rays and UV-light, the pH and OCD parameters of irradiated samples from the absorbed dose, UV spectra of samples at different doses. The transformer oil + water system under study is in a two-phase state due to the insolubility of the oil in water, and the processes that occur during the radiolysis of this system include physico-chemical reactions in the oil layer, water layer and the boundary strip along their contact. The following table shows the dose dependence of the pH parameter of the samples as a result of radiolysis of transformer oil and transformer oil + water system containing 15 mg/kg TCB and PCB under the influence of γ-rays. It should be noted that the pH parameter in the radiolysis process of the transformer oil + water system characterizes the water part of the sample.

Table 8

Transformer oil and transformer oil system containing 15 mg/kg trichlorobenzene + water and polychlorinated biphenyl + water dependence on the absorbed pH of the pH value during radiolysis. The volumes of transformer oil and water are 5 ml and 10 ml, respectively

D, kGy	pH		
	Transformer oil	15-mg / kg TCB + transformer oil + water	15-mg / kg PCB + transformer oil + water
0	5.6	5.1	6.5
4.1	4.9	4.9	6.1
27.4	4.3	4.8	5.9
68.4	4.1	4.6	5.6
136.8	3.5	4.3	5.3

As can be seen, an increase in dose during radiolysis of all 3 systems leads to a decrease in pH (table 8). This decrease is due to the formation of hydrochloric acid from the process of radiolytic dechlorination of organic acids and chlorinated compounds formed as oxidation products during the radiolysis of transformer oil. Due to the complex composition of transformer oil, the elementary reactions of its radiolysis include the conversion of alkanes, cycloalkanes, aromatic and polyaromatic compounds, the reaction of ionic and excited particles formed in the process with the hydrocarbons in the oil. On the other hand, the dissolved oxygen in the oil can take an active part in the conversion process. Table 9 shows the dependence of the COD index on the absorbed dose during the radiolysis of the transformer oil and the transformer oil system containing 15 mg/kg of trichlorobenzene + water and polychlorinated biphenyl + water.

Table 9

Dose dependence of COD from absorbed dose during radiolysis of transformer oil and transformer oil system containing 15 mg/kg trichlorobenzene + water and polychlorinated biphenyl + water. The volumes of transformer oil and water are 5 ml and 10 ml, respectively

D, kGy	COD, mq O/L	
	15-mg/kg TCB + transformer oil + water	15-mg/kg PCB + transformer oil + water
0	683	433
4.1	600	600
27.4	516	766
68.4	433	933
136.8	350	1266

As can be seen from the table 9, if the COD index of 15 mg/kg TCB + transformer oil + water samples decreases with increasing dose, the dose increase during the radiolysis of 15 mg/kg PCB + transformer oil + water system leads to an increase in COD. The decrease in COD of + transformer oil + water samples containing 15 mg/kg TCB is due to the fact that the TCB molecule breaks down under the influence of γ-rays and the concentration of organic matter decreases. Unlike PCBs, where PCBs are composed of a large number of isomers and homologues, the radiolytic conversion of PCBs in the system under consideration results in the dechlorination of PCBs with more chlorine atoms to form PCB homologues with less chlorine atoms. On the other hand, chlorine atoms formed during the radiolytic decomposition of PCBs react with the components of the transformer oil, causing their chlorination. As a result, COD is observed to increase with increasing dose as the concentration of organic matter in the system containing PCBs increases.

H_2O_2 and CO_2 are also formed during radiolysis of the mentioned systems under consideration. Table 10 shows the dose dependence of the concentration of H_2O_2 during the radiolysis of transformer oil + water system containing TCB and PCB.

Table 10

Dose dependence of H_2O_2 concentration during radiolysis of transformer oil and transformer oil system containing 15 mg/kg trichlorobenzene + water and polychlorinated biphenyl + water. The volumes of transformer oil and water are 5 ml and 10 ml, respectively

D, kGy	$H_2O_2 \cdot 10^{-5}$, q/ml		
	Transformer oil	15 mg/kg TCB + transformer oil + water	15 mg/kg PCB + transformer oil + water
4.1	5.1	6.0	5.9
27.4	6.0	7.9	7.9
68.4	4.3	6.1	4.3
136,8	4.1	5.1	4.3

As can be seen from the table, the dose dependence of the H_2O_2-concentration during the radiolysis of all 3 systems is extreme. Thus, an increase in the dose leads to an increase in the concentration of $H_2O_2$and a decrease after ~27 kGy. This dependence indicates the participation of H_2O_2 in the conversion of large doses during radiolysis of the system. In the presence of TCB and PCB in the system, the radiation-chemical yield of H_2O_2 is 4,2 molecules/100 eV.

It should be noted that the values of the obtained radiation-chemical yield are 6-8 times higher than the radiation-chemical yield of H_2O_2 during the radiolysis of water, which indicates that the formation of H_2O_2 during the radiolysis of the two-phase system under consideration is due to additional channels.

Table 11 shows the change of CO_2 concentration depending on the absorbed dose in the irradiated system.

As can be seen from the table, the concentration of carbon dioxide formed during the radiolysis of transformer oil reaches a maximum value of 27 kg, its concentration decreases with increasing dose, and the concentration of carbon dioxide increases with increasing dose during radiolysis of the system with TCB and PCB compounds being added to the system. Radiation-chemical yields of carbon dioxide in the system are 0.33 molecules/100 eV in the presence of TCB, 0.39 molecules/100 eV in the presence of PCBs and 0.18 molecules/100 eV in the radiolysis of pure transformer oil. The results show that the presence of chlorinated organic compounds in the system increases the rate of carbon dioxide formation.

Table 11

Dose dependence of CO_2 concentration absorbed during radiolysis of transformer oil and transformer oil system containing 15 mg/kg of trichlorobenzene + water and polychlorinated biphenyl + water. The volumes of transformer oil and water are 5 ml and 10 ml, respectively

D, kGy	$CO_2 \cdot 10^{17}$, molec/g		
	Transformer oil	15 mg/kg TCB + transformer oil + water	15 mg/kg PCB + transformer oil + water
4,1	0,5	2,5	0,9
27,4	2,3	2,6	1,1
68,4	0,3	3,3	1,2
136,8	0,4	6,5	2,5

Along with the study of kinetic regularities of physical and chemical parameters in the process of radiolysis of the considered systems, UV spectra were drawn at different absorption doses of irradiated samples. Figure 14 below shows the absorption spectra at different radiation doses.

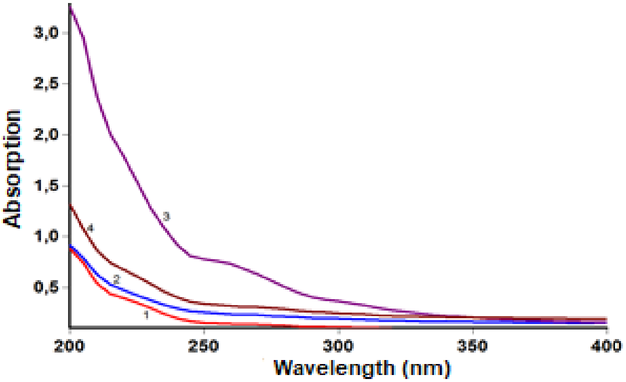


Figure 14. Absorption spectra of samples: 5 mg/kg TCB in 5 ml of transformer oil +10 ml of water (water part) Absorption spectra of the system in different doses (200-400 nm). 1) D= 0; 2) 4.1 kGy; 3) 27.4 kGy; 4) 68.4 kGy.

As can be seen from the figure, the optical density of the samples increases with increasing dose and decreases at values greater than 27.4 kGy. The observed absorption covers the region from ~300 nm to 200 nm.

During the radiolysis of the systems in question, the radiation energy is absorbed by water and transformer oil molecules, which are the main components of the systems. For this reason, the reactions of the primary products of padiolysis of these components with chlorinated compounds play an important role.

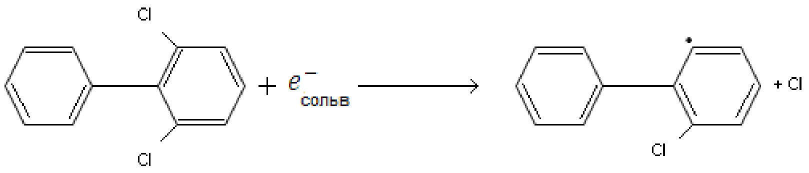
Radiation-chemical yields of intermediate products of water radiolysis 1/100 eV are given below:

$$H_2O \rightarrow OH(2{,}8) + e^-_{aq}(2{,}7) + H(0{,}6) + H_2(0{,}45) + H_2O_2(0{,}72) + \\ + H^+_{aq}(3{,}2) + OH^-_{aq}(0{,}5)$$

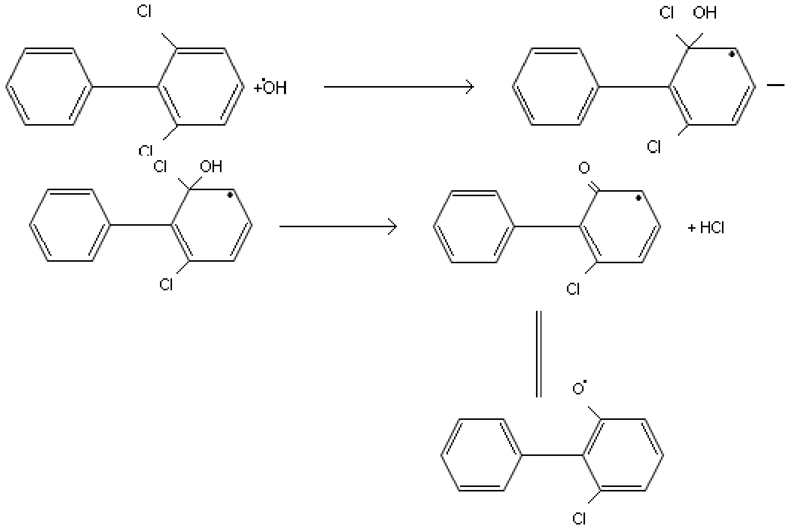
Since H atoms and OH radicals do not react with water molecules at room temperature, they can react in recombination or with PCB molecules in the system.

Chlorinated aromatic hydrocarbons have a high electron affinity, so the most likely mechanism for the dechlorination of PCBs is the reaction with hydrated electrons (Sherman mechanism). The rate constants of the reaction of hydrated electrons with PCB molecules increase with the increase of chlorine in the molecule. The rate constants of the reactions of the hydrated electrons with the molecules of dichlorobiphenyl, tetrachlorobiphenyl, and decachlorobiphenyl are $2{\cdot}10^9$, $3{\cdot}10^9$, and $7{\cdot}10^9$ $k{\cdot}mol^{-1}{\cdot}s^{-1}$, respectively. The rate constants of the reaction of H and OH – with PCB molecules are not known, but it was determined by pulsed radiolysis that the rate constants for chlorinated phenols are k (OH + 4-Cl-PhOH = $1{,}5{\cdot}10^{10}$ $dm^3{\cdot}M^{-1}$, $1{\cdot}s^{-1}$ and k (H + 4-Cl-PhOH=$2{\cdot}10^9$ $dm^3{\cdot}M^{-1}{\cdot}s^{-1}$) respectively. The rate constants of similar reactions are assumed to be in this range.

The capture of solvated electrons causes the C-Cl bond to break and Cl^- ions to form. In the reactions of PCB molecules and OH radicals, new products are formed as a result of the decomposition of adducts.



A similar situation occurs in the reactions of PCB molecules with H $^+$ atoms.



In the process of radiolysis of PCB + water system, the final products are acidic. The regularities observed during the radiolysis of a two-phase system are explained by the formation of Cl$^-$ ions and changes in pH, the radiolysis of PCB oil and the reactions of primary particles of radiolysis of water, in particular the reactions of hydrated electrons with PCB molecules leading to dechlorination.

Due to the lack of information on the intermediate products of radiolysis of transformer oil, if the general mechanisms of radiolysis of alkanes, cycloalkanes and aromatic compounds, which are its main components are taken as a basis, then general information on intermediates of radiolysis of hexane, cyclohexane and benzene, respectively, can also be used as a basis for analysis.

Some of the active particles formed are captured by aromatic hydrocarbons, for example, hydrogen atoms react effectively with benzene. For this reason, the role of these reactions in the degradation process of chlorinated organic compounds is small, as the relative rate of the reaction of active particles with chlorinated organic compounds is small.

In Chapter VI, the kinetic regularities of the radiolysis process of PCB-containing oils were studied in the presence of polar and non-polar organic solvents, as well as alkalis. The urgency of this issue is due to the need to study the application of radiation-chemical technology for the treatment of PCB-containing wastes generated during the washing of transformers with organic solvents after their removal from the volume for cleaning PCBs. The following figures show the results of the study of the effect of gamma rays on the transformation processes of Sovtol-type PCB oil in the presence of hexane and isopropyl alcohol.

Figure 15 shows the dependence of changes in the concentration of PCB isomers and homologues identified during radiolysis of the system taken in the amounts of "Sovtol 10" type PCB oil, hexane and isopropyl alcohol, respectively (0.25 g + 8 ml + 0.5 ml) shown. Identified PCBs include PCB (149 + 118) hexa-pentachlorobiphenyl, PCB (101) pentachlorobiphenyl, PCB (153) hexachlorobiphenyl, PCB (138) hexachlorobiphenyl, PCB (52) tetrachlorbiphenyl.

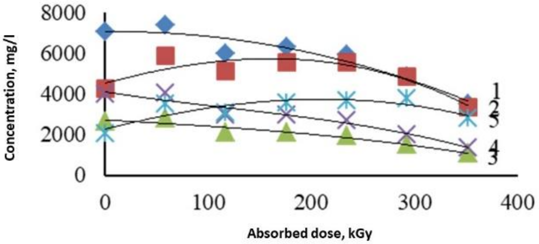


Figure 15. Kinetics of change of concentration of PCB isomers depending on the dose absorbed during radiolysis of PCB + hexane + isopropyl alcohol system (I = 0.30 Gr / s). 1 - PCB (149 + 118) hexa-pentachlorobiphenyl; 2 - PCB (101) pentachlorobiphenyl; 3 - PCB (153) hexachlorobiphenyl; 4 - PCB (138) hexachlorobiphenyl; 5 - PCB (52) tetrachlorobiphenyl.

As shown in the figure, the concentration of hexachlorobiphenyls decreases with increasing dose. The concentration of tetrachlorine and pentachlorine decreases to certain dose values, and in large doses the concentration of these PCBs also decreases. Dose-dependent changes in the concentration of PCBs containing less chlorine occur in a similar way. Thus, the concentration of trichlorobiphenyl and tetrachlorobiphenyls increases with dose, while the concentration of heptachlorobiphenyl decreases in the considered dose range.

In small doses, low-chlorine PCB isomers and homologues are likely to be formed in addition. Radiation-chemical yields of the relevant processes were calculated based on the initial parts of the kinetic curves during the radiolysis of the mixture of PCB + hexane + isopropyl alcohol and are shown in Table 12.

Table 12

Radiation-chemical yields of relevant PCBs during radiolysis of PCB + hexane + isopropyl alcohol mixture

PCB isomers	Radiation-chemical yield, G (molecule/100 eV)
PCB-18	0.280
PCB-31+28	0.094
PCB-44	0.32
PCB-101	0.210
PCB-149+118	- 0.024
PCB-153	- 0.081
PCB-138	- 0.156
PCB-180	- 0.023
PCB-52	0.28
Total cost of PCB degradation	1.468

* "Negative" sign indicates consumption.

Thus, the final yield of PCB isomers is 0.90 molecules/100 eV. Decreases in the initial concentration of isomers and homologues containing PCB are observed at doses above 240 kGy.

As noted, the decomposition of chlorinated biphenyls occurs primarily in reactions with solvated electrons. Although hexane is a major component in the radiolysis of the system under consideration, the yield of solvated electrons in its radiolysis is very small (~0.12 electrons/100 eV). For this reason, since the electron affinity of propyl alcohol molecules is high, the free electrons are mainly absorbed by these molecules in the system under consideration, and the resulting $(CH_3)_2CO^-$ anion radicals react effectively with PCB molecules:

$$(CH_3)_2CO^- + ArCl \rightarrow (CH_3)_2CO + Ar^{\cdot} + Cl^-$$

The addition of alkali to the system in question results from their electrolytic dissociation with formation of OH^- ion radical. As a result of the reaction of OH^- ion radicals with isopropyl alcohol radicals $(CH_3)_2CO^{\cdot-}$ ion formation occurs:

$$(CH_3)_2C^{\cdot}OH + OH^- \leftrightarrow (CH_3)_2CO^- + H_2O$$

Figure 16 shows the concentration of PCB isomers (149 + 118) during radiolysis of PCB (0.25 ml) + hexane (8 ml) + isopropyl alcohol (0.5 ml) system in different doses. (1 - 46 kGy, 2 - 333 kGy, 3 - 460 kGy), PCB (18) (4 - 460 kGy, 5 - 46 kGy) KOH (0.05; 0.1; 0.5 g) dependence is shown.

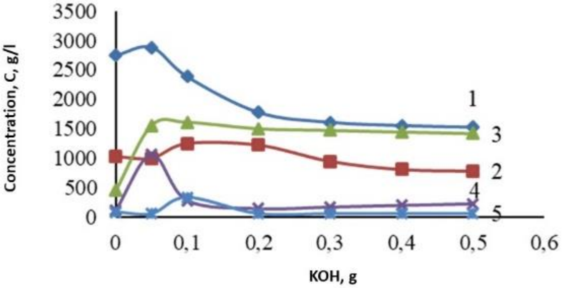


Figure 16. Determination of PCB isomers (149 + 118) (1 - 46 kGy, 2 - 333 kGy, 3 - 460 kGy), PCB (18) (4 - 460 kGy, 5 - 46 kGy) quantity dependence curves.

As can be seen from the figure, the change in the concentration of PCB isomers depending on the amount of KOH during the radiolysis of the systems under consideration is extreme, and the maximum change is observed when 0.5-0.1 g of KOH.

During the radiolysis of the system under the influence of gamma rays, a sharp decrease in the pH of the irradiated samples and the formation of chloride ions are observed as a result of radiolytic conversion of PCBs. An increase in the concentration of KOH in the considered concentration range leads to an increase in the steady-state concentration of chloride ions.

Based on the obtained results, a kinetic scheme of 52 elementary reactions of conversion processes under the influence of gamma rays in organic solvents with PCB Sovtol oil and in the presence of KOH was developed and dose-dependent curves of the parameters characterizing the process were obtained by mathematical modeling. The kinetic scheme covers the initial processes of radiolysis of hexane, the main component of the system under consideration, the processes of radiolytic conversion of isopropyl alcohol and PCBs, as well as the processes of electrolytic conversion of KOH:

Table 13

A formal kinetic scheme of the process

№	Reaction	Speed constants, s^{-1}, $M^{-1}s^{-1}$
1	2	3
1	R (CH_3, C_2H_5, C_3H_7, C_4H_9, C_5H_{11}, C_6H_{13}, C_7H_{15}) + $O_2 \rightarrow RO_2$	(CH_3) $4.7 \cdot 10^9$, (C_2H_5) $2.9 \cdot 10^9$, (C_4H_9) $4.9 \cdot 10^9$(cyclohexane)
2	$HO_2 + RH \rightarrow H_2O_2 + R$	10^4
3	$HO_2 + HO_2 \rightarrow H_2O_2 + O_2$	$8.3 \cdot 10^5$
4	$C_6H_{14} \rightarrow C_6H_{14}^+ + e^-$	$1.33 \cdot 10^{-8}$
5	$C_6H_{14}^+ + (CH_3)_2CHOH \rightarrow (CH_3)_2CHOH^+ + C_6H_{14}$	10^{10}-10^{11}
6	$(CH_3)_2CHOH^+ + (CH_3)_2CHOH \rightarrow (CH_3)_2CHOH_2^+ + (CH_3)_2COH^{\cdot}$	10^{10}-10^{11}
7	$(CH_3)_2CHOH_2^+ + e^- \rightarrow (CH_3)_2COH + H$	10^{11}-10^{12}
8	$(CH_3)_2CHOH + H \rightarrow (CH_3)_2COH + H_2$	$9 \cdot 10^7$
9	$2(CH_3)_2COH \rightarrow (CH_3)_2CO + (CH_3)_2COH$	$3.8 \cdot 10^8$
10	$(CH_3)_2COH + O_2 \rightarrow (CH_3)_2C(OO)OH$	$3.9 \cdot 10^9$
11	$(CH_3)_2C(OO)OH \rightarrow (CH_3)_2CO + HO_2$	10^4
12	$(CH_3)_2COH + H_2O_2 \rightarrow (CH_3)_2CO + HO_2 + OH$	$7.0 \cdot 10^5$
13	$(CH_3)_2CHOH + OH \rightarrow (CH_3)_2COH^{\cdot} + H_2O$	$1.6 \cdot 10^9$
14	$KOH \rightarrow K^+ + OH^-$	
15	$(CH_3)_2COH^{\cdot} + OH^- \rightleftarrows (CH_3)_2CO^- + H_2O$	10^8-10^9
16	$(CH_3)_2CO^- + C_{12}H_{10-n}Cl_n \rightarrow (CH_3)_2CO + C^{\cdot}{}_{12}H_{10-n}Cl_{n-1} + Cl^-$ (n=1-10)	n=1' $k_1=1.2 \cdot 10^8$ n=2 $k_2=1.4 \cdot 10^8$ n=3' $k_3=1.6 \cdot 10^8$ n=4 $k_4=1.8 \cdot 10^8$ n=5' $k_5= 2 \cdot 10^8$ n=6' $k_6=2.2 \cdot 10^8$ n=7' $k_7=2.4 \cdot 10^8$ n=8' $k_8=2.6 \cdot 10^8$ n=9' $k_9=2.8 \cdot 10^8$ n=10' $k_{10}= 3 \cdot 10^8$
17	$C^{\cdot}{}_{12}H_{10-n}Cl_{n-1} + O_2$ hydroperxide aromatic compound	10^8-10^9
18	$Cl^- + C_6H_{14} \rightarrow C_6H_{13}^{\cdot} + HCl + e^-$	10^8-10^9
19	$e^- + C_{12}H_{10-n}Cl_n \rightarrow C_{12}H_{10-n}Cl_{n-1} + Cl^-$ (n=1-10)	n=1' $k_1=1.5 \cdot 10^9$ n=2 $k_2=2.1 \cdot 10^9$ n=3' $k_3=2.7 \cdot 10^9$ n=4 $k_4=3.3 \cdot 10^9$ n=5' $k_5=3.9 \cdot 10^9$ n=6' $k_6=4.5 \cdot 10^9$ n=7' $k_7=5.1 \cdot 10^9$

Continued table 13

1	2	3

		n=8' $k_8=5.7\cdot10^9$ n=9' $k_9=6.3\cdot10^9$ n=10 $k_{10}=6.9\cdot10^9$
20	$C_{12}H_{10-n}Cl_{n-1}+ (CH_3)_2CHOH \rightarrow C_{12}H_{10-n+1}Cl_{n-1}+ (CH_3)_2C^{\cdot}OH$	10^6-10^7
21	$R_iOO + C_6H_{14} \rightarrow R_iOOH + C_6H_{13}$	10^5
22	$R_iOOH \rightarrow R_iO + OH$	$2\cdot10^{-4}$
23	$R_iO + C_6H_{14} \rightarrow R_iOH + C_6H_{15}$	10^7
24	$R_IO + (CH_3)_2CHOH \rightarrow R_iOH + (CH_3)_2COH$	$5\cdot10^7$
25	$e + O_2 \rightarrow O_2^-$	$1.9\cdot 10^{10}$
26	$(CH_3)_2CHOH_2^+ + O_2^- \rightarrow (CH_3)_2CHOH + HO_2$	10^{11}

The symbol next to the reaction number (') indicates a value based on a similar reaction.

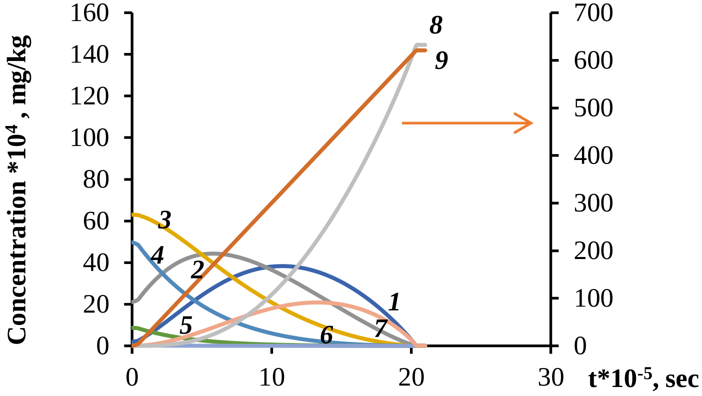


Figure 17. PCB isomers and products formed during irradiation of PCB (0.25 ml) + hexane (8 ml) + isopropyl alcohol (0.5 ml) + KOH (0.05; 0.1; 0.5 g) system - Dependence of the concentration of biphenyl PCB-1 and chlorine ions on the irradiation time (I = 0.30 Gy/sec). 1) PCB 18; 2) PCB 52; 3) PCB 101; 4) PCB 138; 5) PCB 180; 6) PCB 194; 7) PCB 1; 8) Biphenyl; 9) Cl_m.

As can be seen, the nature of the change in isomer density depending on the dose is different for different isomers. PCB - (18) (2,2',5-trichlorobiphenyl), PCB - (31 + 28) (2,4,4'-trichlorobiphenyl + 2,4',5-trichlorobiphenyl), PCB - (44) (2,2',3,5'-tetrachlorobi-phenyl), PCB - (101) (2,2',4,5,5'-pentachlorobiphenyl), PCB-(52) (2,2',5,5'-tetrachlorobiphenyl) isomers' concentration the absorbed dose increases as the absorbed dose increases. In contrast, PCB (149 + 118)

(2,3',4,4',5-pentachlorobibenyl + 2,2',3,4',5',6-hexachlorobi-benyl), PCB - (153) (2,2',4,4',5,5'-hexachlorobiphenyl), PCB - (138) (2,2',3,4,4',5'-hexachlorobiphenyl), PCB-180 (2,2',3,4,4',5,5'-heptachlorbiphenyl) The concentration of PCB isomers decreases monotonically depending on the absorbed dose.

As can be seen, the kinetic curves of the change in density depending on the irradiation time reach a maximum at relatively low doses (t~$0.5\cdot10^5$ sec) with relatively stable values of concentration and subsequent increase in monochlorobiphenyl, PCB 52 and PCB 18 t~$12\cdot10^5$ sec, respectively (360 kGy), $10\cdot10^5$ sec (300 kGy) and $5\cdot10^5$ sec (150 kGy). These PCB isomers contain three or four chlorine atoms. In contrast to these isomers, the concentrations of relatively high chlorine isomers such as PCB 101, 138, 180, 194 decrease monotonically with increasing radiation time. These isomers contain more than 5 chlorine atoms. The formation of biphenyls, the end product of dechlorination of PCB isomers, occurs during the induction period. Intensive processes of biphenyl formation occur when the irradiation time is t~$5\cdot10^5$ sec (150 kGy). The results show that the dechlorination of PCB isomers occurs in stages. First, chlorine depletion of high chlorine-containing PCB isomers and formation of low-chlorine PCB isomers occur. Then, as the irradiation time increases, the low-chlorine PCB isomers are also dechlorinated and biphenyls are formed. The stability of the concentration of PCB isomers observed at the beginning of irradiation is due to the capture of electrons by oxygen molecules. Because the assessment of the relative rate of electron consumption by PCBs and oxygen molecules shows that at the beginning of the process, oxygen almost completely captures the electrons.

$$\frac{\omega_1}{\omega_2}=\frac{k_1[e][O_2]}{k_2[e][PXB]}=\frac{1{,}9\ 10^{10}4{,}5\ 10^{-3}}{5\ 10^{8}\ 0{,}5\ 10^{-2}}\ \approx 30,$$

here ω_1 , k_1 , $\omega\ _2$, k_2 - O_2 and the rates of electron capture reactions and rate constants by PCB molecules.

When oxygen is completely consumed, the electrons are captured by PCB molecules, which lead to their re-dechlorination.

Based on the kinetic curves, radiation-chemical yields of PCB isomers (PCB-18, 52, monochlorobiphenyls, biphenyls and Cl–) and decomposition (PCB 101, 138, 180) were determined (table 14). PCB isomers are fully used at a dose of ~600 kGy, biphenyls and hydrochloric acid are formed as final products.

The total radiation-chemical yield of the decomposition process of PCBs is 2.7 molecules/100 eV, which is approximately equal to the yield of biphenyl. The yield of hydrochloric acid is higher than the yield of biphenyl, which is explained by the stoichiometry of the dechlorination process.

Table 14

Calculated values of radiation-chemical yields of PCB 18, PCB 52, monochlorobiphenyls, biphenyls and Cl^- formation and decomposition of PCB 101, 138, 180

	PCB-18	PCB-52	PCB-101	PCB-138	PCB-180	Mono-chlorine-biphenyl (PCB 1)	Biphenyl	Cl_m
G, molecul/100 eV	0,45	0,30	-0,76	-0,61	-0,15	0,45	2,1	5,1

In Chapter VII Dose-dependent change in pH during radiolysis of transformer oil containing TCB under the influence of γ-rays with or without the presence of nano-Al_2O_3, CO_2 and H_2O_2, H_2 and hydrocarbon gases (CH_4, C_2H_4, C_2H_6, C_3H_8, C_4H_{10}, C_5H_{12}, C_6H_{14}, C_7H_{16}) formation kinetics were studied. The following figure shows the dependence of the pH on the absorbed dose.

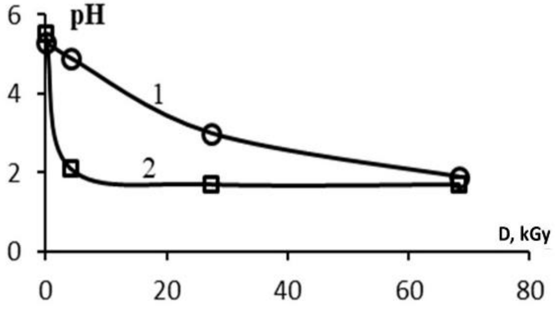


Figure 18. Dependence of the pH of transformer oil containing 15 mg/kg TCB on the absorbed dose. 1) transformer oil; 2) transformer oil + 0.1 g nano-γ-Al_2O_3.

The acidity of the oil increases in both cases, but a stronger increase in acidity has been found in the presence of nano-γ-Al_2O_3. In this case, the steady-state value of acidity is obtained at a dose approximately 7 times lower, ie ~10 kGy. In addition, as the concentration of TCB in transformer oil increases, the rate of acidity increases, which is due to the increase in the rate of dechlorination of TCB at high concentrations.

Another possible way to increase the acidity during irradiation of the above system is the oxidation of the main components dissolved in the transformer oil.

The radiolytic conversion of TCBs is due to the radiolysis of high-density transformer oil in the irradiated system. When nanoparticles are added to the system, the process of decomposition of transformer oil components takes place in the presence of uneven charge carriers - electrons and holes - formed on the surface of nanoparticles.

The formation of carbon dioxide and hydrogen peroxide under the influence of γ-rays in the presence of oxygen dissolved in transformer oil has been studied experimentally.

Table 15 shows the values of radiation-chemical yields of CO_2 and H_2O_2 formed during the radiolysis of a homogeneous system of transformer oil containing different concentrations of TCB and transformer oil containing transformer oil containing TCB in the range of 5-40 mg/kg + nano-γ-Al_2O_3.

Table 15

Radiation chemical yields of H_2O_2 and CO_2 during radiolysis of TCB + transformer oil and TCB + transformer oil + nano-γ-Al_2O_3 systems:

TCB, mg/kg	G, molec/100eV			
	TCB + transformer oil		TCB + transformer oil + 0.1q nano-γ-Al_2O_3	
	CO_2	H_2O_2	CO_2	H_2O_2
5	1.78	4.7	1.26	3.55
15	1.39	5.4	0.66	4.11
40	1.18	6.0	0.47	5.42

As can be seen, as the initial concentrations of TCB increase in both systems, the radiation-chemical yield of CO_2 decreases, while in the presence of nanoparticles in the system, the radiation-chemical yield of CO_2 decreases even more.

Unlike CO_2, the cost of radiation-chemical yield of H_2O_2

increases as the initial concentration of TCB in the system increases, but decreases with the presence of nano-γ-Al_2O_3.

Thus, in both systems (TCB + transformer oil, TCB + transformer oil + 0.1 g nano-γ- Al_2O_3) as the initial concentrations of TCB increase, the radiation-chemical yield of CO_2 decreases, while in the system there are nano-particles, the radiation of CO_2 -chemical yield is further reduced.

Unlike CO_2, the radiation-chemical yield of H_2O_2 increases as the initial concentration of TCB in the system increases, but decreases with the presence of nano-γ-Al_2O_3. In both cases, the acidity of the oil increases, but in the presence of nano-γ-Al_2O_3, the acidity increases even more. In this case, the stationary value of acidity is obtained at a dose of 10 kGy, as it becomes stationary at a dose of ~7 times less. As the concentration of TCB in transformer oil increases, the rate of acidity increases, which is explained by the increase in the rate of dechlorination at relatively high concentrations of TCB. Table 16 shows the dependence of the radiation-chemical yield of hydrogen on the initial concentration of TCB in the radiolysis of the system studied.

Table 16

Dependence of radiation-chemical yield of hydrogen on the initial concentration of TCB in the radiolysis of the studied system

Concentration TCB, mg / kg	G, molec/100 eV	
	Transformer oil	Transformer oil + nano-γ-Al_2O_3
5	0.39	1.25
15	0.42	1.10
40	0.43	0.99

When TCB is 40 mg/kg in the mixture, i.e. when TCB is added to the transformer oil, the radiation-chemical yield of hydrogen increases slightly from 0.37 to 0.43 molec/100 eV. When nano-γ-Al_2O_3 is added to the system, an increase in G (H_2) to 1.25 molecular weight/100 eV is observed, a decrease in G (H_2) with increasing TCB concentration, and G (H_2) for 40 mg/kg TCB.) Is equal to ~1 molec/100 eV.

The kinetics of formation of hydrocarbon gases (CH_4, C_2H_4, C_2H_6, C_3H_8, C_4H_{10}, C_5H_{12}, C_6H_{14}, C_7H_{16}) depending on the absorbed dose was studied and the radiation-chemical yields of gas products are given in Table 17:

Table 17

Dependence of radiation-chemical yield of hydrocarbon gases in the radiolysis of the studied system on the initial concentration of TCB

TCB, mg/kg	G, molec/100 eV, 10^{-3}							
	CH_4		C_2H_4		C_2H_6		C_3H_8	
	1	2	1	2	1	2	1	2
5	2.00	2.56	0.30	1.220	0.55	0.98	0.31	0.48
15	1.30	1.97	0.45	0.390	0.47	0.90	0.29	0.43
40	0.80	1.57	0.43	0.196	0.35	0.87	0.28	0.39

1) Transformer oil + TCB
2) Transformer oil + TCB + nano-γ-Al_2O_3

As can be seen from the table, as the concentration of TCB increases, the radiation-chemical yields of methane, ethane and propane decrease.

When nano-γ-Al_2O_3 is added to the system, the radiation-chemical yields of methane, ethane, and propane increase in all cases, but the increase in the initial concentration of TCB leads to a decrease in their radiation-chemical yields, as observed in radiolysis of homogeneous systems. The cost of radiation-chemical yields of heavier hydrocarbons is less than ~10^{-4} molecules/100 eV. Because TCBs are well soluble in transformer oil, their mixture is single-phase and homogeneous. The radiation-chemical processes in these systems are continued with active particles corresponding to the electronic density of each component formed during the radiolysis of the main components of the transformer oil.

The results show that the speed of radiation-chemical processes increases in the presence of nano-γ-Al_2O_3. In the presence of nano-γ-Al_2O_3, the conversion rate of transformer oil components increases and the yield of hydrogen and hydrocarbon gases increases.

Figure 19 shows the IR spectra of non-irradiated transformer oil containing 15 mg/kg TCB, obtained in 19 b with the addition of nano-γ-Al_2O_3 to the same sample. As can be seen, Abs_{max} 3180, 2973, 2854, 2200, 1450, 1330 cm-1 bands are observed in the spectrum.

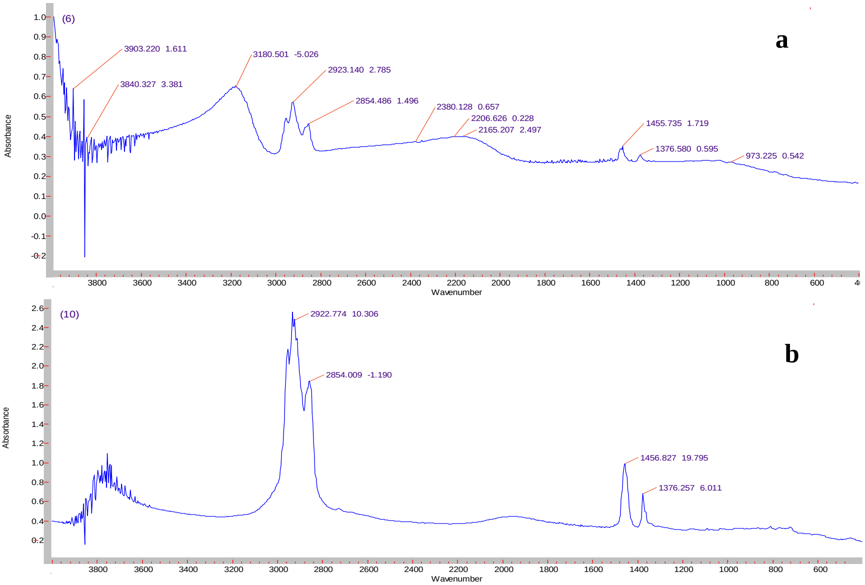


Figure 19. Non-radiation transformer oil (a) containing 15 mg / kg TCB and 15 mg / kg TCB + transformer oil + 0.1 g nano-γ-Al_2O_3 IR spectra (b)

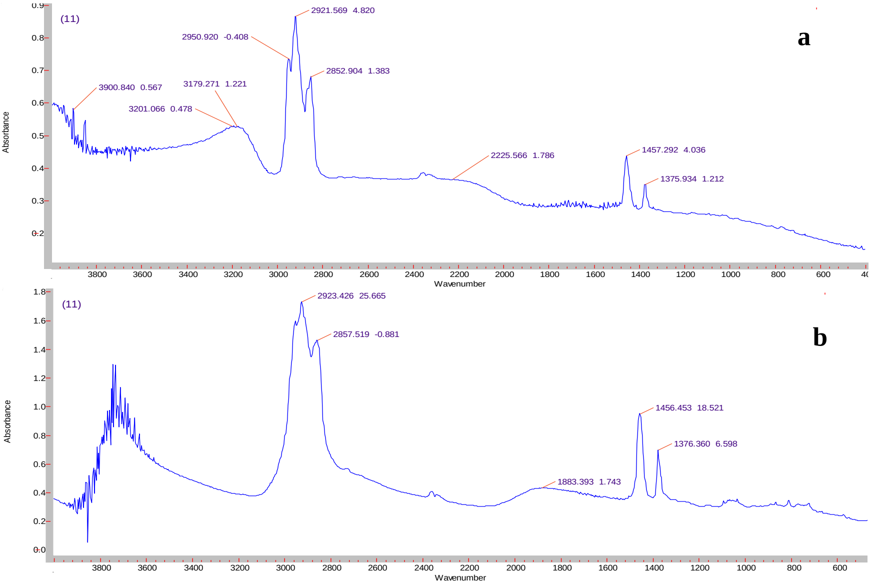


Figure 20. Transformer oil (a) irradiated at a dose of 68.4 kGy and containing 15 mg/kg TCB and 15 mg/kg TCB + transformer oil + 0.1 g nano-γ-Al_2O_3 IR spectra (b).

When nano-γ-Al_2O_3 is added to the system, Abs$_{max}$=3180 cm^{-1} wide band is lost, instead Abs$_{max}$ is increased by 4 times for other bands. This is due to the adsorption of transformer oil components, which increases their concentration on the surface. The reason for the disappearance of the 3180 cm^{-1} strip is not clear.

Figure 20a shows the IR spectra of transformer oil samples containing 15 mg/kg TCB at an absorption dose of 68.4 kGy. In the IR spectra given in Figure 20 b, the opposite picture of the Abs$_{max}$ change is observed when irradiating a mixture of transformer oil + TCB + nano-γ-Al_2O_3.

The kinetics of Abs$_{max}$ change depending on the absorbed dose are given in Table 18.

Table 18

Abs$_{max}$ values of the bands in the spectra of samples irradiated at different absorption doses: (1) 3180 cm^{-1}; (2) 2960-2947 cm^{-1}; (3) 2922-2924 cm^{-1}; (4) 2851-2857 cm^{-1}; (5) 1960-1883 cm^{-1}; (6) 1456 cm^{-1}; (7) 1376 cm^{-1}

D, kGy	Abs$_{max}$ values													
	1	2	1	2	1	2	1	2	1	2	1	2	1	2
0	0.65	0	0.50	2.20	0.58	2.50	0.48	1.85	0.44	0.50	0.35	1.00	0.33	0.70
4.1	0.56	0	0.82	1.25	0.94	1.35	0.67	1.40	0.35	0.50	0.42	0.90	0.35	0.65
27.4	0.54	0	0.61	2.00	0.65	1.65	0.52	1.80	0.38	-	0.36	1.10	0.32	0.75
68.4	0.54	0	0.65	2.10	0.70	1.75	0.60	1.70	0.42	0.50	0.49	1.00	0.40	0.75

1) Transformer oil + TCB
2) Transformer oil + TCB + nano-γ- Al_2O_3

Determination of absorption bands was carried out in accordance with [5]:

(1) – 3180 cm^{-1} ≡C–H valent oscillations in aromatic compounds;
(2) – 2960-2947 cm^{-1} –CH_3, –CH_2, valent dances;
(3) – 2922-2924 cm^{-1} –CH_2 valent dances;
(4) – 2851-2857 cm^{-1} C-H valence dances in alkanes;
(5) – 1960-1883 cm^{-1} C-H non-plane dances;
(6) – 1456 cm^{-1} –CH_2 valent dances.

As can be seen from the table, when irradiating transformer oil containing 15 mg/kg TCB, Abs$_{max}$ for bands 2; 3 and 4 increases to 4.1 kGy, a subsequent increase in dose leads to a decrease in Abs$_{max}$, and the stationary value of Absmax is determined. When nano-γ-Al_2O_3 is added to the system, the dose dependence of Abs$_{max}$ is of antibat nature, the lowest value of Abs_{max} is observed for this band at a dose of 4.1 kGy, for other bands Abs_{max} does not change depending on the absorbed dose. The following figures show the IR spectra of radiolysis products in the dose range of 4.1-68.4 kGy in the presence of nano-γ-Al_2O_3 of transformer oil containing 5; 15 and 40 mg/kg TCB.

Dose-dependent pH changes during radiolysis of transformer oil containing different amounts of PCB under the influence of γ-rays with or without the presence of nano-Al_2O_3, CO_2 və H_2O_2, H_2 and hydrocarbon gases (CH_4, C_2H_4, C_2H_6, C_3H_8, C_4H_{10}, C_5H_{12}, C_6H_{14}, C_7H_{16}) the kinetics of the formation were studied and given on the basis of the results.

Used transformer oil (Sovtol-10) containing PCB isomers and homologues and 10% trichlorobenzene was used. This oil was taken in different amounts and added to the new T-1500 transformer oil. Methods of sample preparation, irradiation and product analysis are given in Chapter 7.1.

The pH values of the samples irradiated at different doses are given in Table 19.

Table 19

Dependence of pH of absorbed transformer oil during radiolysis at different initial concentrations of PCB on transformer oil containing PCB and PCB + transformer oil + 0.1 g of nano-γ-Al_2O_3

D, kGy	pH					
	PCB			PCB+0.1 q nano-γ-A_2O_3		
	5 mg/kg	15 mg/kg	40 mg/kg	5 mg/kg	15 mg/kg	40 mg/kqg
0	5.5	4.7	4.5	5.30	5.1	4.20
4.1	5.2	4.6	4.2	4.92	5.0	3.72
27.4	4.8	4.3	3.9	4.35	4.0	3.30
68.4	4.5	3.9	3.7	4.00	3.6	3.20
136.8	4.4	3.7	3.5	3.50	3.2	3.11
Conversion degree	20%	21.2%	22.2%	37.7 %	37.2 %	26%

As can be seen, the acidity of the oil increases in both cases, in the first case (without the presence of nano-γ-Al_2O_3) the acidity increases to 20-22%, in the second case (with the presence of nano-γ-

Al_2O_3) the acidity of the mixture at different concentrations of PCB Varies in the range of 26-38%.

The kinetics of hydrogen peroxide and CO_2 formation are shown in Figures 21 and 22.

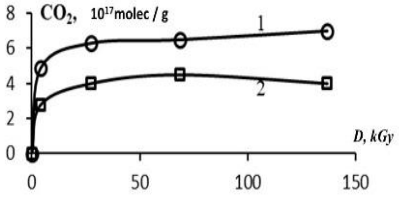


Figure 21. Dose dependence of CO_2 concentration. Contains 15 mg / kg PCB 1) transformer oil and 2) PCB + transformer oil + 0.1 g nano-γ-Al_2O_3

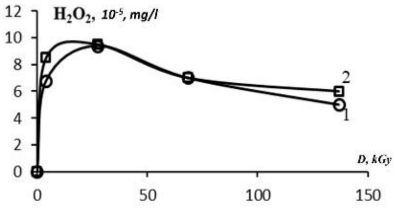


Figure 22. Dependence of the concentration of H_2O_2 on the absorbed dose. Contains 15 mg / kg PCB 1) transformer oil and 2) PCB + transformer oil + 0.1 g nano-γ-Al_2O_3

As can be seen, a sharp increase in the concentration of hydrogen peroxide up to a value of ~30 kGy of the absorbed dose, and a decrease with increasing dose is due to the presence of hydrogen peroxide in the 2nd reaction. Like the formation of CO_2 in the system, the rate of formation of H_2O_2 decreases with the presence of nano-γ-Al_2O_3.

Table 20 shows the values of radiation-chemical yields of CO_2 and H_2O_2 formed during the radiolysis of a homogeneous system such as transformer oil with different concentrations of PCB and transformer oil containing PCB in the range of 5-40 mg/kg + heterogeneous system such as nano-γ-Al_2O_3 is given.

Table 20

Radiation chemical yields of H_2O_2 and CO_2 during radiolysis of PCB + transformer oil and PCB + transformer oil + nano-γ-Al_2O_3 systems

PCB, mg/kg	G, molecules/100 eV			
	PCB + Transformer oil		PCB + Transformer oil + 0.1 q nano-γ-Al_2O_3	
	CO_2	H_2O_2	CO_2	H_2O_2
5	1.1	3.9	4.9	4.1
15	1.9	4.7	1.1	5.9
40	2.3	5.9	0.8	6.9

As can be seen, as the initial concentrations of PCBs increase in both systems, the radiation-chemical yields of CO_2 decrease, while in the presence of nanoparticles in the system, the radiation-chemical yields of CO_2 decrease further.

Thus, in both systems (PCB + transformer oil, PCB + transformer oil + 0.1 g nano-γ-Al_2O_3) as the initial concentrations of PCB increase, the radiation-chemical yield of CO_2 decreases, while in the system there are nano-particles, CO_2 radiation - chemical yield is further reduced.

Unlike CO_2, the radiation-chemical yield of H_2O_2 increases with increasing initial PCB concentration in the system, but decreases with the presence of nano-γ-Al_2O_3. In both cases there is an increase in the acidity of the oil. In the first case, the rate of acidity increase in the absence of nano-γ-Al_2O_3 is 20-22%, in the second case, the acidity in the presence of nano-γ-Al_2O_3 varies in the range of 26-38% in different concentrations of PCB. In addition to spectroscopic studies, radiolysis of the investigated system was studied to clarify the effect of nano-γ-Al_2O_3 on the formation of the hydrogen molecule.

Table 21 shows the dependence of the radiation-chemical yield of hydrogen on the initial concentration of PCB in the radiolysis of the studied systems.

Table 21

Dependence of radiation-chemical yield of hydrogen on the initial concentration of PCB in PCB + Transformer oil and PCB + Transformer oil + nano-γ-Al_2O_3 systems

Concentration of PCB, mg / kg	$G(H_2)$, molec/100 eV	
	Transformer oil	Transformer oil +nano-γ-Al_2O_3
5	0.24	0.91
15	0.26	0.72
40	0.27	0.10

When PCB is 40 mg/kg in the mixture, i.e. when PCB is added to the transformer oil, the radiation-chemical yield of hydrogen increases slightly from 0.24 to 0.27 molecules/100 eV. When nano- γ-Al_2O_3 is added to the system, an increase in G (H_2) to 0.91 molecules/100 eV is observed, a decrease in G (H_2) with an increase in PCB concentration, and G (H_2) for 40 mg/kg PCB is equal to ~0.1 molecules/100 eV. Radiation-chemical yields of hydrocarbon gases depending on the absorbed dose are given in Table 22.

Table 22

Dependence of radiation-chemical yield of hydrocarbon gases on the initial concentration of PCB in the radiolysis of PCB + Transformer oil and PCB + Transformer oil + nano-γ-Al_2O_3 systems

PCB, mg/kg	G, molec/100 eV, 10^{-3}							
	CH_4		C_2H_4		C_2H_6		C_3H_8	
	1	2	1	2	1	2	1	2
5	0.47	1.20	0.29	0.50	0.190	0.35	0.04	0.35
15	0.44	1.10	0.15	0.45	0.105	0.24	0.08	0.32
40	0.51	0.81	0.20	0.40	0.124	0.15	0.12	0.28

1) Transformer oil + PCB
2) Transformer oil + PCB +nano-γ- Al_2O_3

As can be seen from the table, the radiation-chemical yields of methane, ethane and propane decrease as the concentration of PCB increases. When nano-γ-Al_2O_3 is added to the system, the radiation-chemical yields of methane, ethane, and propane increase in all cases, but the increase in the initial concentration of PCBs leads to a decrease in their radiation-chemical yields, as observed in radiolysis of homogeneous systems. The cost of radiation-chemical yields of heavier hydrocarbons is below ~ 10^{-4} molecules/100eV.

Figure 23a shows the IR spectra of non-radiated transformer oil containing 15 mg/kg PCB. As can be seen, Abs_{max} 3180, 2973, 2854, 2200, 1450, 1330 cm^{-1} bands are observed in the spectrum.

When nano-γ-Al_2O_3 is added to the system, Abs_{max}=3180 cm^{-1} wide band is lost, instead Abs_{max} is increased by 4 times for other bands. This is due to the adsorption of transformer oil components on the surface, which increases their density (Figure 23 b). The reason for the disappearance of the 3180 cm^{-1} strip is not clear. As can be seen, the $Absc_{max}$ of all bands observed in the first series irradiated samples increases.

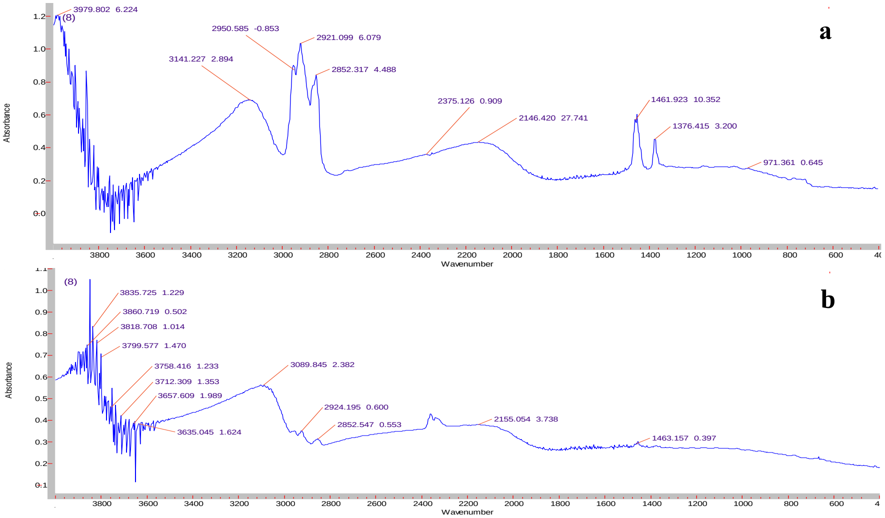


Figure 23. IR spectra of non-irradiated transformer oil (a) containing 15 mg/kg PCB, 15 mg/kg PCB + transformer oil + 0.1 g nano-γ-Al_2O_3 (b).

To study the effect of water on the radiolysis process of the transformer oil + nano-γ-Al_2O_3 system containing PCB, the dose dependence of pH, H_2O_2, CO_2 and OCT in the radiolysis of this system was studied.

Table 23

Dose dependence of pH, H_2O_2, CO_2 concentration, OCT in radiolysis of transformer oil + water +0.1 g nano-γ-Al_2O_3 system containing 15 mg/kg PCB

D, kGy	PCB + 10 ml water +0,1 q nano-γ-Al_2O_3 (15 mg/kg PCB)			
	pH	$H_2O_2 \cdot 10^{-5}$, g/ml	$CO_2 \cdot 10^{17}$molec/g	OKT, mg O/l
0	5.0	0	0	517
4.1	4.8	6.8	0.72	433
27.4	4.5	8.0	1.25	350
68.4	4.2	6.0	1.00	267
136.8	4.0	6.0	1.00	183

The calculated radiation-chemical yields of H_2O_2 and CO_2 are given in Table 24. As can be seen from the table, the radiation-chemical yields of H_2O_2 and CO_2 increase as the initial concentration of PCB increases during the radiolysis process of transformer oil + nano-γ-Al_2O_3 + water system containing (5, 15, 40)

Table 24

Radiation-chemical yields of H_2O_2 and CO_2 formed during the radiolysis process of transformer oil + nano-γ-Al_2O_3 + water system containing (5, 15, 40) mg/kg PCB

N, mg/kg	G, molecul/100 eV	
	H_2O_2	CO_2
0	0.8	
5	4.1	0.15
15	4.7	0.28
40	5.2	0.39

In Chapter VIII, the possibilities of application of radiation-chemical technology for the neutralization of chlorinated organic compounds and the cost and toxicity level of the dose required for the purification of transformer oils from PCBs and waste water from chloroform were evaluated.

The assessment of the required dose and toxicity during the purification of oils from PCBs was based on the dependence of the concentration and conversion rate of PCBs on the absorbed dose. Figure 24 shows the conversion rate (curve 1) and concentration of low-density isomers in the presence of KOH (0.1 g) during radiolysis of the PCB (0.25 ml) + hexane (8 ml) + isopropyl alcohol (0.5 ml) system. curve 2) the kinetics of change depending on the absorbed dose are given.

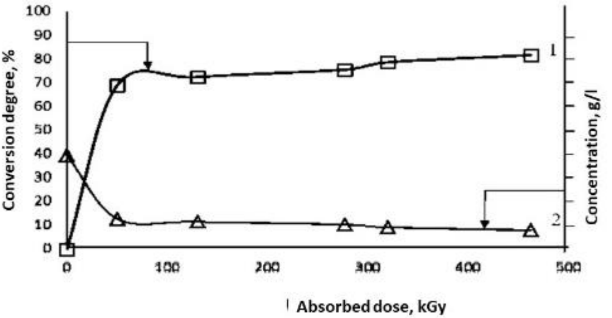


Figure 24. Absorption of conversion rate (curve 1) and concentration (curve 2) of low-density isomers in the presence of KOH (0.1 g) during radiolysis of PCB (0.25 ml) + hexane (8 ml) + isopropyl alcohol (0.5 ml) system dose-dependent kinetics.

Similar dependencies have also been studied for relatively high-density isomers.

The kinetic curve of the change in density is expressed by the following equation

$$C = C_0 \exp\left(-\frac{kD}{I}\right),$$

here: C_0 – initial concentration of PCB, mg/l;
C – allowable concentration in water (10^{-3} mg/l);
I – dose rate, Gy/s;
k – rate constant of PCB decomposition, s^{-1};
D – dose rate for the decomposition of PCB to the allowable concentration, kGy.

This equation can also be written as: $D = \frac{I}{k} \ln \frac{C_0}{C}$

I=0,30 Gy/s, C_0= 40 mg/l, C= 10^{-3} mg/l and k=$0,4 \cdot 10^{-5}$ c^{-1} we get when

$$D=0.3 \cdot 10,7/\ 0,4 \cdot 10^{-5} = 8 \cdot 10^5 \text{ Gy}=800 \text{ kGy}.$$

Thus, when the isomer concentration in the aqueous medium is 40 mg/l, the value of the absorbed dose for the decomposition of PCB-194 to the allowable concentration is 800 kGy.

Acceptable values of environmentally safe waste containing 40 mg/l PCB are 2~3 mg/l when transformer oil is removed from PCB. In this case, the dose required for oil refining is: D=0.75×105×2.57=193 kGy.

The results are the equivalent toxicity values of the products (TEC – Toxic Equivalent Concentrations) the toxicity equivalent factor of the concentration values of individual PCB congeners (TEF–Toxic Equivalent Factor) allows you to estimate by multiplying the appropriate prices.

Based on the data in Figure 24, it was found that during radiolysis of this system, the total amount of PCB isomers decreased from 21,200 mg/l to 4,321 mg/l at a dose of 470 kGy. This corresponds to a reduction of TEC of 212-43 mg/l, ie an 80% reduction in the value of the equivalent toxic concentration.

Using similar equations for the purification of chloroform from water, we obtain D = 34 kGy for the value of the absorption dose required for purification up to the allowable concentration at the following values of the decomposition rate and concentration of chloroform.

MAIN RESULTS

1. It has been established that during the radiolysis of chlorinated compounds of methane, benzene and biphenyls in water and organic solvents, the processes of radiolytic decomposition, oxidation and dechlorination of these compounds occur in parallel. The kinetics and mechanism of the processes depending on the absorbed dose of the parameters characterizing the processes corresponding to different physicochemical methods (initial concentration, OCT and pH, density of gas and liquid products, intensities of UV and IR spectra of the resulting products) were studied. [1, 2, 3, 5, 6, 7, 8, 9, 11, 20, 23]
2. During the radiolysis of an aqueous solution of chloroform, the appropriate parameters of its chain decomposition were determined and for the first time the kinetics of this process was calculated on the basis of 68 elementary reactions. According to the kinetic model, the values of the parameters characterizing the process are calculated and the correspondence between the experimental values suggests that the proposed mechanism is adequate to the radiolysis process of the system. [3, 4, 25, 29, 55]
3. For the first time, the kinetics of dose-dependent variation of physicochemical parameters (pH, OCT, H_2O_2, CO_2 concentrations, UV spectrum intensity) characterizing the process of radiolysis of 1,2,4-trichlorobenzene (TCB) in the aqueous medium were studied. The results show that during the radiolysis of the system under consideration, the process of oxidation and dechlorination of TCB took place in parallel. Similar kinetic patterns were observed during radiolysis of PCBs in water. However, in this case, due to the presence of transformer oil in the system under consideration, along with PCBs, the OCT parameter in the process of radiolysis increases with increasing dose. [44, 48, 22, 30, 40, 35, 41, 49, 51]
4. For the first time, the kinetic regularities of the decomposition processes of PCBs and 1,2,4-trichlorobenzene under the influence of gamma rays were studied. The total radiation-chemical yield of

studied PCBs and radiation-chemical yields of the Sovtol-10 PCB containing oil's low chlorine containing PCB compounds were determined. [14, 17, 19, 34, 45, 46, 47, 52, 64]

5. The dependence of the physicochemical and electrophysical parameters of these oils on the irradiation time was studied to characterize the conversion processes of PCB-containing oils during UV photolysis. It has been shown that the specific resistance of the oil decreases linearly as a result of UV radiation. The temperature dependence of electrical conductivity was studied and it was shown that the activation energy of the change in electrical conductivity decreases with increasing radiation time and is ~1 kcal / mol during 3.5 hours of radiation. The viscosity of the oil also decreases with increasing radiation time and is ~34.8 mm^2/sec for 3.5 hours. Similar dependencies are observed during radiolysis of PCBs under the influence of γ-rays. [10, 21, 24, 28, 33, 38, 42, 54]
6. It was found that the nature of the dose-dependent change in the concentration of PCBs during radiolysis of solutions of PCBs in organic solvents is determined by the number and location of chlorine atoms in PCB molecules. This dependence is due to the formation of relatively low chlorine PCBs as a result of radiolytic decomposition of high chlorine PCBs during radiolysis of the solution of PCBs in organic solvents. It was found that the addition of KOH to solutions of PCBs in organic solvents leads to an increase in the rate of radiolytic conversion of PCBs. The observed dependence is due to the participation of OH-ions formed as a result of electrolytic dissociation in the solution in the presence of KOH in the solution in the decomposition of PCBs. For the first time, kinetic modeling of the process of radiolysis of PCB oil + hexane + isopropyl alcohol + KOH system was carried out and radiation-chemical yields of PCB decomposition, isopropyl alcohol, radiolysis products of hexane (H_2, C_2 -C_{12}) were calculated and compared with appropriate prices in the literature. and the observed consistency indicates that the proposed formal kinetic scheme is adequate to the radiolysis process. [12, 13, 15, 16, 18, 31, 36, 39]
7. The effect of nano-γ-Al_2O_3 on the radiolysis process of trichlorobenzene and polychlorinated biphenyls in transformer oil

has been studied by various physicochemical methods and shown that the addition of nano-catalysts to these systems reduces the radiation-chemical yield of oxidation products CO_2 and H_2O_2. (H_2, C_1-C_{12}) costs are increasing. As the initial concentration of chlorinated compounds increases, the yield of products other than H_2O_2 decreases. In the considered dose range (up to 70 kGy), the maximum is observed in the kinetics of H_2O_2 formation (10-15 kGy), unlike other products. [56, 58, 60]

8. Possibilities of application of radiation-chemical technology for neutralization of chlorinated organic compounds were analyzed and reduction of toxicity rate as a result of exposure to ionizing radiation was determined. If the transformer oil contains PCBs with a concentration of ~ 40 mg/l, the dose rate required to purify it to the permissible concentration (10-3 mg/l) is 800 kg, to purify the water from the chloroform to the permissible level ($6 \cdot 10^{-3}$ mg/l). An absorption dose of 34 kGy was determined. The results show that radiation-chemical technology at low values of the concentration of chlorinated organic compounds is a promising method for cleaning the environment from these toxic components. [27, 37, 41, 43, 50, 53, 57, 59, 61, 62, 63, 65]

LIST OF PUBLICATIONS ON THE MAIN RESULTS OF THE DISSERTATION

1. Курбанов, М.А., Способ очистки метана от сероводорода, Авторское свидетельство №1632475, СССР / Мамедов Х.Ф., Мустафаев И.И., Искендерова З.И. – 1991.
2. Курбанов, М.А., Искендерова, З.И. Роль хлорных соединений во вторичном загрязнении атмосферы // Nəsrəddin Tusinin 800 illik yubileyinə həsr edilmiş Respublika Elmi konfransının Materialları, – Azərbaycan, Bakı: – 02-03 aprel, – 2001, – s. 2
3. Qurbanov, M.Ə., İskəndərova, Z.İ., Şəfiyeva, Ş.M. Hava mühitində xloroformun termiki çevrilmə prosesinin kinetikası // “Ekologiya və Həyat Fəaliyyətinin Mühafizəsi” mövzusunda V Beynəlxalq elmi konfransın materialları, – Azərbaycan, Bakı: – 26-27 noyabr, – 2004.

4. Ahmedov, S.A., Gurbanov, M.A., Iskenderova, Z.I., Abdullayev, E.T., Ibadov, N.A. Radiation-chemical degradation of chloroform in water solutions // The fourth Eurasian conference "Nuclear Science and its Application", – Azerbaijan, Baku: – October 31-November 03, – 2006, – p.192 -193.
5. Qurbanov, M.Ə., Qurbanov, Ə.H., İskəndərova, Z.İ., Abdullayev, E.T., Şəfiyeva, Ş.M. polixlorbifenilli yağların ionlaşdırıcı və ultrabənövşəyi şüalarm təsiri ilə çevrilmə qanunauyğunluqlarının tədqiqatı // Abşeron yarımadasmm Radioekoloji Durumuna neft-qaz istehsalının təsirinə həsr edilmiş konfrans materialları, – Azərbaycan, Bakı: – 05-07 dekabr, – 2007, – s. 23-24.
6. İskəndərova, Z.İ.,Qurbanov, M.Ə., Şəfıyeva, Ş.M., Su mühitlərinin bioloji və kimyəvi təmizlənməsində yeni texnologiyalar // «Müasir dövr və Azərbaycanda ekoloji siyasət” mövzusunda elmi-nəzəri konfrans, – Azərbaycan, Bakı: – 21-22 dekabr, – 2007, – s. 111-112.
7. Gurbanov, M.A., Gurbanov, A.H., Abdullayev, E.T, Ahmadov, S.A., İskenderova, Z.İ., Aliyeva, S.H., Shefieva, Sh.M. Radiation-chemical processes in PCB oils and its watcr solutioııs // The Fifth Eurasion Conference on Nuclear Science and its Application, – Turkey, – 14-17 october, – 2008, – p. 188-189.
8. Qurbanov, M.Ə., Qurbanov, Ə.H., İskəndərova, Z.İ., Şəfiyeva, Ş.M., Əliyeva, S.H. Tərkibində polixlorbifenil olan transformator yağlarınm ioıılaşdırıcı şüalarm təsiri ilə radiolizi nəticəsində çevrilmə qanunauyğunluqlarmın tədqiqi // Akademik M.F.Nağıyevin 100 illik yubileyinə həsr olunmuş elmi konfrans, – Azərbaycan, Bakı: – 10-11 noyabr, – 2008, – p. 302.
9. Qurbanov, M.Ə., Qurbanov, Ə.H., İskəndərova, Z.İ. Radiasiya texnologiyasının energetikanın ekoloji məsələlərinin həllinə tətbiqi // Akademik Mahmud Kərimovun anadan olmasının 60 illiyinə həsr olunmuş beynəlxalq konfrans, – Azərbaycan, Bakı: – 10-12 dekabr, – 2008, – s. 24.
10. Qurbanov, M.Ə., İskəndərova, Z.İ., Abdullayev, E.T., Qurbanov, Ə.H., Şəfiyeva, Ş.M., Balayev, V.S. Polixlorbifenilin sulu məhlullarının fotolizi və radiolizinin tədqiqi // VII Бакинская международная Мамедалиевская конференция по нефтехимии,

посвященная 80-летию института нефтехимических процессов НАН Азербайджана, – Azərbaycan, Bakı: – 29 sentyabr-02 oktyabr, – 2009, – s. 102-103.

11. Qurbanov, M.Ə., Qurbanov, Ə.H., Abdullayev, E.T., İskəndərova, Z.İ., Şəfiyeva, Ş.M., Əliyeva, S.H. İonlaşdırıcı şüaların təsiri ilə polixlorbifenilli yağların fiziki-kimyəvi xassələrinin öyrənilməsi // VII Бакинская международная Мамедалиевская конференция по нефтехимии, посвященная 80-летию института нефтехимических процессов НАН Азербайджана, – Azərbaycan, Bakı: – 29 sentyabr – 02 oktyabr, – 2009, – s. 100-101.
12. Qurbanov, M.Ə., Qurbanov, Ə.H., İskəndərova, Z.İ., İbadov, N.Ə., Şəfiyeva, Ş.M. Polixlorbifenil-propil spirti sisteminin radiolizi zamanı polixlorbifenilin xlorsuzlaşdırılması prosesinin tədqiqi // Azərbaycan Milli Elmlər Akademiyası Radiasiya Problemləıi İnstitutunun 40 illik yubileyinə həsr olunmuş Beynəlxalq konfrans, – Azərbaycan, Bakı: – 03-05 noyabr, – 2009, – s. 30-32.
13. Qurbanov, M.Ə. polixlorbifenilli transformator yağlarının heksan və propil spirti iştirakı ilə radiolizi / M.Ə.Qurbanov, E.T.Abdullayev, Ə.H.Qurbanov [və b.] // Azərbaycan Kimya Jurnalı, – Bakı: – 2010. №3, – s. 75-78.
14. Qurbanov, M.Ə. Polixlorbilenilli (polixlorbifenil) yağların γ şüaların təsiri ilə çevrilmə qanıınaııyğunluqlarının tədqiqi / M.Ə.Qurbanov, Z.İ.İskəndərova, E.T.Abdullayev [və b.] // Kimya Problemləri, – Bakı: – 2010. №2, – s. 292-295.
15. Qurbanov, M.Ə., Abdullayev, E.T., Qurbanov, Ə.H., İbadov, N.Ə., İskəndərova, Z.İ. polixlorbifenilli transformator yağlarının heksan və propil spirtinin iştirakı ilə radiolizi // RPİ-nin direktoru, AMEA-nın həqiqi üzvü, Əməkdar elm xadimi Adil Qəribovun 60 illik yubileyinə həsr olunmuş “Radiasiya və Ətraf Mühit” mövzusunda konfrans, – Azərbaycan, Bakı: – 01-02 iyun, – 2010, – s. 18-19.
16. Qurbanov, M.Ə., İskəndərova, Z.İ., Şəfiyeva, Ş.M., Əliyeva, S.H. polixlorbifenilli yağların spirtli məhlulunun radioliz prosesinə KOH-ın təsiri // M.M.Məlikzadənin 100 illik yubileyinə həsr

olunmuş “Nüvə enerjisinin dinc məqsədlərlə istifadəsi” mövzusunda beynəlxalq konfrans, – Azərbaycan, Bakı: – 08-10 noyabr, – 2010, – s. 60-61.

17. Qurbanov, M.Ə., Qurbanov, Ə.H., İskəndərova, Z.İ., Əliyeva, S.H., Şəfiyeva, Ş.M. polixlorbifenilli yağların Radiasiya kimyəvi üsulla təmizlənməsi // Akademik T.H Şahtaxtiniskinin 85 illik yubileyinə həsr olunmuş Respublika Elmi konfransı, – Azərbaycan, Bakı: – 27-28 oktyabr, – 2011, – s. 216-217.
18. Qurbanov, M.Ə., Qurbanov, Ə.H., İskəndərova, Z.İ., Şəfiyeva, Ş.M., Əliyeva, S.H., Cavanşirova, Ə.Ə. polixlorbifenilli transformator yağlarının kalim hidroksidin iştirakı ilə radiolizi // “Nüvə Enejisinin Dinc Məqsədlərlə İstifadəsi Perspektivləri” mövzusunda IV Beynəlxalq konfrans, – Azərbaycan, Bakı: – 23-25 noyabr, – 2011, – s. 115.
19. Qurbanov, M.Ə., İskəndərova, Z.İ., Qurbanov, Ə.H., Şəfiyeva, Ş.M., Abdullayev, E.T., Əliyeva, S.H. polixlorbifenil tərkibli transformator yağlarının radiolizi // “Nüvə Enejisinin Dinc Məqsədlərlə İstifadəsi Perspektivləri” mövzusunda IV Beynəlxalq konfrans, – Azərbaycan, Bakı: – 23-25 noyabr, – 2011, – s. 116.
20. Gurbanov, M.A., Iskenderova, Z.I., Gurbanov, A.G., Abdullayev, E.T. Radiation technology application for cleaning of water from admixtures of phenol, PAC and PCBs // International Conference on Nuclear Science and its Application, – Uzbekistan, Tashkent: – September 25-28, – 2012, – p. 396-398.
21. Qurbanov, M.Ə., İskəndərova, Z.İ., Şəfiyeva, S.M., Abdullayev, E.T., Cavanşirova, Ə.Ə. Hidrogenin polixlorbifenilli Yağların Fotokimyəvi Xlorsuzlaşma Prosesinə Təsiri / The V International Conference on Perspectives of Peaceful Use of Nuclear Energy, – Azerbaijan, Baku: – November 21-23, – 2012, – p. 125.
22. Курбанов, М.А. Радиолиз двухфазной системы полихлорбифенилы-вода / М.А. Курбанов, З.И.Искендерова, У.А.Гулиева, У.А. [и др.] // Химические Проблемы, – 2012. №2, – с. 292-296.
23. Курбанов, М.А., Искендерова, З.И., Джамалов, П.Дж., Алиева, С.Г. Исследование фотохимического разложение

ПХБ содержащего масла методом УФ спектроскопии // Akademik M.K.Kərimovun 65 illik yubileyinə həsr olunmuş “Radiasiya Tədqiqatları və onların praktiki aspektləri” mövzusunda VIII konfrans, – Azərbaycan, Bakı: – 20-21 noyabr, – 2013, – s. 144-145.

24. Iskenderova, Z.I., Gurbanov, M.A. UV photolysis of cross PCB-s contaminated transformer oils / “Nüvə elmi və onun tətbiqi” mövzusunda 7-ci Avrasiya konfransı, - Azərbaycan, Bakı: –21-24 oktyabr, – 2014, – s.133-134.
25. Алиева, Р.А., Шукурли, С.А., Искендерова, З.И., Аминбеков, А.С., Курбанов, М.А., Радиационно-химическая очистка воды от хлороформа / IV Всероссийская конференция с международным участием «Актуальные вопросы химической технологии и защиты окружающей среды» , – Россия, Москва: – 21-22 ноября, – 2014, – с. 39.
26. Курбанов, М.А., Мамедов, С.Г., Кулиева, У.А., Искендерова, З.И. Газообразования в жидких радиоактивных отходах // 10-я международная конференция по теме «Ядерная и радиационная физика», – Казахстан, Алматы: – 08-11 сентября, – 2015, – с. 47.
27. Qurbanov, M.Ə., İskəndərova, Z.İ., Hidayətov, B.H. Enerji sektorunda xlorlaşmış bifenillər (polixlorbifenil) problemi və əlaqədar risklər // FHN-in yaradılmasının 10 illik yubileyinə həsr olunmuş “Fövqəladə hallar və təhlükəsiz həyat” mövzusunda elmi-praktiki konfrans, – Azərbaycan, Bakı: – 09-11 sentyabr, – 2015.
28. Jamalov, P.J. Comparative study of the radiolysis and photolysis of the ethanol solutions of polychlorinebiphenyls / P.J.Jamalov, E.T.Abdullayev, M.A.Gurbanov [et al.] // European Journal of Analytical and Applied Chemistry, – 2015. №2, – p. 49-53.
29. Iskenderova, Z.I., Gurbanov, M.A. Kinetic regularities of radiolytic degradation of chloroform in water solutions // Journal of Radiation Researches, – 2015. 2(2), – p. 51-56.
30. Искендерова, З.И., Джаванширова, А.А., Курбанов, М.А. Фотохимическая деградация полихлорбифенилов в водной среде // VIII международная научно-практическая

конференция по теме «Наука в современном мире», – Украина, Киев: – 12-14 апреля, – 2016, – с. 13-17.

31. Джаваншировa, А.А., Искендерова, З.И., Курбанов, М.А., Абдуллаев, Э.Т. Влияние щелочи на процесс радиационно-химического дехлорирования полихлорбифенилов // 4-я международная научно-практической конференция по теме «Проблемы и перспективы современной науки», – Россия, Москва: – 10-12 ноября, – 2016, – с. 142-145.
32. Искендерова, З.И., Джаваншировa, А.А., Курбанов, М.А. Исследование фотолиза полихлорбифенил содержащего трансформаторного масла методом УФ спектроскопии // Журнал «Оптика и спектроскопия», – 2016. 120(5), – р. 877-879.
33. Iskenderova, Z.I., Dvanshirova, A.A., Gurbanov, M.A. A study of photolysis of polychlorobiphenylcontaining transformer oil by UV spectroscopy // Journal of Optics and Spectroscopy, – 2016. 120(5), – p. 823-825.
34. Джаваншировa, А.А. Исследование радиолиза полихлорированных бифенилов под действием γ-излучения / А.А.Джаваншировa, З.И.Искендерова, Э.Т.Абдуллаев [и др.] // Международный журнал прикладных и фундаментальных исследований, – 2016. №4, – с. 898-901.
35. Javanshirova, A.A. Iskenderova, Z.I., Gurbanov, M.A. Research of polychlorinated compounds in used transformer oil // Journal of Radiation Researches, – 2016. 3 (2), – p. 42-47.
36. Джаваншировa, А.А. Особенности кинетики радиационно-химического дехлорирования ПХБ масла (Совтол-10) в присутствии органических растворителей / А.А.Джаваншировa, З.И.Искендерова, Э.Т.Абдуллаев [и др.] // Журнал Фундаментальные Исследования, – 2017. 4 (2), – с. 242-246.
37. Искендерова, З.И., Джаваншировa, А.А., Курбанов, М.А. Применение радиационно-химических технологий для очистки масел от хлоророванных бифенилов // International Scientific Forum on Nuclear Science and Technologies dedicated to the 60th anniversary of the Institute of Nuclear physics, 11th

International conference “Nucleus-2017”, 8th Eurasian Conference on “Nuclear Science and its Application”, – Kazakhstan, Almaty: – 12-15 September, – 2017, – с. 388.

38. Джаваншировa, А.А. Влияние УФ-света и γ-излучения на физико-химические параметры обработанного технического трансформаторного «Совтол-10» и конденсаторного «Совол» масел / А.А.Джаваншировa, З.И.Искендерова, Э.Т.Абдуллаев [и др.] // Международный журнал прикладных и фундаментальных исследований, – 2017. 5 (2), – с. 243-247.
39. Джаваншировa, А.А. Численные моделирование радиационно-химических превращений полихлорированных бифенилов в растворе гексана, изопропилового спирта и щелочи КОН / А.А.Джаваншировa, З.И.Искендерова, С.Г.Маммедов [и др.] // Бюллетень науки и практики (Bulletin of Science and Practice), – 2017. №4, – с. 22-29.
40. Искендерова, З.И., Курбанов, М.А. Радиационно-химическая деградация полихлорбифенилов в водной среде // Journal of Radiation Researches, – 2018. 5 (1), – p. 35-39.
41. Iskenderova, Z.I., Gurbanov, M.A. Changes of operating characteristics of transformer oil under ionizing radiation // 68-я международная конференция «Ядро 2018» по теме «Фундаментальные проблемы ядерной физики, атомной энергетики и ядерных технологий», – Россия, Москва: – 05-07 июня, – 2018, – с. 209.
42. Искендерова, З.И., Курбанов, М.А. Влияния гамма излучения на физико-химические параметры трансформаторного масла // International Conference on Energy of Futures “Challenges and opportunities” (ISEFCO 2018), – Азербайджан, Баку: – 10-13 октября, – 2018, – с. 97-99.
43. Искендерова, З.И., Курбанов, М.А., Джаваншировa, А.А. Оценка токсичности продуктов радиационной очистки трансформаторных масел от хлорированных дифенилов // Международная научно практическая конференция «Экологическая, промышленная и энергетическая безопасность-2018», – Россия, Москва: – 24-27 сентября, – 2018, – с. 485-488.

44. Искендерова, З.И., Курбанов, М.А. Радиационно-химическая деградация 1,2,4-трихлорбензола в водной среде / IV Международная конференция «Актуальные и научные и научно-технические проблемы обеспечения химической безопасности (ASTICS-2018), – Россия, Москва: – 17-18 октября, – 2018, – с. 101.
45. Искендерова, З.И., Курбанов, М.А., Алиев, С.М. Закономерности радиолиза трансформаторного масла в присутствии примесей трихлорбензола // Journal of Radiation Researches, – 2018. 5 (2), – p. 390-394.
46. Искендерова, З.И., Курбанов, М.А. Исследование радиационной стойкости трансформаторного масла в поле ионизирующего излучения // Международный научно-исследовательский журнал «Евразийский Союз Ученых», – 2018. 56 (11), – с. 57-59.
47. Iskenderova, Z.I., Gurbanov, M.A. Radiolysis of transformer oil in the presence of admixtures of polychlorinebiphenyl // International Journal of Modern Research in Engineering Management (IJMREM), – 2018. 1 (8), – p. 1-8.
48. Искендерова, З.И., Курбанов, М.А. Радиационно-химическая деградация 1,2,4-трихлорбензола в водной среде // Химическая безопасность, технологии ликвидации источников химической опасности, – 2018. 2 (2), – с. 112-118.
49. Искендерова, З.И., Курбанов, М.А. Влияние примесей хлорированных бифенилов на радиолиз трансформаторного масла // Журнал Химия высоких энергий, – 2019. 53 (2), – с. 123-126.
50. Искендерова, З.И., Курбанов, М.А. Изменения эксплуатационных характеристик трансформаторного масла под действием ионизирующего излучения // Журнал Химия высоких энергий, – 2019. 53 (6), – с. 459-463.
51. Iskenderova, Z.I. Study of radiation-chemical decomposition of transformer oil by the method of IR-spectroscopy // Journal of Radiation Researches, – 2019. 6 (1), – p. 47-52.
52. Iskenderova, Z.I. A comparative study of the radiolysis of used transformer oil and oil containing 1,2,4-trichlorbenzene under the

influence of gamma-radiation // Вопросы Атомной Науки и Техники, – 2019. 123 (5), – p. 191-195.

53. Iskenderova, Z.I., Kurbanov, M.A. Effect of chlorinated biphenyl admixtures on transformer oil radiolysis // High Energy Chemistry, – 2019. 53 (2), – p. 132-135.
54. Искендерова, З.И. Радиационные и фотохимические методы дехлорирования полихлорбифенилов (обзор) // Химическая безопасность, – 2019. №2, – с. 130-150.
55. Iskenderova, Z.I., Kurbanov, M.A.Experimental study and kinetic modeling of chloroform decomposition in aqueous solutions under the action of γ-radiation // Russian Journal of Physical Chemistry A, – 2019. 93 (1), – p. 102-105.
56. Iskenderova, Z.I. Radiolysis of transformer oil in presence of polychlorobiphenyl and nano-γ-Al_2O_3 // Journal of Radiation Researches, – 2019. 6 (2), – p. 73-79.
57. Iskenderova, Z.I. Polychlorbiphenyls (PCB) problems and related risks in energy sector // International Scientific-practical Conference on “Radiation and Chemical Safety Problems”, – Baku, Azerbaijan, – 05-06 November, – 2019, – p. 204-205.
58. Искендерова, З.И. Влияние нано-γ-Al_2O_3 на радиолиз трансформаторного масла, содержащего примесей полихлорбифенила // Физика и химия обработки материалов, – 2020. №1, – с. 20-25.
59. Искендерова, З.И. Традиационные методы очистки трансформаторных масел от хлорированных бифенилов (ПХБ) // Journal of Baku Engineering University, – 2019. 3 (2),

– p. 122-135.

60. Искендерова, З.И. Радиолиз трансформаторного масла в присутствии трихлорбензола и нано-γ-Al_2O_3 // Физика и химия обработки материалов, – 2021. №2, – с. 80-85.
61. İskəndərova, Z.İ. İşğal olunmuş ərazilərdə xlorlaşmış bifenillər və ətraf mühitə təsir riskləri / AZMİU tərəfindən keçirilən “İşğal olunmuş ərazilərdə fövqəladə hal riskləri” mövzusunda elmi-texniki konfrans, – Azərbaycan, Bakı: – 21 may, –2021, – s .67-68.
62. İskəndərova, Z.İ. İşğaldan azad olunmuş ərazilərdə energetik qurğulardakı xlorlaşmış bifenillərin ətraf mühitdə yaratdığı risklər // “İşğaldan azad olunmuş ərazilərdə radioloji və kimyəvi risklər” mövzusunda Respublika elmi-texniki konfransı, – Bakı: – 28-29 oktyabr, – 2022, – s. 71-72.
63. Iskenderova, Z.I. Methodics of technico-economical estimation of radiation technology application (review) // Azerbaijan Journal of Chemical News, – 2022. 4 (2), – p. 76-83.
64. İskəndərova, Z., Həsənova, R. Xlorlu aromatik birləşmələrin transformator yağının radiolitik oksidləşmə prosesinə təsiri // Ulu öndər Heydər Əliyevin anadan olmasının 100 illiyinə həsr olunmuş “Radiasiya texnologiyaları və onun tətbiqi” elmi-texniki konfransı, – Bakı: – 5 may, – 2023, – s.35-36.
65. Zeynalova F., İskəndərova, Z. Radioaktiv tullantılar və onların ətraf mühitə təsiri // “Elmi iş” beynəlxalq elmi jurnal, – 2024. 17 (10), – s. 88-93.

The defense will be held on 26 September 2024 at 14:00 hours at the meeting of the Dissertation Council BED 1.21 of Supreme Attestation Comission under the President of the Republic of Azerbaijan operating at the Institute of Radiation Problems of the Ministry of Science and Education of the Republic of Azerbaijan.

Address: 9 Bakhtiyar Vahabzade str., Baku AZ 1143, Azerbaijan

Dissertation is accessible at the library of the Institute of Radiation Problems of Ministry of Science and Education of the Republic of Azerbaijan.

Electronic versions of dissertation and its abstract are available on the official website of the Institute of Radiation Problems of Ministry of Science and Education of the Republic of Azerbaijan (www.irp.science.az).

Abstract was sent to the required addresses on 20 August 2024.

Signed for print: _____ . ______ 2024

Paper format: A5

Volume: 92821

Number of hard copies: 20