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CHROMATOGRAPHIC STUDY OF RADIOLITIC DECOMPOSITION OF ORGANOCHLORINE PESTICIDES IN SOILS UNDER GAMMA RADIATION

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Abstract: This study aimed to investigate the radiolitic decomposition of OCPs products in soil samples using chromatographic methods and systems (GC/ECD and GC/MS). The chromatograms of the studied samples in the different absorbed doses were analyzed. Changes in concentrations and retention times were identified for investigated compounds.

Keywords: gamma-irradiation, OCPs, degree of decomposition, GC/ECD, GC/MS chromatography.

1. Introduction

Chromatography is widely used in researches on quantity study of products of chemical transformation of various chemicals under initiating factors. In this regard, the application of gas chromatography and mass spectrometer products transportations of OCPs under ionizing radiation in various mediums, including of soil matrix is important that allows the provide the quantity estimation of product of chemical transformations of OCPs [1-6]. This work aims to study of products of radiolitic transformation of OCPs in soil under γ radiation by gas chromatography and chromatography-mass spectrometer.

2. Material and methods

For this study 16 OCPs were investigated: α-, β-, γ- and δ- (HCH), p,p'-DDE, p,p'-DDD, p,p'-DDT, dieldrin, α-, β- endosulfan, endosulfan sulfate, endrin aldehyde. Pesticide standards and other reagents were purchased from LGC and Sigma-Aldrich Co. The mixed stock solution for calibration of the GC/ECD, containing all OCPs, was prepared in n-hexane.

Solvents used in the extraction and cleanup procedures including methylene chloride and acetone exchanged to n-hexane before analysis. All solvents were in gas chromatographic quality grade and each solvent was free of phthalates. EPA Method 8081B [7] was used as the base method for the determinations of OCPs. For irradiation of soil samples, ^{60}Co was used as a source; the rate of absorbed dose is about 0,2 Gy/sec. Samples irradiated in static conditions at room temperature.

The concentration of OCPs before and after γ-irradiation in the samples was determined using capillary gas chromatography and chromatography-mass spectrometry systems. The measurement procedure was carried out in the following conditions:
- Gas chromatograph (GC) Varian 3800 (Varian, Inc. (USA)), detector - ECD (^{63}Ni), on column 30 m x 0,250 mm x 0,25 µm, phase DB-5MS, temperature programming was used; The oven temperature was programmed starting at 80ºC and held for 0.5 min, followed by increases of 26ºC/min to 175ºC, then 6,5ºC/min to 235ºC, and then 15ºC/min to 300ºC and held 6 min. The injection port was at 250ºC splitless mode, and the detection was carried out at 340ºC. Nitrogen

(purity≥99.999%) was used as carrier gas at a constant flow rate of 3.0 mL/min, whereas nitrogen (purity≥99.999%) was employed as makeup gas at a flow of 27 mL/min. The system was operated by GC Solution Star Workstation software [8, 9].

In addition, the real samples with positive results by GC/ECD were analyzed using GC/MS (Thermo-Electron Ultra Trace DSQ, Quadruple (Finnigan, (USA)). Thermo Trace-Ultra gas chromatography coupled to a quadruple mass detector Thermo DSQ, operated in the electron impact ionization (EI) at 70 eV. The ion source temperature was 250 C and the MS transfer temperature, 250 C. The system was operated by Xcalibur 1.3 version software. Confirmation of residues was carried out by GC-MS/SIM using an Agilent column fitted with a DB-5MS (30 m 0.25 mm, 0.25 μm film thickness) column operating in the splitless mode; helium was used as carrier gas at a constant flow rate of 1.3 mL/min. The injector was maintained at 240 C. The oven temperature was programmed starting at 40 C and held for 2 min, followed by increases of 30 C/min to 220 C, held for 5 min, then 10 C/min to 270 C, and held for 1 min. For the identification of pesticides, the retention time, and three ions, the NIST and Wiley pesticide libraries were used. The SIM conditions were fixed for each compound, trying to select as precursor ion the one with the highest m/z ratio and abundance.

Soil samples were taken from 5 different points from depths of 30 ÷ 45 cm, from heavy clay soil. Samples from five points were dried at room temperature for 12 hours and a homogeneous mixture was prepared by mixing. After sieving to a maximum particle size of <2 mm, the soil was kept in a plastic bag at 4 C for 14 days before use.

For irradiation of soil samples by γ-irradiation (^{60}Co) used glass ampoules. The ampoules were prepared in a special cylindrical shape. After adding the dried and homogenized soil to the ampoules, they were sealed by forging to ensure complete isolation from the air. For the calculation of the concentration of compounds used external standard calibration procedure. The use of Calibration Factors (CF) is the preferred approach to determine the relationship between the detector response and the analyte and collective range concentrations. It is also permissible to utilize linear regression to calculate the slope and y-intercept that best describes the linear relationship between the analyte and collective range concentrations and the instrument response.

Prepared of OCPs calibration standards from the Stock Standard Solution at five concentrations (10, 25, 50, 75, and 100 ng/ml) by adding volumes of stock standard solutions to vials, and diluting to volume with and hexane, respectively, and injected each calibration standard into the gas chromatograph using the injection volume (2μL) that will be used to introduce the "actual" samples. The ratio of area response to the concentration injected, defined as the calibration factor (CF), was calculated for analytes using Equation 1. The percent relative standard deviation (%RSD) of the calibration factor must be equal to or less than 25% over the working range for the analyte of interest, as determined using Equation 2. When this condition is met, linearity through the origin may be assumed, and the average calibration factor may be used instead of a calibration curve.

Equation 1 Calibration Factor: Target OCPs Analytes	$Calibration\ Factor\ (CF) = \dfrac{Area\ of\ peak}{concentration\ injected\ (ng\ /\ uL)}$
Equation 2 Percent Relative Standard Deviation	$\%RSD = \dfrac{Stand\ Dev\ of\ 5\ CFs}{Mean\ of\ 5\ CFs}\ x\ 100$

The concentration of components in soil samples (C) is calculated from the following equation (3):

$$C = [(A_s) \times (V_{extr}) \times (D)] \, / \, [(CF) \times (M_{samp})] \qquad (3)$$

Where:

C - concentration of the compound of interest in solid sample, µg/kg;

As - peak area of the compound of interest;

V_{extr} - volume of extract, ml;

D - dilution factor;

CF - calibration factor of analyte;

M_{samp} - dry mass of sample taken for extraction, g;

Continuing Calibration Standard (CCS) - A mid-range (50 ng/ml each component in hexane) continuing calibration standard, prepared from the same stock standard solution used to develop the calibration curve, must be analyzed before sample analysis to verify the calibration state of the instrument. However, it should be noted that a mid-range continuing calibration standard is required after every 20 samples or every 24 hours (whichever comes first) and at the end of the analytical sequence. If the percent difference or percent drift of an analyte within the continuing calibration standard varies from the predicted response by more than 25%, a new five-point calibration must be performed for that analyte.

3. Results and discussion

The chromatograms of the pesticide degradation in soil samples under gamma irradiation are shown in Figure 1-3.
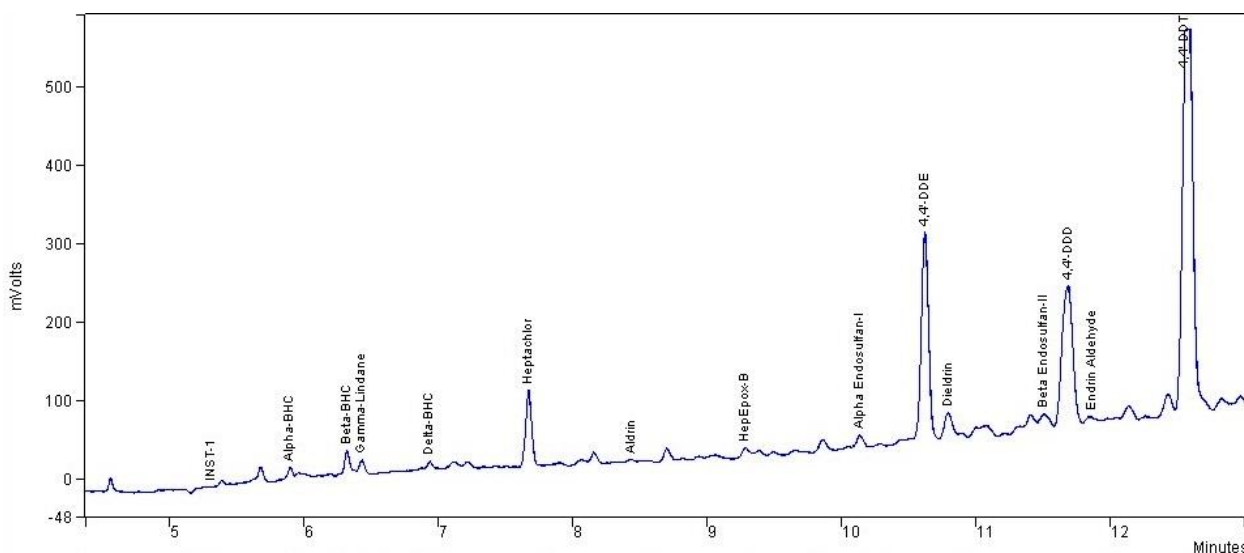

*Fig 1. Chromatograms of initial sample **0 kGy** (Dilution factor of extract equal to 10) (extracted mass of sample equal to 20 g, volume of sample extracts equal to 2 ml)*

Retention time and Quantitation Ions of the OCPs compounds in chromatograms are shown in Table 1. In Figures 2 and 3 the chromatograms of the irradiated samples are shown.

Table 1. Retention time and Quantitation Ions of the OCPs compounds in chromatograms.

| Compound	CAS#	Molecular Formula	Molecular Weight, g/mol	Retention Time, min	Quantitation Ions for GCMS SIM mode, m/z
Alpha-BHC	319-84-6	$C_6H_6Cl_6$	290.83	5.892	181
Beta-BHC	319-85-7	$C_6H_6Cl_6$	290.83	6.318	181
Gamma-BHC	58-89-9	$C_6H_6Cl_6$	290.83	6.427	183
Delta-BHC	319-86-8	$C_6H_6Cl_6$	290.83	6.934	181
Heptachlor	76-44-8	$C_{10}H_5Cl_7$	373.32	7.669	100
Aldrin	309-00-2	$C_{12}H_8Cl_6$	364.91	8.350	66
Heptachlor Epoxide Isomer B	1024-57-3	$C_{10}H_5Cl_7O$	389.32	9.284	81
Endosulfan I (Alpha)	959-98-8	$C_9H_6Cl_6O_3S$	406.93	10.136	195
4 , 4 ' – DDE	72-55-9	$C_{14}H_8Cl_4$	318.03	10.619	246
Dieldrin	60-57-1	$C_{12}H_8Cl_6O$	380.91	10.796	79
Endrin	72-20-8	$C_{12}H_8Cl_6O$	380.91	11.212	263
Endosulfan II (Beta)	33213-65-9	$C_9H_6Cl_6O_3S$	406.9	11.507	195
4 , 4 ' – DDD	72-54-8	$C_{14}H_{10}Cl_4$	320.04	11.507	235
Endrin Aldehyde	7421-93-4	$C_{12}H_8Cl_6O$	380.9	11.864	279
Endosulfan Sulfate	1031-07-8	$C_9H_6Cl_6O_4S$	422.9	12.323	272
4 , 4 ' – DDT	50-29-3	$C_{14}H_9Cl_5$	354.49	12.482	235
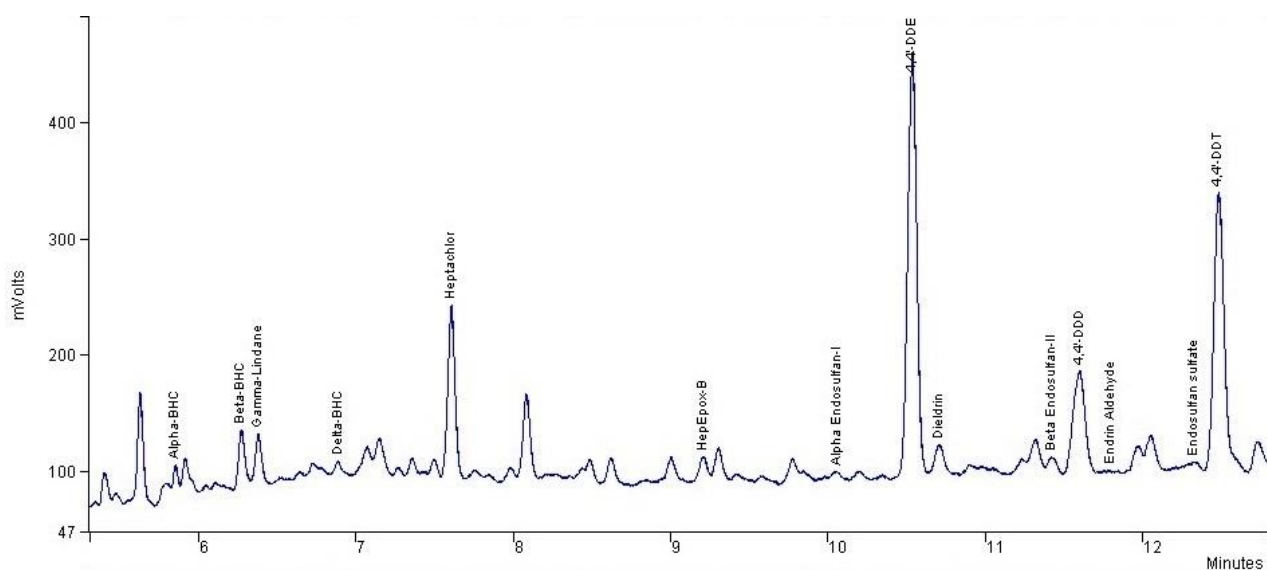
Fig. 2. Chromatograms of 10.8 kGy (Dilution factor of extract equal to 2) (extracted mass of sample equal to 9.5 g, volume of sample extracts equal to 1 ml)
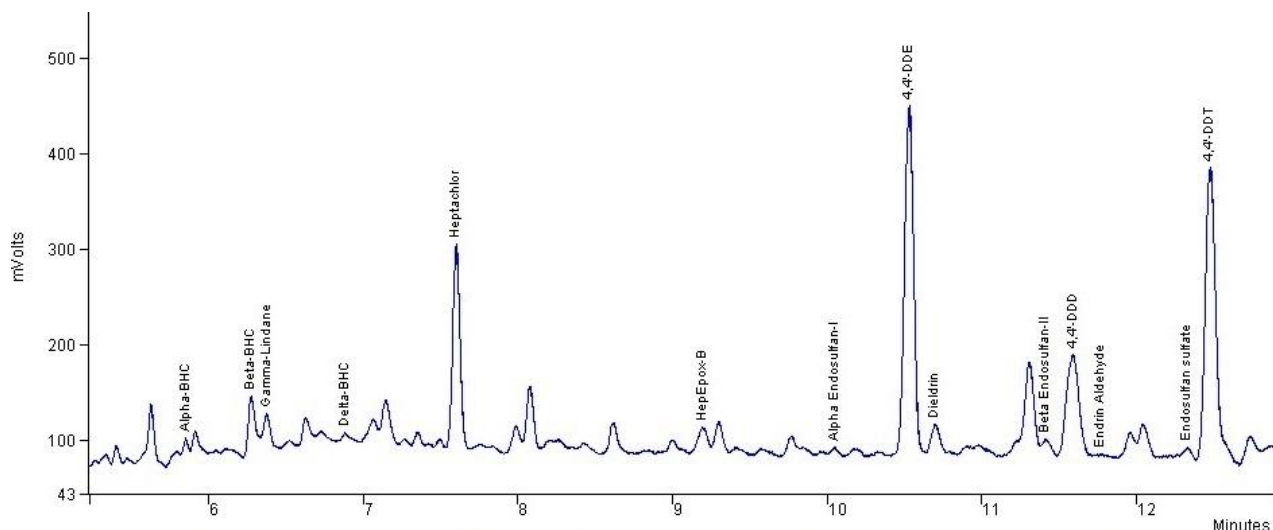
Fig. 3. Chromatograms of 36 kGy (Dilution factor of extract equal to 2) (extracted mass of sample equal to 10 g, volume of sample extracts equal to 1 ml)

Despite the appearance and changes of the degradation products is expected, but quantity analyses are not possible due to the unavailability of relevant standards. Therefore we provide the quantitative analyses of the concentration changes of the initial OCPs components at different absorbed doses. Results are given in the following diagrams figures 4 and 5.
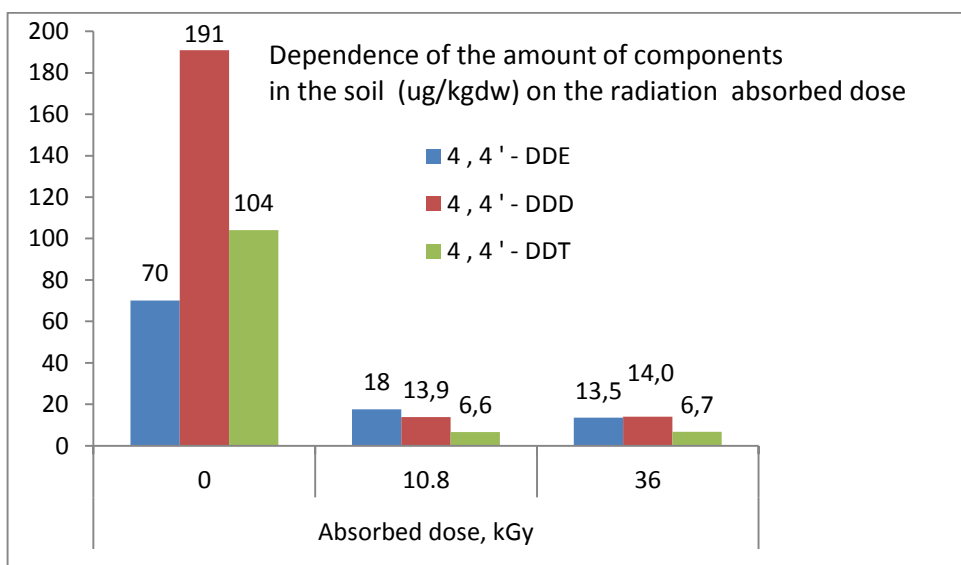

Fig.4 Dependence of the concentration of the 4,4'-DDT (red), 4,4'-DDE(blue), and 4,4'-DDD(grey) on absorbed doses
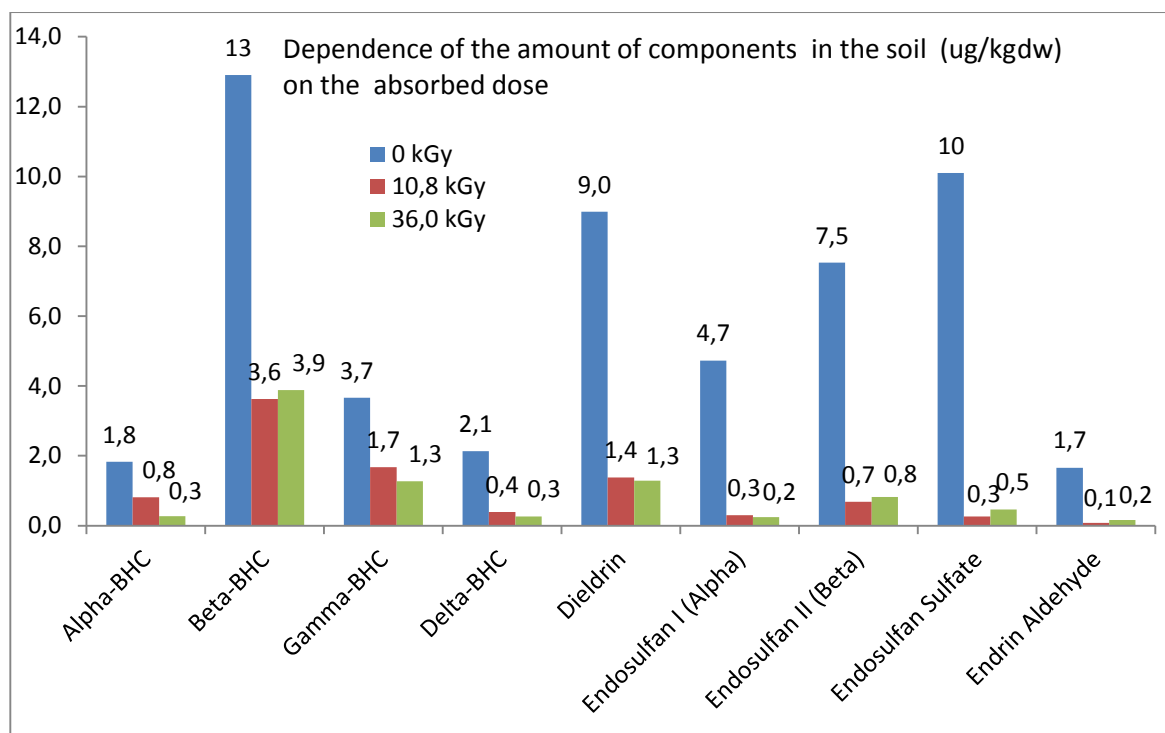
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Fig.5. Dependence of the concentration of the BHC isomers, Dieldrin, Endosulfan (alpha&beta), Endosulfan Sulfate and Endrin Aldehyde on absorbed doses

The obtained results show the decreasing of initial concentration of OCPs components by the increasing of absorbed doses.

4. Conclusion

The obtained results show that application GC and GC/MS analyses methods allow providing the correct quantity estimation of the changes in irradiated samples and can be considered as perspective methods for the OCPs analysis.

References

1. Stephen W.C. Chung *, Benedict L.S. Chen (2011), Determination of organochlorine pesticide residues in fatty foods: A critical review on the analytical methods and their testing capabilities. Journal of Chromatography A, 1218 (2011) 5555–5567.
2. Linda L Sibali, Jonathan O Okwonkwo and Rob I McCrindle (2008). Determination of selected organochlorine pesticide (OCP) compounds from the Jukskei River catchment area in Gauteng, South Africa. ISSN 0378-4738 = Water SA Vol, 34 No, 5 October 2008, 611-622.
3. Kong, WJ., Liu, QT., Kong, DD. *et al.* (2016). Trace analysis of multi-class pesticide residues in Chinese medicinal health wines using gas chromatography with electron capture detection. Sci Rep 6, 21558 (2016). https://doi.org/10.1038/srep21558

4. Rashid A, Nawaz S, Barker H, Ahmad I, Ashraf M.(2010). // J Chromatogr A., 2010, Apr 23;1217(17):2933-9. doi: 10.1016/j.chroma.2010.02.060. Epub 2010 Mar 3.PMID: 20303092.

5. Lijuan Jia, Yunyun Deng. Determination of organochlorine pesticides in soils using gas chromatography-tandem mass spectrometry// Se Pu, 2008, 26(6):697-703.

6. Fernandes V.C., Domingues V.F., Mateus N.&Delerue-Matos C (2012). Analysing organochlorine pesticides in strawberry jams using GC-ECD, GC-MS/MS and QuEChERS sample preparation. Food Additives & Contaminants: Part A, Volume 29, 2012 - Issue 7, pp. 1074-1084. http://www.tandfonline.com/loi/tfac20.

7. US EPA Method 8081B Organochlorine Pesticides By Gas Chromatography.

8. Ibadov N. A., Humbatov F.Y., Samedov M.A., Mammadzade S.Sh. and Karimova N.Sh.(2018). Determination of organochlorine pesticides and radionuclides in soil and sediment samples taken from the Kura-Aras river systems. Journal of Radiation Researches, Baku, vol.5, №2, pp.307-315. irp.science.az › pdf › 84)_irp_journal-2018-2_493-499

9. Voogt P., Klamer J.C. and Govers H.(1986). Simultaneous clean up and fractionation of organo-chlorine compounds by adsorption chromatography // J. of Chromatography.- V.363, pp. 407-411. https://doi.org/10.1016/S0021-9673(01)83765-1

ХРОМАТОГРАФИЧЕСКОЕ ИССЛЕДОВАНИЕ РАДИОЛИТИЧЕСКОГО РАЗЛОЖЕНИЯ ОРГАНОХЛОРИРОВАННЫХ ПЕСТИЦИДОВ ПОД ДЕЙСТВИЕМ ГАММА-ИЗЛУЧЕНИЯ

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Резюме: Целью данного исследования является изучение радиолитического разложения продуктов ХОП в образцах почвы с использованием хроматографических методов и систем (ГХ/ЭЗД и ГХ/МС). Проанализированы хроматограммы исследуемых образцов при различных поглощенных дозах. Для исследуемых соединений выявлены изменения концентрации и время удерживания.

Ключевые слова: гамма-облучение, ХОП, степень разложения, ГХ/ЭЗД, ГХ/МС.

GAMMA RADİASİYASI İLƏ TORPAQDA XLORÜZVİ PESTİSİDLƏRİN RADİOLİTİK PARÇALANMASININ XROMATOQRAFİK TƏDQİQİ

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Xülasə: **T**ədqiqat işi QX/ETD (GC/ECD) xromatoqrafik metoddan və QX/Kütlə-spektrometrik cihazlarından (GC&GC/MS) istifadə etməklə torpaq nümunələrində XÜP-lərin radiolitik parçalanmasının araşdırılmasına həsr olunub. Müxtəlif dozalarda tədqiq olunan nümunələrin xromatoqramları analiz edilmişdir. Tədqiq olunan birləşmələrin konsentrasiyaları və udma müddətinin dəyişməsi aşkar edilmişdir.

Açar sözlər: qamma-şüalanma, XÜP-lər, parçalanma dərəcəsi, GC/ECD, GC/MS