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Original Article

THE USE OF EPR SIGNALS OF PLANTS AS BIOINDICATIVE PARAMETERSIN THESTUDY OF ENVIRONMENTAL POLLUTION

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ABSTRACT

Objective: The change of the signal intensity of the electron paramagnetic resonance (EPR) of plants as privet-*Ligustrum japonicum,* olive – *Olea europea and* pyrocantha – *Pyracantha coccinea* was studied. İn the study of environmental pollution was used EPR signals of plants.

Methods: In all study areas the exposure dose rate (EDR) was measured using a MKS- 1125 AT, Atomtex dosimeter - radiometer. EPR spectra of dry plant objects were recorded using "BRUKER" EPR spectrometer. Radionuclide composition and specific activity of radionuclides in the samples were determined by gamma spectrometry.

Results: It is shown that the intensity of the broad EPR signal ($\Delta H \approx 450$ G, $g = 2.32$) that presumably belong to iron oxide nanoparticles, rises with the increase of environmental pollution. The comparative analysis of intensity changes of broad EPR signals depending on the level of contamination was studied. EDR of the areas where plants were collected was measured. The elemental and radionuclide composition was determined and the specific activity of radionuclides in the leaves of test plants was measured.

Conclusion: The obtained results allow us to use the EPR spectra that belong to nanoparticles of iron oxide as bio indicative parameters of environmental pollution.

Keywords: magnetic nanoparticles, EPR signal, environment, pollution.

INTRODUCTION

It is known that the environmental pollution occurring as a result of radioactive emissions of chemical and industrial production and other anthropogenic factors violate ecological balance and create danger to living organisms. The serious problem is contamination of soil and water caused by the production of oil and gas industries [1]. Because of the development of oil and gas industries the environment, especially the surface of the Earth is being contaminated by heavy metals and radionuclides [2].

At the mean time, during the last decade it was revealed that different types of nanoparticles, especially metal nanoparticles may cause dangerous diseases as nanopotologies while entering the human body. It is known that the metal nanoparticles can penetrate into the human body in different ways: through the mucous membranes of the respiratory and digestive tracts, transdermally (e. g., using cosmetics), via the bloodstream comprising vaccine and sera. While studying the influence of contamination of the dominant species of plants characterized for Absheron Peninsula for the first the magnetic nanoparticles in the plants were revealed by using the EPR method [3]. They showed that parameters of broad EPR signal registered in plant leaves and its change during the decrease of registration temperature are identical to the characteristics of broad EPR signals in the synthesized nanoparticles of magnetite. This is especially true broadening of these signals and their amplitude with decreasing temperature to 80 K [4].

Therefore, the study of the influence of radio ecological factors on plants, on the formation of metal nanoparticles in them is of great scientific and practical interest. Also, it can be argued that the identification of ways and means of influence of metal nanoparticles on plants-this is extremely important and urgent work.

In this paper, the objects of our study were three types of plants: Ligustrum japonicum, Olea europea, (Oleaceae), Pyracantha coccinea (Rosaceae) growing in three different areas of the city of Baku, which differ in the degree of contamination. These territories are the first zone (control), which is environmentally friendly, is a countryside (Botanical Garden of the National Academy of Sciences of Azerbaijan), second industrial zone of the city of Baku (Absheron Peninsula), the third area of high traffic (airport). Measured EDR sites where plants were collected under investigation. By EPR method studied the formation of magnetic nanoparticles in the studied plants. It is shown that the contamination has a significant influence on the formation of magnetic nanoparticles in these plants. With increasing degree of pollution, an increase broad EPR signal belonging presumably magnetic iron oxide nanoparticles.

Ligustrum japonicum Olea europea Pyracantha coccinea

MATERIALS AND METHODS

Investigations were carried out on some plant species ((Ligustrum japonicum, Olea europea, (Oleaceae) and Pyracantha coccinea (Rosaceae) growing in three different areas of the Absheron Peninsula: 1-zone, which represents the countryside-Botanical Garden of the National Academy of Sciences (ANAS) (this area will be called the control group), 2-industrial zone of Baku (Absheron peninsula), 3-high traffic area (airport).

In all study areas, DER was measured using a MKS-1125 AT, Atomtex (Belarus) dosimeter-radiometer. The Back ground of radiation in these areas did not exceed 2.8-3.5 mkR / hr.

Freshly harvested leaves of the above plants were used in the experiments. Plants harvested in spring were dried naturally at a room temperature 25-27 °C. Before EPR studies samples were crushed to powder.

EPR spectra of dry plant objects were recorded using "BRUKER" (Germany) ESR spectrometer model at room temperature with the following recording conditions: microwave power 10 mW, modulation amplitude of the RF magnetic field 4 G, temperature 297 K. The EPR spectra shown in the fig. were normalized according to the amount of material in the sample.

Radionuclide composition and specific activity of radionuclides in the samples were determined by gamma spectrometry. For this purpose, the collected plant samples were dried and placed in sealed containers of Marinelli. The radionuclide composition and specific activity of radionuclides was determined after three days storage of samples under these conditions with the gamma spectrometer of "Canberra" detector HP Ge. The time (4 hours) and conditions was the same for all the samples.

The elemental composition of the samples was determined by X-ray fluorescence spectrometer of "XRF-Analyzer, Innov-X Company (USA)".

RESULTS AND DISCUSSION

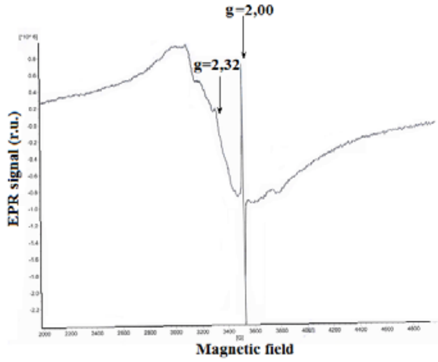


Fig. 1: Typical EPR spectrum of dried at room temperature leaves of Olea europea

EPR spectra: fig. 1 shows a typical EPR spectrum of dried at room temperature leaves of Olea europea, collected from plants growing at the airport. It is obvious that the main contribution to the EPR spectrum includes relatively broad signal with g-factor g ≈ 2.32 and a half-width ΔH ≈ 450 G. Further we will refer to the signals of this type "broad EPR signals". Fig. 2 shows the EPR spectra (at room temperature) of the dried leaves of privet (Ligustrum japonicum) collected from plants growing in three different areas of Absheron.

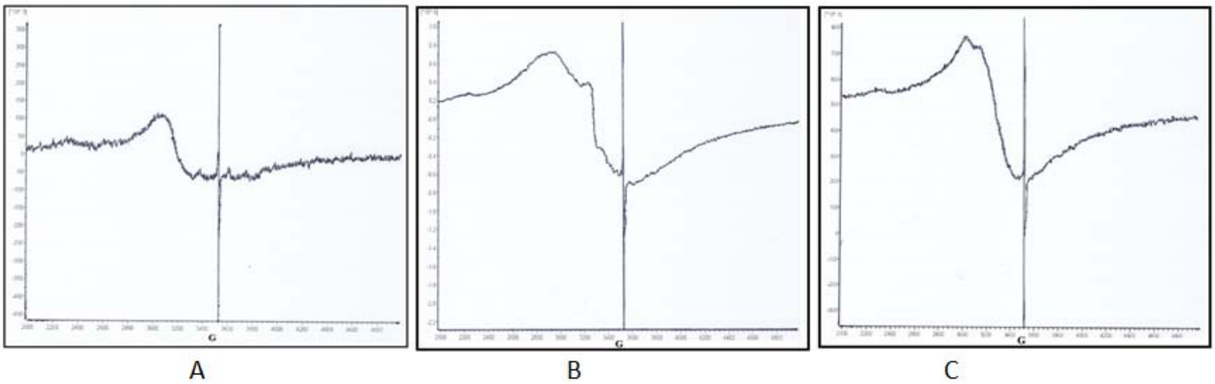


Fig. 2: EPR spectra od dried at a room temperature leaves of privet (Ligustrum japonicum) collected from different areas of Absheron: A Botanical Garden of Academy of Sciences of Azerbaijan, C-industrial area of Baku, in-area high traffic (airport). Conditions of registration: center field: 3480G, sweep width: 3000G, mod / amplitude: 10 G, power: 0,667 mW, temperature 297 K.

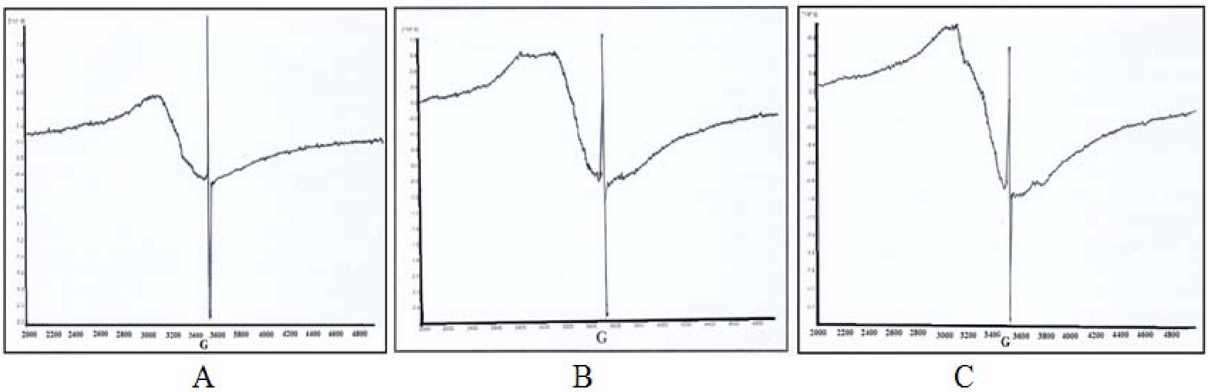


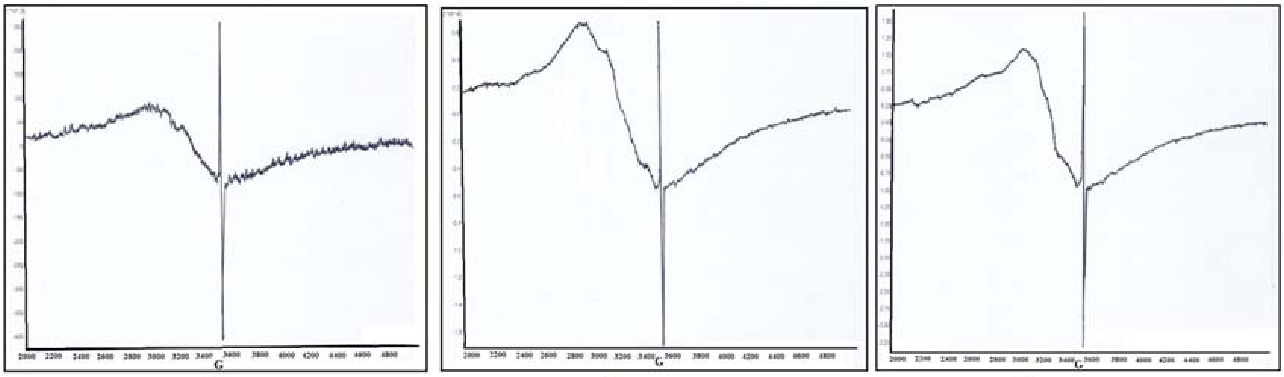
Fig. 3: EPR spectra of dried at a room temperature leaves of olive (Olea europea) collected from different areas of Absheron: A-botanical garden ANAS, B-Industrial Zone of Baku, from the area of high traffic (airport). Conditions of registration: center field: 3480G, sweep width: 3000G, mod / amplitude: 10 G, power: 0,667 mW, temperature 297 K.

The fig. 2 shows that the main contribution to these spectra makes a wide EPR signal. This is accompanied by the following pattern: in the leaves from the control area, in the botanical garden the EPR signal intensity is less than intensity of analogical signal of plants from relatively polluted areas.

The amplitude of the wide EPR signal was significantly higher in plants collected from the industrial area of Baku city. Apart from a wide signal the narrow EPR signal of free radicals (g = 2.00) is detected in the spectrum.

This pattern was observed in plants of the olive (Olea europea) and pyracantha-Pyracantha coccinea (fig. 3, fig. 4).

Radionuclide and elemental composition: table 1 shows the radionuclide composition and specific activity of radionuclides in leaves of privet (Ligustrum japonicum), Olive-Olea europea, (Oleaceae) and pyracantha-Pyracantha coccinea (Rosaceae) collected from three different areas of Absheron with different level of pollution. The natural radionuclides (^{7}Be, ^{40}K, ^{226}Ra, ^{228}Ra, ^{235}U) were detected in the studied samples. In the samples of the plants collected from control areas (A) (i.e. plants collected from the Botanical Garden of ANAS) the specific activity of some radionuclides (^{40}K, ^{226}Ra, ^{228}Ra) was significantly less than the specific activity of plants collected from the territories of airport and industrial zones of Baku city.



A B C

Fig. 4: EPR spectra, of dried at room temperature leaves of pyracantha-Pyracantha coccinea collected from different areas of Absheron: A botanical garden ANAS, B Industrial Zone of Baku, from the area of high traffic (airport). Conditions of registration: center field: 3480G, sweep width: 3000G, mod / amplitude: 10 G, power: 0,667 mW, temperature 297 K.

Table 1: Radionuclide composition and specific activity of the plant leaves grown on contaminated and control areas of Absheron. A, B, C corresponds to the caption indicated below the fig. 2-4

Element	Specific activity of radionuclides (Bq / kg)								
	Privet *Ligustrum japonicum*			Olive *Olea europea*			Pyracantha *Pyracantha coccinea*		
	A	B	C	A	B	C	A	B	C
^{7}Be	5.9±0.4	2.8±0.2	5.7±0.6	4.1±0.5	5.9±0.3	3.8±0.6	3.9±0.4	5.3±0.4	5.7±0.4
^{40}K	460±12	563±21	567±19	554±18	627±17	657±18	601±13	760±13	820±18
^{226}Ra	3.9±0.2	4.9±0.2	4.8±0.3	3.5±0.1	12.9±0.1	12.8±0.2	11.9±0.2	14.8±0.2	13.4±0.3
^{228}Ra	2.8±0.1	8.9±0.3	9.7±0.2	8.1±0.3	11.8±0.2	10,8±0.3	10.9±0.1	10.9±0.3	11.1±0.1
^{235}U	1.5±0.2	3.2±0.1	0.5±0.2	3.2±0.2	0.9±0.1	2.8±0.1	3.4±0.2	3.8±0.2	2.5±0.1

Table 2: The elemental composition of the plant leaves grown on contaminated and control areas of Absheron

Element	Privet *Ligustrum japonicum*			Olive *Olea europea*			Pyrocantha *Pyracantha coccinea*		
	A	B	C	A	B	C	A	B	C
Ti	0,082	0,16	0.17	0.013	0.0889	0.15	0.0326	0.16	0.0463
V	-	0,0552	0.0453	0.0841	0.0633	0.068	0.0395	0.09	0.0483
Fe	0,78	0,23	0.55	0.87	0.17	0.31	0.44	0.99	0.72
Cu	0,49	0.55	0.84	0.12	0.14	0.85	0.23	0.65	0.41
Pb	0,16	0.0298	0.0186	0.023	0.33	0.54	0.0686	0.0121	0.52
Bi		0.0442	-		0.21	0.22	0.0136	0.0131	0.23
Zn	0.29	0.2	0.0102	0.2	0.19	0.01	0.2	0.32	0.0113
Zr	0.18	0.2	0.24	-	0.3	0.18	0.24	0.0539	0.31
Cd	0.6	-	-	-	0.45	-	-	0.0231	0.38

The strong concentration of the isotope ^{40}K in the test plant leaves was observed. The minimum concentration of isotope $^{235}U$was observed in all plant leaves. No pattern was observed in the concentration of the isotope ^{7}Be.

CONCLUSION

In addition, we determined the elemental composition of the test plants collected from different areas of Absheron, which is shown in table 2. As saw from the table in all plants investigated concentration of Fe and Cu was significantly larger than the other elements. The elements Ti, V, Zn и Zr were observed in plants least of all. Despite that the plant leaves of privet (Ligustrum japonicum) and olive (Olea europea) contain iron (Fe) in the control areas more than in polluted areas, the amplitude of wide EPR signals that characterizes magnetic nanoparticles of iron oxide is less in control samples that in plants from polluted areas.

In the early studies of L. A. Blumenfeld, he and his coworkers found that relatively broad EPR signals are recorded in yeast cells [5,6]. These signals may belong to the magnetic nanoparticles that contain iron. In our works, we discovered wide EPR signals in the tissues of plant origin [3,4]. These signals resemble broad EPR signals in synthetic nanoparticles preparations of magnetite (eg, Fe_3O_4 in polyacrylamide matrix) [6-8].

The authors of the work [8,9] obtained EPR signals (g=2.25; ΔH≈320 G) typical for superparamagnetic iron oxide particles characteristic in the natural systems and in the samples of colloidal particles of paraffin oil. The effective g-factor that is considerably larger than value 2 and characterized for paramagnetic ferric, indicates ferromagnetic magnetism and significant magnetization of nanoparticles present in the sample. Electron microscopic images of these samples also showed that the unit consists of iron oxide nanoparticles [10]. Our experiments and measurements have shown that an increase in the degree of pollution in plant leaves growing in these areas, the amplitude of broad EPR signals characterized for magnetic nanoparticles increases. This pattern was observed in all plant species studied by us. These signals have been shown in [2,5] works belong to magnetic nanoparticles.

Therefore, the EPR signals that belong to the magnetic nanoparticles of an environment can be used as bio-indicative parameters in the study and monitoring of the environment.

CONFLICT OF INTERESTS

Declared None

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