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Investigation of generation of magnetic nanoparticles in plants by EPR spectroscopy

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Abstract
By Electron Paramagnet Resonance (EPR) method was studied many plants growing in Lankaran. EPR spectra of samples have recorded. Signals of ferrous magnetic nanoparticles were found in EPR spectra of most of these samples (80%). Angular variations were recorded in EPR spectra. Temperature and frequency dependence of magnetic properties of iron oxide magnetic nanoparticles was studied. When the temperature dependence of EPR spectra of the investigated plants was studied, abnormalities were observed at 120-125 K temperatures characteristic for Vervey transition phase in magnetite. The radionuclide content and elemental analysis of the studied plant and soil samples were determined.

Keywords: EPR signals, magnetic nanoparticles, citrus plants, soil samples

Introduction

All living things, from bacteria to humans, are rich in natural iron oxide nanoparticles that generated by biomineralization processes. In living organisms, the most common magnetic nanoparticles are magnetite, maghemite and ferrihydrite (in the core of the protein of ferritin). These nanoparticles play an important role in the functioning of living systems, as well as the development of brain cancer, tumor processes and other pathological situations. These nanoparticles bring about the generation of magnetic properties in Biosystems and the formation of EPR signal [1]. In modern age, synthesis of magnetic materials in the nanoscale is an area of intensive research [2]. Magnetic nanoparticles are widely used for various purposes, including biomedical [2, 3, 4].

In our previous studies, we investigated the EPR spectra on the leaves of tree and shrub vegetation in different parts of the Absheron peninsula. For the first time, we have demonstrated the formation of iron oxide magnetic nanoparticles in plants by EPR [5]. Generally, we have studied by EPR plants has been growing in ecologically clean and ecologically polluted areas, such as near various factories, on the edges of intensive transport routes, and so on. At the same time, EPR spectra of plants that grow in the same area in different seasons of the year have been studied. Our plural researches have shown that stress factor causes formation of magnetic properties in plants. The obtained results were correlated with the obtained results from our experiences with the seedlings of irradiated plant seeds in different doses in laboratory conditions.

Materials and Research Methods

In the presented study, we investigated the generation of magnetic nanoparticles on the leaves of five types of plants (lemon (*Citrus limon*), magnolia (*Magnolia)*, tangerine (*Citrus reticulata)*, feykhoa *(Feijoa)*, kumquat (*Fortunella)*) in Lankaran region by EPR method. We have determined the temperature dependence of paramagnetic resonance spectra of these particles. In addition, along with the leaves of these plants, EPR spectra of soil samples collected from their sown area were studied. Measurements were carried out on the EPR spectrometer (Bruker - Germany). EPR spectra measurements were registered out up to 4 K from room temperature (297 K) at a wide range of temperatures.

In addition, also were analyzed radionuclide and elemental composition of soil samples of plants and their cultivated areas.

Citrus limon ***Magnolia*** ***Citrus reticulate*** ***Feijoa*** ***Fortunella***

Fig 1

Result and Discussions

Both plant and soil samples were naturally dried and prepared in laboratory conditions for EPR studies. It has been determined that, two types of signals are observed in the EPR spectrum of the leaf samples (fig.1A).

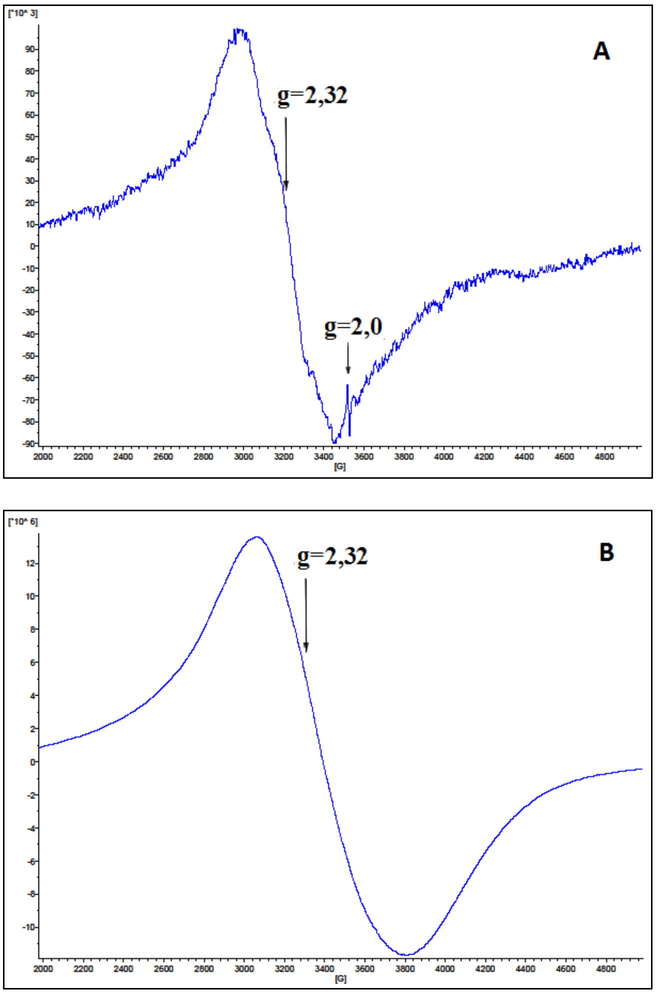


Fig 1: EPR signals taken from dried leaves of lemon plant (A) and soil sample (B), where this plant grows.

One of them is narrow signal compatible to g = 2.0 and corresponds to the free radical signal. The other is intensive signal compatible to g = 2.32 and is almost was recorded in all plant samples collected from this area. The parameters of the signal which received from the leaves of the lemon plant (g = 2.32, ΔH = 500 Qs) indicate that iron oxide magnetic nanoparticles exist on these leaves. We can say that the received signal according to their parameters (fig. 1A) belong to the magnetic nanoparticles. Sometimes at room temperature received this signal is superposition of two signals with parameters $g_1 = 2.34$; $\Delta H_1 = 260$ Qs and $g_2 = 2.22$, $\Delta H = 380$ Qs. At the same time, we observed EPR signals of paramagnetic centers characterizing the iron components in soil samples collected from the plant growing area (fig. 1B).

Along with the lemon plant, we investigated EPR signals of leaves of feykhoa, tangerine, magnolia and kumquat plants harvested from Lankaran. In these plants have observed wide EPR signals characterizing iron oxide magnetic nanoparticles.

We have researched the EPR spectra of the magnolia leaves and the soil from the area where this plant grows (fig.2). It has been determined that in the spectra of the leaves were recorded three types of signals. As shown in the figure, wide EPR signal captures the main place in this spectrum (g = 2.4). At the same time, in many samples it is also observed a weak signal of the trivalent iron complexes (g = 3.4) and the signal of the free radicals corresponding to g = 2.0.

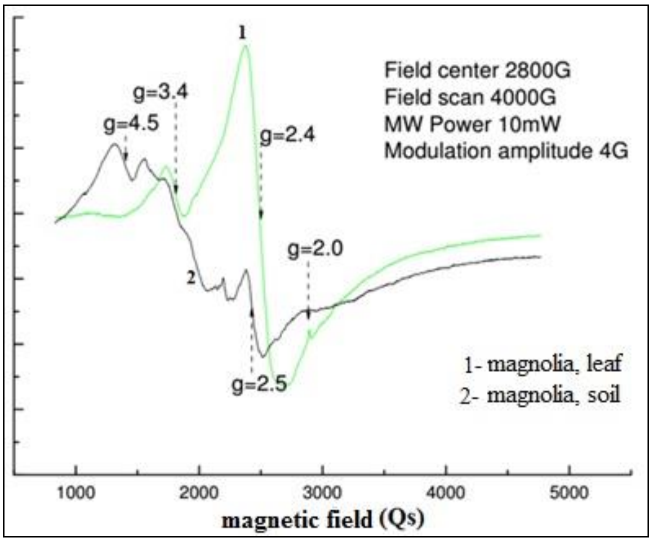
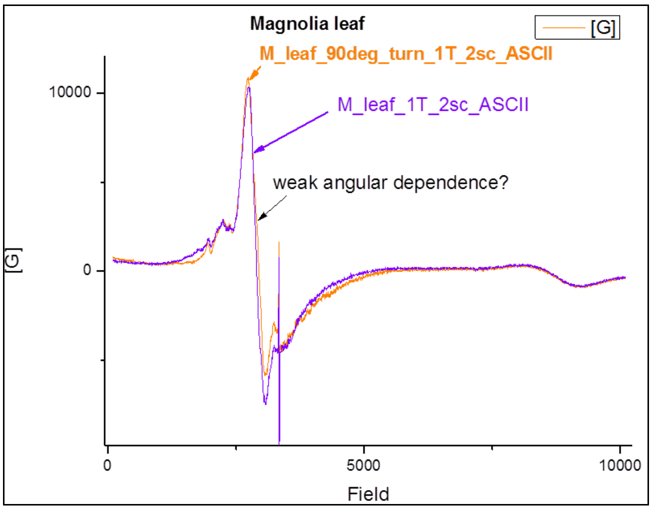


Fig 2: EPR signals of the 1- leaves of magnolia and 2- soil samples of this area.

For learn the characteristics of the specific wide EPR signal that characterizes iron oxide nanoparticles we have researched EPR signal of magnolia plant changing the parameters of the radio spectrometer and we have determined that this signal has magnetic anisotropy. So that, we have studied glass ampoule, where samples are located at different angles (90º, 180º) for determine the angle variation in the resonator and we have observed that the shape of EPR signal had changed slightly (Figure 3). In the resonator of spectrometer when we rotated 90° glass ampules where samples are located we have observed that the EPR signal has shifted slightly to the left, and when turning 180 ° again returned to its previous state. Such behavior of signals has found for Fe2O3 and Fe3O4 superparamagnetic nanoparticles [6, 7, 8, 10]. This indicates that the paramagnetic centers responsible for the EPR signal have a compound structure.



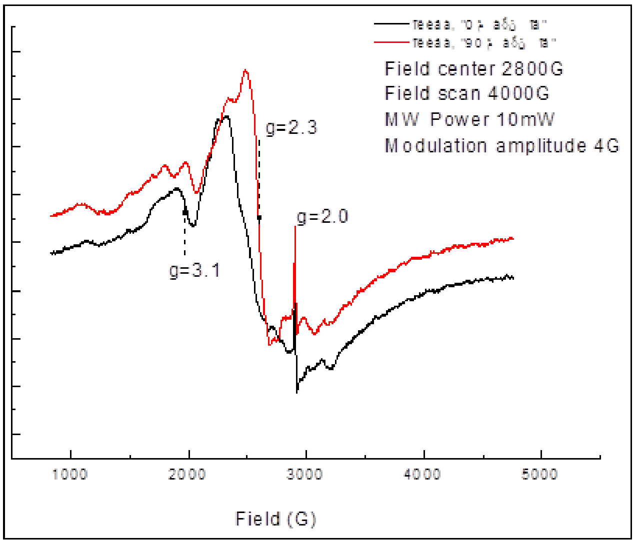


Fig 3: EPR signals of dried magnolia leaves.

We have studied the temperature dependence of spectra for the identification of obtained signals. It was revealed that these spectra change depending on the temperature (Figure 4).

When the temperature decreases from room temperature to 120-125 K, amplitude of the signal increases rapidly and reaches maximum on T ≈ 120-125 K. During the subsequent decrease of temperature, the amplitude of the signal decreases sharply. When we study the dependence of the width of signal on the temperature, we observe behavior specific to superparamagnetic nanoparticles in the temperature range, which we are researching, so at temperature of 120-125 K, the width of the signal is reach the minimum.

The similar lowering of g-factor at low temperatures was observed in magnetite nanoparticles, which was previously placed on the polymer matrix, and explained by the crossing to the situation compatible to spin bottle of the system [9, 11, 12]. With such a low-temperature anomaly, only large particles (greater than 10^{-6} m) have been characterized [13]. The variation behavior of the parameters indicates that two types of particles, which differ in size, may be in the system [14].

The critical temperature for both types of particles is ≈ 125-130 K. It is observed the variation of behavior of g-factor, changes of the intensity character of the signal and the minimization of the width of signal, at this temperature. It is known that during the decrease of temperature the expansion of the EPR signal and the replacement to the smaller magnetic field are characteristic for super paramagnetic nanoparticles [15, 16].

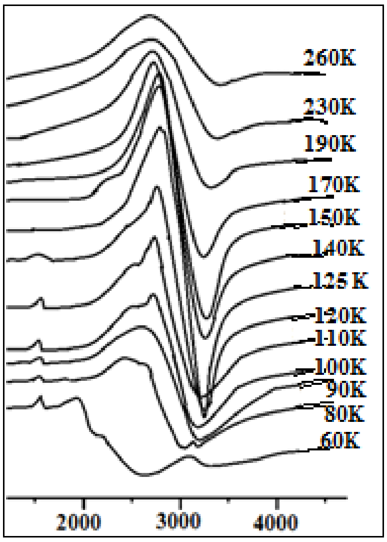


Fig 4: Temperature dependence of magnolia leaves EPR spectra in the range of 60K - 260K

Compatible behavior of EPR signal has observed in the magnetic resonance signals of the ferritin in healthy human tissues also.

In addition, were also analyzed radionuclide and element composition of Lankaran plants and soil samples of this area.

Table 1

Bq/kg	Magnolia-leaf	Magnoli-soil	Lemon-leaf	Lemon -soil
Ra226	<3.8	15.1	<4.9	17.1
Th232(Ra228)	<2.8	17.8	<3.5	21.8
K40	248.6	439.1	178.5	571.3
Co60	<1.9	<0.7	<2.4	<1
Cs134	<1.8	<0.8	<2.3	<1.1
Cs137	<1.9	1.8	<2.4	9.2

Table 2

Elements/ Names of samples	Unit	S	Cl	K	Ca	Ti	Cr	Mn	Fe
Lemon(*Citrus limon*)leaf	ppm	35070	<LOD	102672	259999	<LOD	<LOD	247	1508
Magnolia (*Magnolia*)leaf	ppm	41502	<LOD	37558	77087	<LOD	80	588	852
Feykhoa (*Feijoa*) leaf	ppm	<LOD	5565	76709	24189	<LOD	89	229	913
Magnolia (*Magnolia*)soil	ppm	<LOD	<LOD	26306	29523	5839	165	863	47659
Lemon (*Citrus limon*)soil	ppm	<LOD	<LOD	23042	28890	6589	193	738	56607
Feykhoa (*Feijoa*) soil	ppm	<LOD	<LOD	26305	34335	5635	157	1115	51033

Table 3

Elements/ Names of samples	Unit	Sr	Zr	Mo	Ba	Co	Cu	Zn	As	Rb
Lemon(*Citrus limon*)leaf	ppm	633	60	<LOD	<LOD	<LOD	<LOD	71	<LOD	20
Magnolia (*Magnolia*)leaf	ppm	141	82	83	<LOD	<LOD	<LOD	63	<LOD	22
Feykhoa (*Feijoa*) leaf	ppm	69	65	67	<LOD	<LOD	<LOD	59	<LOD	37
Magnolia (*Magnolia*)soil	ppm	476	101	<LOD	456	<LOD	<LOD	72	<LOD	67
Lemon (*Citrus limon*)soil	ppm	523	87	<LOD	499	<LOD	<LOD	52	<LOD	63
Feykhoa (*Feijoa*) soil	ppm	584	83	<LOD	506	<LOD	<LOD	95	20	64

It was determined that in both of soil and plant samples the quantity of elements K, Ca, Fe, Sr was sufficient. Although S, Cl, Mo elements were observed on the leaves, these elements were not found in soil samples collected from that area. Although Ti, Ba elements are in the soil samples, on plant leaves were not found.

References

1. Yurtaeva SV, Efimov VV, Salnikov VV. EMR signals in biological systems and their informative value for biomedical research. Biophysics of single molecules. Nanobiotechnology, 2015, 339.
2. Tevhide Ozkaya, Muhammet Toprak S, Abdulhadi Baykal, Huseyin Kavas, Yuksel Koseoglu, Bekir Aktas. Synthesis of Fe3O4 nanoparticles at 100^0 C and its magnetic characterization. Journal of Alloys and Compounds, 2009, 18-23.
3. Koseoqlu Y, Aktash B. ESR studies on superparamagnetic Fe3O4 nanoparticles. Phys. stat. sol. 2004; (c)1:12. / www.pss-c.com.
4. Abolfazl Akbarzadeh, Leila Kafshdooz, Zohre Razban, Ali Dastranj Tbrizi, Shadi Rasoulpour, Rovshan Khalilov, Taras Kavetskyy, *et al*. An overview application of silver nanoparticles in inhibition of herpes simplex virus. Artificial Cells, Nanomedicine, and Biotechnology. 2018; 46(2):263-267.
5. Khalilov RI, Nasibova AN, Serezhenkov VA, Ramazanov MA, Kerimov MK, Garibov AA, *et al*. Accumulation of Magnetic Nanoparticles in Plants Grown on Soils of Apsheron Peninsula. Biophysics. 2011; l56(N2):316-322.
6. Rovshan Khalilov I, Aygun Nasibova N, Naglaa Youssef. The use of EPR signals of plants as bioindicative parameters in the study of environmental pollution. // International Journal of Journal of Pharmacy and Pharmaceutical Sciences. 2015; 97:S.1:172-175.
7. Peyman Hassanpour, Yunes Panahi, Abbas Ebrahimi-Kalan, Abolfazl Akbarzadeh, Soodabeh Davaran, Aygun Nasibova V, *et al*. Biomedical applications of aluminium oxide nanoparticles. J. Micro & Nano Letters. 2018; 13(9):1227-1231.
8. Nasibova AN, Khalilov RI. Preliminary studies on generating metal nanoparticles in pomegranates (*Punica Granatum*) under stress. // International Journal of Development Research. 2016; 6(3):7071-7078, March, 2016.
9. Nasibova AN, Fridunbayov İY, Khalilov RI. Interaction of magnetite nanoparticles with plants. European Journal of Biotechnology and Bioscience. 2017; 5(3):14-16.
10. Arash Hasanzadeh, Rovshan Khalilov, Elham Abasi, Siamak Saghfi, Aygun Nasibova, Abolfazl Akbarzadeh. Development of doxorubicin – adsorbed magnetic nanoparticles modified with biocompatible copolymers for targeted drug delivery in lung cancer. Advances in Biology and Earth Sciences. 2017; 2:5-21.
11. Nasibova AN, Fridunbayov IY, Nabiyev NN, Khalilov RI. Influence of UV and GAMMA radiation on paramagnetic properties in fragments of photosystem 2. International Journal of Pharmacy and Pharmaceutical Research. 2016; 7(4):24-32.
12. Noginova N, Weaver T, Giannelis EP, Bourlinos AB, Atsarkin VA, Demidov VV. Observation of multiple quantum transitions in magnetic nanoparticles», Phys. Rev. B 77, 014403, 2008.
13. Olga Sorokina N, Alexander Kovarski L, Marina Lagutina A, Sergey A. Dubrovskii 2and Fridrikh S. Dzheparov. Magnetic Nanoparticles Aggregation in Magnetic Gel Studied by Electron Magnetic Resonance (EMR). Applied sciences, 2012, 342-350.
14. Guskos N, Typek J, Zolnierkiewicz G. // FMR study of magnetic nanoparticles embedded in nonmagnetic matrices. Current Topics in Biophysics. 2010; 33(suppl A):77-80.
15. Robert Usselman J, Klem MT, Allen M, Eric Walter D, Gilmore K, Douglas T. Singel // Electron magnetic resonance of iron oxide nanoparticles mineralized in protein cages. Journal of applied physics. 2005; N97:10.
16. Gubin SP, Yu A, Koksharov GB, Khomutov G. Yurkov. Magnetic nanoparticles: preparation, structure and properties. Russian Chemical Reviews. 2005; 74(6):489-520.