EPR-spectroscopy of dry aerosols

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The method of dry aerosols sampling with the use of powder substrate is suggested, and the results of experimental test of the method efficiency are presented. Methodical aspects of dry aerosols study by EPR-spectroscopy are discussed.

Introduction

The geochemical estimate of the environment is based on the data, obtained from ecological-geochemical investigations, the main direction of which is tracing the migration of heavy metals. In the investigation of the latter a prominent place is occupied by aerosols, participating in a wide range of processes, connected with the environmental monitoring.[1,2] It has been noted in this connection that the share of contaminants precipitating with dry aerosols is by 15–20% greater than with wet aerosols,[3] and the total content in atmospheric precipitation is 10–20%, that makes important the study of dry aerosol composition in the ground air. At the same time, dry aerosols contain 100% of particles, being a serious hazard in terms of hygiene. The sizes d of these particles are less than 0.3 μm. Therefore, they are not caught by filters of the controlling detectors and by dust-collecting devices.[5] This requires the methods of analytical control and monitoring of air pollution by dry aerosols to be improved.

The goal of this work is to demonstrate the potentiality of a new method of collection of dry aerosols, as well as methodical aspects of studying the aerosol composition by the electron paramagnetic resonance (EPR-spectroscopy) method.

The method

The method is based on the process of passive precipitation of particles from air flows, which allows identification of particles, precipitated under action of the turbulent diffusion (d = 0.1–10.0 μm) for the subsequent chemical analysis. The interaction of such particles both with each other in the air flow and with the substrate surface at precipitation is determined by the van der Waals forces. It is known that near the surface the air flow velocity varies greatly and a so-called boundary layer is formed. Because air is transparent for solar radiation, its temperature in the atmospheric boundary layer depends on heating of the particles, and, consequently, its magnitude depends on the solar radiation intensity. The more is the number of particles in the atmospheric boundary layer and the higher is its temperature, the more active is the molecular mixing. While heating, particles transfer a part of their kinetic energy to air molecules. The number of particle collisions increases, they begin to contact with the surface and are caught by it. This phenomenon, called adhesion, refers to the category of surface phenomena, which occur at the boundary of adjoining phases.[6] The adhesion is always preceded by the adsorption, accompanied by a change of the matter concentration at the interphase boundary. The process goes at different interphase surfaces, on which any matters can be adsorbed. In this case the dynamic adsorption equilibrium is rapidly established, i.e., the equilibrium distribution of matter between the boundary layer and adjacent phases.[7]

If the forces of interaction between two particles are stronger than between a particle and the surface, then in the boundary layer the particle enlargement (autohesion) takes place.[6] The gravity forces begin to affect the particle precipitation in the atmospheric boundary layer. This process is favored by the fact that at the contact of aerosol particles a liquid layer is formed between them due to the capillary condensation, i.e., vapor condensation to the liquid at the pressure, which is less than the pressure of the saturated vapor.

A necessary condition for formation of a capillary layer is the hydrophility of contacting surfaces. The manifestation of the capillarity in the particle contact zone can be observed already at a relative air humidity higher 50%, and at a humidity of 70% just the capillary forces determine the magnitude of the particle adhesion. The adhesion particle interaction and the wettability of their surfaces are realized at the cost of molecular – surface processes.

Besides, it is well-known that most of solid surfaces have areas of different activity, and the traditional surface reactions on solids proceed mainly at the localized active adsorption areas, which occupy different parts of the surface of different materials. Consequently, the surface of mineral grain relative to dry aerosol precipitation is chemically inhomogeneous: the area, which is active for some matter, is not surely active for another. The presence of two or more solid matters on the surface intensifies its chemical inhomogeneity, greatly increasing its adsorption characteristics. Therefore, as a depositing substrate for collecting dry aerosols, the chemically inert finely dispersed mineral powders were used, for which the presence of large areas of active surface is typical. In this case, the natural passive precipitation of dry aerosols of necessary dimensions on the substrate surface is gained.

Description of the device

Figure 1 shows the device for collecting dry aerosols. The device consists of the container *6* made of the material having a high heat capacity and being chemically inert to the atmospheric components. The device can be designed in the form of a hollow cylinder, frustum of a cone, or a polyhedron with open bottom part of the container.

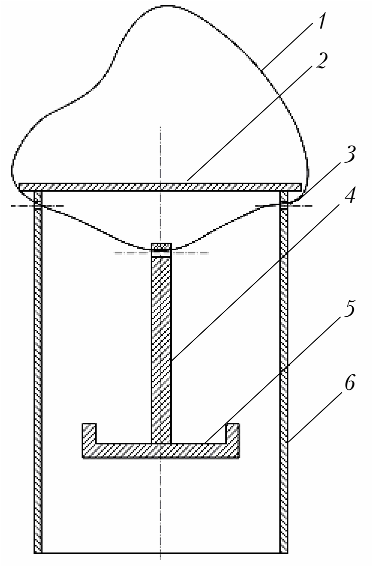

Fig. 1. The device for collecting dry aerosols.

The container can be made, for example, of the plastic, or wood, or composite material (carbon plastic, metal plastic, glass reinforced plastic). The top part of the container is closed by a dead-end cover (*2*) with a ledge-visor, in the periphery of which the holes are made (*3*) for generation of convective and turbulent air flows inside the container. A round cradle (*5*) is placed inside the container, attached immovably to the lower part of the rod (*4*).

The heat capacity of the cradle material should be lower than of the container material in order to create the temperature gradient. A thin layer of chemically inert finely dispersed powder substrate, which has a high specific active surface, is placed on the cradle. The container and the rod with the cradle are attached to the fixture (*1*) for the device fixation in the hanging position. The fixture is made as a loop of nylon filament, which allows one to change the powder substrate at the site.

The device works in the following way. Under the impact of solar radiation and due to difference in heat capacities between the cradle and container materials, there appears the temperature gradient inside the device. The air flow with aerosol particles enters the device through the open bottom part of the container. The presence of the temperature gradient and holes (perforation) in the upper part of the container create inside the device conditions for generation of convective and turbulent air flows.

Experiment

Sampling of dry aerosols was performed at a site, located in the suburban green zone, by the following procedure. Nine devices were hung at the site area, on trees and bushes at a height of 0.6–2.0 m.

As a substrate, chemically inert finely dispersed powders of Al_2O_3, MgO, $CaCO_3$ (all powders of X4 mark) were used. The powder (300–500 mg) was poured by thin layer on the cradle. The exposure time was 18 days.

EPR-spectroscopy

Spectra of EPR were studied in the “Spectroscopic Investigation Centre” of the Institute of Geology, Komi SC UB RAS using a serial radio-spectrometer SE/X-2547 (Radio/PAN, Poland) in the X-frequency range with HF modulation of 100 kHz at the room temperature of samples. The rectangular cavity RX102 with TE_{102} mode was used. Pairs of samples (Al_2O_3, MgO, $CaCO_3$) were studied at a triple repetition. Every pair included a standard (control) and exhibited samples of one sorbent. When recording the spectra, the weight of samples was about 200 mg. Powders were placed in a quartz test tube. The test tube signals were eliminated from the obtained spectra by the mathematical processing of spectra.

Results and discussion

Figure 2*a* shows the spectra of standard and exhibited Al_2O_3 powders. The spectrum of standard sample (Fig. 2*a*, *1*) comprises the broadened components, which are identified with lines of ions Fe^{3+} localized in the ions structural positions of aluminum oxide, substituting aluminum, and in amorphous parts of the matter (*g*-factor of curve is 4.27).[8]

Besides, in the spectral range at magnetic field value about 300 mT there is a wide band, which is produced by small quantities of oxides and/or iron hydroxide impurities. In the EPR spectrum of the exhibited sample (Fig. 2*a*, curve *2*) lines of impurity iron ions in the lattice of aluminum oxide remained unchanged, and the wide-band intensity with $g = 2.1$ somewhat grew, which is indicative of adsorption by the surface of aluminum oxide of aerosol particles of iron oxides. Note that the aluminum oxide refers to a very stable chemical compound: the exposition did not disturb the material structure.

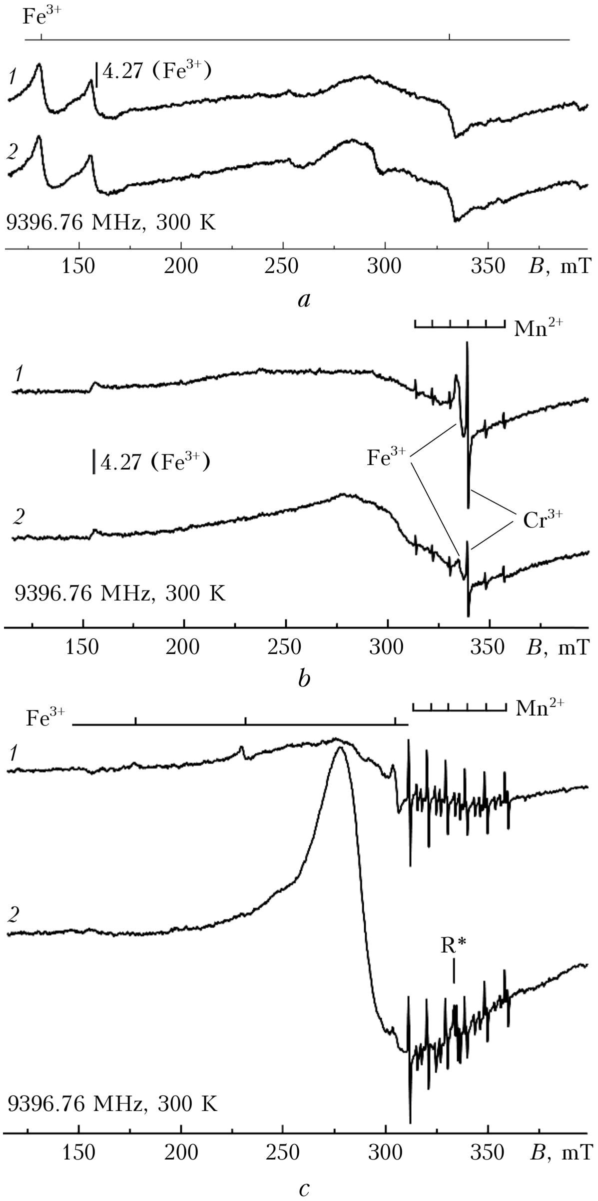

Fig. 2. EPR spectra of standard (*1*) and exhibited (*2*) samples for sorbents: Al_2O_3 (*a*), MgO (*b*), $CaCO_3$ (*c*). *B*, mT (polarizing magnetic field in millitesla).

Figure 2*b* shows the spectrum of standard and exhibited powder of MgO. In the spectrum of standard sample (Fig. 2*b*, curve *1*) a sextet of narrow peaks and one narrow line are detected, connected with Mn^{2+} and Cr^{3+} ions in the Mg positions, respectively.[9] Signals from Fe^{3+} ions, localized in the substituting structural positions of a magnesium oxide ($g = 2$), aluminum oxide, as well as in amorphous parts of material ($g = 4.27$) are also detected. A wide component of impurity oxy-hydroxide phases of iron is present as well. In the exhibited samples (Fig. 2*b*, curve *2*), a decrease of intensity of oxonium ion lines, the impurity ions of manganese and especially chromium is fixed. These variations can be connected with hydration of the surface of MgO grains. The intensity increase of the wide line is indicative of the presence of adsorption of iron-containing compounds on the material surface.

Note that a given increase of the wide line intensity is irregular. For some exhibited samples the EPR signal with a very intense wide band was detected, but in other cases the growth of the signal is insignificant. Possibly, this was connected with irregular aerosol particle precipitation on the substrate surface due to the turbulent diffusion.

Figure 2*c* shows spectra of standard and exhibited $CaCO_3$ powder. In the spectrum of the standard sample (Fig. 2*c*, curve *1*) two systems of lines are detected connected with the presence in the structure of material of calcium substituting Fe^{3+} and Mn^{2+} [Ref. 10]. A low-intensity wide component of impurity iron phases is also noticed in the spectrum. In the exhibited sample (Fig. 2*c*, curve *2*) the Mn^{2+} signal intensity remained constant, and lines of structural ions of iron lowered in the intensity; however an intensive asymmetric line of adsorbed phases of iron oxides appeared. The decrease of line intensities of ions of structural iron as differentiated from lines of manganese ions can be explained by the fact that iron ions are localized in the surface layers of $CaCO_3$ grains and, therefore, their paramagnetism to a greater extent depends on the contamination of grain surface by magnetic particles. These changes were recorded in the EPR spectra of all exhibited $CaCO_3$ samples. A good reproducibility of the band of finely dispersed iron oxide phases offers possibilities of indication of iron-containing compounds, which are constituents of dry aerosols at aerotechnogenic contamination of the surface on the base of EPR carbonate sorbents.

A peculiarity of the exhibited sample of calcium carbonate ($CaCO_3$) (Fig. 2*c*, curve *2*), when comparing it with the standard one (Fig. 2*c*, curve *1*), is the emergence in the spectrum of EPR of a polycomponent EPR signal in the region of free radicals (Fig. 3, curve *2*). Only the central part of the spectrum in the form of a pair of peaks with $g = 2.0059$ and 2.0035 is recorded distinctly.

After computer processing of spectra, there appeared additional components located almost symmetrically relative to the central pair of lines (Fig. 3, curve *3*). Because of the low signal intensity, it is difficult to identify the radical or their composition defining a given spectrum. Assumingly, the radical is organic. The distinguished polycomponent spectrum does not correspond to the case of rapid chaotic rotation of molecules in gas and liquid phases ("isotropic spectrum"), but has evident traces of orientational broadening of lines into "anisotropic" bands. Hence, the paramagnetic molecules, responsible for the spectrum, form a coupling with ions of the carbonate matrix in such a way that their space orientation is fixed or only strongly hindered anisotropic rotation is allowed.

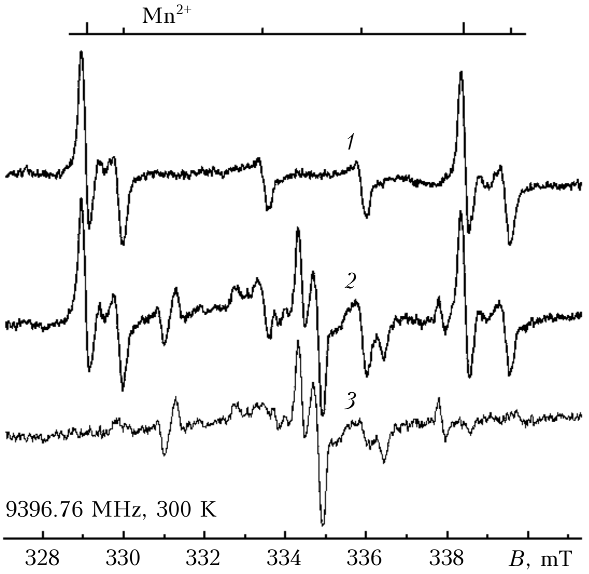

Fig. 3. EPR spectrum of organic radicals on the $CaCO_3$ surface: standard sample (*1*); exhibited sample (*2*); a focused signal of organic radicals in the exhibited sample (*3*). *B*, mT (polarizing magnetic field in millitesla).

Evidently, the appearance of a given spectrum is conditioned by a free-radical oxidation of organic material, photo-induced by the solar radiation, and coupling of reaction products with ions of substrate surface. Results of investigation of the interaction of organic compounds with the surface of powdered oxides of silicon, aluminum, and magnesium make the basis for this assumption.[11]

Note that the above spectrum was observed steadily in all exhibited samples of the carbonate, but it was not found in any sample of other materials. Among three tested mineral sorbents, just carbonates have a coplanar-compatible structure relative to the organic matter.[12] At the same time, the presence of traces of organic radicals in amounts, detectable by the EPR method, is traditional for natural dispersed carbonates of different origins. Possibly, the photochemical mechanism of fixation of organic molecules on the carbonate is realized under natural conditions as well, therefore, the determined EPR effect can be used in studies of the organic phase of aerosols.

Conclusion

The obtained results allow one to well define the dry aerosol problems solvable by the EPR-spectroscopy method. Thus, the presence of EPR lines of structural impurity ions of metals in the control (not exhibited) samples allows their use as stable inner standards, when comparing the spectral intensities of exhibited samples, studying the atmospheric cycle of migration of heavy metals, and contaminating the surface via aerotechnogenic processes. The EPR spectroscopy enables one to selectively detect both the adsorbed mineral phases and the organic molecules on the surface of substrate grain. Taking the latter into account, the study of the qualitative composition of organic phase of dry aerosols becomes possible.

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