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Abstract

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THE EFFECT OF EXTERNAL IRRADIATION ON THE SORPTION PROPERTIES OF $BaSO_4$

In previous communications ([1], [2]) the authors showed that the sorption capacity of radioactive precipitates of barium sulfate with respect to various dyes depends on the nature of the dye, as well as on the character and intensity of the radiation of the radioactive isotope introduced. It was also noted in ([2]) that prolonged radioactive decay of S^{35} occurring in $BaSO_4$ preparations leads to a decrease in the absorptive capacity of the sorbent. This peculiar phenomenon has now been studied in greater detail with the use of external radiation. Samples of barium sulfate were irradiated with high-energy electrons, after which their sorption of dyes was determined as a function of the dose rate and of the absorbed integral radiation dose. Several experiments were also carried out with $BaSO_4$ preparations irradiated by a proton flux.

Electrons with an energy of 800 keV were obtained by means of an accelerating tube powered by a cascade valve capacitor voltage multiplier at 1.2 MeV. The intensity of the electron beam reaching the barium sulfate sample was monitored by the magnitude of the current absorbed in the exit beryllium window of the accelerating tube; for this purpose an appropriate calibration was performed.

Protons with an energy of 1.5 MeV for irradiation of $BaSO_4$ were obtained on an electrostatic generator at 2.5 MeV*. The work was carried out in a vacuum of 10^{-5}–10^{-6} mm Hg. Despite cooling of the target with water, the preparation heated during the experiment to a temperature of 100–150°. No induced activity was detected in the samples after irradiation with protons.

The procedure of the investigation was as follows. Chemically pure barium sulfate was calcined for 2 hours in vacuum (10^{-3} mm Hg) at 300–350° in a special cylinder made of stainless steel. Then nitrogen was admitted into the vessel containing the dehydrated $BaSO_4$, and its pressure was brought up to 5 atm. The preparations treated in this way were subsequently used for irradiation with both electrons and protons. Electron bombardment was carried out in a special aluminum cuvette with water cooling in a nitrogen atmosphere. Conducting the experiments in a nitrogen atmosphere and saturating the initial $BaSO_4$ preparations with nitrogen excluded the possibility of occlusion by barium sulfate of ozone formed from atmospheric oxygen under the action of accelerated electrons, which could have distorted the results of the experiments.

Intensive water cooling made it possible to conduct experiments at 30–60°. The change in temperature during the experiments was monitored with a copper-constantan thermocouple. The weight of the samples after irradiation with both protons and electrons did not change.

Thirty to forty minutes after irradiation, the $BaSO_4$ samples were transferred into flasks with solutions of the dyes acid orange or methylene blue, shaken for 1 hour, and the magnitude of dye sorption was determined. Flasks with nonirradiated $BaSO_4$ precipitates were shaken simultaneously. The ratio of the solid and liquid phases in the experiments was 0.4 g $BaSO_4$ per 25 ml of acid orange solution and 3 g $BaSO_4$ per 25 ml of methylene blue solution.

* Irradiation of $BaSO_4$ with protons was carried out at the Physical Institute of the Academy of Sciences of the USSR in the laboratory of I. Ya. Barit.

Measurement of the concentration of dyes in solution was carried out on an SF-2M spectrophotometer. Before the measurements, samples of the solution were centrifuged. The error in determining the magnitude of sorption from three or four parallel experiments was 3-4% for acid orange and 5-8% for methylene blue. The initial solutions used had concentrations of 50, 100, 200, 300, and 450 mg/l at pH 5-6 in the case of acid orange, and 25, 50, 100, and 150 mg/l at pH 5-5.5 for methylene blue.

Fig. 1. Sorption of methylene blue by $BaSO_4$ precipitates irradiated with electrons. 1 –unirradiated sample; samples that absorbed radiation doses, eV/g: 2 $-1.3 \cdot 10^{22}$, 3 $-1.3 \cdot 10^{23}$, 4 $-1.3 \cdot 10^{24}$, 5 $-1.3 \cdot 10^{23}$

Fig. 2. Sorption of acid orange by $BaSO_4$ precipitates irradiated with electrons and protons. 1 –unirradiated sample; samples that absorbed doses of electron radiation, eV/g: 2 $-1.3 \cdot 10^{21}$, 3 $-1.3 \cdot 10^{22}$, 4 $-1.3 \cdot 10^{23}$, 5 $-1.3 \cdot 10^{24}$, 6 $-1.3 \cdot 10^{23}$, 7 $-0.4 \cdot 10^{21}$; irradiation was carried out with protons

Figures 1 and 2 show the change in the degree of absorption of methylene blue and acid orange by $BaSO_4$ precipitates as a function of the absorbed integral dose and the radiation dose rate.

Curves 2, 3, 4 in Fig. 1 and 2, 3, 4, 5 in Fig. 2 refer to samples irradiated with electrons for different times (different integral doses) at the same dose rate, equal to $1.3 \cdot 10^{20}$ eV/g • sec. Curve 5 in Fig. 1 and curve 6 in Fig. 2 show the change in sorption of dyes by the $BaSO_4$ precipitate when the dose rate is decreased to $1.3 \cdot 10^{19}$ eV/g • sec. As follows from Figs. 1 and 2 and Table 1, with an increase in the absorbed integral dose of electron radiation, the sorption capacity of barium sulfate samples decreases, independently of the nature of the dye used. This is also evident from Fig. 3.

Table 1

Effect of radiation dose rate on the sorption properties of $BaSO_4$

Type of irradiation	Absorbed dose, eV/g	Dose rate, eV/g · sec	Maximum dye sorption, g/m^2	Dye
Electrons	$1.3 \cdot 10^{23}$	$1.3 \cdot 10^{20}$	22.5	Methylene blue
Electrons	$1.3 \cdot 10^{23}$	$1.3 \cdot 10^{19}$	17.5	Methylene blue
Electrons	$1.3 \cdot 10^{23}$	$1.3 \cdot 10^{20}$	300.0	Acid orange
Electrons	$1.3 \cdot 10^{23}$	$1.3 \cdot 10^{19}$	235.0	Acid orange
Protons	$0.4 \cdot 10^{21}$	$0.5 \cdot 10^{19}$	250.0	Acid orange

It should be noted that, on passing from electron irradiation to proton irradiation, the sorption capacity of $BaSO_4$ with respect to acid orange decreases very sharply (Table 1).

As is seen from the data in Table 1, at the same absorbed dose, less intense irradiation of $BaSO_4$ with electrons of the same energy gives a greater effect of lowering the sorption capacity. Consequently, with prolonged action of the β-particles emitted by sulfur-35 introduced into $BaSO_4^*$, a decrease in the sorption capacity of $BaSO_4^*$ should indeed be observed, although the energy of the β-particles of sulfur-35 is only 162 keV.

It could be supposed that powerful electron and proton irradiation changes the surface area of $BaSO_4$, evidently decreasing it. This could be the cause of the decrease in the degree of sorption of dyes. However, as follows from the data given below, the surface of $BaSO_4$ before and after irradiation remains constant* and, consequently, the decrease in sorption capacity does not depend on this factor.

It remains to suggest that external irradiation, without changing the magnitude of the surface area, reduces the number of active centers, as if "polishing" the surface of $BaSO_4$, and thereby lowers the sorption capacity of the irradiated samples. However, such energetic "smoothing" of the surface may be only one of the reasons lowering the sorption of dyes. Another reason for such a decrease is apparently radiation effects in the sorbent itself, which consist in a disturbance of the normal distribution of electron density in the substance during its irradiation ([3–5]). In particular, an external sign of the radiation effect of electrons and protons on $BaSO_4$ is a change in the color of the irradiated samples: from white it changes to light gray or light brown. This coloration disappeared both in air and in an atmosphere of nitrogen after approximately a week. However, the sorption properties of $BaSO_4$ were not restored. After calcination for 1 hour at 200–250°, the coloration of the preparations disappeared, and the sorption capacity of the irradiated samples increased somewhat, but nevertheless

Fig. 3. Sorption of dyes by $BaSO_4$ precipitates as a function of the absorbed dose of external electron irradiation. 1 —acid orange, 2 —methylene blue.

Figure 1: Fig. 3. Sorption of dyes by $BaSO_4$ precipitates as a function of the absorbed dose of external electron irradiation. 1 —acid orange, 2 —methylene blue.

remained lower than that of the unirradiated ones. The weight of the colored preparations did not change during calcination.

Table 2

Sample	Specific surface area, m^2/g
Unirradiated	7.7
Irradiated with electrons.	7.8
Absorbed dose $1.3 \cdot 10^{22}$ eV/g	
Irradiated with electrons.	7.7
Absorbed dose $1.3 \cdot 10^{24}$ eV/g	
Irradiated with protons.	7.7
Absorbed dose $0.4 \cdot 10^{21}$ eV/g	

Fig. 3. Sorption of dyes by $BaSO_4$ precipitates as a function of the absorbed dose of external electron irradiation. 1 —acid orange, 2 —methylene blue.

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* Measurement of the surface area of $BaSO_4$ precipitates was carried out on a Deryagin apparatus. It was preliminarily shown, by nitrogen sorption, that the $BaSO_4$ used in the experiments had no blind pores (with an accuracy of up to 10%).

Note: Figure translations are in progress. See original paper for figures.

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