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## IR SPECTROSCOPIC STUDY OF THE PHASE COMPOSITION OF BORIC ACID AS A COMPONENT OF GLASS BATCH

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Analytically pure reagent “boric acid,” used in batches for preparing glass, was investigated by IR spectroscopy. It was found that the reagent consisted of three components — meta- and orthoboric acids and glassy boron oxide, water was present in two forms — molecular and in the form of OH groups, and impurities of organic substances and carbon dioxide were not very probable. The orthoboric acid bands at 1450, 1195, 883, 815, and 548  $\text{cm}^{-1}$  were found for the first time and were not indicated in the previously published reference spectrum.

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Borosilicate compositions are widely used in chemical engineering of glass — Pyrex, medical, container, vacuum, optical, artistic, for glass solder, glass fibers and wool, microspheres, burial of radioactive wastes, etc. The molar content of  $\text{B}_2\text{O}_3$  can vary from 0.04 to 40% (RF Patents Nos. 2033978, 2035415, 2036171, and 2036856) [1].

In laboratory practice, boric acid is frequently used for adding  $\text{B}_2\text{O}_3$  to glass-forming compositions. Its normal aggregate state is a finely disperse powder that absorbs water vapors from the atmosphere (caking or clumping of boric acid is well known). Water is retained on the surface of the particles by hydrogen bonds with the OH groups of the acid, which can be represented as  $\text{B}(\text{OH})_3$ . When heated or left in a dry atmosphere for a long time, low vapor pressure is created over its surface and structural fragments of the  $[\text{B}(\text{O})_{4-x}(\text{OH})_x]$  type ( $x = 0-4$ ) are formed due to loss of water. Boron can coordinate from three to four oxygen atoms, so that the formation of two- and three-dimensional structures is probable — planar boroxol rings of  $[\text{BO}_3]$  groups, chains of different length, and networks of  $[\text{BO}_4]$  tetrahedrons. There are intermediate structures formed when these polyhedrons are joined. In the trigonal structure, the boron atom is slightly above the plane formed by three oxygen atoms, i.e.,  $[\text{BO}_3]$  is actually not a two-, but a three-dimensional figure in the form of a strongly distorted tetrahedron [2]. Boron four-coordinated with respect to oxygen can be incorporated in a silicate network, while three-coordinated boron forms its own structure, causing liquation.

The features of the structure of  $\text{B}_2\text{O}_3$  and its compounds complicate interpretation of analytical data, but as physico-

chemical research techniques evolve, these negative phenomena can be surmounted. In 32 of the studies we have on this subject, the IR spectrum was not studied any further than 1857  $\text{cm}^{-1}$  and data up to 3703  $\text{cm}^{-1}$  are only reported in 5 studies.

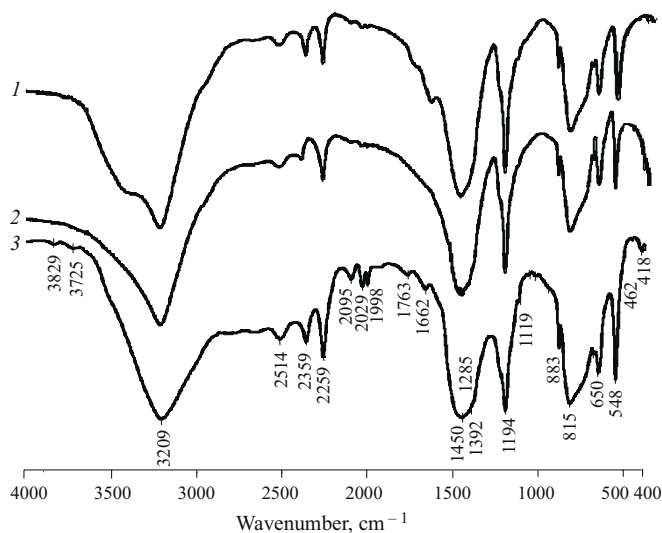
The results of a study of analytically pure boric acid used for synthesis of batches in aqueous medium with the sol-gel method for fabrication of microspheres (RF Patent Nos. 2033978, 2036171, and 2036856) are reported here. The spectra were obtained on a Nexus IR spectrometer in the transmission (TR) and diffuse reflection (DR) modes.

The method of conducting the analysis consisted of the following. A Satrogosm balance with accuracy of  $\pm 0.02$  mg was used to sample 0.001 g of substance, which was mixed with potassium bromide KBr; 0.38 g of the mixture was ground for 1 min in a vibrator with steel ShKh15 grinding bodies (GOST 801–78, balls). The mixture obtained was placed in a mold with a 13-mm inner diameter and held under 10-tons pressure for 5 min. The TR spectra were recorded in the 4000–400  $\text{cm}^{-1}$  region with resolution of 4–8  $\text{cm}^{-1}$ . The reference spectra (background) were made with no sample in the cuvette compartment of the spectrometer and with previously molded KBr pellets. Molding was not used for taking the spectrum in the DR mode; the prepared mixture was placed in a sample holder and then in the DR module, and the IR spectrum of KBr powder was recorded as background. The analysis of the spectra recorded in the different modes allowed most completely detecting the bands in the Fourier-transform IR spectrum (FIRS) of reagent “boric acid”.

The spectra contain bands with sharp (s.) peaks and broad (b.) peaks; some of the bands are represented by shoulders (sh.). Bands whose relative intensity was less than 10%

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**Fig. 1.** Transmission (1, 2) and diffuse reflection (3) spectra. Background: 1) air; 2, 3) KBr.

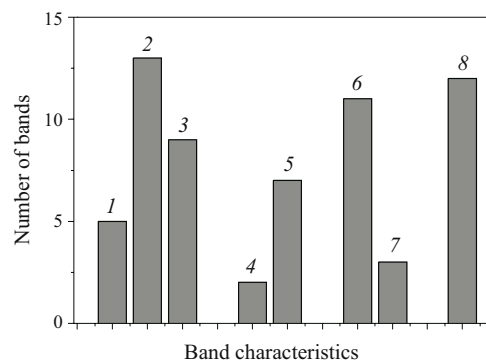
of  $I_{\max}$  (100%) were considered very weak (v.w.), 10–15% of  $I_{\max}$  were considered weak (w.), 15–35% were considered of medium intensity (m.), 80% were considered strong (st.), and over 80% were considered very strong (v.s.). The FIRS (PR and DR) of the sample of the acid and the diagram demonstrating their individual features are shown in Figs. 1 and 2 and in Tables 1 and 2. In the DR spectrum, the bands at 3209 and 1450  $\text{cm}^{-1}$  were most intense. The intensity was set at 100% ( $I_{\max}$ ) and the relative intensities of each band were then calculated:

$$I_p = \frac{h_p}{h_{\max}} I_{\max},$$

where  $h_p$  is the peak height, mm (for convenience, the up-down direction was selected as positive).

We will subsequently basically examine the DR spectrum. The 3829–1300  $\text{cm}^{-1}$  region in which many bands are broadened, except for the bands at 2359, 2259, 2029, and 1998  $\text{cm}^{-1}$ , is the most complex. The broadening could be due to the presence of different forms of water, which is characteristic of boric acid or contaminants that absorb IR radiation in a close or the same range as the basic substance. One-third of the bands (33%) is poorly resolved and is represented by shoulders. This can be attributed to overlapping of the vibrations of different atom groups in the sample of boric acid investigated.

The IR spectrum (IRS) of boric acid in the 1460–450  $\text{cm}^{-1}$  region is reported in [3]; the bands were classified as described above (see Table 2). Since the short-wave region was not investigated, the 1453–415  $\text{cm}^{-1}$  region was separated in the FIRS for comparative analysis and the line spectrograms were constructed (Fig. 3); they were very similar. To be able to correctly compare the IRS [3] and FIRS of the investigated sample of acid obtained 30 years apart on dif-



**Fig. 2.** Band distribution in spectrum 3 shown in Fig. 1 by individual qualitative traits. Peak: 1) strong sharp; 2) strong; 3) medium; 4) weak; 5) very weak; 6) sharp; 7) broad; 8) shoulder.

ferent generations of instruments [3] and relative to the isolated part of the FIRS of the experimental sample of acid, the line spectrograms (Fig. 3) were plotted and brought to the same size by conversion with the equation

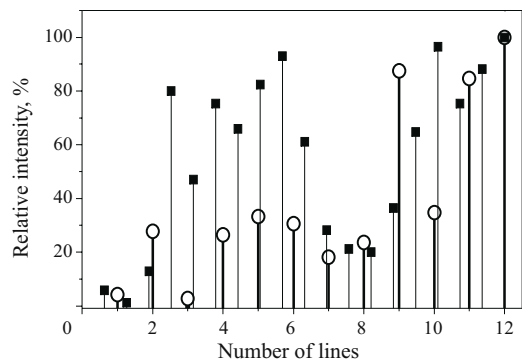
$$N_{\text{re}} = N_{\text{in}} \frac{12}{19},$$

where  $N_{\text{re}}$  is the number of bands reported for the isolated part of the FIRS;  $N_{\text{in}}$  is the initial number of bands there,  $N_{\text{in}} = 19$  bands (see Figs. 2 and 3); 12 is the number of bands in the IRS [3].

The line spectrograms satisfactorily matched with respect to the position of the lines but differed with respect to

**TABLE 1**

Position in spectrum, $\text{cm}^{-1}$	Peak height, mm	Relative intensity, %	Position in spectrum, $\text{cm}^{-1}$	Peak height, mm	Relative intensity, %
418 v.w.	2.5	5.9	1392 v.s., sh.	41.5	98.0
462 v.w.	0.5	1.2	1450 v.s., b., sh.	42.5	100.0
508 v.w.,	5.5	12.9	1577 st., b., sh.	16.0	37.6
548 st., s.	34.0	80.0	1662 m., b.	12.0	28.2
623 st., sh.	20.0	47.1	1763 m., b.	7.5	17.6
650 st., s.	32.0	75.3	1927 m., b., sh.	6.5	15.3
676 st., s.	28.0	65.9	1998 m., s.	11.0	25.9
746 st., b., sh.	35.0	82.3	2029 m., s.	11.0	25.9
815 v.s.	39.5	92.9	2095 m., s.	9.5	22.3
883 st., s.	26.0	61.2	2259 st., s.	28.0	65.9
938 m., b., sh.	12.0	28.2	2359 st., s.	24.5	57.6
1015 m., b.	9.0	21.2	2514 st., b.	23.5	55.3
1062 m., b.	8.5	20.0	2677 w., b.	22.0	51.8
1119 m., s.	15.5	36.5	3209 v.s., b.	42.5	100.0
1177 st., sh.	27.5	64.7	3500 w., b., sh.	14.5	34.1
1195 v.s., s.	41.0	96.5	3614 v.w., b., sh.	4.0	9.4
1230 st., sh.	32.0	75.3	3725 v.w., b.	2.0	4.7
1285 v.s., sh.	37.5	88.2	3829 v.w., b.	1.0	2.4



**Fig. 3.** Line spectrograms of boric acid: ○) data from [3]; ■) relative to the isolated region of the spectrum of the investigated reagent.

the intensity (the first number in the parentheses refers to the IRS in [3] and the second to the FIRS,  $\text{cm}^{-1}$ ): 1 (450 – 462), 2 (550 – 548), 4 (650 – 650), 5 (829 – 815), 6 (890 – 883), 7 (1018 – 1015), 8 (1118 – 1119), 9 (1200 – 1195), 10 (1254 – 1230), 11 (1409 – 1392); the last was detected in the 1450 – 1300  $\text{cm}^{-1}$  region in the FIRS in determining the structure of the spectrum with the Gauss method), 12 (1460 – 1450). The finer structure of the FIRS was established due to the high sensitivity of the Fourier IR spectrometer. The difference in the number of bonds of strong and medium intensities is most probably due to the quality of the samples — we used analytically pure boric acid, while the reagent in [3] was perhaps less pure. In comparison to the IRS, the shift of the bands in the isolated region of the FIRS was basically to the long-wave region. This could indicate the presence of a contaminant.

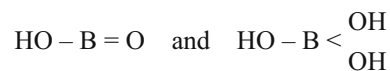
Taking the spectrum of the study in [3] as reference, we note that the bands at 547, 650, 883, 1015, 1119, 1195, 1392, and 1450  $\text{cm}^{-1}$  in the FIRS belong to boric acid  $\text{H}_3\text{BO}_3$ . In [3], the band at 418  $\text{cm}^{-1}$  belongs to deformation vibrations of the B – O bond in the B – O – B boron–oxygen bridge (550 – 400  $\text{cm}^{-1}$ ), but in [4], the band at 415  $\text{cm}^{-1}$  close to it, like the bands at 461, 462, and 477  $\text{cm}^{-1}$ , belong to  $\text{B}_3\text{O}_3(\text{OH})_3$  in the structure of metaboric acid of the ortho-

rhombic system. The band at 477  $\text{cm}^{-1}$  is assigned in [5] to  $\text{B}_2\text{O}_3$ . Since the band in the FIRS at 418  $\text{cm}^{-1}$ , which appeared when KBr was used as the background substance, is very weak, we hypothesized that metaboric acid or boric oxide impurity was present in the sample of reagent “boric acid.”

The band at 548  $\text{cm}^{-1}$  — the basic band in the 600 – 418  $\text{cm}^{-1}$  region — belongs to  $\text{H}_3\text{BO}_3$  [3, 6]. The band of medium intensity at 631  $\text{cm}^{-1}$ , represented by a shoulder near the well-resolved band of boric acid at 650  $\text{cm}^{-1}$  [3], is due to deformation vibrations of the atoms in the B – O bond. The slight broadening indicates the presence of water, but not molecular water, but water in the form of structure-forming OH groups. Bands characteristic of molecular water are located in another region of the FIRS.

The band at 676  $\text{cm}^{-1}$  in [7] is assigned to vibrations  $\nu_4$  of  $[\text{BO}_3]^{3-}$  structural group [7], B – O – B bridge [8], or to vibrations of the atoms that form  $[\text{B}(\text{O}, \text{OH})_4]$  tetrahedrons [6]. A sharp peak of medium intensity within a complex wide band 940 – 650  $\text{cm}^{-1}$  (see Fig. 1 and Table 1) can't be attributed to the additive and thus the band at 676  $\text{cm}^{-1}$  is to be attributed to  $\text{H}_3\text{BO}_3$ .

The band at 746  $\text{cm}^{-1}$  in [6] is assigned to  $\nu_4$  vibrations of atoms in B – O bonds, but Parsons [4] assigns it to the structure-forming  $\text{B}_3^{10}\text{O}_3(\text{OH})_3$  group in metaboric acid  $\text{HBO}_2$  (see Fig. 1). The broad band indicates the presence of water, perhaps in the form of OH groups. The same also applies to the next band at 815  $\text{cm}^{-1}$ , and both bands form a common contour. According to Raman's data, the band at  $819 \pm 5 \text{ cm}^{-1}$  (in the absence of the original source, we cite [4]) belongs to metaboric acid, although the close band at 829  $\text{cm}^{-1}$  is assigned to orthoboric acid  $\text{H}_3\text{BO}_3$  in [3]. The structural formulas of both acids



contain a common element,  $[\text{HO} - \text{B}]^{2-}$ , vibrations of its atoms could cause the closeness of these bands in the spectrum, and the important width of the peak could be due to the OH groups of the acids and to adsorbed molecular water. In the FIRS, the band at 1194  $\text{cm}^{-1}$  was probably caused by vibrations of atoms in the – O – B < bond in the structure of orthoboric acid [9]. For this reason, the strong band at 815  $\text{cm}^{-1}$  should be assigned to the spectrum of  $\text{H}_3\text{BO}_3$  containing three times as many OH groups than metaboric acid, which could be an impurity in view of the classification of the substance that we used. The poorly resolved, very weak band at 938  $\text{cm}^{-1}$ , represented by a shoulder, indicates the presence of an impurity; this is probably metaboric acid [4].

The weak bands at 1062 – 1015  $\text{cm}^{-1}$  [6 – 10] indicate formation of structure-forming  $[\text{BO}_4]$  groups; they are perhaps glassy  $\text{B}_2\text{O}_3$  impurity that appears in heat treatment of boric acid in the process cycle of manufacturing the reagent.

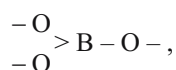
**TABLE 2**

Position in spectrum, $\text{cm}^{-1}$	Peak height, mm	Relative intensity, %	Position in spectrum, $\text{cm}^{-1}$	Peak height, mm	Relative intensity, %
450 v.w., b.*	1.5	4.2	1018 v.w., b.*	6.5	18.1
550 st., s.	10.0	27.8	1118 w., b.*	8.5	23.6
576 v.w., b.*	1.0	2.8	1200 v.s., s.	31.5	87.5
650 m., b.	9.5	26.4	1254 st., b., sh.*	12.5	34.7
829 st., b.	12.0	33.3	1409 v.s., sh.*	30.5	84.7
890 m., s.	11.0	30.6	1460 v.s., b.	36.0	100.0

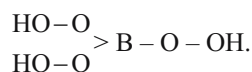
\* We determined the position of the bands, and the remainder are from the data in [3].

The shoulder at  $1230\text{ cm}^{-1}$  could be caused by  $-\text{B(III)}-\text{O}-\text{V(IV)}-$  bond vibrations (III, IV — coordination numbers of boron with respect to oxygen) [9] or assigned [3] to the  $[\text{BO}_3]$  structural motif, including formation of double  $[\text{B}_{3/2}]$  fragments. Together with the band at  $1195\text{ cm}^{-1}$ , it forms a complex contour in the  $1300-1000\text{ cm}^{-1}$  region, like the bands at  $1200$  and  $1254\text{ cm}^{-1}$  in the IRS [10] (see Figs. 1–3 and Tables 1 and 2). In addition, the line spectrograms of both spectra coincided in the examined region — lines 9, 10. For this reason, the band at  $1230\text{ cm}^{-1}$  in the FIRS should be considered a band that belongs to the spectrum of boric acid, although the presence of glassy  $\text{B}_2\text{O}_3$  or  $\text{HBO}_2$  impurity is not excluded.

The very strong band at  $1392\text{ cm}^{-1}$ , represented by a shoulder in the contour of the also very strong and very broad band in the  $1800-1250\text{ cm}^{-1}$  region could be caused [6–10] by vibrations of the atoms in the  $\text{B(III)}-\text{O}^-$  bond in structure-forming  $[\text{BO}_3]$  or  $\text{B}_3^{\text{I}}\text{O}_3(\text{OH})_3$  groups [4]. The last substance, which contains the trigonal fragment



can be represented as



As a consequence, trigonal coordination of boron with respect to oxygen occurs, but it is difficult to unambiguously say this in the oxide or metaboric acid, since impurities of both substances are equally probable.

The bands at  $1625-1709\text{ cm}^{-1}$  (see Fig. 1, spectrum 1) and  $1569-1662\text{ cm}^{-1}$  (see Fig. 1, spectrum 3)<sup>2</sup> indicate the presence of molecular water, since they are positioned in the region of its deformation vibrations [5, 6]. Water could be adsorbed from the atmosphere on particles of boric acid powder. To confirm this hypothesis, we will use the method in [5] and determine the ratios of the frequencies of the bands forming the contour in this region:

$$\begin{aligned} 1709 : 1662 &= 1.0283; & 1662 : 1625 &= 1.0228; \\ 1625 : 1569 &= 1.0359. \end{aligned}$$

Let us simplify the data obtained by selecting the largest and determining the ratio of each result to the largest:

$$\begin{aligned} 1.0283 : 1.0359 &= 0.99; & 1.0228 : 1.0359 &= 0.99; \\ 1.0359 : 1.0359 &= 1. \end{aligned}$$

The equality of the ratios indicates the same type of symmetry in all three cases, i.e., all three bands belong to the same form of water.

The bands at  $1763$ ,  $1927$ ,  $1998$ ,  $2029$ ,  $2095$ ,  $2259$ , and  $2359\text{ cm}^{-1}$  could be caused by stretching vibrations of atoms

in the  $\text{C}-\text{O}$  bond [7] of gaseous  $\text{CO}_2$  sorbed in the powder analyzed. However, there are also bands of  $\text{B}_2\text{O}_3$  in the same region [6], i.e., the complex contour of this part of the spectrum is most probably the result of superposition of the bands of both substances, although no other  $\text{CO}_2$  bands were established.

Stretching vibrations of different forms of water appear in the  $3840-2400\text{ cm}^{-1}$  region of the spectrum. We will use the method in [5] to confirm this conclusion:

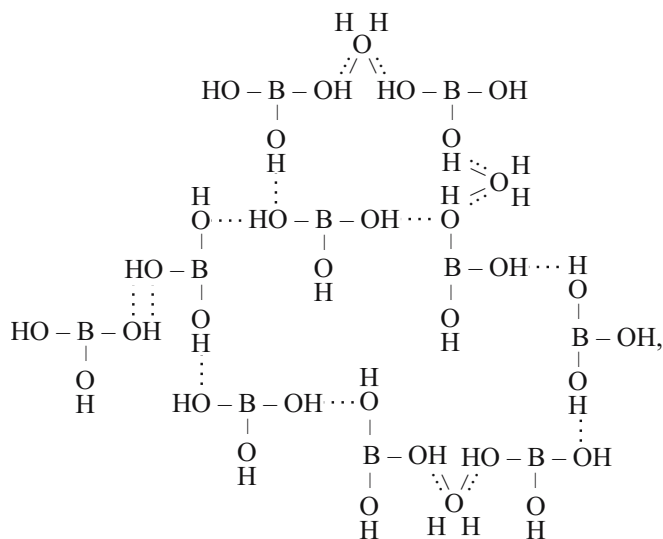
$$\begin{aligned} 3829 : 3725 &= 1.0279; & 3725 : 3615 &= 1.0304; \\ 3615 : 3500 &= 1.0329; \\ 3500 : 3404 &= 1.0282; & 3404 : 3209 &= 1.0608; \\ 3209 : 2514 &= 1.2764. \end{aligned}$$

After simplification, the following expressions were obtained:

$$\begin{aligned} 1.0279 : 1.2764 &= 0.81; & 1.0304 : 1.2764 &= 0.81; \\ 1.0329 : 1.2764 &= 0.81; \\ 1.0282 : 1.2764 &= 0.81; & 1.0608 : 1.2764 &= 0.83; \\ 1.2764 : 1.2764 &= 1. \end{aligned}$$

Water, whose band is located in the long-wave region of the separated FIRS contour, had important differences: the weak band at  $2514\text{ cm}^{-1}$  most likely indicated molecular water impurity adsorbed on particles of the acid from the atmosphere. The next bands, including the band at  $3209\text{ cm}^{-1}$  with the highest peak height, belong to water of similar structural type but different from the preceding type. After combining the results obtained in two groups ( $1.0279-1.0608$  and  $1.2764$  or  $0.81-0.83$  and  $1$ ), it is not difficult to see that there are two forms of water. Let us explain this graphically.

#### Diagram of Particles and Structure of Boric Acid



where  $\dots$  is a hydrogen bond in formation of a bridge between the OH groups of the acid;  $\vdots\vdots$  are bonds formed in adsorption of atmospheric water on an acid particle.

<sup>2</sup> The bands at  $1709$ ,  $1625$ ,  $3615$ ,  $3500$ , and  $3404\text{ cm}^{-1}$  appeared in determining the regions of the spectrum by the Gauss method.

Closely positioned molecules of boric acid associate due to the formation of “bridge” hydrogen bonds between neighboring OH groups. Some of the OH groups remain in the free state, do not participate in “bridge” formation, are directed inside the powder particles, and do not react with atmospheric water. Other “free” OH groups are directed to the outside and are potentially sites for adsorption of molecular water from the atmosphere. Since the normal aggregate state of boric acid is a solid powder, the amount of adsorbed water cannot be greater than the amount of “intrinsic” structurally bound water in the form of OH groups; otherwise, there would be no solid particles but a solution of the acid. This is why a broad band consisting of bands of very strong, strong, and medium intensity is present in the region of stretching vibrations (high-frequency region of the IRS and FIRS) of boric acid, and the broad band of deformation vibrations of water is well expressed. Molecular water, as an impurity from the atmosphere, is represented by weak and very weak bands.

Analytically pure reagent “boric acid” is thus a mixture of several substances: boric (orthoboric) acid, metaboric acid, and glassy boron oxide. During storage of the reagent in air, adsorption of organic impurities and carbon dioxide is not very probable.

The bands at 1450, 1195, 883, 815, and 548  $\text{cm}^{-1}$ , absent in the spectrum in [3] but established in our study, belong to the spectrum of orthoboric acid.

Reagent “boric acid” contains two forms of water: molecular, as an impurity from the atmosphere, and in the form

of structure-forming OH groups — bridge and “free” — on the surface and inside the particles of the substance.

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