Analysis of surface layers of container colourless glass.

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The aim of undertaken investigations was to study the regularity of surface layers structure forming of container from colourless glass.

The experiments were carried out with bottles and jars of different capacity, manufactured in different days. The stability of dissolution rate of jars and bottles surface layers was investigated at a depth of 10 μm in dependence of glass layer thickness, dissolved in one etching. The section etching by the HF solution and lighted microscopy were applied to analyze the container glass layers structure, the microhardness was also measured.

Key words:

bottle, jar, container glass, section etching, dissolution rate, surface layer, structure.

1. Introduction

The stability of chemical and some physical properties of glass depend on the stability of composition and the structure of its surface layers. Different physico-chemical analysis methods are involved for investigation of glass surface. [1 2 3] The thickness of the analyzed layers consists from one monolayer to some μm. Every method of analysis has its own field of applying and restrictions.

The aim of the undertaken investigations was to study the regularity of surface layers structure forming container from colourless glass.

The section etching with the HF solution is used as the main analysis method of the composition and structure of glass surface layers.[4 5] The essence of the method consists in dissolution glass of one layer at a time and in extract analysis after etching. The section etching method is worked out in the University of Budapest.[6]

The most important advantage of the section etching method by HF solution is the possibility of the thickness range of one analyzed layer in very large limits - from 10 μm to many several dozens of μm, that is not possible by using other methods of analysis.

2. Experimental procedures

The objects of investigation were bottles and jars of different capacity. Jars were manufactured by section machine IS-8-2, bottles - by rotary machine BB-12. Jars and bottles were picked out just after annealing.

The chemical composition of the colourless glass on the first stage of the experiment (mass content in %) – 72.00 SiO_2, 1.97 Al_2O_3, 0.07 Fe_2O_3, 7.07 CaO, 4.79 MgO, 13.68 Na_2O, 0.32 SO_3. At the following experiments the variations SiO_2, Al_2O_3, CaO, MgO and Na_2O in the glass composition did not exceed ± 0,1 %.

Experimental method. Glass samples with area - from 10 to 30 cm^2, were cut from bottles or jars. The samples ends were ground. Before etching the samples were washed with distilled water, dried and weighed. After that, the samples were tied up by polymer fiber and put into a weak solution HF (0,1-1,0 % by mass). The solution volume was not changed in any experiment and consisted 1 litre. In each run of experiments there were etching by three samples at a time. While etching the samples were in stationary position.

After etching the samples were fast washed with water, dried and weighed again. The thickness of dissolved glass surface was defined by the formula:

$$h = \frac{\Delta m \cdot 10}{S\rho}$$

where h - thickness layer, μm;
Δm - mass losses of glass, mg;
S - surface of glass, cm^2;
P - glass density , g/cm^3.

Attention should be paid to that that an error is introduced while calculating rate of glass dissolution and thickness of an etched layer. It is connected with non-precise determination of density of a surface layer which usually differs from density of the bulk. Besides it is considered, that all surface samples are etched with the same rate.

Dissolution rate of the samples is defined from the relation:

$$\upsilon = \frac{\Delta m \cdot 100}{S \cdot \tau}$$

where υ – dissolution rate of the glass, mg/(dm^2 of glass surface · min);
τ- duration of etching, min.

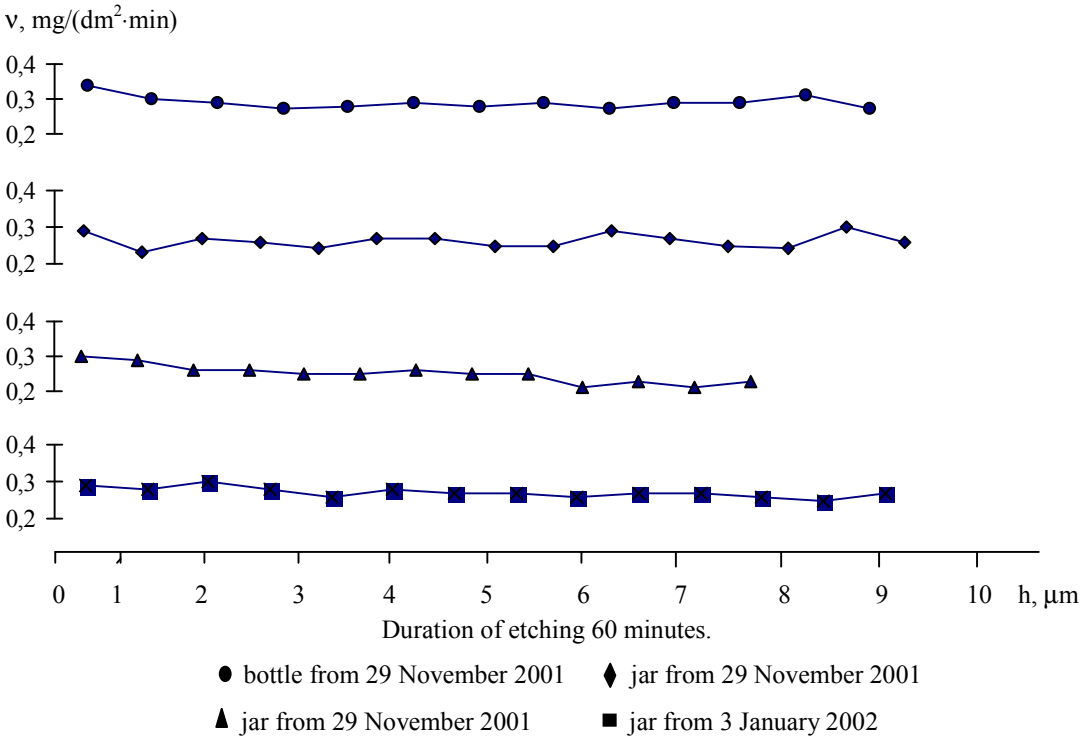
A relative error of experiment did not exceed ± 5 %. By the method of flame photometry concentration of Na^+, K^+, and Ca^{2+} were measured in extracts after etching. A relative error of experiment did not exceed ± 6 %.
For the control of change in the extent of compactness at glass surface layer we measured microhardness with the help of Vickers diamond pyramid. The load on indenter made 0,5 N. Relative error in measuring microhardness did not exceed ± 4 %.The samples were viewed at the microscope with magnification from 100 to 500^x.

3. Results and discussion

Preliminary experiments showed that the dissolution rate of container glasses depends on the temperature of the HF solution and its concentration, the volume of the solution and the time of its action on the samples and hydrodynamics conditions. The temperature of the solution HF (30 ^{0}C), its volume remained unchanged in all experiments.
The thickness of the glass layer dissolved in one etching range from 0,05 to 10 μm. It was achieved with the help of changing of the solution concentration and time of the etching. For the same experiment series the concentration of solution HF and time of the etching did not change.
Stability of the dissolving rate of glass depends heavily on the thickness of layer dissolved in one etching.
On figure 1 graphics are given of the dissolving rate of glass samples, which were an etching of 60 minutes.
The first thing to be paid attention to is that in all experiments the first subsurface layer with the thickness ≈ 1,5 μm dissolves quickly, than the following layers. That is connected as with the feature of the forming structure of subsurface layers, so with its defects. The average dissolution rate both bottles and jars is similar and it has a stable character.
Graphics 2 and 3 on the figure 1 characterize the dissolving rate of jars picked out from the

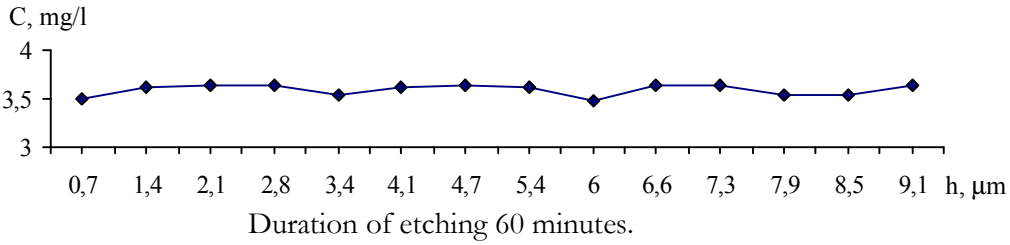
same section of glass forming machine at the same time. They present results we can say, that the structure of glass surface layers, produced in the same conditions, is almost similar. But separate layers in two different jars by compactness of structure differ between themselves (difference of dissolution rate is 10-20 %).
Figure 1 also shows, that the graphics of samples dissolution rate, cut from the jars, produced in different days, are similar.

Figure 1. Dissolution rate of bottles and jars in the HF solution



So, the structure compactness of container colourless glass for separate layer with thickness of 0,7 µm depends little on the method of wares forming and on the manufacturing time.
The dependence of concentration changing of Na^+ in extracts after samples etching, cut from jars is shown in the figure 2.

Figure 2. Concentration of Na+ in jar glass from 3 January 2002



The results show, that between dissolution rate of separate layers and concentration in them do not give an intimate correlation.
In other series of experiments the etching time was 30 minutes. In the figure 3 is given the date etching of jars glass, on figure 4 the concentration of Na^+ for this glass.
Comparison by the results in figure 1 and figure 3 we can say, that glass structures in

separate layers with thickness 0,3 and 0,6 μm are almost alike.

Figure 3. Dissolution rate of jars from 3 January 2002 in the HF solution

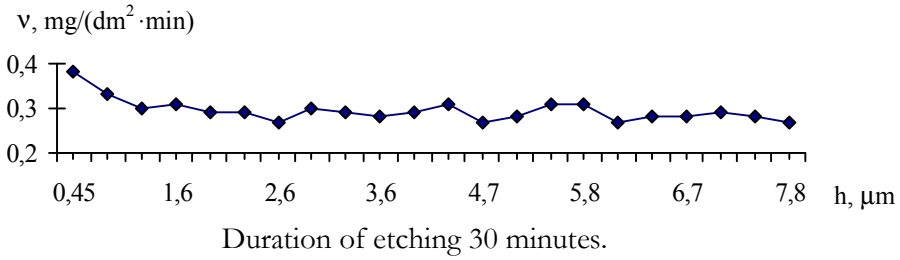
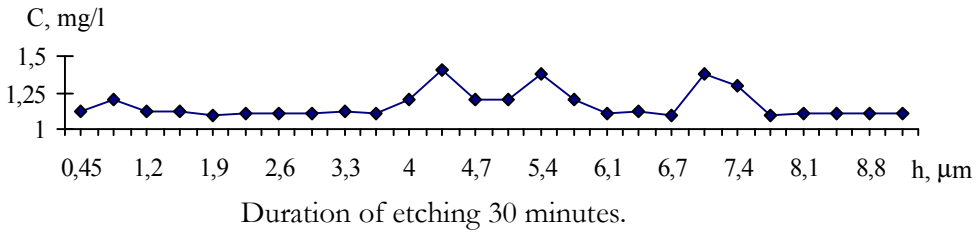
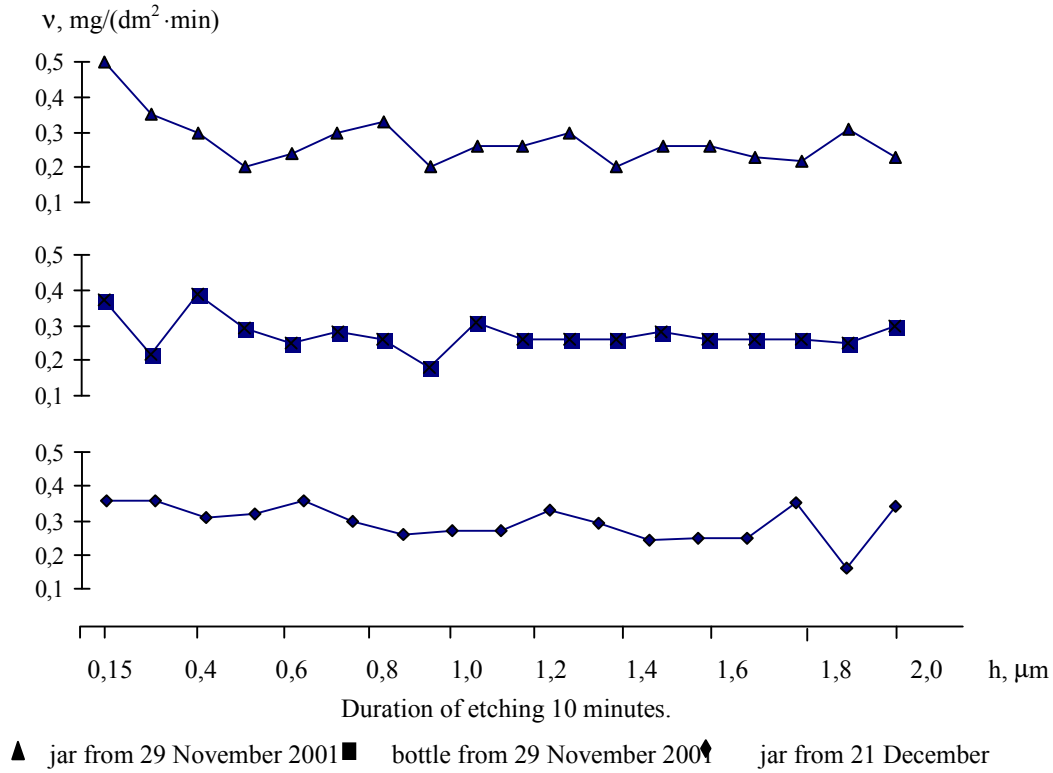


Figure 4. Concentration of Na+ in jar glass from 3 January 2002



We got another results, when the etching time was 10 minutes (figure 5).

Figure 5. Dissolution rate of bottles and jars in the HF solution



Firstly, all graphics of glass etching rate do not have the smooth character. Secondly, there is

no correlation between the graphics . We think, this shows the stratified structure of container glass. Comparing by the results in figure 1 and figure 5 we can conclude: thickness of separate glass layers, that differ between themselves in durability to action the HF, consists less than 0,3 μm.
The correlation between dissolution rate of separate layers and content of Na^+, K^+, Ca^{2+} in them, is not revealed.
Stratificated container glass structure is proved by lighted microscopy. Layers have different form and different size in different places of article.
The microhardness of bottles and jars was at the same level in the undertaken experiments (in the limits of errors measure).
So, knowing the mechanism of the glass layers structure forming we can maintain necessary physico-chemical glassware properties.

4. Conclusion

The method of container glass surface layers dissolution, with the thickness - from 10 nm to 10 μm and more, is worked out.
Stability of the container glass dissolution rate depends heavily on the surface thickness dissolved in one etching.
The experimental data show the presence of stratified structure in container glass.

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[1] Rupertus V., Bange K. in *Proc. Int. Congr. Glass,* 2001, p. 1-10.

[2] Mazzoldi P. in *Proc. XVI ICG,* 1992, p. 197-217.

[3] Hench L. L., Riv. Stn. Spr. Vetro **20**, p. 123-135 (1990).

[4] Sharagov V., Azarenco O., Kubac V., Tsurcan D. in *Proc. of the 5-th ESG Conf.,* 1999, p. C2-39 - C2-45.

[5] Sharagov V., Azarenco O. in *Proc. of the ICG Annual meeting 2000,* 2000, PS. 4.3, p. 1-7.

[6] Csakvari B., Boksay Z. and Bouquet G., Anal. Chim. Acta. **56**, p. 279-284 (1971).