SURFACE DAMAGE OF TWO DIFFERENT WINEGLASSES DURING DISHWASHING PROCESS

VIERA PETRUŠKOVÁ, PETER VRÁBEL, PETER ŠIMURKA, PAVOL ŠAJGALÍK*, MATRIN MARYŠKA**

RONA, j.s.c., 02 061 Lednické Rovne, Slovak Republic
*Institute of Inorganic Chemistry, Slovak Academy of Sciences, Dúbravská cesta 9, 842 36 Bratislava, Slovak Republic
**Department of Glass and Ceramics, Institute of Chemical Technology, Prague, Technická 5, 166 28 Prague, Czech Republic

E-mail: petruskova@rona.sk

White cover (milky effect), iridescence and mechanical scratches on the glass surface are consequences of an automatic dishwashing process. Controlled dishwashing conditions were used to study the iridescence and milky effect created on the glass product. Glass surface, cutting cross-section and depth profile measurement of an unwashed and washed glass product at two different glass types were investigated. Measured areas were analysed using optical microscopy, Scanning Electron Microscopy (SEM), Electron Microprobe Analysis (EDX) and Electron Spectroscopy for Chemical Analysis (ESCA). A presence of foreign components eventually their combinations were detected on the outer side of the washed damaged glass surface. Small concentration changes were found on the inner side of washed glasses. Both glass surface and depth profile analyses of corroded glass samples showed increasing concentration of Na, Ba, Ca and Al towards bulk glass. Barium crystal glass containing aluminium was more corrosion resistant.

INTRODUCTION

Although the glass is considered as a stable material, various mechanical/chemical mechanisms proceed on the glass surface during production or during polishing and cleaning procedures of the glass when surfaces are in touch with an aqueous solution. The chemical composition of the glass surface is influenced by various interactions, which occur on the top-most atomic layers. As a consequence of the interaction between the glass and a solution, irreversible changes in glass as well as in attacked solution can be observed. Most important of them are as follows: dissolution of the glass, transfer of glass components into the solution, changes of glass surface composition, especially the depletion of alkali and alkali earth ions, and creation of secondary precipitated layers on the glass surface [1,2]. Long-term dishwashing process of the glass also can develop an irreversible surface degradation. White clouding, iridescence and other optical changes appear on the glass surface. Many research papers have already intensively studied the glass surface damages induced by various dishwashing detergents, at different washing temperatures and with different water hardness [3, 4]. White clouding was found to be caused by surface adsorption of disilicate-containing detergent impurities [3]. Buchmeier [3] also proposed that an uneven temperature distribution at the glass surface during glass production lead to diffusion of alkali ions from warmer to colder regions of the glass surface. The areas of high alkali ion concentration after excessive alkali leaching during intensive dishwashing give rise to the characteristic ring-shaped clouding. Lohmeyer [5] pointed out those local differences in chemical composition due to melting-off and annealing produced local differences in resistance to attack by various media. Gebhardt [6] proved by SEM and IR reflection spectroscopy that round-melted mouth rim of drinking glass is enriched by the alkali ions. In both cases white clouding on the glass surface was observed after dishwashing. Evaporation of the volatile species from warmer regions and their condensation onto colder areas of the glass surface during the flame treatment of a rim and consequently the craters formation was identified by Martinek [7]. Sharma [8] proposed that the glass surface can become chemically heterogeneous due to the operations applied during glass shaping. It was hypothesized that products formed by rapid glass expansion (as in the case of pressing and/or blow process), have just prior to the rapid forming step lower surface temperature (more viscous) compared to the interior. This fact causes the lost of some volatile modifier ions. Carnali [9] has focused on the development of corrosion pattern during corrosion process and explained why the different regions on the glass surface separated by distances of millimeters have same/similar susceptibilities to the corrosion process.

Concentration changes in the glass surface layers caused by glass corrosion can be detected by determination of concentration profiles of some elements. The changes in modification in the surface of soda-lime glasses obtained by different corrosion experiments in water were investigated by a multi-method approach of surface-sensitive techniques [10, 11, 12, 13, 14]. Significant changes in the alkali distribution were found using ESCA on the surface of tested glasses in various corrosion environments [3, 8, 15, 16, 17].

The present paper analyses the glass surface, glass cross-section and depth profile of glasses before and after dishwashing process by optical microscopy, SEM, EDX and ESCA. The aim of the paper is to understand the differences in chemical composition of unwashed and washed glass surfaces of two glass types. The simple model of corrosion is suggested.

EXPERIMENTAL

Samples

Two different machine made barium crystal wineglass marked as S and SA were used in the study. The initial chemical composition of both glasses is listed in the Table 1. Standard analytical norms were used to chemical analysis of glasses. Wineglasses were shaped and fabricated by machine process. The wineglasses were washed/corroded in domestic dishwasher for 220 washing cycles. Each washing cycle was performed at 65°C, and the residual water hardness was kept about 5. *Fairy activ Pulver* was used as a detergent. The composition of the detergent given by the producer is as follows: more than 30 % of phosphate, less then 5 % of aliphatic hydrocarbons, nonionic surfactants, enzymes, 5-15 % of oxygen based bleaching agents.

Table 2 summarizes the visual observations of the wineglasses before (S and SA samples) and after (SW and SAW samples) 220 washing cycles. All wineglass-

es were visually inspected regularly after every 50 washing cycles. Glass surface damages were classified by scale from 0 to 4, where 0 means no visible glass surface damage; the grate of 1 was identified using neon light and black background. The damage grate of 2 was visible by free eye without neon light and the grate of 3 showed the stronger visible damage (iridescence and fine white cover). The grate of 4 was identified for maximal strong surface damage, especially white cover.

Analysis

Samples of size 2 × 2 cm used for further analysis were cut from the wineglass goblet just 2 cm beneath the glass mouth rim. All samples were cleaned before each particular analysis with distilled water and acetone p.a. for ESCA analysis. Optical microscopy (with incident light, JENAVERT, Carl Zeiss Jena) and Scanning Electron Microscopy (JEOL 24S III) were used for the identification of (i) the surface and (ii) cross-section morphological changes. EDX (EDS analyser NORAN, accelerating voltage 10kV, emission current 15mA) was used for the chemical analysis of (i) glass surfaces and (ii) glass cross-sections. The EDX analysis of glass cross-section was performed in three spots: directly at the sample surface (0 μm), at the distance of 1 μm and 20 μm from the sample surface.

Glass surface of all glass samples was analyzed by X-ray photoelectronic spectrometer ESCA 3Mk II (VG Scientific) using the AlKα line (hv = 1486.6 eV). The pressure of the remaining gas in the sample chamber was 3 10^{-10} Pa. The voltage of 11.5 kV and the current of 20 mA were applied in the X-ray lamp. The photoemission lines of O(1s), Si (2p), Ca(2p), Na(1s), K(2p), Al(2s) and Ba(3d5/2) (also Zn(2p), Auger line of Mg($K_1L_{23}L_{23}$) were used for the quantitative analysis. Depth concentration profiles of glass forming elements were measured by XPS (ESCA) method (XPS spectra were recorded on a Kratos XSAM 800 spectrometer

Table 1. Chemical composition of studied crystal wine glasses (at.%).

Sample	Na	Si	K	Ca	Ba	Al	O
S	7.29	25.83	2.33	3.22	0.68	0.12	60.54
SA	7.24	25.50	2.41	3.23	0.64	0.47	60.47

Table 2. Characterisation of glass samples.

	Sample	Detergent	Washing cycles	Damage
S	unwashed glass	-	0	-
SW	washed glass	Fairy activ pulver	220	strong white cover
SA	unwashed glass	-	0	-
SAW	washed glass	Fairy activ Pulver	220	iridescence, fine white cover

operated in fixed analyser transmission mode using Mg K$\alpha_{1,2}$ (1253.6 eV) excitation, pass energy 80 eV and 40 eV, steps 0.5 and 0.1 event. Ion etch depth profiling was done by 2.5 keV Ar$^+$ ions).

RESULTS AND DISCUSSION

Morphology of washed surfaces

After visual evaluation, each dishwashed sample was inspected by the optical microscopy. In both SW and SAW samples the surface defects were observed, these can be classified as follows: (i) iridescence, white spot and their combination; (ii) mechanical damage in the form of cracks, riffles, uncovered cords and (iii) glass corrosion (jelly layer - surface enrichment by SiO$_2$ [18]) in the form of very fine "cracks". Optical microscopy observation confirmed some differences in the extent of damage of outer surfaces of both tested glasses. While the glass sample SW contained strong white spot (so-called milky effect) with the mechanical scratches on the outer surface, only fine iridescence and weak white spots were observed on the outer surface of sample SAW. Iridescence is probably caused by the thin film with a refractive index different from the glass.

SEM micrograph of outer surface of unwashed glass sample S showed no visible surface defects, the same is valid for the outer surface of sample SA. Figure 1 shows the washed glass surface on the outer side of sample SW. Micrograph is taken from the strong white spot classified on the defect scale by 4. Figure 2 shows the surface of weak white spot of sample SAW classified on defect scale by 2 after washing cycle. The leached dark areas are much smaller compared to sample SW and the surface fraction of white area is substantially larger. The inner surfaces of both SW and SAW samples were substantially less damaged, (Figures 3, 4)
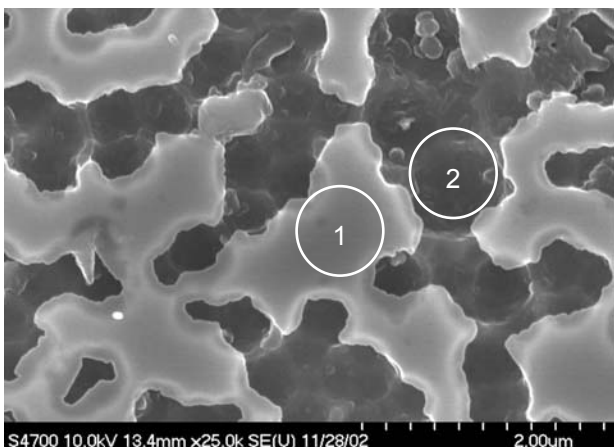

Figure 1. SEM micrograph of washed sample SW, damaged outer surface (strong white cover). EDX analysis of spots 1 and 2 are given in Table 5.
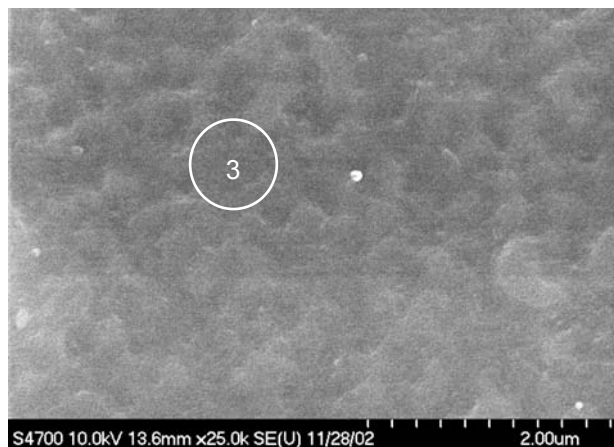

Figure 3. SEM micrograph of washed sample SW, damaged inner surface; (white cover). EDX analysis of spot 3 is given in Table 5.
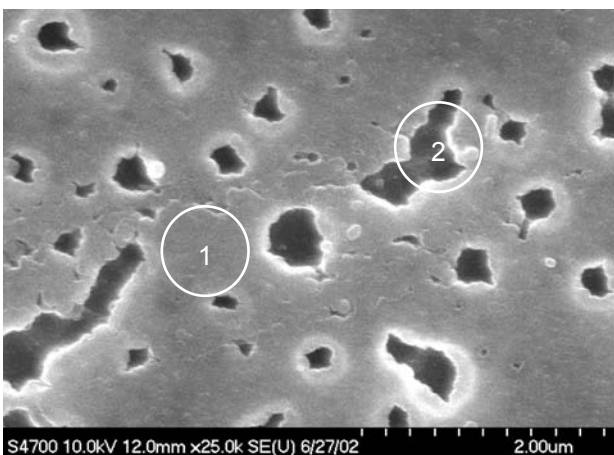

Figure 2. SEM micrograph of washed sample SAW, damaged outer surface (fine white cover). EDX analysis of spots 1 and 2 are given in Table 6.
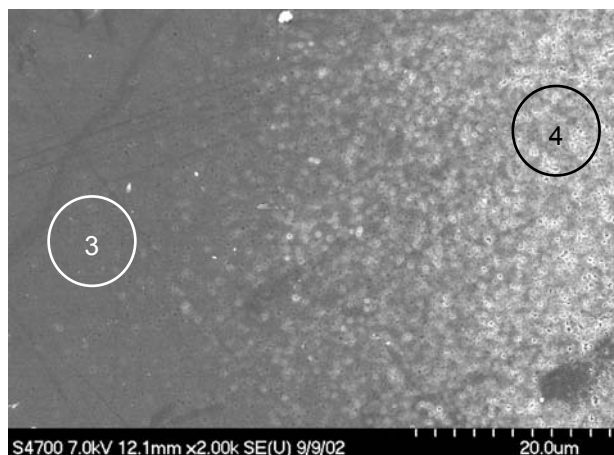

Figure 4. SEM micrograph of washed sample SAW, damaged inner surface (white cover). EDX analysis of spots 3 and 4 are given in Table 6.

The glass cross-section was analyzed by SEM in order to distinguish surface deposits which are located over the original glass surface or as etched glass areas. Figure 5 shows a side view of sample SW. Strong relief is visible, some deposits of size < 1 μm are also recognized. The rest of the glass surface is strongly corroded by the washing process. Sample SAW is shown in Figure 6. The relief is less pronounced compared to the sample SW. The depth of leached craters is about 0.2 μm in the sample SAW and approximately 0.5 μm in the sample SW.

Concentration changes of analysed glasses

Changes in glass surface and cross-section of the unwashed/washed samples were analysed by EDX and depth profiles of the unwashed/washed samples by ESCA. At first the unwashed glasses were measured to compare them with washed glass. All results of surface and cross-section chemical composition were compared with measured glass bulks.

EDX analysis - Unwashed samples (S and SA)

EDX analysis of outer side, inner side and bulk of sample S are listed in Table 3. Outer surface of sample S was slightly enriched by sodium and barium and depleted of silicon with respect to the bulk glass composition. The chemical composition of inner side is very similar to the bulk glass composition. Moderate increased amounts of potassium and calcium and decreased amount of sodium were identified on both surfaces of sample SA, Table 4. Outer surface contained more barium and less silicon than inner surface. Alu-

Table 3. Chemical composition of unwashed glass surfaces (S) analysed by EDX.

Sample S (at.%)	Na	Si	K	Ca	Ba	O
Outer side*	**6.7**	**26.2**	2.6	**2.5**	0.9	60.9
Inner side	6.4	26.8	2.7	2.2	0.8	61.1
Bulk	6.2	26.8	2.6	2.4	0.8	61.2
Standard deviation	± 0.2	± 0.3	± 0.3	± 0.2	± 0.1	± 1.7

* 0.1 % Al; 0.1 % S
The most important concentration differences of elements are noted in bold.

Table 4. Chemical composition of unwashed glass surfaces (SA) analysed by EDX.

Sample SA (at.%)	Na	Si	K	Ca	Ba	Al	O
Outer side	**6.6**	26.0	**2.7**	**2.5**	**1.0**	0.4	60.8
Inner side	**6.4**	26.4	**2.8**	**2.5**	**0.6**	**0.3**	61.0
Bulk	7.3	26.2	2.2	2.2	0.8	0.5	60.8
Standard deviation	± 0.2	± 0.3	± 0.3	± 0.2	± 0.1	± 0.1	± 1.2

The most important concentration differences of elements are noted in bold.
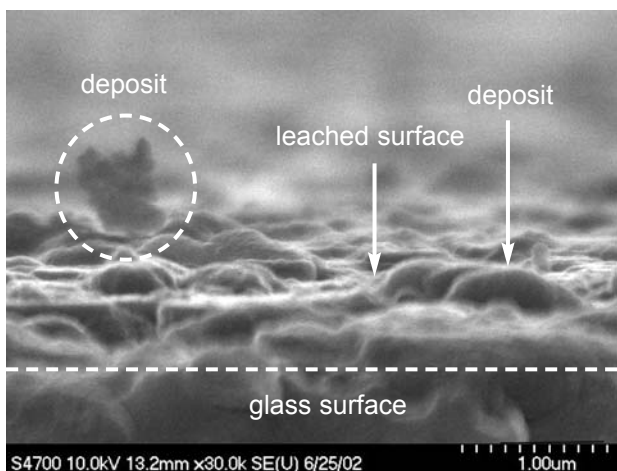

Figure 5. SEM micrograph of washed sample SW, cross-section of damaged outer surface (strong white cover).
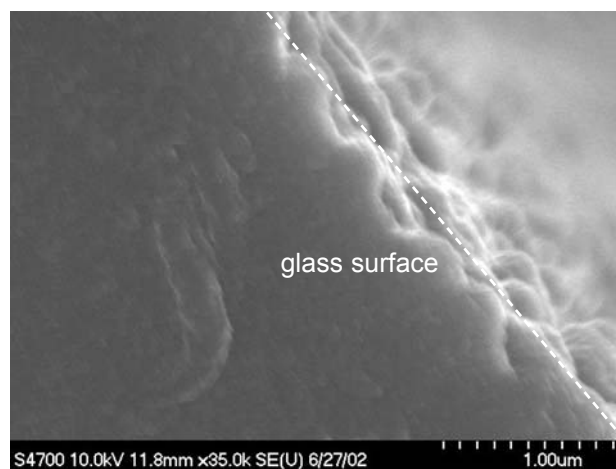

Figure 6. SEM micrograph of washed sample SAW, cross-section of damaged outer surface; (fine white cover). Detection angle of SEM analysis was 60°.

minium is built into glass structure of sample SA and thus its initial composition differs from composition of sample S and therefore these two glasses are not directly comparable.

Sample S has slightly higher content of sodium in the outer surface compared to the inner surface and bulk, while sample SA has this content reverse, i.e. higher sodium content in the bulk compared to the inner and outer surface. Potassium content in the sample SA is higher in the outer and inner side compared to the bulk. Rest of the elements is approximately at the same level, i.e. within the rangiest experimental error, independent on the location of the measurement. The different content of Na and K in the bulk and surfaces is attributed to the thermal history of the glass, when it is supposed that the alkali elements have higher tendency to evaporation and condensation [7, 8]. Figures 7 and 8 show the concentration profiles of the elements along the cross section of the samples S and SA, respectively. In spite of the fact that the profiles of the sample S are not changed very much across the sample section, some tendencies can be observed. Potassium and calcium concentration slightly decreases from the outer surface to the inner one in this sample. 1 µm beneath outer surface of sample S is observed remarkable increase of potassium and simultaneous decrease of barium in comparison with glass bulk. It was probably given by local glass chemical inhomogeneity due to different ion diffusion during the thermal treatment of the glass surface.

In the sample SA a remarkable increase of the calcium content in the inner part of the sample can be observed, slight decrease of the aluminium content towards the inner surface of the sample and depletion of sodium in the middle (glass bulk) of the sample cross section. Na concentration differences obtained by cross-section analysis against surface analysis could be caused by selection of glass sample from glass product. Mouth edge is influenced by flame in place about 1 cm from edge. Alkali evaporate and diffuse from warmer regions into colder areas of the glass surface and this areas are enriched by alkali. The analyzed glass samples came from alkali enriched and depleted area, respectively.

EDX analysis - Washed samples (SW and SAW)

EDX analysis of washed samples shows that the situation is much more complicated compared to the unwashed ones. In the case of sample SW, the surface area, visually characterized as not damaged (outer side 1, Table 5) has almost the same composition as the sample S (Table 3). The situation is rapidly changed when the analysis is taken from the damaged area. EDX analysis taken from the outer side 2 (Figure 1, location 1) listed in the Table 5 shows that concentration of all elements is changed with the exception of oxygen. Increased content of sodium, potassium and barium is

Table 5. Chemical composition of washed glass surface (SW) analysed by EDX.

Sample SW (at.%)	Na	Si	K	Ca	Ba	O	S	Cl
Outer side 1	**6.6**	26.6	**2.9**	2.4	0.6	60.9	-	-
Outer side 2 (F.1, 1)	**7.8**	**25.8**	**3.5**	**0.9**	**1.9**	60.1	-	-
Outer side 3 (F.1, 2)	**8.6**	**25.7**	**1.8**	**3.7**	**0.0**	60.2	-	-
Inner side (F.3, 3)	**6.6**	26.6	2.4	2.3	0.8	61.0	0.1	0.2
Bulk	6.2	26.8	2.6	2.4	0.8	61.2	-	-

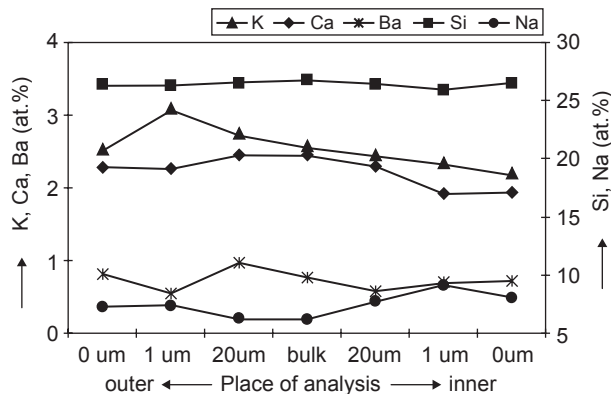*The most important concentration differences of elements are noted in bold.*

Figure 7. EDX cross-section analysis of unwashed sample S, outer side, inner side in comparison with glass bulk.
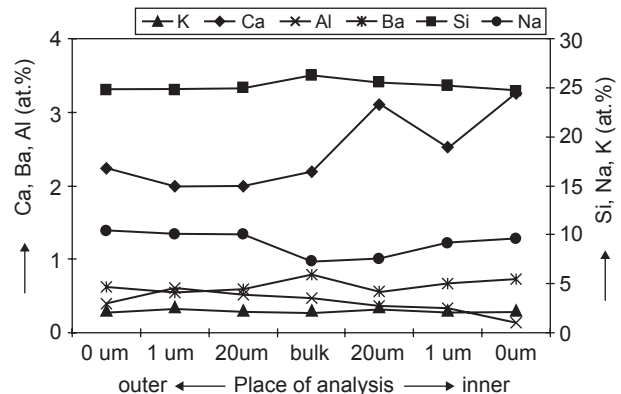
Figure 8. EDX cross-section analysis of unwashed sample SA, outer side, inner side in comparison with glass bulk.

observed while decrease of the concentration of silicon and calcium is documented. The same analysis of the outer side 3 (Figure 1, location 2) in the Table 5 shows increased content of sodium and calcium, and decreased content of silicon and potassium and simultaneous disappearance of barium. Based on those results the simple schematic model shown in Figure 9 can be drawn. The empty space drawn in Figure 9 represents the glass leached by the detergent water solution. Silicon is very probably dissolved into the water solution at the formation of silicon acid and that is the reason of its depletion. Potassium and barium with larger atomic radius (133 and 135 pm, respectively) react with the detergent solution and probably form compounds, which precipitate at the glass surface. Smaller atoms as sodium and calcium (95 and 99 pm, respectively) are deposited at the bottom of the crater, Figure 9.

The inner part of the sample SW differs from the bulk insignificantly, Table 5. Outer glass surface of sample SAW (Table 6) was less damaged and detected concentration differences were not as significant as for sample SW. This fact corresponded well to observation obtained by the optical and electron microscopy. No significant concentration changes on this side were measured although the concentrations of calcium, barium eventually potassium and aluminium were slightly increased. The significance of these findings is very low because the EDX detection depth is few micrometers, which is much higher than the thickness of the observed white spots (about 0.2 μm).
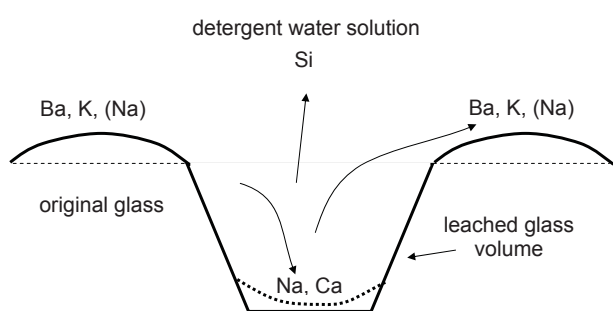

Figure 9. Schematic model of the surface damage of sample SW.

Significant depletion of sodium and barium on the inner part of the sample SAW was observed, Table 6. This depletion is more pronounced in the visually more damaged spot, Figure 4, location 4.

Foreign elements as sulphur, chlorine, magnesium and nitrogen, which were not a part of the original glass composition were identified on both sides of the sample SAW. Probably they originate from detergent or from insufficiently softened water (5°dH).

Aluminium content is not changed significantly on both sides and it is similar to that of the glass bulk. This probably means that aluminium as a network former is strongly bonded in the glass structure. By addition of this element the glass structure is more stable and less opened for the leaching by the detergent solution. EDX cross-section elements analyses of sample SW are shown in Figure 10. The labels 1 and 2 represent the different locations of the EDX analysis taken from the outer surface, accordingly to the Figure 1. This analysis documents the diffusion processes taking place in the glass after the washing process. Concentration of small sodium atom increases towards the outer surface, Figure 10, which was not observed in unwashed glass S, Figure 7. On the other hand concentration of large potassium atom decreases towards the outer surface when we take into account only undamaged zone starting from 1 μm under the both surfaces. The same is valid for the concentration of calcium atom and moderately also for silicon. Concentration of barium increases towards both inner and outer surface. Concentration of barium seems to be decisive for the diffusion of other metallic ions/atoms. If barium diffuses from glass bulk towards the surfaces, inner and outer surface are a present case, it can create a local stress on the surface because of its high atomic/ionic size. This local stress can support diffusion of the other ions towards this surface [23]. It could explain why the concentration of calcium and potassium increases towards the inner surface.

In the case of sample SAW, when we adopt the same approach that only concentrations 1 μm under the surface will be taken into account, one can see evidently the increase of the barium concentration towards the outer surface (Figure 11), in opposite to the sample SW. Supporting the previous speculation, also in this case, the calcium and potassium follow the increased concen-

Table 6. Chemical composition of washed glass surface (SAW) analysed by EDX.

Sample SAW (at.%)	Na	Si	K	Ca	Ba	Al	S	Cl	Mg	N	O
Outer side 1 (F.2, 1)	**7.6**	**25.7**	**1.9**	**2.5**	0.8	0.5	**0.2**	-	**0.1**	-	60.7
Outer side 2 (F.2, 2)	**7.6**	**25.6**	2.4	2.3	0.8	0.6	**0.1**	-	0.1	-	60.5
Inner side 1 (F.4, 3)	**5.9**	26.5	2.4	**2.5**	**0.1**	0.3	**0.4**	0.3	-	-	61.6
Inner side 2 (F.4, 4)	**4.8**	27.0	2.0	2.1	**0.5**	0.5	**0.1**	-	**0.3**	1.3	61.4
Bulk	7.3	26.2	2.2	2.2	0.8	0.5	-	-	-	-	60.8

The most important concentration differences of elements are noted in bold.

tration of barium in this direction. In both cases the concentration of sodium has an opposite trend compared to barium. The likely reason for this behavior is that the large diameter of barium ion limits the motion of small univalent metals (Na^+) and reduces their mobility [20].

Comparable Si concentration with glass bulk or its slight increased amount was identified especially on the inner side of both washed glass samples (SW, SAW). The inner washed glass side was less damaged than outer side therefore the elements concentration did not differ on the inner side markedly.

Analysis of damaged surface layer without basic glass (the peeled off part of the most damaged surface layer - white cover) was performed in case of sample SAW. These results are presented in Table 7. Two different locations were analysed and compared with bulk glass SA. The compositions of these surface spots are rather different to the original SA glass sample. Significantly increased concentrations of sodium, potassium, sulphur, aluminium and chlorine and small amount of magnesium without any barium were measured. This indicates that the detergent solution damages glass structure, even in the case of glass SA, which contains aluminium. Measured significant depletion of silicon confirms previous speculation that silicon is dissolved in water at formation of the silicon acid. The glass forming and modifying elements create compounds with the components of the detergent and these new, in water insoluble, compounds precipitate at the glass surface.

ESCA measurement

Depth profile analysis of samples SA and SAW

Figures 12 and 13 show the ESCA measurements of the depth concentration profiles of samples SA and SAW, respectively. The measurement was accomplished always after ion etching of the sample surface. The concentration profiles of the elements in the unwashed sample SA are roughly comparable with the results obtained by EDX, Figure 10. The same can be concluded for the measurements taken from surface of the SAW sample.

The concentration profiles of barium, calcium and aluminium in the case of sample SAW seems to be different compared to the profiles of the sample SAW obtained by EDX but one must keep in mind the scale of y axis of Figure 13. ESCA takes only a few surface atomic layers and thus analysis of the glass surface is extremely sensitive on the selection of the analyzed spot, but measured quantities of Ba and Al are in the range obtained by EDX, only lower concentration level of calcium was measured by ESCA. The negligible amount of sodium in the sample (with the exception of the surface layer) can be explained by sodium volatilization during the ion etching of the sample surface. The same/similar argument can be used for more then two times lower concentration of calcium. Both these elements (Na, Ca) concentration are the smallest in the composition obtained by ESCA analysis.

Table 7. Chemical composition of peeled off washed layer (SAW) analysed by EDX.

Sample SAW (at.%)	Na	Si	K	Ca	Ba	Al	S	Cl	Mg	O
Place 1	**16.7**	1.7	14.1	**2.9**	**0.0**	**0.9**	**3.9**	**24.0**	**0.5**	35.3
Place 2	**16.1**	5.4	**8.2**	**1.8**	**0.0**	**3.9**	**3.7**	**16.2**	**1.5**	43.2
Bulk	7.3	26.2	2.2	2.2	0.8	0.5	-	-	-	60.8

The most important concentration differences of elements are noted in bold.
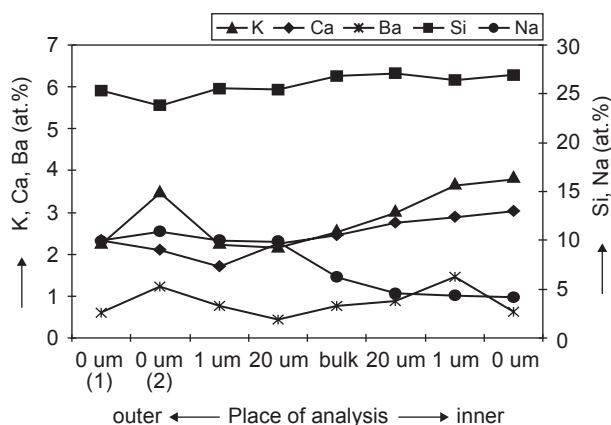

Figure 10. EDX cross-section analysis of washed sample SW, outer side, inner side in comparison with glass bulk.
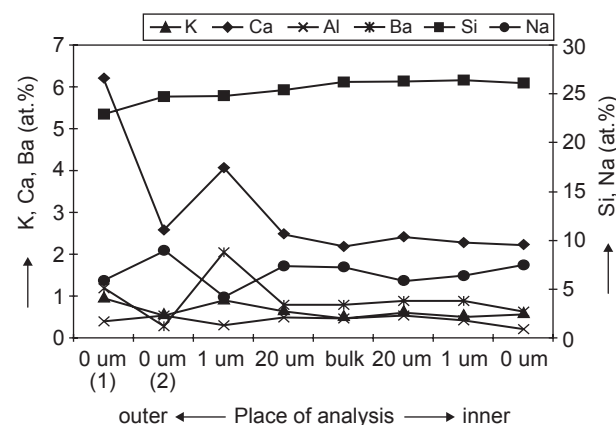

Figure 11. EDX cross-section analysis of washed sample SAW, outer side, inner side in comparison with glass bulk.

Surface analysis of washed sample SAW

ESCA method is able to detect directly the glass surface in depth of 2-10 nm, therefore it provides more accurate information about surface character than EDX method (depth detection about 2 μm). Table 8 presents chemical composition of damaged glass surface in case of iridescence and white cover on the outer and inner glass side. Outer side of damaged glass surface was significantly depleted in sodium, potassium and calcium at both damage types. Higher amount of silicon in comparison with unwashed glass surface was found at all analysed types of damaged surface. Zinc and magnesium were also identified but only in case of analysis of white cover and aluminium in case of iridescence. The possible reason is using a zeolite as ionic-exchanger in dishwashers, which consists from Al, Zn and Si. These components are able to create zinc or magnesium silicates.

No barium was found at any analysed damaged surface. It results in barium depleted glass surface because of its leaching from glass surface layer into water solution. Dimension of hydrated/unhydrated cation play significant role in case of the ionic exchange reaction. The higher radius of unhydrated ion, the higher exchange force of ion. It means the less hydrated ion is removed from solution instead of more hydrated ion in preference, which is released from solid state into solution.

Therefore exchange force of barium is higher than that of calcium and the exchange force of potassium than sodium [24]. High amount of barium released from the glass was proved by ICP analysis of leaching solution after flow-through leaching test [25].

Comparison of results obtained by optical microscopy, SEM, EDX and ESCA

Results of the optical and electron microscopy showed that the morphology of inner side was more homogenous and less damaged with respect to the outer side. Aluminium containing barium crystal glass SA (damaged glass SAW) was more resistant with respect to the surface morphology (Figures 1 and 2). Washed aluminium-free glass (SW) was covered by higher white deposits and iridescence defect. Surface and cross-section analysis by optical and electron microscopy showed that the washing process leads to a reopening of fine surfaces cracks and subsurface damage, iridescence and so-called milky effect formation. The craters analysed at aluminium contained glass were smaller in diameter and in depth than at aluminium-free glass.

Comparison of cross-section analysis with surface analysis for both glass types S and SA, respectively by EDX shows that the concentration changes (enriching

Table 8. Chemical composition of unwashed/washed glass surface (SA, SAW) analysed by ESCA.

Sample SAW (at.%)	Na	Si	K	Ca	Ba	Al	Zn	Mg	O
Unwashed outer glass side (SA)	3.80	28.30	1.85	2.98	0.15	0.60	-	-	62.33
Washed outer side, iridescence (SAW)	**0.78**	**32.46**	**0.54**	**0.87**	-	**1.38**	-	-	63.97
Washed outer side, white cover (SAW)	**0.86**	**32.53**	**0.67**	**1.51**	-	0.50	**0.62**	**0.23**	63.07
Unwashed inner glass side (SA)	4.07	29.95	1.43	2.94	0.11	0.51	-	-	60.99
Washed inner side, iridescence (SAW)	**0.91**	**31.46**	**0.63**	**2.64**	-	0.59	**0.59**	**0.63**	62.51

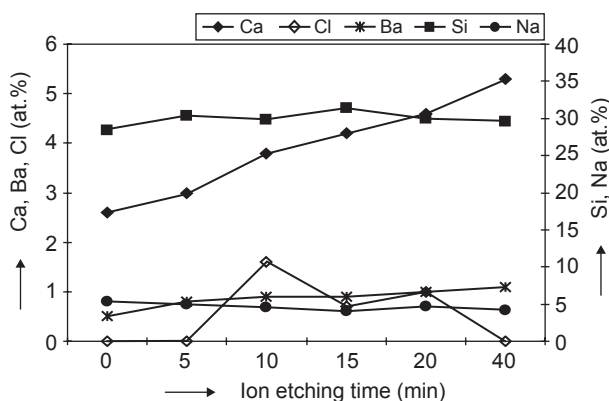*The most important concentration differences of elements are noted in bold.*

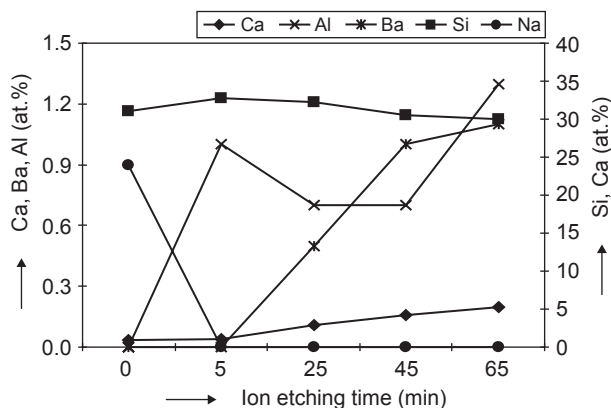Figure 12. ESCA depth profile analysis of unwashed sample SA, outer side.

Figure 13. ESCA depth profile analysis of washed sample SAW, outer side.

or depletion) of elements were comparable. The biggest varieties were observed on damaged surfaces, in spots of 0 μm and 1 μm, i.e. at the interface between basic glass and the washing solution.

Depth profile analysis of unwashed glass (SA) by both EDX and ESCA methods shows almost the same results; increasing concentration of Ba, Ca and Si towards glass bulk. However, ESCA is able to detect direct glass surface in depth of 2-10 nm, therefore it provides more accurate information about surface character. Surface analysis using both methods showed also the same results: depletion of barium, alkali/earth alkali enrichment and depletion related to the analysed glass side and spots and especially the presence of foreign components. Very low amount of calcium, sodium and potassium were identified by ESCA because of its analysed detection depth (2-10 nm) and also due to volatilization in the course of ion etching.

Tested glass probes, cut out about 2 cm from the mouth rim, were used for dishwashing test and chemical analysis. It is reasonable to suppose that a phase separation occurred during the secondary edge melting process and isolated phase was preferentially dissolved or scaled off in the detergent. In the re-melting area the alkali and earth alkali ions might evaporate and condense on the colder area. Ion migration and phase separation could take place [7, 19]. This was visualized especially after dishwashing process. Chemical composition of both the glass surface and bulk supported this assumption in case of unwashed glass (Tables 3 and 4). The presence of different surface morphology in case of craters and elevations, especially on the outer glass side, proves the above mentioned flame attack to the glass. The craters (dark places, Figures 1 to 4, Tables 5 and 6) were more depleted and enriched on alkali and alkali earth related to the analysed glass side and spots. These findings are explained by corrosion process: transfer of glass components into the solution, changes of glass surface composition, especially the depletion of alkali and alkali earth ions. The precipitation of elements from solution on the glass surface and/or back precipitation of glass elements already dissolved are next stages of glass surface damage [1, 2]. Precipitates on glass surface in form of white cover may give rise to localized differences in chemical composition and result in different resistance to attack by tested media. The analysed corrosion products, especially by EDX, were formed by ion exchange of H_3O^+ with Na^+ or K^+ in the glass. During this process the glass network can dissolve and the durability of the whole surface is reduced. Obtained precipitates of white cover contained higher concentration of alkali/earth alkali, Al, S, P, Cl and Mg. The last mentioned elements were not a part of glass composition and came from detergent washing solution. A combination of applied detergent in tested process allows the explanation above mentioned compounds as follows: (i) Sodium tripolyphosphate or its hydrated forms, phosphates of inorganic condensates and alkali sulphate were formed by reaction between compounds originated from detergent and glass structure. (ii) Calcium and magnesium carbonates and/or hydroxides originated in insufficiently softened water (residual water hardness about 5). (iii) Sodium aluminosilicate could be formed from sodium zeolite, which has been used as ionic exchanger between sodium and calcium from water [25]. Therefore it can precipitate on glass surface due to solution attack. Precipitation of elements from solution on the glass surface and/or back precipitation of glass elements already dissolved in solution is another source of aluminosilicate formation. Mentioned reasons resulted in glass corrosion in form of surface dissolution and covering by precipitates.

On the other hand, both methods EDX and ESCA also confirmed more chemical stability of the inner glass side in comparison with the more damaged disturbed outer glass side. The glass surface chemical inhomogeneity of unwashed glass was proved especially in case of sodium concentration. EDX and ESCA detected very low amount % of Na. It confirms the influence of thermal treatment during glass manufacturing (forming and post-forming processes) and washing process as well [7, 8, 19].

CONCLUSION

Surface analyses, cross-section analysis and depth profile measurement were made in case of washed and unwashed glass products by optical microscopy, SEM, EDX and ESCA. Optical and electron microscopy provided the basic information for identification of the state of damaged surface. Surface and cross-section analyses of unwashed glasses confirmed concentration stability of both outer and inner side. Concentration changes of both washed samples were given by increased/decreased amounts of alkali and earth alkali eventually their combinations. These results confirmed the theory of alkali diffusion from glass bulk to surface and/or evaporation from surface, and ion exchange between glass and washing (liquid) solution. Surface and depth analyses proved that no barium was found and foreign elements were detected, which were not a part of initial glass composition. Alkali, especially sodium depletion was identified on the unwashed glass surface due to influence of the thermal treatment in the course of glass manufacturing. Applied methods showed the difference of surface morphology and chemical composition at two various glass types in solution used. Barium crystal glass containing aluminium was more chemical resistant. Chemical changes of analysed surfaces were not so significant in comparison with aluminium-free glass.

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POŠKODENIE POVRCHU DVOCH RÔZNYCH
ÚŽITKOVÝCH SKIEL POČAS UMÝVACIEHO PROCESU

VIERA PETRUŠKOVÁ, PETER VRÁBEL,
PETER ŠIMURKA, PAVOL ŠAJGALÍK*,
MARTIN MARYŠKA**

RONA, a.s., 02 061 Lednické Rovne, Slovenská republika
**Ústav anorganickej chémie, SAV, Dúbravská cesta 9,*
*842 36 Bratislava, Slovenská republika**
***Ústav skla a keramiky,*
Vysoká škola chemicko-technologická v Praze,
Technická 5, 166 28 Praha 6, Česká republika

Vznik bieleho zákalu (milky effect), iridiscencie a mechanického poškodenia na povrchu skla sú výsledkom automatického umývacieho procesu. Iridiscencia a biely zákal tvorený na povrchu sklených výrobkov boli sledované pomocou riadeného umývacieho procesu. Skúmané boli dva typy skiel, bola použitá povrchová analýza a analýza v priečnom reze na neumývanom a umývanom povrchu skla. merané plochy boli analyzované optickým mikroskopom, riadkovacím elektrónovým mikroskopom (SEM), elektrónovou mikroanalýzou (EDX) and fotoelektrónová spektroskopia (ESCA). Na vonkajšom poškodenom umývanom povrchu skla boli identifikované cudzie zložky. Na vnútornom povrchu umývaného skla boli zistené nízke koncentračné rozdiely. Povrchová analýza i hĺbkový profil korodovaného skla ukázal znížené koncentrácie Na, Ba, Ca a Al smerom k jadru skla (bulk). Bárnatý krišťáľ obsahujúci hliník bol chemicky odolnejší.