# LEAD CONCENTRATION PROFILES IN THE SURFACE OF LEAD CRYSTAL GLASS

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*Concentration profiles of lead in the surface of lead crystal glass (24 wt.%) treated by products of decomposition of ammonium chloride at 280 °C and 450 °C were measured by the method of photoelectron spectroscopy. The concentration profiles showed that the dealkalization resulted in a distinct reduction of lead concentration in the glass surface already at the lower treatment temperature (280 °C). The dealkalized surfaces yielded very low extracts of lead even by long-term leaching into 4 vol.% acetic acid at room temperature.*

## INTRODUCTION

Leaching of lead from lead crystal glass ware can be suppressed by suitable surface treatment. The methods employed are aimed in particular at reducing the lead content in the surface of finished products prior to their application in practice. Apart from extraction in solutions of acids, use can also be made of surface dealkalization at elevated temperatures otherwise employed for the purpose of improving the chemical durability of soda-lime glasses. The method is based on interaction of alkalies and possibly other components in the glass surface with reactive gases ($SO_2$, $SO_3$, HCl) at elevated temperatures, whose products either form readily soluble deposits on the surface, or vaporize at the treatment temperature. It is assumed that apart from alkalies, the treatment also removes other components, in particular calcium, and at higher temperatures also other elements (Fe, Pb, B, etc.) [1, 2]. This paper presents the results of measuring the concentration profiles of lead in the surface of lead crystal samples with dealkalized surfaces. The effect of dealkalization on the amounts of lead extracted from the surface by leaching was determined at the same time.

## EXPERIMENTAL PROCEDURES

### Glass specimens
(lead crystal glass with a content of 24 wt.% PbO)

1. Platelets 10 × 10 × 4 mm cut from the cup bottom, the surface treated mechanically by grinding and polishing (samples for measuring the concentration profiles).
2. Drinking glass: goblets of 300 ml capacity (samples for determining the lead extracts).

### Dealkalization of specimen surfaces

Carried out with ammonium chloride at 280 °C and 450 °C. The deposits were washed off the surface with distilled water.

### Measuring the lead concentration profiles

Use was made of X-ray photoelectron spectroscopy in combination with the ion sputtering [3]. The rate of sputtering from the surface was about 0.6 nm $min^{-1}$.

### Determination of lead extracts from the inner surfaces of drinking glass

Leaching of inner surfaces with dilute acetic acid (4 vol.%) at room temperature. The lead content in the extracts was determined by the AAS method.

## RESULTS

Figure 1 shows the concentration profile in the surface of a specimen prepared from the original glass from commercial production by grinding and polishing the surface. The specimens thus prepared were used in dealkalization. Also shown is the concentration profile of lead obtained from the same glass not subjected to additional grinding and polishing.

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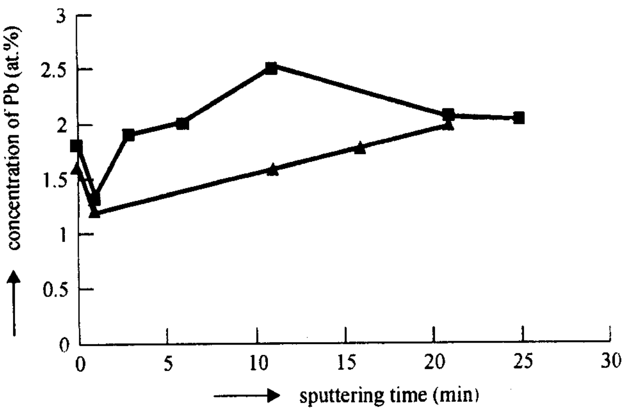


Figure 1. Concentration profiles of lead in the surface of non-dealkalized glass specimens.
■ - original glass from production, ▲ - surface treated mechanically by grinding and polishing

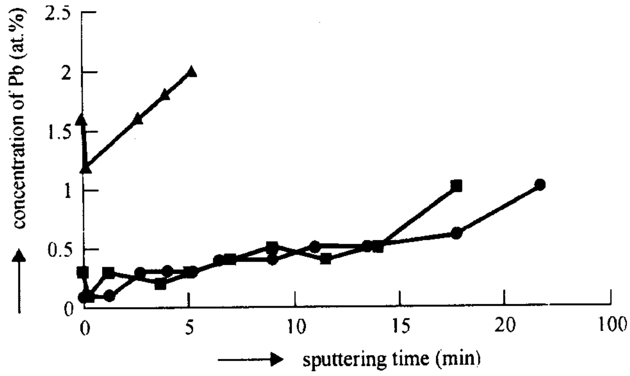


Figure 2. Concentration profiles of lead in the surface of dealkalized glass specimens.
▲ - initial non-dealkalized surface, ■ - dealkalization at 280 °C, ● - dealkalization at 450 °C

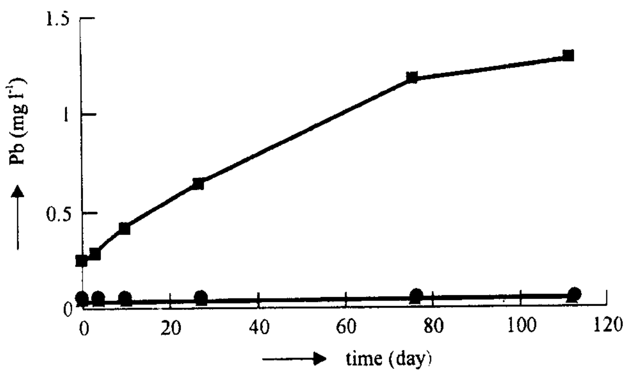


Figure 3. Time dependence of lead concentration in extracts into acetic acid (4 vol.%) at room temperature. 300 ml goblets.
▲ - non-dealkalized surface, ■ - dealkalization at 280 °C, ● - dealkalization at 450 °C

Figure 2 shows the concentration profiles of lead in the surface of ground and polished specimens following their dealkalization at 280 °C and 450 °C respectively, in comparison with the concentration profile of non-dealkalized surface.

Figure 3 shows the time dependence of lead concentration in extracts from drinking glass (goblets of 300 ml capacity) with dealkalized and non-dealkalized inner surfaces, into acetic acid (4 vol.%) at room temperature.

## DISCUSSION

The results of measuring the lead concentration profiles in the surface of non-dealkalized specimens (figure 1) show that the original surface from commercial production (chemically unpolished surface), compared to the additionally mechanically treated one, shows enrichment with lead in the subsurface layers, with a maximum reached after about 10 minutes of sputtering, i.e. at a depth of approximately 6 nm. In the case of specimens with ground and polished surfaces the concentration profile of lead has changed considerably as a result of removal of the surface lead-enriched layer, and obviously as one of partial extraction of lead in the course of grinding and polishing.

The comparison of lead concentration profiles from dealkalized and non-dealkalized glass surfaces (figure 2) shows that lead concentration in the surface of dealkalized glass was significantly reduced (by a factor of about 7). Gradual sputtering of the outer layer of dealkalized surfaces brings about only a very slow increase in lead concentration in the subsurface layers which rises distinctly only after removal of about 30 to 40 nm. Short periods of surface sputtering bring about only minimum differences in the concentration profiles of specimens dealkalized at various temperatures (280 °C and 450 °C). Some differences appear only in the deeper layers where in the layer dealkalized at the lower temperature the lead content starts to rise earlier (after about 55 minutes of sputtering) than in that dealkalized at the higher temperature (after about 70 minutes of sputtering).

The results of extraction from the surface of ware into acetic acid solution at room temperature (figure 3) demonstrate a significant effect of surface dealkalization on suppressing the leaching of lead. Even after long-term leaching (112 days) the concentration of lead in extracts from dealkalized surfaces remained within the detection limits of the analytical method employed (about 0.05 mg $l^{-1}$).

## CONCLUSIONS

The results of measuring the concentration profiles of lead showed that dealkalization by reactive gases at elevated temperatures is a very efficient treatment bringing about removal of lead from the surface layers of glass. The treatment results in a significant reduction of lead leached from the surface of lead crystal ware. The dealkalized surfaces exhibited extremely small values of extracted lead even after long-term leaching in acetic acid.

A comparison of concentration profiles of specimens dealkalized at temperatures of 280 °C and 450 °C respectively indicates that from the standpoint of removing lead from the surface layers of glass, dealkalization at the lower temperature far below the transformation temperature of glass is already adequately effective. Evidence of the efficiency of the treatment even at the lower temperature is provided by the results of extraction of surfaces dealkalized at the lower temperature (280 °C), which showed a significant decrease of the amount of extracted lead compared to non-dealkalized surfaces. Similar results were obtained by dealkalization at the higher temperature (450 °C).

Acknowledgement

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## KONCENTRAČNÍ PROFILY OLOVA V POVRCHU OLOVNATÉHO KŘIŠŤÁLU

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Snížení výluhů olova u výrobků z olovnatého křišťálu je možné dosáhnout vhodnou úpravou povrchu, která vede k extrakci olova z povrchových vrstev skla před jeho použitím.

V práci byl sledován vliv dezalkalizace povrchu olovnatého křišťálu (24 hmot.% PbO) produkty rozkladu chloridu amonného při teplotách 280 °C a 450 °C na obsah olova v povrchových vrstvách skla a na snížení výluhů olova z povrchu výrobků. Koncentrační profily olova byly měřeny metodou fotoelektronové spektroskopie ve spojení s odprašováním povrchu energetickými ionty. Rychlost odprašování povrchových vrstev skla byla přibližně 0,6 nm $min^{-1}$.

Vliv dezalkalizace na vyluhování olova z povrchu byl sledován dlouhodobým (až 112 dní) loužením nápojového skla (sklenice 300 ml) do roztoku kyseliny octové (4 obj.%) za laboratorní teploty.

Na obr.1 je koncentrační profil olova v povrchu základního vzorku připraveného z původního skla z výroby broušením a mechanickým leštěním povrchu. Vzorky s takto upraveným povrchem byly použity pro dezalkalizaci. Současně je zde uveden koncentrační profil olova v povrchu vzorku téhož skla, ale s původním povrchem z výroby dodatečně mechanicky neopracovaným. Z porovnání koncentračních profilů je zřejmé, že původní povrch z výroby (chemicky neleštěný vzorek) vykazuje oproti dodatečně mechanicky opracovanému povrchu obohacení olovem v podpovrchových vrstvách. U vzorku s povrchem dodatečně broušeným a leštěným došlo k výrazné změně koncentračního profilu olova v porovnání s původním vzorkem z výroby v důsledku odstranění povrchové, olovem obohacené vrstvy skla a zřejmě i částečným vyloužením olova z povrchu v průběhu broušení a leštění. Měření koncentračních profilů dezalkalizovaných vzorků ukázalo (obr.2), že koncentrace olova v povrchových vrstvách skla s dezalkalizovaným povrchem výrazně klesla v porovnání s nedezalkalizovaným povrchem (cca 7x), k nárůstu koncentrace olova v hlubších podpovrchových vrstvách dochází jen velmi pozvolně. Koncentrační profily olova u vzorků dezalkalizovaných za různých teplot (280 °C a 450 °C) se při kratších časech odprašování povrchové vrstvy prakticky neliší, určitý rozdíl se začíná projevovat až v hlubších vrstvách (cca 40 nm) pod povrchem skla. Dlouhodobé loužení povrchu výrobků do roztoku kyseliny octové za laboratorní teploty (obr.3) prokázalo výrazné snížení výluhů olova u vzorků s dezalkalizovaným povrchem a to pro obě použité teploty dezalkalizace.

Výsledky měření koncentračních profilů potvrdily, že dezalkalizace účinkem reaktivních plynů za vyšších teplot je velmi účinnou úpravou k extrakci olova z povrchových vrstev skla. Důsledkem této úpravy je výrazné snížení výluhů olova z povrchu výrobků. Dezalkalizované povrchy vykazují velmi nízké výluhy olova i po dlouhodobém loužení v kyselině octové. Účinná je již dezalkalizace za poměrně nízkých teplot (280 °C) hluboko pod transformačním bodem skla.