

# CONDUCTOMETRY ANALYSIS – BENEFICIAL METHOD FOR DETERMINING THE CHEMICAL COMPOSITION OF ALKALINE SILICATE SOLUTIONS

## KONDUKTOMETRIJA – KORISTNA METODA ZA DOLOČITEV KEMIJSKE SESTAVE ALKALNIH SILIKATNIH RAZTOPIN

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The study deals with the methodology for determining the chemical composition of alkaline silicate solutions. Nowadays, the most widely used method in industry is titration, using the color change of an acid-base indicator. This technique is very accurate for the determination of the total alkalinity (i.e., Na<sub>2</sub>O, K<sub>2</sub>O, or Li<sub>2</sub>O). However, a problem arises in the determination of the SiO<sub>2</sub> content, since the color change of the methyl red indicator is very slow and therefore the equivalence point is unclear. The main aim of this work is to present the benefits of conductometric titration, where the equivalence point is indicated by a sudden change in the conductivity. The applicability of the method was verified with other analytical techniques, such as ICP-OES and gravimetric analyses. Their results confirmed the values of the obtained silicate module (the molar ratio of SiO<sub>2</sub> and alkaline oxide) in the cases of sodium, potassium and lithium water glasses. Based on the obtained results, one can say that conductometry is a very promising method providing an accurate, fast and instrumentally undemanding chemical characterization of alkaline silicate solutions, usable even in a manufacturing process.

Keywords: conductometry, titration, chemical composition, alkaline silicate solutions

V članku avtorji opisujejo študijo, ki se ukvarja z metodologijo določevanja kemijske sestave alkalnih silikatnih raztopin. Dandanes je titracija najbolj razširjena in uporabna metoda v industriji pri kateri ovrednotenje temelji na spremembi barve kislega indikatorja. To je zelo natančna metoda za določitev celotne alkalnosti (naprimer Na<sub>2</sub>O, K<sub>2</sub>O, ali Li<sub>2</sub>O). Vendar problem nastopi, če je potrebno določiti koncentracijo SiO<sub>2</sub>, ker je sprememba barve metil oranžnega indikatorja zelo počasna in je zato točka enakosti zelo nejasna. Glavni namen tega dela je bil predstaviti prednosti konduktometrične titracije pri kateri se točka enakosti določi z skokovito spremembo prevodnosti raztopine. Uporabnost te metode so avtorji verificirali z uporabo drugih analitskih tehnik, kot sta ICP-OES (angl.: Inductively Coupled Plasma – Optical Emission Spectrometry) in gravimetrija. Eksperimentalni rezultati so pokazali medsebojno primerljivost vrednosti dobljenega silikatnega modula (molar razmerje med SiO<sub>2</sub> in alkalnimi oksidi) v primeru Na, K in Li vodnih stekel. Na osnovi dobljenih rezultatov avtorji zagotavljajo, da je konduktometrija obetajoča metoda, ki zagotavlja natančno, hitro in instrumentalno nezahtevno kemijsko karakterizacijo alkalnih silikatnih raztopin, ki je uporabna celo v proizvodnih procesih.

Ključne besede: analiza električne prevodnosti elektrolitov (konduktometrija), titracija, kemijska sestava, alkalne silikatne raztopine

## 1 INTRODUCTION

Alkaline silicate solutions (water glasses) are important raw materials for many applications. They are widely used, e.g., in foundry, building, paper, and paint industry.<sup>1-3</sup> The most mass-produced alkaline silicate is sodium silicate, whose production in Europe exceeds 500,000 tons per year, followed by the production of potassium silicate, which is at a level of approximately 21,000 tons per year, and a maximum of 1,000 tons is attributed to the production of lithium silicate, which is a specialized chemical, whose use is limited to the area of coatings.<sup>4</sup> Great demands are placed on its production, regarding its product quality, technological procedures, or certain parameters that the input raw material must

meet. When processing water glasses to obtain a new product with desired properties, it is crucial to know the chemical composition of the water glass used. The analyses can be performed with different methods, of which the most commonly industrially used one is the titrimetric method based on the color change of the indicator.<sup>5</sup> This analysis includes a titration of a water glass sample with a volumetric solution of hydrochloric acid using methyl red as the indicator. The mentioned procedure determines the M<sub>2</sub>O alkali content (i.e., Na<sub>2</sub>O, K<sub>2</sub>O, or Li<sub>2</sub>O) very precisely, but the method is inaccurate for the determination of the SiO<sub>2</sub> content. The main problem is the color change of the indicator during the subsequent titration, which is very gradual and, therefore, the determination of the equivalence point is ambiguous.

From this point of view, a conductometric analysis based on titration with a volumetric solution of hydro-

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chloric acid appears to be a very promising method, which could solve the above-mentioned problem. The method is based on the fact that in solutions of electrolytes the electric-current conduction is realized by the movement of ions. Therefore, the conductivity can be referred to as ionic or electrolytic.<sup>6</sup> However, what is very important for conductometric titrations is the fact that different ions can have different conductivities, so there can be changes in conductivities during the titration. The specific conductivity of an electrolyte solution depends not only on the type of ion, but also on its concentration. The most concentrated solutions of titration agents are used for the determination in order to avoid deformation of the linear dependence by diluting the titrated solution. The end of the titration is determined by the break in the titration curve.<sup>7</sup>

The aim of this article is to verify the applicability of conductometry analysis for the purpose of fast and accurate determination of the chemical compositions of various types of alkaline silicate solutions on an industrial scale. The measured results were compared with the currently used titrimetric method based on the color change of the acid-base indicator and subsequently verified using the ICP-OES and gravimetric determinations.

## 2 EXPERIMENTAL PART

### 2.1 Materials

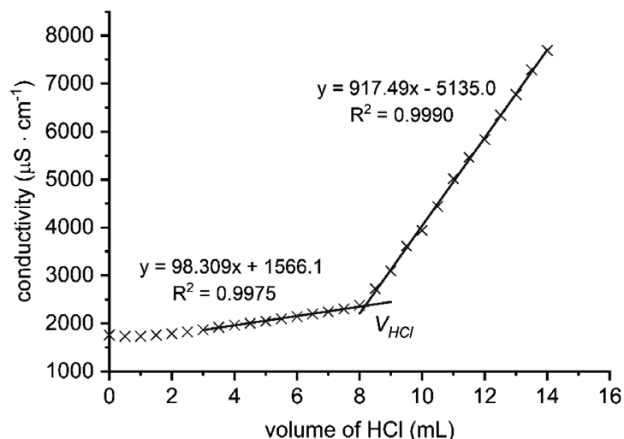
The sodium (Na-WG), potassium (K-WG) and lithium (Li-WG) silicate solutions (water glasses) used for the chemical analyses described below were supplied by the SChem a.s. company. The silicate modules as well as alkali and silica contents provided by the manufacturer are summarized in **Table 1**.

**Table 1:** Chemical-composition data of water glasses according to the supplier

	$w_{M_2O}$ (w/%)	$w_{SiO_2}$ (w/%)	$M_s$
Na-WG	16.65	31.66	1.96
K-WG	25.50	28.38	1.75
Li-WG	not specified	not specified	2.64

### 2.2 Conductometric titration

The procedure itself consists of two titrations, one of which determines the content of  $M_2O$  and the other the content of  $SiO_2$ . When water glass is titrated with a standard volumetric solution of hydrochloric acid and the silicate modulus (molar ratio of  $SiO_2$  and alkaline oxide) of the water glass is approximately 2, or higher, only reaction (2) applies, so only one sudden change in the conductivity appears in the obtained titration curve, which corresponds to the total  $M_2O$ . An example of an obtained titration curve is shown in **Figure 1**, where the intersection point of two linear parts corresponds to the volume of volumetric solution of HCl at the equivalence point –  $V_{HCl}$  in Equation (3).



**Figure 1:** Example of a measured conductometric curve for the determination of  $M_2O$



The determination process itself proceeded as follows. An amount of approximately 1 g to 2 g of a water-glass sample was weighed on an analytical balance, and transferred to a 400 mL plastic beaker using distilled water. It was filled up with water to a volume of approximately 200 mL. The resulting solution was placed on a magnetic stirrer. The solution was titrated conductometrically (Mettler Toledo conductometer In Lab 731) with 1 M hydrochloric acid. Conductivity values were recorded at each addition of 0.5 mL of volumetric HCl solution. The percentage of  $M_2O$  was calculated with Equation (3):

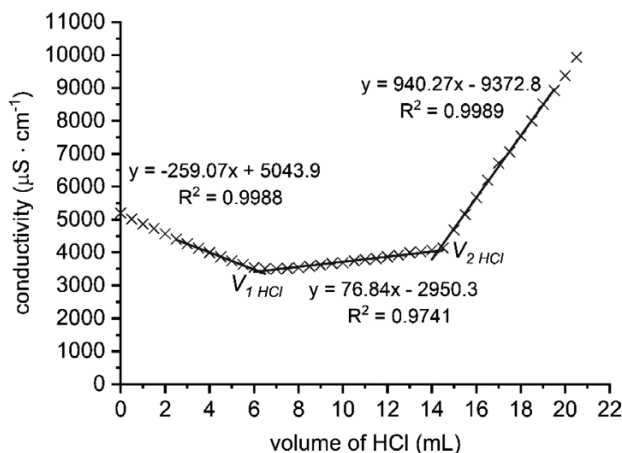
$$w_{M_2O} = \frac{1}{2} \frac{c_{HCl} \cdot V_{HCl}}{1000} M_{M_2O} \cdot \frac{100}{m_s} \quad (3)$$

where  $w_{M_2O}$  represents the percentage weight amount of  $M_2O$  in the water-glass sample (w/%),  $c_{HCl}$  is the concentration of the HCl measuring solution ( $mol \cdot L^{-1}$ ),  $V_{HCl}$  is the consumption of volumetric solution of HCl (mL),  $M_{M_2O}$  is the molar mass of  $M_2O$  ( $g \cdot mol^{-1}$ ), and  $m_s$  is the weight of the water-glass sample (g).

For the determination of  $SiO_2$ , before starting the conductometric titration, a suitable excess of the corresponding alkali metal hydroxide (LiOH, NaOH, or KOH) was added to the water glass, which also brought equation (1) into play; as a result, two breaks are visible on the titration curve. The first break corresponds to the titration of  $OH^-$  and  $SiO_3^{2-}$ , while the second one corresponds to the titration of  $HSiO_3^-$ . An example of the obtained titration curve is shown in **Figure 2**, where the intersection points of three linear parts correspond to the volume of volumetric solution of HCl –  $V_{1HCl}$  and  $V_{2HCl}$ .

Subsequently, the percentage of  $SiO_2$  was calculated with Equation (4),

$$w_{SiO_2} = \frac{c_{HCl} \cdot (V_{2HCl} - V_{1HCl})}{1000} \cdot M_{SiO_2} \cdot \frac{100}{m_s} \quad (4)$$



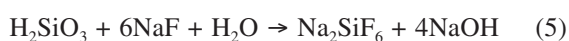
**Figure 2:** Example of the measured conductometric curve for the determination of  $\text{SiO}_2$

where  $w_{\text{SiO}_2}$  represents the percentage weight amount of  $\text{SiO}_2$  in the water-glass sample ( $w/\%$ ),  $c_{\text{HCl}}$  is the concentration of the HCl measuring solution ( $\text{mol}\cdot\text{L}^{-1}$ ),  $V_{\text{HCl}}$  is the consumed volume of the HCl solution (mL) corresponding to the titrated sum of  $\text{OH}^-$  and  $\text{SiO}_3^{2-}$  ions,  $V_{2\text{HCl}}$  is the consumed volume of the HCl solution (mL) corresponding to the titrated amount of  $\text{HSiO}_3^-$ ,  $M_{\text{SiO}_2}$  is the molar mass of  $\text{SiO}_2$  ( $\text{g}\cdot\text{mol}^{-1}$ ), and  $m_s$  is the weight of the water-glass sample (g).

### 2.3 Titrimetric method with an acid-base indicator

The principle of total alkalinity determination is the titration with a standard volumetric solution of hydrochloric acid, in the presence of methyl red as the indicator. Approximately 1 g of the water-glass sample was weighed on the analytical balance, and transferred to a plastic beaker with a volume of 400 mL. 50 mL of distilled water and 5 drops of the methyl red indicator were added to the sample. Subsequently, the solution was titrated with 1M HCl to the equivalence point, i.e., until a red-violet coloration appeared. The percentage of  $\text{M}_2\text{O}$  was calculated with Equation (3), where  $w_{\text{M}_2\text{O}}$  represents the percentage weight amount of  $\text{Li}_2\text{O}$ ,  $\text{Na}_2\text{O}$  or  $\text{K}_2\text{O}$  in the water-glass sample ( $w/\%$ ),  $c_{\text{HCl}}$  is the concentration of the HCl measuring solution ( $\text{mol}\cdot\text{L}^{-1}$ ),  $V_{\text{HCl}}$  is the consumption of the volumetric solution of HCl (mL),  $M_{\text{M}_2\text{O}}$  is the molar mass of  $\text{M}_2\text{O}$  ( $\text{g}\cdot\text{mol}^{-1}$ ), and  $m_s$  is the weight of the water-glass sample (g).

The principle of the silica-content determination is in an addition of sodium fluoride, which reacts with silicic acid, forming an equivalent quantity of sodium hydroxide (5) followed by neutralization with a solution of hydrochloric acid (6).



100 mL of a 5-% sodium fluoride solution was added to the solution created during the determination of total alkalinity. The resulting solution was titrated with 1M

HCl to the equivalence point, i.e., to a red color. Subsequently, the percentage of  $\text{SiO}_2$  was calculated with Equation (7),

$$w_{\text{SiO}_2} = \frac{c_{\text{HCl}} \cdot (V_1 - V_0) \cdot M_{\text{SiO}_2}}{40m_s} \quad (7)$$

where  $w_{\text{SiO}_2}$  represents the percentage weight amount of  $\text{SiO}_2$  in the water-glass sample ( $w/\%$ ),  $c_{\text{HCl}}$  is the concentration of the HCl measuring solution ( $\text{mol}\cdot\text{L}^{-1}$ ),  $V_1$  is the consumed volume of the HCl solution (mL),  $V_0$  is the volume of the HCl solution (mL) added for the blank test,  $M_{\text{SiO}_2}$  is the molar mass of  $\text{SiO}_2$  ( $\text{g}\cdot\text{mol}^{-1}$ ), and  $m_s$  is the weight of the water-glass sample (g).

### 2.4 Induction coupled plasma-optical emission spectroscopy (ICP-OES)

The high accuracy of the chemical determination of sodium silicate solutions was achieved using ICP-OES (Horiba Scientific Ultima 2). Exactly 0.10 mL of the water-glass sample was added to a 100 mL plastic volumetric flask using an automatic pipette. The flask was filled with distilled water to its calibration mark. The prepared solution was diluted 1000 $\times$ . The sample was then subjected to an ICP-OES determination by transport via a peristaltic pump to a nebulizer and further carried by argon to a torch. The measured concentrations of elements were obtained in  $\text{mg}\cdot\text{L}^{-1}$ . These values were converted to molar concentrations of the given oxides, from which the silicate modulus was calculated.

### 2.5 Gravimetric determination of $\text{SiO}_2$

For the gravimetric determination of  $\text{SiO}_2$ , approximately 1 g of the water-glass sample was weighed and transferred to a porcelain dish with 20 mL of distilled water. The solution in the porcelain dish was covered with a watch glass and 10 mL of concentrated HCl was slowly added to it. The dish was then placed on a hot plate, where the decomposition of the sample was completed at a temperature of 80 °C. Subsequently, the watch glass was rinsed with distilled water and a few drops of concentrated  $\text{HNO}_3$ . The dish was left on the hot plate until the solution was evaporated to dryness, then the dish was placed in an oven preheated to 105 °C for 10 min to completely dehydrate the precipitated silicic acid. After being removed from the oven, the dish was placed again on the hot plate and moistened with 5 mL of concentrated HCl. After 3 min, 100 mL of hot water was poured into the solution. The excluded silicic acid was filtered through ashless filter paper with a high pore density. The filter was washed 3 times with 5 mL of hot 1-% HCl solution. The paper filter with expelled silicic acid was inserted into an annealed crucible and placed in a triangle high above a Meker burner. The annealing process was lasted until the contents of the crucible dried and the filter paper was ashed. Then the crucible was placed in a laboratory furnace, where it was annealed to



Figure 3: Color transition in the determination of the SiO<sub>2</sub> content by the titrimetric method

Table 2: Chemical compositions of used water glasses determined with the titrimetric method using the color change of the acid-base indicator

	titrimetric method (color change from yellow to red)						titrimetric method (color change from yellow to orange)					
	Na-WG		K-WG		Li-WG		Na-WG		K-WG		Li-WG	
	W <sub>Na2O</sub>	W <sub>SiO2</sub>	W <sub>K2O</sub>	W <sub>SiO2</sub>	W <sub>Li2O</sub>	W <sub>SiO2</sub>	W <sub>Na2O</sub>	W <sub>SiO2</sub>	W <sub>K2O</sub>	W <sub>SiO2</sub>	W <sub>Li2O</sub>	W <sub>SiO2</sub>
1	17.00	39.08	25.97	35.95	3.31	20.25	16.73	32.91	25.17	28.44	3.27	17.33
2	16.70	39.46	25.80	35.94	3.33	20.35	16.67	32.89	25.32	28.88	3.20	17.36
3	16.17	39.65	26.11	36.06	3.28	20.25	16.69	32.50	25.51	27.92	3.26	17.34
4	16.47	39.77	26.25	36.19	3.32	20.37	16.79	31.93	25.40	28.15	3.24	17.37
5	16.49	39.65	26.11	36.23	3.14	19.16	16.48	31.95	25.19	28.96	3.24	17.34
6	16.86	39.84	25.89	36.13	3.26	20.24	16.19	31.87	25.10	28.80	3.25	17.40
<b>Avg.</b>	<b>16.62</b>	<b>39.57</b>	<b>26.02</b>	<b>36.08</b>	<b>3.27</b>	<b>20.10</b>	<b>16.59</b>	<b>32.34</b>	<b>25.28</b>	<b>28.53</b>	<b>3.24</b>	<b>17.35</b>
<b>SD</b>	<b>0.30</b>	<b>0.27</b>	<b>0.17</b>	<b>0.12</b>	<b>0.07</b>	<b>0.47</b>	<b>0.22</b>	<b>0.49</b>	<b>0.16</b>	<b>0.42</b>	<b>0.02</b>	<b>0.03</b>
<b>Ms</b>	<b>2.46</b>		<b>2.17</b>		<b>3.05</b>		<b>2.01</b>		<b>1.77</b>		<b>2.66</b>	
<b>Ms (ICP-OES)</b>	<b>1.84</b>		<b>1.74</b>		<b>2.60</b>		<b>1.84</b>		<b>1.74</b>		<b>2.60</b>	

Table 3: Chemical compositions of used water glasses determined with the conductometric analysis

	conductometric analysis					
	Na-WG		K-WG		Li-WG	
	W <sub>Na2O</sub>	W <sub>SiO2</sub>	W <sub>K2O</sub>	W <sub>SiO2</sub>	W <sub>Li2O</sub>	W <sub>SiO2</sub>
1	16.81	32.06	25.61	28.36	3.22	17.15
2	17.02	32.60	25.48	28.92	3.24	17.16
3	16.56	31.97	25.31	28.13	3.23	17.15
4	16.92	32.15	25.52	28.62	3.25	17.14
5	16.80	32.37	25.49	28.83	3.26	17.17
6	17.01	32.08	25.43	28.76	3.24	17.15
<b>Avg.</b>	<b>16.85</b>	<b>32.20</b>	<b>25.47</b>	<b>28.60</b>	<b>3.24</b>	<b>17.15</b>
<b>SD</b>	<b>0.17</b>	<b>0.24</b>	<b>0.10</b>	<b>0.30</b>	<b>0.01</b>	<b>0.01</b>
<b>Ms</b>	<b>1.97</b>		<b>1.76</b>		<b>2.63</b>	
<b>Ms (ICP-OES)</b>	<b>1.84</b>		<b>1.74</b>		<b>2.60</b>	

a constant weight at 1100 °C; after cooling it down in a desiccator, the crucible with silica was weighed to the nearest 0.1 mg. The entire procedure was repeated 3 times. From the obtained values, the percentage of SiO<sub>2</sub> in the water-glass sample was calculated with Equation (8),

$$w_{\text{SiO}_2} = 100 \cdot \frac{(m_2 - m_1)}{m_s} \quad (8)$$

where  $w_{\text{SiO}_2}$  represents the percentage weight amount of SiO<sub>2</sub> in the water-glass sample (w/%),  $m_1$  is the weight of an empty annealed porcelain crucible (g),  $m_2$  is the weight of the annealed sample and crucible (g), and  $m_s$  is the weight of the water-glass sample (g).

### 3 RESULTS AND DISCUSSION

The titrimetric method using the color change of the acid-base indicator was chosen as the most widely used industrial analysis of alkaline silicate solutions for the verification of the chemical composition declared by the manufacturer. Total alkalinity determination for different types of water glasses provided results without any significant deviation (Table 2). The color change of the methyl red indicator showed a sharp transition from yellow to red at the equivalence point. However, complications occurred during the silica content determination. According to the work procedure described in the experimental part, the neutralization process with the hydrochloric acid solution changes the indicator color again

from yellow to red. However, as can be seen (**Figure 3**), the color transition in this case is very unclear at different stages of the titration. In the first phase, the equivalence point is determined as a bright red-violet coloration, which corresponds approximately to the seventh shade in **Figure 3** (from left to right). The results of the SiO<sub>2</sub> content showed a relatively small deviation (**Table 2** – left side); nevertheless, the total silica content and subsequently calculated silica modulus differed considerably from the declared composition (**Table 1**). For this reason, the approach to determining the equivalence point was changed. It was found from several measurements that the equivalence point belongs to an orange shade from **Figure 3** (the fourth from the left). Such determination has already produced results corresponding to the declared chemical composition as well as the results obtained from ICP-OES analyses.

The problematic determination of the silica content gives reason to use another method of evaluation such as conductometric analysis. Its results are included in **Table 3**. Both the alkali metal and silica contents are always in good agreement with the values given by the manufacturer. The volume consumptions of the HCl volumetric solution were determined from the intersections of linear parts of conductometric curves and not from color transitions. This fact allows a more accurate measurement in contrast to the titrimetric method using an acid-based indicator where the accuracy may be affected by subjective color perception. Moreover, measurement deviations are very low, and the results are more consistent with the results of ICP-OES.

The accuracy of the achieved results was also assessed from gravimetric determinations of SiO<sub>2</sub>. The average values of three measurements were 32.07 w% of SiO<sub>2</sub> in sodium water glass, 28.34 w% in potassium water glass, and 17.16 w% in lithium water glass. Comparing these results with those of the conductometric analysis, marginal differences were observed. The verification using the mentioned analyses proves that conductometry provides meaningful results and can also be used advantageously in industrial practice.

## 4 CONCLUSIONS

The presented method for determining the chemical composition of the used water glasses, based on a conductometric analysis, provides satisfactory and accurate results, verified with other analytical methods. The currently used titrimetric method using the color change of the acid-base indicator had been shown to be misleading, especially in the determination of SiO<sub>2</sub>. Another reason for its unsuitability lies in the use of sodium fluoride, which is classified as a highly toxic substance. On the contrary, in the determination of total alkalinity of alkaline silicate solutions, this method provides representative results. For this reason, a combination of the conductometry analysis and the titrimetric method based on the color change of the acid-base indicator can also be considered.

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