

Precise analysis of pure sodium fluorosilicate: Unusual results

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ABSTRACT

A sample of pure sodium fluorosilicate (Na_2SiF_6), not contaminated with silicic acid, was prepared and used as a standard to develop a potentiometric technique for its alkali titration and determination of the silicic acid content. A surprising difference in the end point and the equivalence point of titration was observed. Influence of the dissolved colloidal silicic acid on the results of this titration was investigated. It is shown that no hitherto well-known analytical procedure can give the correct result of this titration, and that only precise potentiometric titration could explain the obtained results.

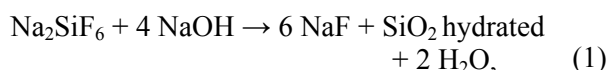
KEYWORDS: sodium fluorosilicate, silicic acid, alkali titration, potentiometric titration

INTRODUCTION

Sodium fluorosilicate is a promising material to produce silicon for use in solar batteries [1-3], but the samples obtained from water solutions always contain some percent of silicic acid (hydrated silicon oxide), which hinders silicon production. The technology of silicon production involves heating of Na_2SiF_6 with the formation of gaseous SiF_4 , which is later reduced with some active metals (Na, Mg), or converted into SiH_4 with subsequent thermal decomposition to give solar grade silicon. This technology demands sodium fluorosilicate of special quality since silicon oxide can react with silicon tetrafluoride on heating to produce volatile silicon oxyfluoride. The latter

contaminates tetrafluoride and the final silicon with oxygen-containing products; it also distorts the results of thermal decomposition pressure measurements of sodium fluorosilicate. It was shown recently [4] that a usual content of 2-3% of silicic acid in sodium fluorosilicate results in 20-30% contamination of silicon tetrafluoride produced.

Therefore it is necessary to analyze Na_2SiF_6 for the silicic acid contamination, and this analysis is usually made by alkali titration of sodium fluorosilicate:



with a widely used phenolphthalein as indicator [5-9] or with bromothymol blue, as recommended in [10]. But when a sample of pure Na_2SiF_6 free from silicic acid was prepared, it was unexpectedly discovered that all the well known methods of its alkali titration give too high results, and the content of silicic acid is appreciably underestimated. Thus it became clear that these strange results could be explained only after the detailed investigation of the titration reaction 1 using the most precise, potentiometric method.

MATERIALS AND METHODS

The starting sodium fluorosilicate was synthesized in the usual way, by pouring together the concentrated solutions of sodium chloride and hexafluorosilicic acid (excess 50%), both of reagent grade purity; laboratory polyethylene and polypropylene wares were used. A sample of pure sodium fluorosilicate was obtained by multiple treatments with concentrated hydrofluoric and

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hexafluorosilicic acids. Its purity and absence of silicic acid was confirmed by infra-red and X-ray spectra. Fourier-transform infrared spectra were obtained on FT-02 spectrometer. Powder X-ray diffraction patterns were recorded on DRON-3 diffractometer.

Chemical analysis of Na_2SiF_6 was carried out by its alkali titration using a universal ionmeter EV-74 and modified electrodes: platinum (quinhydrone) indicator (EPL-02) and silver chloride (EVL-1M4) reference electrodes. Glass parts of these electrodes were protected from the destroying influence of hydrofluoric acid using a layer of special composition, obtained by saturation of molten paraffin with polyethylene [11]. Processes of Na_2SiF_6 alkali titration and of sodium hydroxide titrant standardization were investigated thoroughly to obtain the best accuracy $\pm 0.1\%$ [12]. The standard HCl solution was prepared from an azeotrope [13], and the precision of its concentration was verified gravimetrically using AgCl precipitation. Two equivalence points were detected if the alkali titrant (NaOH) contained some carbonate [12]; this phenomenon could prevent the obtaining of accurate result for Na_2SiF_6 titration. Therefore it was necessary to prepare the standard alkali solution without carbonate [13] and to protect the analyte and titrant from absorbing carbon dioxide from air.

RESULTS AND DISCUSSION

The prepared pure sodium fluorosilicate was used to verify the results of its potentiometric titration

(Figure 1). Equivalence volume of the standard NaOH solution used for Na_2SiF_6 titration was calculated from the mass of the analyzed sample according to reaction 1. In figure 1 the results are shown for 0.0856 g of Na_2SiF_6 and 0.1082 M NaOH. The titration end point was found, as usual, at the maximum of the first derivative of the titration curve. A surprising difference in the end point and the equivalence point of titration can be seen in figure 1 (0.25 ml i.e. 1.5%).

Thus the titration end point found in the usual manner results in overestimation of the fluorosilicate content and, accordingly, in appropriate underestimation of the silicic acid content. Indicator titration with phenolphthalein (pH range 8.3-10) gives a much larger error, and even use of bromothymol blue (pH range 6.0-7.6) does not give the true result, which corresponds to $\text{pH} = 6.09 \pm 0.08$ (Figure 1).

What is the reason for such a strange difference in the end point and the equivalence point as can be seen in figure 1? As it is evident from equation 1, this process differs from a usual acid- or salt-base titration by the formation of colloidal silicic acid. Hence it was necessary to study its probable influence on the titration results, especially since there are data in the literature [14, 15] concerning adsorption of charge-determining ions OH^- onto the surface of disperse silica.

Special experiments were carried out to detect the possible sorption of OH^- by colloidal silicic acid and its influence on the potentiometric titration

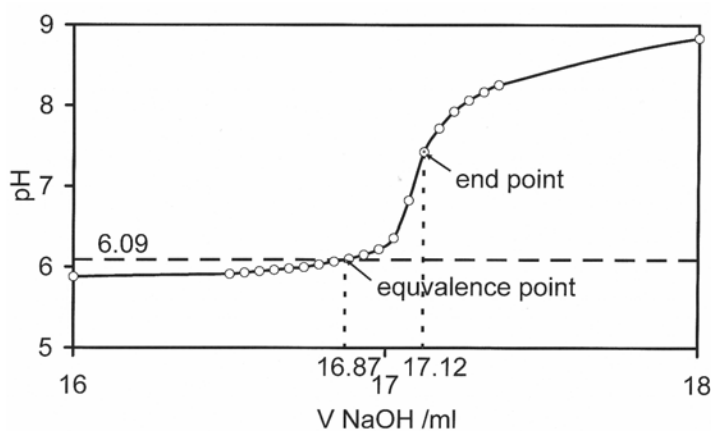


Figure 1. Titration curve of pure sodium fluorosilicate with NaOH standard solution.

results. The initial colloidal solutions were prepared from the weighed samples of $\text{Na}_2\text{SiO}_3 \cdot 4.43\text{H}_2\text{O}$ and the calculated amounts of HCl; the obtained solutions were quite clear and showed no signs of coagulation. Concentrations of these solutions were conditionally defined as mass percent of SiO_2 .

In the preliminary series of titrations solutions with nearly equal concentrations of HCl but different silicic acid concentrations were titrated with the standard NaOH solution. Both titration curves (Figure 2) were superposed at $\text{pH} = 4$, at which sorption of OH^- ions becomes negligible [13, 14]. These curves distinctly show the effect of OH^- sorption by colloidal silicic acid. This effect was never observed earlier, and hence we

examined it again and again in more strict conditions.

The next experiments were organized in such a way that in each series of titrations the analyte contained constant amounts of all the substances except colloidal silicic acid, which was added to the initial acid (HCl) solutions in differing concentrations. The results are shown in figure 3.

Finally, different concentrations of colloidal silicic acid were added to the titrated Na_2SiF_6 samples. In order to compare the results obtained for somewhat different samples, they were recalculated for the mass of Na_2SiF_6 equal to 0.1000 g (Figure 4).

The results shown in figures 2-4 prove the correctness of the hypothesis on the role of silicic acid in the

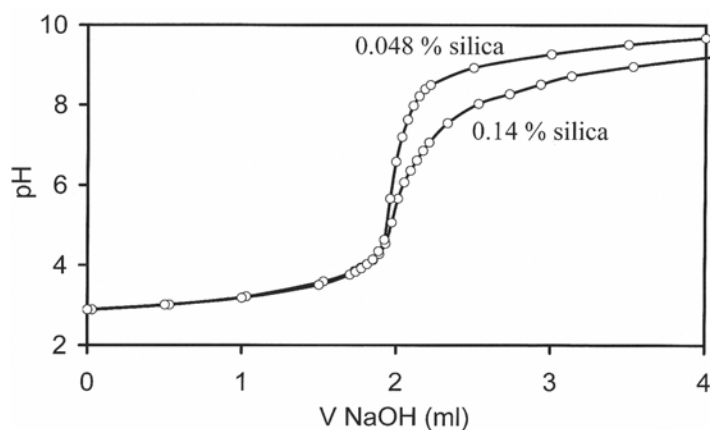


Figure 2. Titration curves of the same HCl solutions with different silicic acid concentrations (mass percent of SiO_2).

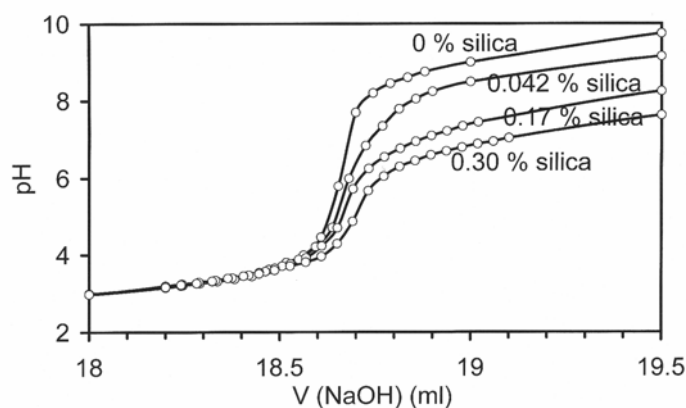


Figure 3. Titration curves of HCl solutions with different silicic acid concentrations and constant amounts of other substances (mass percent of SiO_2).

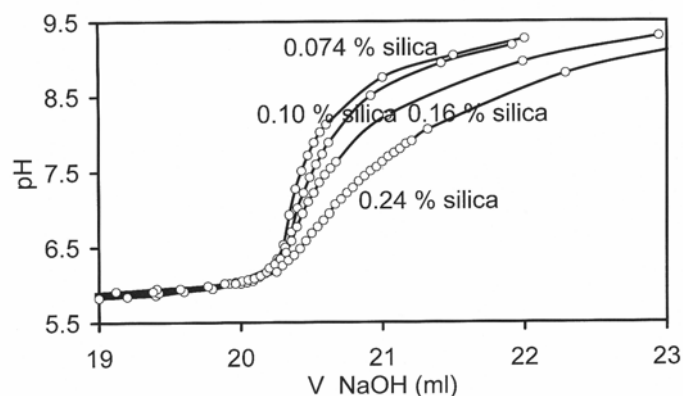


Figure 4. Titration curves of Na_2SiF_6 samples with different silicic acid concentrations, calculated for end points (mass percent of SiO_2).

Table 1. Analysis results of the same Na_2SiF_6 samples.

Volumetric method	Na_2SiF_6 content (%)	Volumetric method	Na_2SiF_6 content (%)
Potentiometric titration (pH = 6.09)	98.1 ± 0.4 (true value)	Titration with bromothymol blue (pH = 6-7.6)	100.0 ± 0.1
Potentiometric titration (derivative maximum, pH = 7-7.5)	99.9 ± 0.2	Titration with phenolphthalein at 20 °C (pH = 8.3-10)	101.1 ± 0.2
Titration with methyl red (pH = 4.2-6.2)	98.2 ± 0.2	Titration with phenolphthalein at 90 °C (pH = 8.3-10)	101.2 ± 0.2

unusual phenomenon – the surprising difference in the end point and the equivalence point of sodium fluorosilicate alkali titration; the obtained end point result also includes the alkali absorbed by colloidal silicic acid.

The results of Na_2SiF_6 analysis, obtained by different volumetric methods, are compared in table 1 with the true value of Na_2SiF_6 content found using the precise potentiometric titration (pH = 6.09). All these results were obtained in the identical conditions: the standard NaOH solution was the same and practically free from carbonate, it was protected from absorbing carbon dioxide from air; pure argon was bubbled through the analyte for the same.

One can see that the usual potentiometric titration (maximum of the first derivative) overestimates

Na_2SiF_6 content by $1.8 \pm 0.6\%$, and that is in good agreement with the data shown in figure 1 (1.5%). Practically the same is the result of titration with bromothymol blue. Volumetric titration with methyl red (to pure yellow) is the only indicator method that gives the result practically identical to the true value of sodium fluorosilicate content; for pure Na_2SiF_6 it also gives the true result $100 \pm 0.1\%$. Titration with phenolphthalein, either at 20 °C or at 90 °C, gives a deviation at the level of 3%.

CONCLUSION

A sample of pure sodium fluorosilicate, not contaminated with silicic acid, was prepared and carefully titrated with sodium hydroxide without carbonate. A surprising difference in the end point and the equivalence point of this titration was

observed. Thus it was shown that no hitherto well-known analytical procedure can give the correct result of this titration, and the difference amounts to 3 percent in the case of phenolphthalein as indicator. A detailed investigation of the titration reaction was undertaken using the most precise, potentiometric method, and the obtained results were explained by sorption of some alkali by colloidal silicic acid, formed in this reaction. Two titrimetric procedures are proposed to obtain the precise results of sodium fluorosilicate alkali titration: either potentiometric titration at pH = 6.09, or the indicator titration with methyl red. The observed phenomenon ought to be true for any other metal fluorosilicate alkali titration.

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CONFLICT OF INTEREST STATEMENT

The authors declare no conflict of interest.

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