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DETERMINATION OF THE ACTIVITY OF ALKALI METAL OXIDES IN MELTS OF THE $Na_2O-K_2O-SiO_2$ SYSTEM USING AN ION-MOLECULAR EQUILIBRIUM METHOD

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Multicomponent silicate systems containing several alkali metal oxides are the basis of many industrial glasses and play a significant role in pyrometallurgical processes. Silicate slags including potassium and sodium oxides are at the center of interest in the development of new carbon-fuel energy technologies. To study these systems various physicochemical methods, including solution calorimetry [1] and mass-spectrometry are used as well as an approach based on a model of the ideal mixing of complex phases [2, 3].

The fullest thermodynamic information can be obtained from high-temperature mass-spectrometry. To study multicomponent silicate systems the Belton–Fruehan method is most often used [4-9]. This method considers the quasibinary section of the multicomponent system. For example, in the case of the $Na_2O-K_2O-SiO_2$ system the sections $(\eta = \text{const})\{(1 - \xi) \cdot Na_2O \cdot (SiO_2)_\eta + \xi K_2O \cdot (SiO_2)_\eta\}$ run through this section and for several other compositions (the change in ξ from 0 to 1 with a constant η) we can obtain the ratios of the partial pressures of sodium and potassium. For this purpose the ratio of the ion fluxes of Na^+ and K^+ obtained as a result of the ionization by electron bombardment of the molecular beam are measured experimentally. Integration with respect to the Gibbs-Duhem equation makes it possible to calculate the activities of selected components in the quasi-binary section and the excess thermodynamic functions of their mixing. We must point out that to carry out the integration it is necessary to study a fair number of compositions and this makes this method cumbersome.

Wagner [10] proposed a mathematical transformation with the help of which for a three-component system it is possible to determine using the Belton—Fruehan method the activities of all three oxides; in this case the volume of experimental work and the processing of the data are intensely increased. In particular it becomes necessary to make measurements for several series of compositions with different mole fractions of silicon oxide (with different η).

By contrast the ion-molecular equilibrium method makes it possible to determine the activities of alkali metal oxides for each composition, independently of each other. This approach was considered in [11] on the example of the Na_2O—SiO_2 system. The basic idea lies in the fact that in the vapor over the experimental melt, suitable ions, for example, CrO_3^-, CrO_4^-, and $NaCrO_4^-$ are generated by adding an easily ionized addition. The partial pressure of oxygen can be determined from the following relationship:

$$p(O_2) = \frac{p^2(CrO_3^-)}{p^2(CrO_4^-)} \frac{1}{K_{eq}^2(1)},$$

where $K_{eq}(1)$ is the equilibrium constant of the reaction

$$CrO_3^- + \frac{1}{2}O_2 = CrO_4^-, \tag{1}$$

whose numerical values have been determined in advance. The ratio of the partial pressures of the ions are calculated from the measured ion streams [12, 13].

$$\frac{p(CrO_4^-)}{p(CrO_3^-)} = \frac{I(CrO_4^-)}{I(CrO_3^-)} = \frac{M(CrO_4^-)}{M(CrO_3^-)}.$$

where I is the ion stream measured on the electron multiplier and M is the molecular mass of the ion.

The pressure of sodium is determined analogously from the ratio of the ion streams of $NaCrO_4^-$ and CrO_4^- and the equilibrium constant of the reaction

$$CrO_4^- + Na = NaCrO_4^-. \tag{2}$$

In the case of the reaction

$$Na_2O(liq) = 2Na + \frac{1}{2}O_2 \tag{3}$$

the equilibrium constant is well known and therefore we can calculate the activity of sodium oxide from the partial pressures of sodium and oxygen.

The extent of the effect of the addition on the values to be determined can be found by planning the experiment specifically.

In this study the ion-molecular equilibrium method is used to determine the activities of the alkali metal oxides in the Na_2O—K_2O—SiO_2 system. Particular attention has been paid to the problem of the effect of the nature of the additive and the material of the crucible on the result of the measurements.

Experiment. To determine the activities of the alkali metal oxides in the Na_2O—K_2O—SiO_2 system we used an MX-1303 mass spectrometer refitted to investigate the ion-molecular equilibria [13].

Sodium and potassium carbonates and also silicon oxide used in the synthesis were "analytically pure" grade. The glass-melting process was carried out in Pt crucibles. The analysis of the specimens obtained was carried out at the Grebenshchikov Institute of Silicate Chemistry (Academy of Sciences, Leningrad).

Over the 1300-1430 K temperature interval three compositions were studied:

Composition I, $0.242Na_2O$—$0.102K_2O$—$0.656SiO_2$,

Composition II, $0.172Na_2O$—$0.161K_2O$—$0.667SiO_2$,

Composition III, $0.116Na_2O$—$0.223K_2O$—$0.661SiO_2$.

The duration of the experiment was chosen so that the change in the concentration of each of the alkali metal oxides as a result of evaporation should not exceed 0.0015 mole fractions.

Unless particularly specified, a Pt crucible (diameter 12 and height 14 mm) was used in the study. The ratio of the area of evaporation to the area of the effusion aperture was ~200-900. The crucible plus the material in it was heated in an Mc resistance furnace. The temperature was measured by a Pt—Rh (10% Rh) thermocouple to an accuracy of ±3 K. The constancy of the temperature was held by a VRT-3 controller to an accuracy of 1 K.

TABLE 1. Mass Spectra of Negative Ions in the Vapor over a Melt of the $Na_2O-K_2O-SiO_2$ System (relative units)

Expt. No.	Composition	Addition, mole %	$I(CrO_4^-)$	$I(NaCrO_4^-)$	$I(KCrO_4^-)$
1	I	Cr_2O_3 0.040	14.9	5.3	6.8
2		Li_2CrO_4 0.019	46.7	10.4	13.1
3		Cs_2CrO_4 0.015	38.6	15.1	19.2
4	II	Cr_2O_3 0.020	31.9	9.6	22.6
5		Li_2CrO_4 0.020	52.1	11.6	22.9
6		Cs_2CrO_4 0.032	14.8	7.1	16.5
7	III	Cr_2O_3 0.032	4.5	2.0	8.5
8		Li_2CrO_4 0.040	18.8	4.6	20.8

Note. $I(CrO_3^-)$ = 100,000 for all compositions.

The ion streams were measured by a VÉU-6 electron channel multiplier. In the case of the chromium-containing ions we measured the ^{52}Cr isotopes and for the potassium-containing ions, the ^{39}K.

In order to generate the required negative ions in the vapor of the experimental silicate system, we added a small addition of chromium-containing compounds. This ensured the presence of CrO_3^-, CrO_4^-, $NaCrO_4^-$, and $KCrO_4^-$ ions in the measured concentration.

To study the effect of the nature of the addition in measurements using the same composition, chromates of various alkali metal oxides and the chromium oxide, Cr_2O_3 were used.

Table 1 gives the relative intensities of the ion streams and the values of the additives.

The experiment was conducted in accordance with the scheme proposed in [11]. When comparing the data from individual experiments, this system made it possible to take advantage of the help of a single-factor dispersion analysis [14], i.e., it provides an opportunity to evaluate independently the statistical spread. The procedure includes the following. At one temperature we recorded several mass-spectra (one series), then we changed the temperature and again recorded several mass-spectra. After the passage of some time we returned to the first temperature. Thus, at precisely the same temperature we obtained several series of mass-spectra recorded at different times in the experiment. The measurement time for one series was $\approx$10 min and the interval between the same temperatures was $\approx$40 min. The recording of the mass-spectra began 20 min after the beginning of the experiment.

Discussion of the Results. The Effect of an Additive on the Partial Pressures of Oxygen, Sodium, and Potassium in the System $Na_2O-K_2O-SiO_2$. Table 2 shows the log ratios of the following ion streams: CrO_4^- and Cr_3^-, $NaCrO_4^-$ and CrO_4^-, $KCrO_4^-$ and CrO_4^- obtained by taking the average over the whole series of measurements at a given temperature. From these data we calculated the partial pressures of oxygen, sodium, and potassium, established in the system $Na_2O-K_2O-SiO_2$ plus the additive. The required values of the equilibrium constant of reactions (1) and (2) and

$$CrO_4^- + K = KCrO_4^- \tag{4}$$
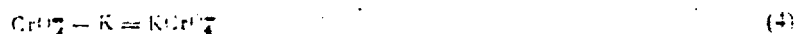
were calculated from the thermodynamic characteristics of the ions and of O_2, Na, and K [15, 16]. The results are given in Table 2.

It is clear that the partial pressures of oxygen, sodium, and potassium corresponding to the experiments with different additives for the same composition differ significantly (sometimes as much as tenfold). A similar fact was also noted previously with the introduction of an additive to the Na_2O-SiO_2 system [17]. Nevertheless, as we shall show later, the products $p(O_2)^{1/2}p(Na)^2$ and $p(O_2)^{1/2}p(K)^2$ remain constant within the experimental error. This can be explained by the fact that the additive "distorts" the oxygen pressure in the original system and the measured values of $p(O_2)$ refer to a new four-component system.

Thus, the partial pressures of oxygen, sodium, and potassium found here cannot refer to the original system.

The Effect of the Nature of the Additive on the Activity of Oxides of Alkali Metals in the System $Na_2O-K_2O-SiO_2$. The measured pressures of oxygen and sodium in combination with the equilibrium constant of reaction (3) make it possible to determine the activity of sodium oxide. By expressing the partial pressures of O_2 and Na in terms of the ion streams we obtain the calculation equation (for more detail, see [11])

TABLE 2. Partial Pressures of Oxygen, Sodium, and Potassium in the $Na_2O-K_2O-SiO_2$ System at 1387 K

Composition	Additive	$\ln \frac{I(CrO)}{I(CrO_4)}$	$\ln \frac{I(NaCrO_4)}{I(CrO_4)}$	$\ln \frac{I(KCrO_4)}{I(CrO_4)}$	n	$p(O_2)$, Pa	$p(Na)$, Pa	$p(O_2)$, Pa
I	Cr_2O_3	−8.81	−1.04	−0.79	9	0.014	0.098	0.06?
	Cs_2CrO_4	−7.86	−0.92	−0.70	6	0.090	0.110	0.060
	Li_2CrO_4	−7.67	−1.50	−1.27	6	0.130	0.062	0.039
II	Cr_2O_3	−8.05	−1.20	−0.37	9	0.062	0.083	0.097
	Li_2CrO_4	−7.56	−1.50	−0.82	12	0.174	0.062	0.062
	Cs_2CrO_4	−8.82	−0.73	0.11	3	0.013	0.130	0.160
III	Cr_2O_3	−10.00	−0.82	0.62	3	0.0013	0.120	0.260
	Li_2CrO_4	−8.58	−1.40	0.10	9	0.022	0.068	0.16

Note. n is the number of measurements.

$$\ln a(Na_2O) = \ln \frac{I(NaCrO_4)^2}{I(CrO_4) \cdot I(CrO_4)} + 0.51 - \ln K_{eq}(1)\, K_{eq}(2)^2\, K_{eq}(3).$$

and the numerical constant arises with a change to ion streams.

An analogous expression is also obtained for the activity of potassium oxide

$$\ln a(K_2O) = \ln \frac{I(KCrO_4)^2}{I(CrO_4) \cdot I(CrO_4)} + 0.87 - \ln K_{eq}(1)\, K_{eq}(4)^2\, K_{eq}(5).$$

where $K_{eq}(5)$ is the equilibrium constant of the reaction

$$K_2O\ (liq) = 2K + \frac{1}{2}O_2. \tag{5}$$

The equilibrium constants of reactions (3) and (5) were calculated from the thermodynamic characteristics of Na_2O and SiO_2 [18] and K_2O [2].

Like the pressures of O_2, Na, and K, the activities obtained for sodium and potassium oxides generally speaking refer to the four-component system $Na_2O-K_2O-SiO_2$-additive. However, since the amount of the additive is not very great, there are grounds for assuming that it cannot significantly change the activities of the main components. Thus, the effect of an addition of potassium chromate to the Na_2O-SiO_2 system on the activity of sodium oxide was studied by us in advance. It was shown that the activity obtained for sodium oxide does not change, within the experimental error, with a change in the mole fraction of K_2CrO_4 from 0.003 to 0.04 which is in satisfactory agreement with the published data on the activity of Na_2O in the Na_2O-SiO_2 binary system [11].

In the present work we studied the effect of the nature of the additive at a concentration of ≈0.03 mole fraction on the measured activities of Na_2O and K_2O. For all the compositions we used chromium oxide and lithium chromate as the additives since these generate the required negative ions and for compositions I and II we also used cesium chromate. Sodium and potassium chromates were not used in order to avoid a direct increase in the mole fractions of Na_2O and K_2O. The results of the measurements at 1387 K are shown in Table 3.

The activities obtained for the alkali metal oxides in experiments with additions of chromium oxide and lithium chromate are in satisfactory agreement with each other. The experimental results with cesium chromate for Composition II agree on the whole with the values obtained with the additions of Cr_2O_3 and Li_2CrO_4. In the case of Composition I an addition of cesium chromate to the region richer in sodium oxide led to a 2.5-fold increase in the activity of alkali metal oxides.

We propose the following interpretation of the results obtained. The chemical affinity of chromium oxide and lithium chromate to silicon oxide is less than that of cesium oxide and therefore the experiments with additions of Li_2CrO_4 and Cr_2O_3 demonstrate the activities of alkali metal oxides closer to the original three-component system. In the case of the addition of cesium chromate a mixed-alkali effect is clearly observed [19] and its effect is exerted in the region richer in sodium oxide. We must point out that the actual mechanism of the effect of the cesium chromate addition on the activity of alkali metal oxides is not yet clear and requires a special examination.

From the methodological point of view we can state the fairly obvious conclusion. When using the ion-molecular equilibria method it is necessary to apply compounds which are chemically inert in the given medium as the additive.

TABLE 3. Activities of the Oxides of Sodium and Potassium Obtained in Experiments with Various Additives at 1387 K

Composition	Additive	Y_{Na_2O}	s	$\ln a_{Na_2O}$	Y_{K_2O}	s	$\ln a_{K_2O}$
i	Cr_2O_3	−10.89	0.31	−18.57	−10.39	0.27	−21.16
	Li_2CrO_4	−10.67	0.12	−18.35	−10.20	0.13	−23.97
	Cs_2CrO_4	−9.69	0.09	−17.57	−9.2?	0.27	−3?.93
II	Cr_2O_3	−10.46	0.13	−18.17	−8.78	0.11	−22.7?
	Li_2CrO_4	−10.51	0.23	−18.19	−9.13	0.17	−22.9?
	Cs_2CrO_4	−10.28	0.02	−17.96	−8.60	0.10	−22.??
III	Cr_2O_3	−11.64	0.39	−19.32	−8.76	0.57	−22.5?
	Li_2CrO_4	−11.38	0.14	−19.06	−8.8?	0.15	−22.16

Note. s is the standard deviation of an individual measurement from the average; n is the number of measurements; $Y_{Na_2O} = \ln [I(NaCrO_4^-)^2/I(CrO_3^-) \cdot I(CrO_4^-)]$, $Y_{K_2O} = \ln [I(KCrO_4^-)^2/I(CrO_3^-) \cdot I(CrO_4^-)]$.

TABLE 4. Log of the Ratio of the Ion Streams Required for Calculating the Activities of Sodium and Potassium Oxides

Composition	T, K	Y_{Na_2O}	s_h	s_p	Y_{K_2O}	s_h	s_p	ΣJ_i	
I	1300	−10.44	0.06	0.16	−9.93	0.09	0.24	6	2
	1347	−10.43	0.35	0.12	−9.97	0.27	0.17	15	5
	1387	−10.81	0.34	0.23	−10.32	0.33	0.16	15	5
	1430	−10.44	0.52	0.22	−10.10	0.25	0.22	15	5
II	1300	−10.56	0.41	0.23	−8.72	0.38	0.11	19	7
	1347	−10.51	+0.16	0.08	−8.89	0.15	0.05	17	
	1387	−10.49	0.27	0.14	−8.97	0.40	0.10	21	7
	1430	−10.26	0.02	0.15	−9.03	0.00	0.11	6	2
III	1344	−11.56	0.15	0.28	−8.11	0.23	0.21	12	4
	1387	−11.44	0.30	0.21	−8.45	0.38	0.30	12	4
	1430	−11.52	0.21	0.27	−8.64	0.44	0.20	11	4

Notes. s_h is the interserial standard deviation; s_p is the intraserial standard deviation; ΣJ_i is the number of measurements; 1 is the serial No. $Y_{Na_2O} = \ln [I(NaCrO_4^-)^2/I(CrO_3^-) \cdot I(CrO_4^-)]$. $Y_{K_2O} = \ln [I(KCrO_4^-)^2/I(CrO_3^-) \cdot I(CrO_4^-)]$.

Activities of Sodium and Potassium Oxides. A Comparison with the Model of an Ideal Mixing of Complex Phases. Table 4 gives the average log ratios of the ion streams as required for determining the activities of sodium and potassium oxides. The averages were taken only from the experiments where the additive was chromium oxide or lithium chromate; the experiments with the cesium chromate additive were not taken into account. Table 4 also shows the results of a single-factor dispersion analysis: intraserial, s_p and interserial s_h dispersions. On the whole according to Fisher's criterion they differ significantly from each other. This is confirmation of the fact that within the experimental errors, the results of the tests with additions of chromium oxide and lithium chromate match one another [11, 14].

Although several studies [7-9] have dealt with the system $Na_2O-K_2O-SiO_2$ it is not possible to make a direct comparison of the results since additional transformations are required and a recalculation of the values found. It is planned to discuss this separately.

At a given stage a comparison is made between the experimental data for the activities of Na_2O and K_2O and the data calculated in accordance with the model of ideal mixing of complex phases proposed by Hastie and Bonnell [2]. The solution is considered as an ideal mixture of components and known or hypothetical liquids which can form as a result of the interactions. As the components we chose compounds which are known from the phase diagram [20, 21]. The thermodynamic data for the constants of formation of these complexes were taken from [2]. Comparing the results obtained with the values found in this way

Composi-tion	T, K	ln a_{Na_2O}		ln a_{K_2O}	
		experiment	mode*	experiment	mode*
I	1300	—19.04	—20.65	—25.16	—24.31
	1341	—18.55	—20.12	—24.23	—24.15
	1387	—18.55	—19.43	—24.00	—23.35
	1430	—17.71	—18.88	—23.21	—22.61
II	1300	—19.06	—21.00	—23.95	—24.50
	1344	—18.63	—20.47	—23.35	—23.72
	1387	—18.17	—19.83	—22.74	—22.98
	1430	—17.53	—19.30	—22.14	—22.27
III	1344	—19.58	—20.52	—22.57	—22.93
	1387	—19.12	—19.99	—22.25	—22.22
	1430	—18.79	—19.39	—21.75	—21.55

*Calculated in accordance with the model of ideal mixing of complex components.

TABLE 6. Evaporation of the $Na_2O-K_2O-SiO_2$ System from a Molybdenum Crucible

T, K	O_2, Pa	Na, Pa	K, Pa	ln a_{Na_2O}	ln a_{K_2O}
1344	$1.8 \cdot 10^{-7}$	0.060	0.029	—24.11	—30.14
1387	$6.4 \cdot 10^{-7}$	0.073	0.043	—24.65	—30.68

(Table 5) we can conclude that the model calculation reflects the qualitative course of the change in the activities and gives values close to the experimental.

The Effect of the Material of the Crucible on the Evaporation of Silicate Systems. In the mass-spectral studies, as well as Pt effusion cells of other metals are frequently used (Mo, Ta, Ni) [7, 22]. At the same time, we can assume that the material of the crucible will take part in the chemical interaction with the original reagents and thus will lower the pressure of oxygen. As a check, experiments were carried out with composition II in an Mo crucible. However, in this case the addition of lithium chromate did not provide measurable concentrations of all the required ions and the normally most intense CrO_3^- appeared only at high temperatures in insignificant amounts. The ions MoO_3^-, $KMoO_4^-$, and $NaMoO_4^-$ arising as a result of the participation of the crucible material were observed. Therefore, as the additive in the next experiment we used MnO_3 and $LiPO_3$. Phosphorus-containing negative ions have previously been used to determine low oxygen pressures [23]. In the mass-spectrum we recorded the following ions: PO_2^- (13); PO_3^- (100); MoO_3^- (41), $KMoO_4^-$ (5.5), and $NaMoO_4^-$ (3.5) (figures in brackets denote the relative intensities). In the case of Mo-containing ions we measured the ^{98}Mo isotope streams.

The treatment of the results was carried out in an analogous way. From the measured ion streams and the equilibrium constants of the reactions

$$MoO_3^- + PO_3^- + Na = NaMoO_4^- + PO_2^-. \tag{6}$$

$$MoO_3^- + PO_3^- + K = KMoO_4^- + PO_2^-. \tag{7}$$

$$PO_2^- + \tfrac{1}{2} O_2 = PO_3^- \tag{8}$$
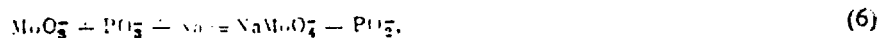
we determined the partial pressures of Na, K, and O_2. In calculating the equilibrium constants of reactions (6)-(8) we used the thermodynamic functions of the ions as recommended in [15, 23].

The partial pressures of O_2, Na, and K and the activities of Na_2O and K_2O obtained in the experiments using a molybdenum crucible are shown in Table 6. These values confirm the hypothesis about the interaction between the material of the effusion cell and the system. As a result, the oxygen pressure is sharply reduced (Tables 6 and 2) and the values of the activity of Na_2O and K_2O are found to be significantly lower than in the experiments using a Pt crucible.

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Conclusions. Using the IME method, the activities of Na_2O and K_2O in melts of the $Na_2O-K_2O-SiO_2$ system have been determined. It is shown that, as the additive which generates the required ions, it is necessary to use Li_2CrO_4 and Cr_2O_3. The use of $CsCrO_4$ provides rather high values of the activities of Na_2O and K_2O. The significant effect of the crucible material on the oxygen pressure has been established while the partial pressures of the alkali metals on evaporation from various effusion cells do not change.

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STRUCTURE FORMATION IN THE SURFACE OF MULTICOMPONENT
SILICATE GLASS IN THE PRODUCTION BY DRAWING FROM
A MELT IN ATMOSPHERES OF DIFFERENT COMPOSITIONS

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From the energy point of view, the formation of the surface of a glass product is a combination of processes directed towards reducing excess surface energy. The process can be divided into two groups. Firstly, there is the absorption processes of surface-active components from the gas phase or melt. In the gas phase there is mainly water vapor and carbon dioxide gas [1] while in the melt there are oxides of alkalis or alkali metals (more accurately, ions of these metals) [2]. Secondly, the lowering of excess surface energy is possible as a result of the regrouping of the structural elements of the glass in the surface layer as is characteristic of all silicates [3]. Such regrouping is now called the "reconstruction" of the surface [4]. It is obvious that, depending on the conditions of the formation, the contribution from the above processes to the total reduction of surface energy when the glass is cooled may be different.

In the present study we attempted to analyze the features of the formation of the structure of the surface layers of a multicomponent, industrial, silicate, window-type glass in an atmosphere of various compositions. To do this we made use of the data on the concentration of Na, Ca, and Si in the surface layer and on their distribution over the surface layer. We also used the IR-reflection spectra of the surface. In parallel we studied the properties of freshly formed specimens of glass determined by the state of the surface, including chemical stability, microhardness, compressive strength, and thermal-shock resistance.

For the tests and analyses we used rods, diameter 4.5-4.6 mm, obtained by drawing from the surface of a glass melt of the following composition, mole%: SiO_2, 71.8; Al_2O_3, 1.59; CaO, 8.63; MgO, 3.61; Na_2O, 13.47; Fe_2O_3, 0.33; and SO_3, 0.39. The drawing rate was 0.3 m/sec. Drawing was carried out using equipment which would provide the required composition of the atmosphere in the forming zone until the surface of the rods reached a temperature of 250°C.

The change in the concentration of the main components in the surface layer of the glass specimens and also in the uniformity of their distribution over the surface was determined using a JXA-733 microanalyzer from the change in the intensity of the K_a lines of Na, Ca, and Si. A study of the change in intensity of the characteristic x-ray radiation was made by scanning the specimens with a fixed position of the electron beam at intervals of 2 μm at 200 points on the surface. The accelerating voltage of the electron beam was 15 kV, the current of the beam, $0.43 \cdot 10^{-7}$ A. It is well known that Na and Ca migrate under the action of the electron beam from the analyzed zone and thus the intensity of the characteristic x-ray radiation during its measurement can change significantly [5]. To determine the errors in the above measurements, multiple (n = 200) determinations were made of the intensities at a fixed point on the specimen after stabilization of the intensity of the above lines over a period of time.