

## Laboratory and Computing Methods

### THE POSSIBILITIES OF POTENTIOMETRIC DETERMINATION OF POTASSIUM IN SOME SILICATE RAW MATERIALS

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*Potentiometry using the potassium ion-selective electrode can be conveniently employed to determine rapidly the approximate content of  $K_2O$  in silicate raw materials. For the determination, the dried and ignited sample of the material is decomposed by reflux boiling in hydrochloric acid ( $9 \text{ mol dm}^{-3}$ ). Aliquots are taken from the suspension obtained so as to receive a resulting  $K_2O$  content over the range of  $10^{-2}$  to  $1.5 \times 10^{-5} \text{ mol dm}^{-3}$  at pH of 0.7 to 0.9. Under the given conditions, the interfering effect of hydrogen ions occurs only at  $pK^+ = 5$ .*

#### INTRODUCTION

The present study had the aim to study the properties of the potassium ionically selective electrode (ISE) and its use for the determination of potassium content in raw materials for the silicate industry. Nowadays, the content of potassium oxide in kaolins and other raw materials is usually determined by flame photometry [1], which is a tedious and financially demanding method.

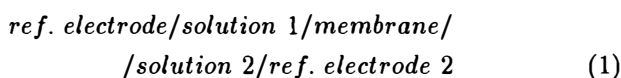
In the determination of potassium, use is made of several types of ion-selective electrodes (ISE) [2], such as the ISE formed by a heterogeneous membrane containing  $K_2Zn[Fe(CN)_6]$  or the LISE type with a liquid membrane enclosed in plasticized PVC. These electrodes basically differ in the active component contained in the membrane. The first ionophore (i. e. the electro-active substance from the group of neutral carriers) employed was nonactin, then there was the group of cyclic polyethers, such as the frequently employed dimethyl-dibenzo-30-crown-10. Recently, membranes of tetraphenylborate or tetra(p-chlorophenyl)borate solution in o-nitrotoluene, and membranes with valinomycin (belonging among cyclodepsipeptides, i. e. substances composed alternately of  $\alpha$ -amino acids and  $\alpha$ -hydroxy acids) are finding increasing application.

Nowadays, most frequent use is made of electrodes based on the valinomycin ionophore, because of their high selectivity towards potassium compared to that towards sodium. Esters of phthalic acid serve as solvents of the active component in the membrane. To improve fixation of potassium in the membrane and to suppress anionic interference in the membrane,

a potassium salt of hydrophobic tetraphenylborate or tetra(p-chlorophenyl)borate anions was built into the membrane. This type of electrodes is manufactured by PRECIOSA, a. s. Turnov under the trade mark Crytur 19-25.

#### Potential of the potassium ion-selective electrode

In ISE potentiometry, the electromotive force (hereafter EMF) of the following cell is measured:



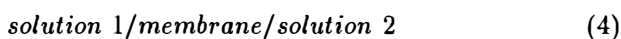
where "solution 1" is the solution being analyzed, and "solution 2" is the so-called inner ISE solution. The voltage of the cell is defined by the relationship

$$EMF = E_{ISE} - E_1 \quad (2)$$

and the electrode's own potential is then

$$E_{ISE} = E_2 - \Phi_M \quad (3)$$

where  $E_2$  is the potential of reference electrode 2 and  $\Phi_M$  is the membrane potential [3]. Its definition is based on the scheme



and in the case of the potassium electrode is expressed by the equation

$$\Phi_M = \frac{RT}{F} \ln \frac{a_K(1)}{a_K(2)} \quad (5)$$

Table I

The content of sodium and potassium oxides in some raw materials for the silicate industry

Type of material	Name of material (country of origin)	Content in wt. %	
		K <sub>2</sub> O	Na <sub>2</sub> O
kaolin	KD Podbořany (CZ)	0.85	0.12
kaolin	KDH Podbořany (CZ)	0.37	0.06
kaolin	Ia Sedlec (CZ)	0.94	0.11
kaolin	Kentucky Tile Blend (USA)	0.7	0.2
kaolin	HTP Gleason (USA)	0.7	0.1
clay	HC Cheb (CZ)	1.56	0.07
clay	CH Cheb (CZ)	2.04	0.12
clay	BD Cheb (CZ)	2.12	0.12
clay	IBV Cheb (CZ)	2.33	0.09
clay	B1 Cheb (CZ)	2.36	0.14
clay	B2 Cheb (CZ)	2.61	0.18
clay	KY Special Mayfield (USA)	0.9	0.2
clay	Tennessee 1-SGP (USA)	1.2	0.2

By joining equations (3) and (5) one obtains the Nernst equation for the potassium ISE in the form

$$E_{\text{ISE}} = \text{const.} + \frac{RT}{F} \ln a_{\text{K}}(1) \quad (6)$$

In fact, however, the solution being measured does not contain only potassium ions, and moreover no ISE is absolutely selective. The ISE potential is also affected by other interfering ions such as Na<sup>+</sup>, H<sup>+</sup>, NH<sub>4</sub><sup>+</sup>, etc. In the present case, the effect of ammonium ions can be ruled out because they are absent in the samples following the decomposition process. The effect of sodium ions, which always accompany potassium ones in silicate materials, is more significant. The manufacturer claims a sodium ion selectivity coefficient of  $K_{\text{Na}} = 2 \times 10^{-4}$ . This means that the effect of the sodium ions presence on the potential of the potassium ion-selective electrode will start at a 100-fold excess of these ions with respect to the content of potassium ions. As follows from Table I, the content of the ions in both natural and processed materials is usually much lower than that of potassium, so that their effect, in terms of the selectivity coefficient value specified by the manufacturer for the given electrode ( $2 \times 10^{-4}$ ), can be neglected.

The hydrogen cation is therefore the only virtually interfering ion. Its effect on the membrane potential is described by the equation

$$\Phi_{\text{M}} = \frac{RT}{F} \ln \frac{a_{\text{K}}(1) + K_{\text{H}}a_{\text{H}}(1)}{a_{\text{K}}(2)} \quad (7)$$

and the so-called Nikolsky equation then holds for the ISE potential [3]:

$$E_{\text{ISE}} = \text{const.} + \frac{RT}{F} \ln [a_{\text{K}}(1) + K_{\text{H}}a_{\text{H}}(1)], \quad (8)$$

where  $K_{\text{H}}$  is the selectivity coefficient of hydrogen cations.

## EXPERIMENTAL

### Laboratory equipment

The pH was measured with the OP 208/1 digital pH-meter and the OP 0808 combined glass electrode made by Radelkis, Budapest, calibrated by two standards for the acidic region (pH 2.11 and 3.556 respectively).

The EMF of the cell comprising the potassium ISE and the reference mercurous chloride electrode was measured with the OP 211/1 digital pH-meter from the same manufacturer. The reference electrode was separated from the solution measured by a salt bridge filled with NH<sub>4</sub>NO<sub>3</sub> solution at a concentration of 0.1 mol dm<sup>-3</sup>.

The following primary solutions were employed: metal-stabilized KCl solution of 0.5 mol dm<sup>-3</sup> concentration, prepared by weighing in KCl C.P. dried for 12 hours at 130°C in an oven. The other primary solution was that of HCl A.R. of 1.05 mol dm<sup>-3</sup> concentration.

The decomposition of samples with concentrated HCl A. R. (9 mol dm<sup>-3</sup>) was effected in a flat-bottom boiling flask of 100 ml capacity under reflux cooler on a sand bath. Boiling flasks of silica glass provided with air condensers were also tested.

### Determination of the selectivity coefficient and the effect of pH on a change in the electrode potential

The selectivity coefficient was determined by the mixed solution method [3]. The dependence of EMF on the pH value at a constant concentration of potassium ions ( $\text{pK}^+=4$ ) was measured. At this concentration, the concentration can be substituted for activity. The result is plotted in Fig. 1. The calculation is based on the following two limiting situations [3]:

1.  $a_{\text{K}}(1) \gg K_{\text{H}}a_{\text{H}}(1)$ : in this case, equation (8) acquires the form of equation (6):

$$E_{\text{ISE}} = \text{const.} + \frac{RT}{F} + \ln a_{\text{K}}(1) \quad (9)$$

with the angular coefficient

$$\frac{dE_{\text{ISE}}}{d \ln a_{\text{K}}} = \frac{RT}{F} \quad (10)$$

2.  $a_{\text{K}} \ll K_{\text{H}}a_{\text{H}}(1)$ : in this case, equation (8) acquires the form

$$E_{\text{ISE}} = \text{const.} + \frac{RT}{F} + \ln K_{\text{H}}a_{\text{H}}(1) \quad (11)$$

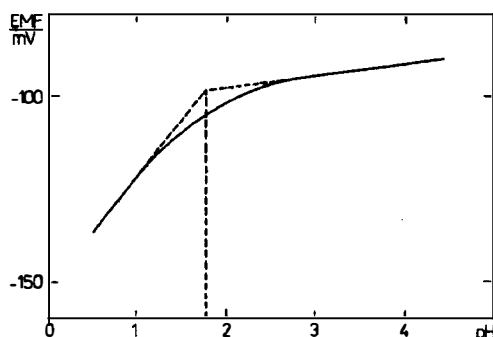


Fig. 1. EMF vs. pH at  $pK^+ = 4$  for selectivity coefficient determination; the EMF was measured by means of  $K^+$ -ISE and SKE, the pH by means of combined glass electrode.

with the angular coefficient

$$\frac{dE_{ISE}}{d \ln a_K} = 0 \tag{12}$$

The transition between the two extremes is curved. The approxiatively determined intersection of the straight lines formed is given by the equation

$$a_K = K_H a_H \tag{13}$$

The measurement for  $a_K = 1 \times 10^{-4}$  yields the value  $a_H = 10^{-1.78}$ , established from the diagram in Fig. 1, which corresponds to a selectivity coefficient value of  $K = 6.03 \times 10^{-3}$ . The value specified by the manufacturer is  $3.9 \times 10^{-4}$ .

The effect of pH on the change in the potential already follows from the diagram in Fig. 1 for the concentration of potassium ions  $pK^+ = 4$ . In view of

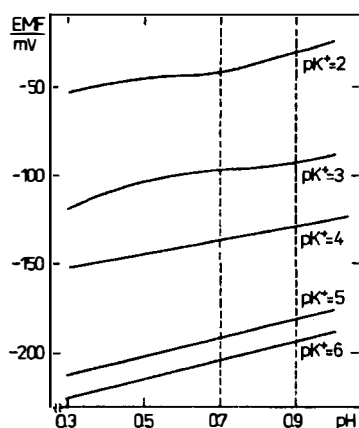


Fig. 2. EMF vs. pH in the strongly acidic region at various  $pK^+$  values, for the purpose of assessing the interfering effect of  $H^+$  ions.

Table II

A survey of angular coefficient values for the dependence of EMF on pH for various values of  $pK^+$

$pK^+$	$\Delta pH$	$\Delta EMF$ (mV)	$S$ (mV/pH)
2	0.7	28.5	40.7 <sup>a)</sup>
3	0.7	30.5	43.6 <sup>a)</sup>
4	0.7	27.0	38.6
5	0.7	35.0	50.0
6	0.7	36.0	51.4

<sup>a)</sup>extrapolated

the relatively wide region of the linear course taken by the calibration curve, it is very important to know in detail the dependence of EMF on pH for various values of  $pK^+$  in the way plotted in Fig. 2.

In this respect, it is significant to establish the angular coefficient  $S$  expressed as the ratio

$$S = \frac{\Delta EMF}{\Delta pH} \tag{14}$$

The results are summarized in Table II which shows that the angular coefficient increases with decreasing concentration of potassium ions. Figs. 2 and 3 indicate that the optimum range for pH is between 0.7 and 0.9, where it is possible to introduce a correction for the actual value of pH thanks to the linear course of the dependence.

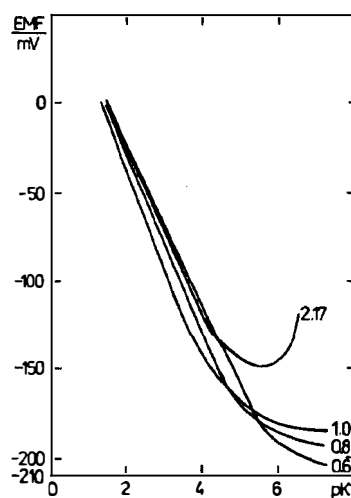


Fig. 3. Calibration curves at various pH values, established in order to assess the effect of pH on the linearity region.

### Calibration of the electrode

The ISE employed was calibrated over the  $K^+$  concentration range of  $1 \times 10^{-2}$  to  $1 \times 10^{-6}$ . In view of the interference of hydrogen cations the calibration was carried out at various pH values. As a result of the use of concentrated HCl in the decomposition of samples, the pH range examined was restricted to pH 0.5 – 1.0, using steps of 0.1, and then for pH 1.78 and 2.17. The results of the measurements are plotted in Fig. 3. The diagram shows the dependence of EMF on the concentration of potassium ions to be linear over a comparatively wide range. The effect of pH on the curvature is already distinct at the lower concentrations. As a result of the interfering effect of hydrogen ions, the linear region of the calibration curve gets narrower with increasing pH values.

### The known addition method

The calculation is based on equations (2) and (6), where the activities are substituted by concentrations for the sake of simplicity. The cell voltage is described by the equation

$$U = E_{ISE} - E_{ref} = \text{const.} + 56.16 \log \frac{c_K V_{ap}}{V_m} - E_{ref} \quad (15)$$

while the voltage of the cell following the known addition is described by the equation

$$U' = E_{ISE} - E_{ref} = \text{const.} + 56.16 \log \frac{c_K V_{ap} + c_s V_s}{V_m} - E_{ref} \quad (16)$$

By subtracting equation (15) from equation (16) and substituting  $\alpha = 10^{(U'-U)/56.16}$  one obtains

$$c_K = \frac{c_s V_s}{2V_{ap}} \frac{1}{\alpha - 1} \quad (17)$$

and

$$c_{K_2O} = \frac{c_s V_s}{2V_{ap}} \frac{1}{\alpha - 1} \quad (18)$$

The content of potassium in the form of potassium oxide is calculated for the equation

$$w_{K_2O} = \frac{c_{K_2O} V_0 M_r 100}{m_0 (1 + f/100)} \quad (19)$$

List of symbols employed in equations (16) through (19) :

$m_0$	sample weight
$f$	ignition loss (wt.%)
$V_0$	volume of primary solution after decomposition
$c_K$	concentration of $K^+$ in primary solution
$c_{K_2O}$	concentration of $K_2O$ in primary solution
$w_{K_2O}$	content of $K_2O$ in sample
$V_{ap}$	volume of aliquot proportion of primary solution
$V_m$	volume of solution for ISE measurement
$V_s$	volume of standard solution added
$c_s$	concentration of standard solution
$M_r$	= 94.195

### The determination procedure

Real samples of materials tend to contain certain proportions of organic admixtures such as wood, coal, etc. Their presence during the determination is undesirable because chemical treatment changes the content of the organic matter. That is why the material in question has to be ignited in a crucible at 600 – 700°C for 2 hours. Crystallically bound water is also partially released by the igniting. The content of sand in the samples is another significant factor. The effect of this variable factor can be eliminated, at least to a certain degree, by removing fraction with grain sizes exceeding 0.063mm [4]. The moisture content is taken care of by drying the sample at  $110 \pm 5^\circ\text{C}$  till constant weight [5].

The dried sample with the required maximum grain size was ignited in a porcelain crucible with lid over a Méker burner. Following thorough cooling down in a desiccator, 0.9 to 1.1g of sample was weighed and introduced into a ground-necked boiling flask and poured over with 15 cm<sup>3</sup> HCl (9 mol dm<sup>-3</sup>). After three hours of reflux boiling on a sand bath, the sample was transferred quantitatively into a 100cm<sup>3</sup> measuring flask. From this primary solution, aliquote proportions were taken so as to obtain a pH of the measuring solution between 0.7 and 0.9, and the  $K_2O$  content over the range of  $1 \times 10^{-2}$  to  $1.5 \times 10^{-5}$  mol dm<sup>-3</sup>.

Because the primary solution prepared on this way contains variable amounts of solid particles (quartz and corundum grains), the effect of the content of these particles on the EMF value established was also studied. The results showed this effect to be negligible, and this is also regarded as one of the advantages of the method.

### Accuracy and correctness of the method

The correctness of the method was assessed by using a standard material, CS Analytical Standard kaolin HB, and by simultaneous determination of

Table III

Determination of K<sub>2</sub>O in the Czechoslovak Analytical Standard – kaolin HB

Determination No.	K <sub>2</sub> O content found wt. %	Deviation from declared value (%)
1	1.19	-16.2
2	1.41	-0.7
3	1.46	+2.8
4	1.54	+8.5
5	1.30	-8.5
6	1.57	+10.6
7	1.26	-11.3
$\bar{x}$	1.39	-2.1
$s_r$ (%)	10.4	

The value declared : 1.42 ± 0.016 wt.% K<sub>2</sub>O

K<sub>2</sub>O in a group of kaolin and clay samples by inductively coupled plasma emission spectroscopy (ICP) on the VARIAN Liberty 200 apparatus using ultrasonic fogging. The result of the determinations are listed in Tables III and IV.

The accuracy of the method was tested by multiple analyses of the CS Analytical Standard, kaolin HB. The results are summarized in Table III.

## RESULTS AND DISCUSSION

The calibration curve method was not applicable in the determination of K<sub>2</sub>O in view of the variable ionic strength of the eluates obtained. Owing to the exclusive character of each sample it was necessary to determine the potassium content by the known addition method [3].

- Assessment of the interfering effect of H<sup>+</sup> ions :
- $K_H$  (exp.) =  $6.03 \times 10^{-3}$
  - the solution being measured :  
pH = 0.8  $c_{HCl} = 0.27 \text{ mol dm}^{-3}$   $I \approx 0.3$   
 $\gamma_H = 0.78$  (activity coefficient)
  - the concentration of potassium ions in the sample (earthen-ware) obtained by calculation :
    - considering the effect of H<sup>+</sup> ions  
...  $5.89 \times 10^{-3} \text{ mol dm}^{-3}$
    - not considering the effect of H<sup>+</sup> ions  
...  $6.19 \times 10^{-3} \text{ mol dm}^{-3}$
  - the difference amounts to about 5%.

The method was verified on four samples from a single region, clays from the Cheb basin, and the

Table IV

Determination of K<sub>2</sub>O content in kaolin and clay samples by the ICP and potentiometric methods

Name of material	Potentiometry		ICP	
	$w_{K_2O}$ (%)	$s_r$ (%)	$w_{K_2O}$	$s_r$ (%)
clay BD	0.60	16.8	0.80	4.5
	0.75	17.9	0.93	3.1
	0.59	12.3	0.82	3.7
clay AGB	2.66	13.1	3.23	4.4
	2.11	13.9	2.42	3.8
	2.07	11.0	2.93	5.1
	2.88	12.5	2.80	5.0
kaolin KD	0.74	9.8	0.73	4.1
	0.80	10.8	0.72	3.3
	0.81	11.5	0.75	4.0

results were compared with the results obtained by flame AAS. The results are listed comprehensively in Table V. The rim of the boiling flask broke off during decomposition of clay B1 1. Prior to the potentiometric determination, the reaction mixture was therefore separated by filtering through a paper filter in order to protect the membrane of the potassium ISE from possible damage. The same procedure was used in the treatment of sample B1 2. The difference found with the B1 clay sample can be explained by sorption of potassium in the paper filter during separation of the solids after sample decomposition. In the other instances the solids were separated by sedimentation.

Table V

The results of determination of K<sub>2</sub>O content in clay samples from the Cheb Basin in wt.%, compared to the results obtained by the AAS method

Name of sample	Sample weight (g)	$w_{ISE}$ (%)	$s_{rel}$ (%)	$w_{AAS}$ (%)	Deviation (%)
AGB 1	1.0213	4.00	0.59	3.98	+0.5
AGB 2	1.0877	3.32	1.65	3.72	-10.7
GE 1	1.1306	2.10	0.39	2.00	+5.0
GE 2	1.1695	1.81	1.52	2.18	+17.0
B1 1	1.0435	1.40	1.35	0.90	+55.6
B1 2	1.0124	1.66	0.73	1.16	+43.1
earthenw.1	1.0994	3.11	0.23	3.44	-9.6
earthenw.2	1.1057	3.64	0.34	4.24	-14.2

## CONCLUSION

On summarizing the results of all the measurements it may be concluded that the membrane potassium ISE made by PRECIOSA exhibits properties meeting all the requirements for the determination of potassium under the given conditions. The data in Tables III through V demonstrate that the method developed for rapid orientation determination of potassium oxide has proved to be satisfactory for routine practice.

The differences of results obtained by potentiometric measurements compared to those yielded by optical methods, in particular ICP (cf. Table IV), are due to the fact that the emission methods also detect the ionic components bound to the surface of microparticles suspended in the solution being analyzed.

## References

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Translated by K. Němeček

## MOŽNOSTI POTENCIOMETRICKÉHO STANOVENÍ V NĚKTERÝCH SILIKÁTOVÝCH SUROVINÁCH

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První část sdělení je věnována studiu vlastností draslíkové ISE. Zahrnuje určení koeficientu selektivity pro kationty  $H^+$  (Obr. 1) a dále zjištění vlivu pH na změnu potenciálu při různých koncentracích draselných iontů (Obr. 2). Dalším bodem studia bylo zjištění průběhu kalibrační křivky v závislosti na různých hodnotách pH (Obr. 3) a cílem určení případné korekce. Navržené stanovení se totiž provádí s ohledem na přípravu vzorků v silně kyselém prostředí ( $pH \approx 0.8$ ) a v této oblasti je potenciál ISE na hodnotě pH závislý. Při použití metody standardního přídatku se však ukázalo, že korekce na vliv pH není nezbytně nutná.

Ve druhé části (vlastním stanovení), je popsána předběžná úprava vzorku, jeho rozklad a samotná analýza včetně výpočtu koncentrace  $K^+$ . Metoda byla ověřena na čtyřech vzorcích jíly Chebské pánve srovnáním paralelních analýz potenciometrickou metodou a AAS a také analýzou československého analytického normálu – kaolinu HB.

S přihlédnutím k účelu metody, jakožto rychlého orientačního stanovení obsahu  $K_2O$ , byly výsledky uspokojivé.

*Obr. 1. Závislost EMF na pH při  $K^+ = 4$  pro určení koeficientu selektivity; EMF měřeno pomocí  $K^+$  ISE a SKE, pH měřeno kombinovanou skleněnou elektrodou.*

*Obr. 2. Závislost EMF na pH v silně kyselé oblasti při různých hodnotách  $pK^+$  pro posouzení rušivého vlivu iontů  $H^+$ .*

*Obr. 3. Kalibrační křivky při různých hodnotách pH pro posouzení vlivu pH na oblast linearity.*