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THE DETERMINATION OF POTASSIUM AND SODIUM IN SILICEOUS, ARGILLACEOUS, AND PHOSPHATIC ROCKS BY THE FLAME PHOTOMETER

By
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This report is preliminary and has not been edited or reviewed for conformity with U. S. Geological Survey standards and nomenclature.

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THE DETERMINATION OF POTASSIUM AND SODIUM IN SILICEOUS, ARGILLACEOUS, AND PHOSPHATIC ROCKS BY THE FLAME PHOTOMETER

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ABSTRACT

A routine method is given for the determination of potassium and sodium in siliceous, argillaceous and phosphatic rocks using the Beckman flame photometer 10300.

The sample is dissolved with HF, HNO_3, and $HClO_4$, evaporated to fumes of perchloric, made up to volume, and the solution atomized. No separations are involved.

Potassium has a pronounced enhancing effect on the flame intensity of sodium but a series of correction curves is used to compensate for this effect. None of the other elements studied caused any serious interference.

The results obtained by this procedure are within $\pm$ 3 percent of the amount of each alkali present in the sample.

INTRODUCTION

This paper describes the flame photometric procedures for the determination of potassium and sodium currently in use by the U. S. Geological Survey. These methods are applicable to siliceous, argillaceous, and phosphatic materials. No separations are required and the results average better than $\pm$ 3 percent of the amount found for each alkali by the J. L. Smith procedure. Supporting data are presented on the effect of Al, Fe, Ca, Mg, P, Na on K, and K on Na. The only serious interference found was

that due to potassium on the sodium determination but this effect is compensated for by the use of correction curves.

REAGENTS AND APPARATUS

KCl, NaCl, HNO_3, HF, $HClO_4$, all A.C.S. grade.

Potassium chloride stock solution: Dissolve 1.5830 g KCl (previously dried at 105 to 110 C for several hours) in redistilled water, dilute to 1 liter in a volumetric flask, and mix thoroughly. This solution contains the equivalent of 1000 ppm K_2O.

Sodium chloride stock solution: Dissolve 1.8858 g NaCl (previously dried at 105 to 110 C for several hours) in redistilled water, dilute to 1 liter in a volumetric flask, and mix thoroughly. This solution contains the equivalent of 1000 ppm Na_2O.

Standard solutions: The concentrations of the solutions are made to correspond to definite percentages of Na_2O or K_2O on the basis of 0.0500 g of rock sample being decomposed and dissolved in a total volume of 100 ml of solution.

Thus, a solution corresponding to 10 percent K_2O in the rock would contain 50 ppm of K_2O. Prepare solutions equivalent to 0.5, 1, 2, 4, 6, 8, and 10 percent K_2O and similar concentrations of Na_2O, by taking 1.25, 2.5, 5, 10, 15, 20, and 25 ml, respectively, of alkali stock solution, adding 5 ml $HClO_4$ to each and diluting each to 500 ml with redistilled water. Mix thoroughly and store in Pyrex bottles. The required volume of alkali stock solutions should be measured in calibrated pipettes or burettes.

The Beckman spectrophotometer, Model DU, with no. 10300 Beckman flame photometer attachment was used in this work. The Beckman instrument was operated from a Nobatron Model E-6-15 in place of a storage battery.

PREPARATION OF THE SOLUTION OF THE SAMPLE

1. Weigh a 0.0500-g sample into a 70-ml platinum dish.

2. Ignite the sample gently to remove organic matter. Cool and moisten the sample with redistilled water.

3. Add 10 ml (1 + 1) HNO_3, 3 ml $HClO_4$, and 5 to 10 ml HF. Evaporate the sample on the steam bath until the volume is about 5 ml. Transfer to a hot plate and fume $HClO_4$ to a volume of about 1 ml.

4. Cool. Add 25 ml redistilled water, digest on steam bath for 5 minutes. Transfer to a 100-ml volumetric flask. Cool. Make up to volume with redistilled water and mix thoroughly.

INSTRUMENTAL DETAILS

1. Turn on Nobatron and adjust it to give 6 volts. Turn switch on Model DU to "1" position; push in phototube positioning knob (red phototube in use); turn resistor selector to position "3" (10,000 megohm resistor in use).

2. Disconnect burner top from base, rinse with water and dry. Clean and dry burner base. Replace.

3. Turn on air, adjusting regulator to 27 lbs/in.^{2}

4. Remove spray chamber, rinse several times and dry by passing air through it. Plug cord into outlet and allow spray chamber to become warm.

5. Clean aspirator and make sure that it is not clogged.

6. <u>TURN ON THE WATER</u>. The water must be turned on <u>before</u> lighting the flame. If this is not done, the solder on the cooling coils of the burner will melt within a few minutes after the strong oxygen-gas flame is started.

7. Turn the gas on full and light the burner. The flame should extend several inches above the top of the chimney, if the gas pressure is high enough.

8. Turn on the oxygen and adjust regulator to 60 inches of water. (If there is a backfire, indicating insufficient gas pressure, the gas should be turned off immediately.)

9. Allow the instrument to warm up for 30 minutes.

PROCEDURE FOR POTASSIUM

1. Set wave length dial at 777 mμ, the slit at 0.1 mm, the transmission dial at 100 percent, gas at 3 cm, oxygen at 30 inches of water, air at 27 lbs, and sensitivity knob between 2 and 4 turns counterclockwise.

2. Transfer about 4 ml of the 10 percent K_2O standard solution to a 5-ml Pyrex beaker. Place under the aspirator.

3. Balance dark current. Open the shutter and balance the needle by means of the sensitivity knob.

4. Close shutter and balance dark current.

5. Open shutter and balance needle.

6. Turn oxygen up and down over the range of 27 to 36 inches to check the pressure for optimum emission; balance needle.

7. Close shutter and balance dark current.

8. Remove 10 percent standard and place unknown under the atomizer.

9. Open shutter and balance needle with transmission knob. Record reading. Repeat for each unknown. This reading will indicate approximate concentration of potassium in the unknowns.

10. Select the standard solution with the nearest higher concentration to the estimated concentration of potassium in the unknown. Transfer about 4 ml of this solution to a 5-ml Pyrex beaker. Place under the atomizer.

11. Check dark current, open shutter and balance needle with the transmission knob. Close shutter and record reading.

12. Transfer about 4 ml of the unknown solution to a 5-ml Pyrex beaker and place under the atomizer.

13. Check dark current, open shutter and balance needle with the transmission knob. Close shutter and record reading.

14. Repeat steps 12 and 13 using the standard solution with the nearest lower concentration to the estimated concentration of potassium in the unknown. Steps 11, 12, 13, and 14 should be done as close together as possible and with all settings constant.

15. Repeat steps 11, 12, 13, and 14, starting with the nearest lower standard and ending with the higher standard.

If the two readings for each solution differ by more than 2 percent transmission, a third set of readings should be taken.

Calculation of percent K_2O.--The percent K_2O is calculated from the following equation:

$$x = (Y-Y_1)\frac{(X_2-X_1)}{(Y_2-Y_1)} + X_1$$

where x = percent of K_2O in the sample

X_1 = percent of K_2O in lower standard

X_2 = percent of K_2O in higher standard

Y = reading for sample solution

Y_1 = reading for lower standard

Y_2 = reading for higher standard

PROCEDURE FOR SODIUM

1. Set wave length dial at 594 mμ, the slit at 0.2 mm, the transmission dial at 100 percent, gas at 1.5 cm, oxygen at 60 inches of water, air at 27 lbs, and sensitivity knob between 2 and 4 turns counterclockwise.

2. Transfer about 4 ml of the 10 percent Na_2O standard solution to a 5-ml Pyrex beaker and place under the aspirator.

3. Follow steps 3-15 under procedure for potassium except that at step 6 set oxygen at near 60 inches of water.

Calculation of percent Na_2O.--The apparent percent of Na_2O is obtained from an analogous formula as given under potassium. The "true" percentage of Na_2O is obtained by correcting for the effect of potassium on sodium. The correction curves are given in figure 1. Potassium enhances the sodium lines and thus corrections are to be subtracted. A simple example will suffice. If the apparent Na_2O is found to be 2.00 percent Na_2O and the sample contains 6 percent K_2O, the correction factor is found from the graph to be 16.5 percent. Then 2 x 0.165 = 0.33. The "true" Na_2O then becomes 2.00-0.33 = 1.67 percent Na_2O.

TURNING OFF THE INSTRUMENT

1. Turn off oxygen and immediately turn off gas. Turn switch on the spectrophotometer to "off".

2. Turn off air, Nobatron and water.

3. Unplug aspirator and check to see if shutter is closed.

TEST OF PROCEDURE

Potassium and sodium were determined on a standard diabase and a standard granite.1/ The flame photometric results are compared with the average of the results of 34 participating analysts below:

Rock	J. L. Smith procedure		Flame photometric procedure
	Spread	Average	
	K_2O		
Granite	5.0-6.0	5.5	5.72
Diabase	0.5-7.7	0.65	0.68
	Na_2O		
Granite	3.0-4.0	3.4	3.45
Diabase	1.8-2.5	2.0	2.23

The results on three National Bureau of Standards standard samples are compared below:

Sample	Nat. Bur. Standards certified analysis (average)	Flame photometric procedure
	Na_2O	
Glass	5.69	5.78
Clay	0.28	0.38
Feldspar	2.38	2.26
	K_2O	
Glass	8.32	8.35
Clay	3.17	3.23
Feldspar	12.58	12.68

1/ Schlecht, W. G., 1951, Cooperative investigation of precision and accuracy in chemical analyses of silicate rocks: Anal. Chemistry, v. 23, p. 1568-1571.

The results obtained flame photometrically on 4 shale samples when analyzed by the Beckman and Perkin-Elmer flame photometers are compared below:

Sample	By Perkin-Elmer instrument 2/	By Beckman instrument
	K_2O	
YB-6-34	4.15	4.46
YB-7-13	3.31	3.54
YB-10-43	4.54	4.74
YB-11-56	4.47	4.69
	Na_2O	
YB-6-34	0.55	0.54
YB-7-13	0.53	0.45
YB-10-43	0.51	0.60
YB-11-56	0.52	0.53

EXPERIMENTS

Data were obtained for the effect of various elements on the determination of potassium and sodium. Two levels of sodium and two levels of potassium concentration were used. The element under study (as the chloride) was tested at various concentrations for each level of sodium or potassium. Each solution contained 1 ml of $HClO_4$ per 100 ml of solution as in the recommended procedure. The results

2/ Brannock, W. W., and Berthold, S. M., 1949, The determination of sodium and potassium in silicate rocks by flame photometer: U. S. Geol. Survey Bull. 992, p. 1-14.

obtained are listed in tables 1 and 2. Data on the enhancing effect of potassium on sodium are given in table 3. Again the percentages are based on 0.05 g of sample.

Table 1.--Effect of various elements on the flame photometric determination of potassium.

K_2O taken (percent)	Element tested (percent)	Apparent K_2O (percent)	Error (percent)
2.06	1 CaO	1.98	-3.9
2.06	10 CaO	2.06	0.0
2.06	20 CaO	2.04	-1.0
2.06	40 CaO	2.14	+4.8
2.06	1 MgO	2.06	0.0
2.06	10 MgO	2.13	+3.3
1.99	1 Fe_2O_3	1.94	-2.5
1.99	5 Fe_2O_3	1.93	-3.0
1.99	10 Fe_2O_3	1.88	-5.5
1.99	20 Fe_2O_3	1.89	-5.0
2.04	1 Al_2O_3	2.04	0.0
2.04	5 Al_2O_3	1.96	-3.9
2.04	10 Al_2O_3	1.96	-3.9
2.04	20 Al_2O_3	1.91	-6.4
2.04	1 Na_2O	2.05	+0.5
2.04	5 Na_2O	2.01	-1.5
2.04	10 Na_2O	2.06	+1.0
2.04	20 Na_2O	2.18	+6.9
2.04	1 P_2O_5	2.02	-1.0
2.04	10 P_2O_5	1.96	-3.9
2.04	20 P_2O_5	1.92	-5.9
2.04	40 P_2O_5	1.88	-7.8
2.04	10 Al_2O_3, 10 Fe_2O_3, 48 CaO, 10 MgO, 40 P_2O_5	2.06	+1.0
10.19	1 CaO	9.99	-1.9
10.19	10 CaO	9.88	-3.0
10.19	20 CaO	9.79	-3.9
10.19	40 CaO	9.96	-2.2
10.27	1 MgO	10.16	-1.0
10.27	10 MgO	10.23	-0.3
10.17	1 Fe_2O_3	10.20	+0.3
10.17	5 Fe_2O_3	10.24	+0.7

Table 1.--Effect of various elements on the flame photometric determination of potassium--Continued.

K_2O taken (percent)	Element tested (percent)	Apparent K_2O (percent)	Error (percent)
10.17	10 Fe_2O_3	10.22	+0.5
10.17	20 Fe_2O_3	10.17	0.0
10.20	1 Al_2O_3	10.50	+2.9
10.20	5 Al_2O_3	10.38	+1.8
10.20	10 Al_2O_3	10.38	+1.8
10.20	20 Al_2O_3	10.44	+2.4
10.07	1 Na_2O	9.84	-2.3
10.07	5 Na_2O	10.22	+1.5
10.07	10 Na_2O	10.42	+3.5
10.07	20 Na_2O	10.52	+4.5
10.17	1 P_2O_5	10.25	+0.8
10.17	10 P_2O_5	10.00	-1.7
10.17	20 P_2O_5	9.90	-2.6
10.17	40 P_2O_5	9.68	-4.8
10.17	10 Al_2O_3, 10 Fe_2O_3, 48 CaO, 10 MgO, 40 P_2O_5, 20 Na_2O	9.85	-3.1

Table 2.--Effect of various elements on the flame photometric determination of sodium.

Na_2O taken (percent)	Element tested (percent)	Apparent Na_2O (percent)	Error (percent)
1.97	1 CaO	2.04	+3.5
1.97	10 CaO	2.05	+4.0
1.97	20 CaO	2.07	+5.0
1.97	40 CaO	2.11	+7.1
1.97	1 MgO	2.03	+3.0
1.97	10 MgO	2.05	+4.0
2.04	1 Fe_2O_3	2.06	+1.0
2.04	5 Fe_2O_3	2.08	+2.0
2.04	10 Fe_2O_3	2.07	+1.5
2.04	20 Fe_2O_3	2.10	+2.9
2.02	1 Al_2O_3	2.08	+2.9
2.02	5 Al_2O_3	2.03	+0.5
2.02	10 Al_2O_3	2.06	+2.0
2.02	20 Al_2O_3	2.02	0.0
2.06	1 P_2O_5	2.05	-0.5
2.06	10 P_2O_5	2.04	-1.0
2.06	20 P_2O_5	2.06	+0.5
2.06	40 P_2O_5	2.03	-1.5
2.06	10 Al_2O_3, 10 Fe_2O_3, 48 CaO, 10 MgO, 40 P_2O_5, 20 K_2O	2.68	+30.0
10.07	1 CaO	10.14	+0.6
10.07	10 CaO	10.21	+1.3
10.07	20 CaO	10.35	+2.7
10.07	40 CaO	10.16	+0.8
10.07	1 MgO	10.12	+0.4
10.07	10 MgO	10.24	+0.6
10.22	1 Fe_2O_3	10.16	-0.6
10.22	5 Fe_2O_3	10.23	+0.1
10.22	10 Fe_2O_3	10.15	-0.7
10.22	20 Fe_2O_3	10.27	+0.5
10.18	1 Al_2O_3	10.12	-0.6
10.18	5 Al_2O_3	10.10	-0.8

Table 2.--Effect of various elements on the flame photometric determination of sodium--Continued.

Na_2O taken (percent)	Element tested (percent)	Apparent Na_2O (percent)	Error (percent)
10.18	10 Al_2O_3	10.18	0.0
10.18	20 Al_2O_3	10.21	+3.0
10.11	1 P_2O_5	10.22	+1.1
10.11	10 P_2O_5	9.84	-2.7
10.11	20 P_2O_5	9.91	-2.0
10.11	40 P_2O_5	9.88	-2.3
10.11	10 Al_2O_3, 10 Fe_2O_3, 47 CaO, 10 MgO, 40 P_2O_5, 20 K_2O	10.86	+6.9

Table 3.--The enhancing effect of K_2O on Na_2O.

Na_2O taken (percent)	K_2O added (percent)	Apparent Na_2O (percent)	Error (percent)
0.099	1	0.140	41.4
0.099	3	0.155	56.6
0.099	5	0.163	64.6
0.099	8	0.169	70.7
0.099	10	0.185	86.9
0.48	1	0.57	18.8
0.48	3	0.60	25.0
0.48	5	0.67	39.6
0.48	8	0.68	41.7
0.48	10	0.72	50.0
0.99	1	1.04	5.1
0.99	3	1.14	15.1
0.99	5	1.22	23.2
0.99	8	1.25	26.3
0.99	10	1.37	41.2
2.03	1	2.14	+5.4
2.03	3	2.27	+11.8
2.03	5	2.35	+15.8
2.03	8	2.46	+21.2
2.03	10	2.54	+25.1
2.03	20	2.68	+32.0
6.08	1	6.25	+2.8
6.08	3	6.55	+7.7
6.08	5	6.75	+11.0
6.08	8	7.03	+15.6
6.08	10	7.21	+18.6
6.08	20	7.34	+20.7
10.06	1	10.37	3.1
9.98	3	10.56	5.8
9.98	5	10.85	8.7
9.98	8	11.05	10.7
9.98	10	11.24	12.6
9.98	20	11.90	19.2

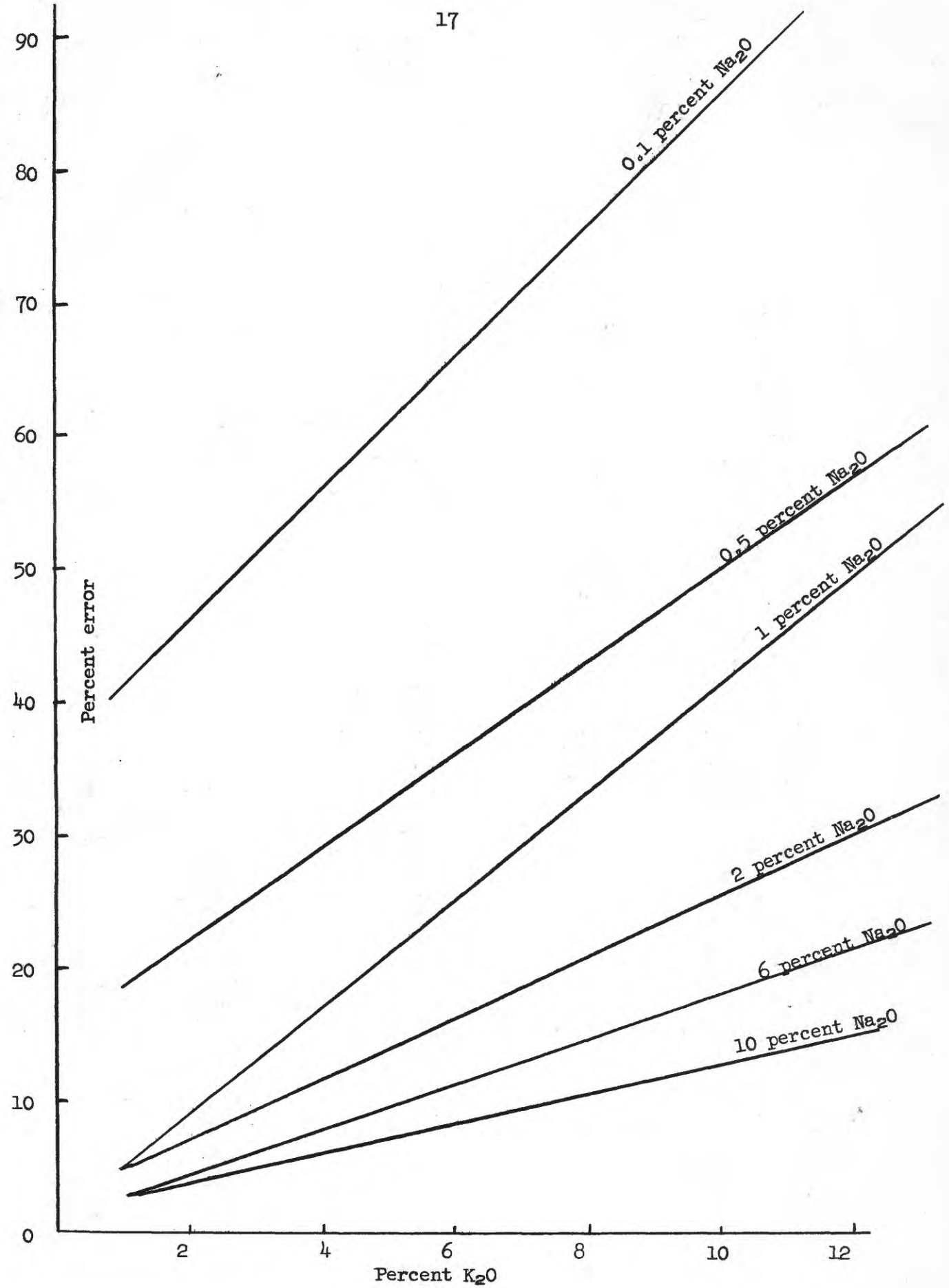

Figure 1.--Corrections for the enhancing effect of potassium on sodium