



Chapter P

Flame photometric determination of K_2O

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U.S. Geological Survey Open File Report 02-223-P

Analytical methods for chemical analysis of geologic and other materials, U.S. Geological Survey

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Codes: E061

T29

Accepted: 3/2/93

Revised: 1/15/02

Principle

Potassium in rocks and mineral separates is determined using flame emission spectrometry (FES) and is reported as an oxide (Cremer and others, 1984; Jackson and others, 1987). The samples are fused with lithium metaborate in graphite crucibles and the fusion beads dissolved in 4 percent (v/v) nitric acid. The sample solution is aspirated into a propane-air flame. Filters are used to isolate the light emitted by the analyte atoms and lithium internal standard. Photomultipliers detect the emitted light. The analyte signals are ratioed to the lithium signal. Use of an internal standard compensates for variations in flame characteristics and sample introduction (aspiration).

Interferences

The only known interference is the presence of rubidium (Rb) in high concentration when potassium (K) content is very low. The effect is ignored in routine work as it occurs rarely and only in certain uncommon minerals.

Scope

The method is applicable to all geologic samples compatible with the lithium metaborate fusion digestion. Approximately 2 days are required for 40 determinations. It is routinely applicable to samples containing K₂O concentrations between 0.025 percent and 15 percent in two ranges (less than 2.9 percent and greater than 2.9 percent). The concentration range should be specified by the submitter- to avoid re-analysis.

Apparatus

Graphite crucibles, high temperature furnace, automatic diluter, and a multi-channel flame photometer with internal standard compensation (e.g., Instrumentation Laboratories (IL) models 343 and 443) is required for this determination.

Reagents

- Water: Deionized (DI) water.
- Dehydrated human blood serum.
- Lithium metaborate, LiBO₂: Anhydrous lithium metaborate, reagent grade powder, specially prepared for fusions. This material can be obtained in 25-pound lots from Southwestern Analytical Chemicals, Inc., Austin, Texas. Each new lot should be checked for freedom from contamination.

4 percent nitric acid, HNO₃ (v/v): Prepare by adding 4 parts 70-71 percent conc HNO₃ (Baker analyzed reagent grade) to 96 parts DI water.

Safety precautions

All safety precautions normally employed in laboratory handling of acids, hot materials from high temperature furnaces, and devices producing flames from potentially explosive gas mixtures must be followed. Workers should wear protective clothing including, but not limited to, lab coats, protective glasses, and face masks when dealing with powdered materials such as flux and sample; insulated gloves when working with the furnace; and protective gloves when working with chemicals. Furnace work and sample digestion are carried out in a hood and the flame photometer is serviced by a fan-driven exhaust device. See the *CHP and MSDS* for further information concerning first-aid treatment and disposal procedures for chemical products used in this method.

Procedure

1. Based on rock description, decide whether high or low standards are to be used for the calibration curve. Specific USGS standard reference materials used, include rock standards G-2, BCR-1, and AGV-1. The division between "high" and "low" occurs at approximately 3.0 percent K_2O . Weigh each standard and blank (sierra quartz) in duplicate. To extend the limited supply of standards, 40-50 samples are run at one time. Two reference standards and one duplicate are included in each run.
2. In a tared, size-00 black porcelain crucible weigh 100 ± 3 mg sample. Add 700 ± 5 mg anhydrous $LiBO_2$. Record both sample weight and total weight. In the same crucible, mix the sample and flux. Samples and standards are weighed on the same day because $LiBO_2$ is somewhat hygroscopic. The purity of each new batch of $LiBO_2$ is checked by emission spectroscopy.
3. Brush out the interior of a high purity graphite crucible and quantitatively transfer the sample-flux mixture to the crucible. New crucibles must be ignited for 2 hours at $1,000^\circ C$ before being put into use.
4. Fuse the contents of the first six crucibles at $950^\circ C$ for 15 min.
5. During the fusion, equip six dry 250-mL polypropylene beakers with dry 1 5/8-in Kel-F magnetic stirring bars. Label six covers. Add 100 mL 4 percent (v/v) HNO_3 ; begin stirring as the time approaches to remove the crucibles from the muffle furnace.
6. At the end of 15 min, using tongs slightly swirl the red hot crucible and pour the molten bead into its corresponding beaker. Place each emptied crucible in same noted order. Cover beakers tightly. Stir for 10 min while fusing the next lot of six. Inspect the solutions for clarity. Cloudy solutions may contain some reducible element, like MnO_2 ; a drop of 30 percent H_2O_2 usually causes the solution to clear.
7. Inspect each cool graphite crucible for adhering particles. Adhering particles, if any, must be dug out with a stainless steel spatula and added to the appropriate beaker. If this is not feasible, a new portion must be fused on another day.
8. Repeat the above procedure for all samples and standards.
9. Use the automatic diluter to dilute samples 1:10 with DI water, dispensing into small 15-mL plastic beakers. The dilution need not be exactly 1:10 but it must be the same for all solutions.

10. On flame photometer, first turn on both the propane gas, then the air.
11. Depress POWER button (flame will automatically ignite). Allow 30 min for warm-up. The warm-up should take place during fusion and dilution steps.
12. Continually aspirate DI water during warm-up. For 5 min during the warm-up, aspirate a dilute solution of reconstituted normal human blood serum (1 drop/25 mL DI water). The blood serum protein coats the spray chamber to minimize formation of water droplets on the chamber walls. Undiluted serum is kept refrigerated.
13. Before operating with rock solutions, check that the aspiration rate is approximately 25 s/mL.
14. On the Digital Printer press RESET to set the sequential counter to 001. Depress ADVANCE to position the paper.
15. For K_2O analysis, aspirate the blank (Sierra Quartz). Adjust the signal display on the lithium response meter so that the red needle comes to rest opposite the black triangle between the horizontal black lines. Set the digital concentration display to zero with the ZERO knob.
16. Aspirate the highest K_2O standard. Check the lithium response and adjust if necessary, using the INTERNAL STANDARD dial at the left of the display. Set the digital concentration to <180.0 (high scale) or <18.0 (low scale), whichever is applicable. The RANGE switch selects the high or low scale. The setting chosen for the high standard is arbitrary. The settings suggested allow for instrument drift since the full span is 0 to 200.0 or 0 to 20.0. The decimal point appears between the second and third digit (e.g., 17.00 for 1.70 percent K_2O); on the high scale it appears between the third and fourth digit (017.0).
17. Aspirate standards and unknowns in the following order, depressing DATA when the display no longer changes, usually after 8-10 s.

All solutions must be read in the same manner.

Typical aspiration order:

- a. duplicate standards
- b. ten unknowns
- c. duplicate standards
- d. repeat the ten unknowns from step #17b
- e. duplicate standards

Drift response is inherent in the operation of the flame photometer. Frequent aspiration of standards to bracket unknowns minimizes errors introduced by instrumental drift. A set of standards and unknowns should not exceed ten of each.

20. Continue the operation until all unknowns have been run. The data collected from steps #17a and c above are weight corrected and used to prepare a linear regression. From this slope-intercept equation the concentration of the unknowns in step #17b is calculated and weight corrected. Data from steps #17c, d, and e are treated in the same manner. The reported value is the average of the two calculated values.

Calculation

A linear calibration curve is prepared using standard results that have been normalized to a 700-mg flux weight and 100-mg sample weight. The equation of this line is used to calculate unknown concentrations that are then weight corrected.

$$\text{Concentration} = [(\text{slope} \times \text{intensity}) + \text{intercept}] \times \text{unknown wt}/100$$

Assignment of uncertainty

Table 1 is the analytical results of K₂O for selected reference materials, duplicate samples, and method blanks by flame emission spectrometry.

Table 1.—Analytical performance summary for K₂O (percent) by FES

[A=Fries, 1991; remaining *pv* from Potts and others, 1992]. See page ix of the introduction to this Methods Manual for an explanation of the abbreviations used in the analytical performance summary tables.

Reference	Description	<i>n</i>	Mean	<i>s</i>	<i>pv</i>	% RSD	% R
Potassium as K₂O							
SRM 88	dolomite	10	0.025	0.005	0.03	<i>cv</i> 20	83
SRM 88b	dolomitic limestone	10	0.106	0.005	0.1030	<i>cv</i> 5	103
AL-1	albite	10	0.137	0.008	0.14	6	98
LK-1	glass	30	1.49	0.01	1.50	A	0.7 99
LK-2	phylite	30	2.22	0.01	2.23	A	0.5 100
HK-1	granodiorite	30	5.55	0.05	5.53	A	0.9 100
HK-2	feldspar	30	13.73	0.07	13.62	A	0.5 101

Table 1.—Continued—Duplicate samples results

Duplicate samples	<i>k</i>	<i>n</i>	Mean	<i>s</i>	% RSD	Concentration range	No of < (total)	No of < (pairs)
K ₂ O	30	2	1.555	0.004	.26	0.368 to 2.168	0	0

Table 1.—Continued—Method blank results 3*s* values are considered the lower limit of detection (LOD), and 5*s* values are considered the lower limit of determination (LLD)

Method blank	<i>n</i>	Mean	<i>s</i>	3 <i>s</i>	5 <i>s</i>
Low K ₂ O	30	0.001	0.005	0.02	0.03
High K ₂ O	30	0.02	0.05	0.1	0.

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