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U.S. DEPARTMENT OF COMMERCE/National Bureau of Standards

Standard Reference Materials:

PREPARATION AND CHARACTERIZATION OF K-411 AND K-412 MINERAL GLASSES FOR MICROANALYSIS: SRM 470

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Standard Reference Materials:

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PREPARATION AND CHARACTERIZATION OF K-411 AND K-412 MINERAL GLASSES FOR MICROANALYSIS: SRM 470

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The two mineral glasses in SRM 470, K-411 and K-412, were quantitatively analyzed for major constituents. The results of wet chemical analyses from two independent laboratories were in excellent agreement; therefore, these results were used for certification. Quantitative electron probe microanalysis also agrees favorably with the certified compositions. Specimens were evaluated for micro- and macrohomogeneity with the electron microprobe by using random sampling and periodic integrator homogeneity trace techniques. Statistical analyses as well as the homogeneity traces showed no obvious composition fluctuations either within each specimen or among different specimens. These glasses are therefore excellent standards for microanalytical techniques. They are primarily composed of silicon, iron, magnesium, calcium, and aluminum oxides, none of which is present in less than 9 weight percent nor more than 55 weight percent.

Key words: chemical analysis; digital periodic integrator; electron probe microanalysis; glass standards; homogeneity testing; microhomogeneity; mineral glasses; Standard Reference Material.

1. Introduction

The Mineral Glasses K-411 and K-412 are the first vitreous materials to be certified as microanalytical standards. At least six other Standard Reference Materials (SRM's) are available for microanalysis [1-6], but these are all binary or tertiary metal alloys. Glasses provide a large number of possibilities for new standard materials. Numerous oxide glass-forming systems offer wide flexibility in selecting matrices in which the elements of analytical interest can be incorporated. Since the resulting glasses are essentially structureless, they can be made homogeneous with a large number of elements present.

The glasses are composed of four and five different oxides, respectively, in concentrations of no less than nine percent by weight for any one oxide. The results of the quantitative analyses and homogeneity evaluation will be described.

2. Preparation

The glasses K-411 and K-412 were developed by D. H. Blackburn and prepared by D. A. Kauffman at NBS. The carbonate and oxides were melted in platinum crucibles and stirred for homogeneity with propeller-type, platinum-10 percent rhodium alloy stirrers. Melting was done in an air atmosphere with electrically heated furnaces. Temperatures for the melting and stirring procedure were in the range of 1450 to 1500 °C. The stirring time was 3 hours. The compounds used in the preparation were high purity crushed quartz, and reagent grade ferric oxide, magnesium oxide, calcium carbonate, and anhydrous aluminum oxide. The glasses were cast into rectangular blocks with approximate dimensions of 9 x 5 x 2 cm. These blocks were annealed at 625 °C.

For SRM distribution, at least 100 specimens were cut from each glass block. Each specimen is approximately 2 x 2 x 20 mm. A precision wafering saw was used with a 0.07 x 15.2 cm (0.028 x 6") 100-grit diamond wheel and a petroleum-based coolant. An acetone-soluble adhesive was used to mount the glass block and slices onto the cutting plate. Several 2 mm slices were cut from the glass block. These slices were in turn cut at 2 mm intervals. The glass slices were removed from the cutting plate and rinsed with acetone several times to remove all traces of adhesive.

3. Chemical Composition

The certified compositions of the glasses K-411 and K-412 are based on classical wet chemical analyses from two independent laboratories. Although the glasses were also analyzed with the electron microprobe (EPMA), the wet chemistry values were selected for certification because they showed consistency between the two analyses and because greater accuracy is usually associated with wet chemical analyses of this type than with EPMA. The accuracy expected from the former is generally better than 1 percent while a conservative estimate of the accuracy associated with the latter is 2 percent. The EPMA results are discussed here for comparative purposes only.

The wet chemical analyses were performed by E. Jarosewich and J. Norberg of the Smithsonian Institution, Washington, D. C. (Lab A) and by J. C. DeVine and N. H. Suhr of the Pennsylvania State University, University Park, Pa. (Lab B). The procedures used are briefly described in Table 1. For a single analysis of each oxide in a glass a 1-gram sample was used. Pieces were broken off the glass bar for this purpose. The results of the analyses from the two independent laboratories and the certified values are in Table 2. There is excellent agreement between the two laboratories.

Lab A did duplicate analyses. Lab B was given only enough sample for a single analysis of each oxide in each glass. The certified values for each oxide are the averages of the two independent results. A 2-sigma (standard deviation) of ±0.20 weight percent was assigned to each of the certified compositions. This is a pooled value taken from all of the oxides and estimated from the ranges between the two laboratories.

Trace or minor amounts of some elements were found in the glasses. These probably originated in the starting materials. Lab A detected the presence of manganese. This was later verified by Lab B which detected MnO by atomic absorption in concentrations of 0.13 weight percent in K-411 and 0.09 weight percent in K-412. A trace of aluminum was also found by Lab B. Less than 0.1 percent aluminum was detected spectrographically but Lab B was unable to chemically observe this small amount.

Table 1. Wet chemical procedures used in the analysis of glasses K-411 and K-412

Lab A

SiO_2 — Gravimetric. Sample fused with sodium carbonate followed by a double dehydration in hydrochloric acid. The hydrated silica is ignited, weighed, and volatilized with hydrofluoric acid. The residue is ignited and weighed. Loss in weight represents silica (SiO_2).

Al_2O_3 — Gravimetric. Aluminum is precipitated from an aliquot of R_2O_3 solution with 8-hydroxyquinoline and weighed as the precipitate.

Fe(total) and Fe_2O_3 — Volumetric titration. Ferric iron is reduced in a silver reductor and titrated with a standard solution of potassium dichromate. Fe_2O_3 is calculated by subtracting FeO from total Fe.

FeO — Volumetric titration. Following dissolution in sulfuric and hydrochloric acids in a non-oxidizing atmosphere, ferrous iron is titrated with a standard solution of potassium dichromate.

CaO — Gravimetric. Precipitation in an ammoniacal solution with ammonium oxalate. Precipitate is dissolved in dilute hydrochloric acid and reprecipitated with the oxalate. The precipitate is ignited and weighed as the oxide.

MgO — Gravimetric. Double precipitation in an ammoniacal solution with dibasic ammonium phosphate. The residue is ignited at 1100 °C and weighed as $Mg_2P_2O_7$.

Lab B

SiO_2 — Same as Lab A.

Al_2O_3 — Gravimetric. Double precipitation with ammonia. Al_2O_3 by difference of total P_2O_3 and Fe_2O_3 and TiO_2. Corrected for SiO_2.

Fe(total) and Fe_2O_3 — Volumetric titration. Ferric iron is reduced with stannous chloride and titrated with a standard solution of potassium dichromate. Fe_2O_3 is calculated by subtracting the Fe_2O_3 equivalent of FeO from total Fe.

FeO — Volumetric titration. Following dissolution in sulfuric and hydrofluoric acids in a non-oxidizing atmosphere, ferrous iron is titrated with a standard solution of potassium permanganate.

CaO — Same as Lab A, but the precipitate is ignited and weighed as calcium carbonate. Calcium recovered from the magnesium precipitate.

MgO — Same as Lab A. Corrected for calcium and manganese.

Table 2. Wet chemical analyses of SRM 470, mineral glasses for microanalysis

	Composition of Oxide in Weight Percent						
	SiO_2	MgO	CaO	Al_2O_3	FeO	Fe_2O_3	Total Fe as FeO
Glass K-411							
Lab A	54.25	14.60	15.61		4.04	11.52	14.47
	54.23	14.67	15.44		4.73	10.93	
Lab B	54.36	14.69	15.41		3.95	11.55	14.34
Certified Value	54.30±0.20[a]	14.67±0.20	15.47±0.20				14.43±0.20
Glass K-412							
Lab A	45.36	19.32	15.33	9.32	2.61	8.21	10.10
	45.40	19.33	15.24	9.20	2.93	8.09	
Lab B	45.32	19.32	15.21	9.28	2.77	7.83	9.82
Certified Value	45.35±0.20[a]	19.33±0.20	15.25±0.20	9.27±0.20			9.96±0.20

[a]The uncertainty of ±0.20 weight percent assigned to the certified values is the 2-sigma value. This error is a pooled value for all oxides estimated from the ranges between the two laboratories using wet chemical techniques.

The two glasses were also analyzed with the electron microprobe by C. E. Fiori at NBS (Lab C). He used an excitation potential of 15 kV, crystal spectrometers, and mineral standards. Matrix corrections were made with COR [7]. The standards used were ENAL 10, Diopside, and Juan de Fuca Basaltic Glass. Their compositions are listed in Table 3. These are well-characterized standards which are used by mineralogists and geologists for quantitative EPMA.

The results of the electron probe analyses are listed in Table 4. The range between experiments for each oxide is less than 2 percent relative except Al_2O_3 which is about 3 percent relative.

4. Homogeneity

The two glasses were tested for both micro- and macrohomogeneity. Periodic integration traces and random sampling techniques were used.

The former procedure which is used to test the transverse microhomogeneity of a specimen is described in detail in a recent NBS Special Publication 260-65 [8]. It uses a stepping motor on the sample stage to move the specimen in a straight line under the electron beam in 1 to 10 μm steps. X-ray counts are accumulated at each step for a preselected time period. The total number of x-ray counts are recorded as an analog signal on a fast strip chart recorder; this signal remains unchanged during the next counting period. In addition, the signal can be digitally multiplied by an appropriate factor and a bias can be applied to subtract any number of counts from the display.

Table 3. Mineral standards used for quantitative EPMA of mineral glasses K-411 and K-412

Composition of Standards in Weight Percent

ENAL 10 (from Geophysical Laboratories)[a]

$[MgSiO_3 + 10\% Al_2O_3]$

Mg	21.80	Al	5.29
Si	25.18	O	47.73

Diopside (from Smithsonian Institution)[b]

$[CaMgSi_2O_6]$

Ca	18.51	Si	25.93
Mg	11.23	O	44.33

Juan de Fuca Basaltic Glass (from Smithsonian Institution)[b]

Si	23.75	Na	1.94
Al	7.44	K	0.16
Fe	9.20	Ti	1.11
Mg	4.05	P	0.0007
Ca	7.95	Mn	0.0017
		O	44.17

[a] A synthetic glass. Composition based on stoichiometry.

[b] These standards were analyzed by wet chemistry; results appear in the following reference.

Jarosevich, E.; Nelen, J. A.; Norberg, J. A. Electron microprobe reference samples for mineral analyses. Mineral Sciences Investigations 1976-1977. Smithsonian Contributions to the Earth Sciences, No. 22. Fudali, R. F., ed. Washington, D.C.; 1979. 73p.

Table 4. Electron probe microanalyses of NBS SRM 470, mineral glasses for microanalysis

	Exp.	Composition of Oxide in Weight Percent[a]				
		SiO_2	FeO	MgO	CaO	Al_2O_3
Glass K-411						
Lab C	1	54.64(E10)	14.39(JdF)	15.05(D)	15.41(D)	
	2	55.50(D)	14.66(JdF)	15.07(D)	15.51(D)	
	3	54.54(JdF)	14.39(JdF)	15.25(E10)	15.56(JdF)	
Avg. (range)		54.89(0.96)	14.48(0.27)	15.12(0.20)	15.49(0.15)	
Glass K-412						
Lab C	1	45.20(E10)	9.88(JdF)	19.57(D)	15.35(D)	9.26(E10)
	2	45.90(D)	10.06(JdF)	19.59(D)	15.46(D)	9.25(E10)
	3	45.13(JdF)	9.88(JdF)	19.82(E10)	15.50(JdF)	9.54(JdF)
Avg. (range)		45.41(0.77)	9.94(0.18)	19.66(0.25)	15.44(0.15)	9.34(0.29)

[a]The standard used for each analysis is noted in parentheses. ENAL 10 (E10); Diopside (D); and Juan de Fuca (JdF).

Examples of homogeneity traces of iron and calcium recorded simultaneously from specimens of glasses K-411 and K-412 are in figures 1a and 1b. Each specimen was moved in 1-μm steps under a 1-μm (approximate diameter) electron beam. Counting periods were 10 s and both elements were analyzed with LiF crystal spectrometers. The specimen current was about 5×10^{-8} A and the excitation potential was 20 kV. The theoretical ±3-sigma limits about the average number of counts per counting period, $\overline{N}$, for the trace are delineated by the double-headed arrows to the right of each trace. Deviations outside this 99.7 confidence limit indicates inhomogeneities within the specimen, assuming that there are no serious instrumental fluctuations.

On the left side of each figure is a time-resolved trace made with a 20 x 20-μm scanning raster. Signal variations for such a trace are due to expected statistical fluctuations, assuming that no systematic instrumental errors are present. Therefore, the variations should lie within the ±3-sigma limits as in fact they do here. For a truly homogeneous specimen, assuming the concentration of an element is high enough to produce a signal above the background, the traces from these moving and stationary specimens should be similar as they are here.

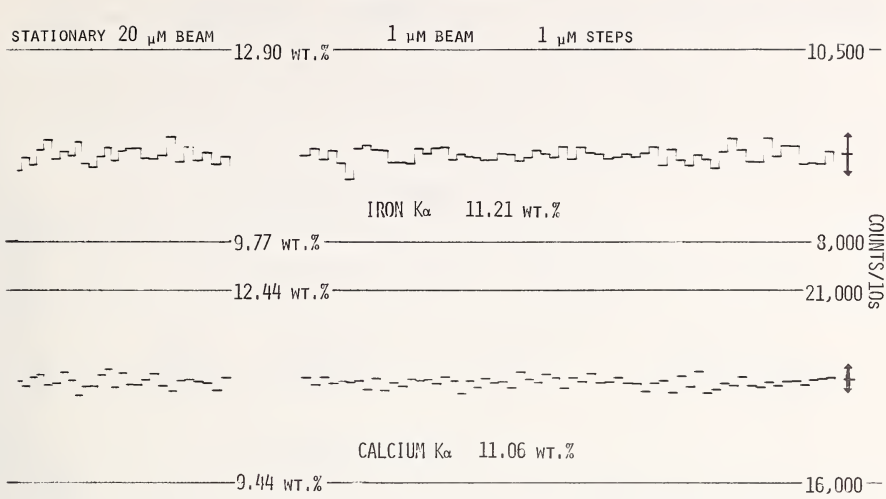

Figure 1a. Periodic integrator homogeneity traces of iron and calcium simultaneously recorded from NBS SRM 470, Mineral Glass K-411 (excitation potential = 20kV, specimen current = 5 x 10^{-8} A). In the traces on the right, the sample was advanced in 1-μm steps under a 1-μm electron beam after each 10-s counting period. To the left, the sample was not moved during repeated 10-s counting periods with a 20 x 20-μm scanning raster. The double-headed arrows to the right represent a range of $\pm 3\sqrt{\bar{N}}$ around the average number of counts per 10 s, $\bar{N}$, for the entire trace.

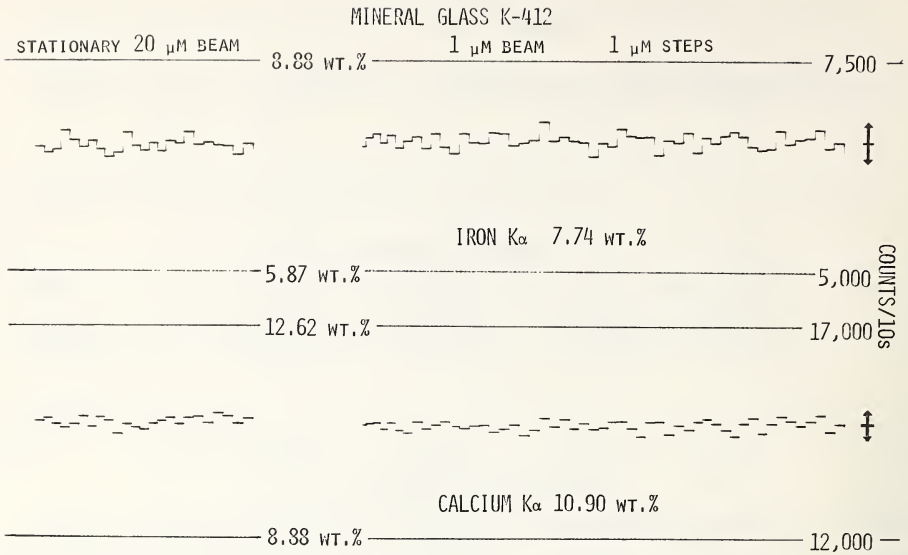

Figure 1b. Periodic integrator homogeneity traces of iron and calcium simultaneously recorded from NBS SRM 470, Mineral Glass K-412 (excitation potential = 20kV, specimen current = 5 x 10^{-8} A). In the traces on the right, the sample was advanced in 1-μm steps under a 1-μm electron beam after each 10-s counting period. To the left, the sample was not moved during repeated 10-s counting periods with a 20 x 20-μm scanning raster. The double-headed arrows to the right represent a range of $\pm 3\sqrt{\bar{N}}$ around the average number of counts per 10 s, $\bar{N}$, for the entire trace.

Two homogeneity traces similar to these were prepared for all major elements from one specimen of each glass. The traces were normal to one another and covered a 50-μm distance across the specimen in 1-μm steps. Duplicate data were taken on each point. The excitation potential was 15 kV. A specimen current of about 3 x 10^{-8} A was used. Counting periods were increased to 40 s in order to improve the counting statistics. This was especially necessary for aluminum and magnesium for which the total number of counts per 40 s was only 4000 to 5000 counts. Higher currents were not used because the 1-μm electron beam appeared to disturb the surface of the glass specimens.

No obvious inhomogeneities were observed in these traces. Fluctuations fell within the ±3-sigma limits about the average number of counts per 40 s, which indicates that these fluctuations were due to counting statistics only. In addition, no differences were observed between the traces from the moving and the stationary specimen.

A statistical evaluation was done on these traces. The equations used and a complete description of the mathematics are in the U. S. NBS Special Publication 260-65 [9]. Using the duplicate data from each point, two standard deviation components were calculated. These were σ_W, the within point component, and σ_B, the between points component. If significant inhomogeneities exist, σ_B would be noticeably larger than σ_W which primarily reflects the statistical fluctuations associated with the inherent experimental errors. The results in Table 5, where the two components are compared, show that no obvious micro-inhomogeneities are reflected in the σ_B component for these 50-μm traces. In fact, in most cases σ_B is smaller than σ_W. Thus the measurement process seems to have a greater error associated with it than does the specimen inhomogeneity.

Table 5. Comparison of statistical data from homogeneity tests (weight percent)

Oxide	Weight Percent	Trace No. or Specimen No.	Homogeneity Trace		Comparison with Random Sampling	
			σ_W	σ_B	σ_{RS}	$\sqrt{\sigma_W^2 + \sigma_B^2}$
Glass K-411						
SiO_2	54.30	#1	0.37	0	0.28	0.37
		#2	0.35	0	0.46	0.35
MgO	14.67	#1	0.24	0.01	0.28	0.24
		#2	0.21	0.11	0.32	0.24
CaO	15.47	#1	0.15	0	0.20	0.15
		#2	0.16	0	0.17	0.16
FeO	14.42	#1	0.18	0	0.13	0.18
		#2	0.19	0	0.24	0.19
Glass K-412						
SiO_2	45.35	#1	0.27	0.21	0.35	0.34
		#2	0.29	0.11	0.29	0.31
MgO	19.33	#1	0.31	0	0.31	0.31
		#2	0.29	0	0.33	0.33
CaO	15.25	#1	0.17	0.03	0.18	0.17
		#2	0.15	0.06	0.14	0.24
FeO	9.96	#1	0.13	0.04	0.15	0.14
		#2	0.13	0.04	0.10	0.14
Al_2O_3	9.27	#1	0.14	0	0.17	0.14
		#2	0.13	0	0.14	0.13

A random sampling test in which two different specimens of each glass were analyzed was also performed to evaluate specimen microhomogeneity. The instrumental parameters, as in the previous tests, were a 15 kV excitation potential and a specimen current of about 3×10^{-8} A. Counting periods were 40 s. Thirty random samplings were made on each glass specimen. One standard deviation, σ_{RS}, was calculated from the thirty points. These values (expressed in weight percent) are listed in Table 5; they agree favorably with the combined components of variance, $\sqrt{\sigma_W^2 + \sigma_B^2}$, obtained from the staticical evaluation of the homogeneity traces.

The errors in Table 5 and in subsequent tables were converted from counts to weight percent concentration. Such a conversion is valid when there is a linear relationship between net counts (background-corrected) and concentration which passes through the origin. For all five elements involved in these analyses such a linear relationship was validated by analyzing several well-characterized minerals containing the elements studied here at concentrations below and above those in the K-411 and K-412 glasses. At least five samplings were taken from each mineral and the average was background-corrected for the plots of net counts vs. weight percent concentration. Wavelength spectrometers were used. A 10 x 10-μm scanning raster was used and counting periods were 40 s. Analyses for silicon, calcium, magnesium, and aluminum were done at an excitation potential of 15 kV and the two different currents of 1.6×10^{-8} A and 3.5×10^{-8} A. Iron data were also taken at 20 kV and 1.6×10^{-8} A. All plots were linear, passing through the origin.

For macrohomogeneity tests five specimens of each glass were randomly selected from the 100 or more samples of each glass that make up the stock for SRM 470. These tests were designed to evaluate differences between specimens as well as differences within each specimen. Counting periods were 20 s. For each element in each glass at least two independent tests on different days were run by two different operators, when possible. For each test, each specimen was randomly sampled six times and duplicate readings were taken at each point. After all five specimens had been tested once, the five specimens were again sampled in random order giving a total of twelve random samplings on each specimen. Testing of a specimen in the first half and again in the second half of an experiment is expected to average out instrumental drifts if any occur. Also, such a sampling procedure can help to distinguish between real specimen differences and instrument fluctuations.

For these homogeneity tests, an NBS electron microprobe was used. With three crystal spectrometers, three elements could be simultaneously tested. The excitation potential was 15 or 20 kV and the beam current was 1.6×10^{-8} A or 3.0×10^{-8} A, depending upon the day of the test. The beam current regulation mode on the instrument was used to minimize current drift during each experiment which took about 1½ hours. A 10 x 10-μm scanning raster was used to minimize specimen contamination. Counting periods were 20 s.

With data from this type of testing procedure, three different contributions to the errors can be estimated. These are σ_S^2, the variance between different specimens, σ_B^2, the variance within specimens on the micrometer scale, and σ_E^2 the variance of a single measurement error. The equations used to derive these components are described in detail in another recent NBS Special Publication 260-70 [6].

In Tables 6 and 7 the individual standard deviations, expressed in weight percent, are given for each oxide in each glass. These standard deviations are all small. There is apparently no significant experimental error, no significant variation within specimens, and no significant variation between specimens. The standard deviation of a single measurement, σ_p, which combines these individual error components is 1.5 percent (relative) or less for glass K-411 (Table 6) and 1.7 percent (relative) or less for glass K-412 (Table 7). For both glasses, the largest values of σ_p are in the iron oxide experiments which were run at a 15 kV excitation potential and at the lower beam current of 1.6×10^{-8} A. A slight improvement in these statistics results when a 20 kV excitation potential is used which is a more favorable overvoltage for iron resulting in more favorable counting statistics. At the lower voltage the total counts per 20 s were about 5000 and 6500 for K-412 and K-411, respectively. At the higher voltage they were about 10,000 and 15,000 respectively. For all other elements, the total counts per 20 s were at least 20,000 in all experiments. The results of better counting statistics can also be seen in experiments G and H for glass K-412 where the higher beam current of

3×10^{-8} A gave improved results not only for iron oxide but also for the oxides of silicon, magnesium and aluminum.

Table 6. Homogeneity evaluation of five specimens of glass K-411

Oxide	Weight Percent	Exp.[b]	Ex. Pot. (kV)	Standard Deviations in Weight Percent of Oxide[a] σ_E	σ_B	σ_S	σ_P(rel.%)
SiO_2	54.30	A	15	0.15	0.15	0.06	0.22(0.4)
		B	15	0.15	0.30	0.15	0.37(0.7)
MgO	14.67	A	15	0.10	0.05	0.05	0.12(0.8)
		B	15	0.10	0.03	0.04	0.11(0.7)
CaO	15.47	C	15	0.07	0.10	0.08	0.15(1.0)
		D	15	0.07	0.04	0.01	0.08(0.5)
FeO	14.42	A	15	0.18	0.07	0.03	0.20(1.4)
		B	15	0.18	0.12	0.0	0.22(1.5)
		C	15	0.14	0.10	0.04	0.18(1.2)
		D	15	0.14	0.07	0.0	0.16(1.1)
		E	20	0.12	0.02	0.04	0.13(0.9)
		F	20	0.11	0.04	0.0	0.12(0.8)

[a]The standard deviations are defined as follows:

σ_E = the error of a single measurement

σ_B = the variation within specimens on a micrometer scale

σ_S = the variation between the different specimens

σ_P = one standard deviation of a single measurement combining the above errors.

$$\sigma_P = \sqrt{\sigma_E^2 + \sigma_B^2 + \sigma_S^2}$$

[b]Beam current for all experiments was 1.6×10^{-8} A.

Table 7. Homogeneity evaluation of five specimens of glass K-412

Oxide	Weight Percent	Exp.[b]	Ex. Pot. (kV)	Standard Deviations in Weight Percent of Oxide[a] σ_E	σ_B	σ_S	σ_p(rel.%)
SiO_2	45.35	A	15	0.14	0.26	0.12	0.32(0.7)
		G	15	0.10	0.15	0.10	0.21(0.5)
		H	15	0.10	0.10	0.03	0.14(0.3)
MgO	19.33	A	15	0.11	0.04	0.02	0.12(0.6)
		G	15	0.08	0.03	0.01	0.09(0.5)
CaO	15.25	C	15	0.09	0.04	0.05	0.11(0.7)
		D	15	0.10	0.18	0.07	0.22(1.4)
FeO	9.96	A	15	0.15	0.0	0.06	0.16(1.6)
		C	15	0.15	0.02	0.06	0.16(1.6)
		D	15	0.14	0.09	0.0	0.17(1.7)
		E	20	0.10	0.07	0.0	0.12(1.2)
		F	20	0.10	0.04	0.02	0.11(1.1)
		G	15	0.11	0.04	0.01	0.12(1.2)
		H	15	0.11	0.0	0.02	0.11(1.1)
Al_2O_3	9.27	C	15	0.07	0.04	0.02	0.08(0.9)
		H	15	0.05	0.03	0.0	0.06(0.7)

[a] Standard deviations defined the same as in Table 6.

[b] Beam current for experiments A, C, D, E, and F was 1.6×10^{-8} A and for experiments G and H the beam current was 3×10^{-8} A.

The uncertainties in the average measurement, $\overline{P}$, for three possible experiments that a user of SRM 470 might perform are summarized in Tables 8 and 9. These uncertainties are calculated for the 99 percent confidence interval for the mean concentration according to the expression $\overline{P} \pm 3\sigma_{\overline{P}}$ where

$$\sigma_{\overline{P}} = \sqrt{\frac{\sigma_S^2}{n_S} + \frac{\sigma_B^2}{n_S n_B} + \frac{\sigma_E^2}{n_S n_B n_E}}$$

and where n_E independent measurements are made at each of n_B randomly chosen points in each of n_S specimens. More details on this equation can be found in the Appendix of reference [6].

The average of each type of error for each oxide in Tables 6 and 7 is used to calculate $\pm 3\sigma_{\overline{P}}$ for the three possible experiments in Tables 8 and 9. For example, the average values of σ_E, σ_B, and σ_S for SiO_2 calculated from experiments A, G, and H for glass K-412 are used to calculate the three different values of $\pm 3\sigma_{\overline{P}}$ (experiments I, II, and III) for SiO_2 in Table 9.

The three possible experiments and the results are meant to be of practical use to the electron probe operator. In experiment I, 16 independent random readings are taken from one specimen; in experiment II, 8 independent readings are taken from one specimen; and in experiment III, 8 independent readings are taken from each of two specimens. For all experiments each point was sampled only once. The best results for both glasses are obtained when using two specimens with eight samplings on each. Sixteen samplings on a single specimen is almost as good. But only eight samplings on one specimen gives noticeably higher errors. The number of specimens and samplings used in each laboratory will

Table 8. Comparison of uncertainty intervals ($\pm 3\sigma_{\bar{p}}$) for glass K-411 in weight percent of oxide

Oxide	Weight Percent	Ex. Pot. (kV)	Experiment I: One Specimen 16 samplings; $n_S=1$; $n_B=16$; $n_E=1$; $\pm 3\sigma_{\bar{p}}$ (rel. %)	Experiment II: One Specimen 8 samplings; $n_S=1$; $n_B=8$; $n_E=1$; $\pm 3\sigma_{\bar{p}}$ (rel. %)	Experiment III: Two Specimens 8 samplings; $n_S=2$; $n_B=8$; $n_E=1$; $\pm 3\sigma_{\bar{p}}$ (rel. %)
SiO_2	54.30	15	±0.41(0.7)	±0.46(0.9)	±0.32(0.6)
MgO	14.67	15	±0.17(1.2)	±0.19(1.3)	±0.13(0.9)
CaO	15.47	15	±0.17(1.1)	±0.19(1.2)	±0.13(0.8)
FeO	14.42	15	±0.15(1.1)	±0.21(1.4)	±0.15(1.0)
		20	±0.11(0.8)	±0.15(1.1)	±0.10(0.7)

Table 9. Comparison of uncertainty intervals ($\pm 3\sigma_{\bar{p}}$) for glass K-412 in weight percent of oxide

Oxide	Weight Percent	Ex. Pot. (kV)	Experiment I: One Specimen 16 samplings; $n_S=1$; $n_B=16$; $n_E=1$; $\pm 3\sigma_{\bar{p}}$ (rel. %)	Experiment II: One Specimen 8 samplings; $n_S=1$; $n_B=8$; $n_E=1$; $\pm 3\sigma_{\bar{p}}$ (rel. %)	Experiment III: Two Specimens 8 samplings; $n_S=2$; $n_B=8$; $n_E=1$; $\pm 3\sigma_{\bar{p}}$ (rel. %)
SiO_2	45.35	15	±0.29(0.6)	±0.33(0.7)	±0.23(0.5)
MgO	19.33	15	±0.10(0.5)	±0.13(0.7)	±0.09(0.5)
CaO	15.25	15	±0.22(1.4)	±0.25(1.6)	±0.17(1.2)
FeO	9.96	15	±0.14(1.4)	±0.17(1.7)	±0.12(1.2)
		20	±0.09(0.9)	±0.13(1.7)	±0.09(0.9)
Al_2O_3	9.27	15	±0.06(0.7)	±0.08(0.9)	±0.06(0.6)

depend upon the acceptable uncertainty interval for the specific analysis and the experimental imprecision of the individual laboratory. The numbers in Tables 8 and 9, however, are only applicable to the NBS electron microprobe used to obtain the estimates of σ_S, σ_B, and σ_E. The value of σ_E will be different for each operator's instrument.

5. Conclusions

These glasses have been shown to be excellent Standard Reference Materials for use in microanalysis techniques such as EPMA and secondary ion mass spectrometry. Independent wet chemical analyses are in very good agreement and homogeneity tests have shown that all oxides in K-411 and K-412 are homogeneous on both the micrometer level and from specimen to specimen.

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U.S. Department of Commerce
Juanita M. Kreps
Secretary

National Bureau of Standards
Ernest Ambler, Director

National Bureau of Standards Certificate of Analysis

Standard Reference Material 470

Mineral Glasses for Microanalysis

These glasses have been fabricated for use in microanalysis techniques such as electron probe microanalysis (EPMA) and secondary ion mass spectrometry (SIMS). The glasses are homogeneous and are especially useful as standards for the analysis of minerals, glasses, and ceramics.

Composition in Weight Percent

Constituent	SiO_2	FeO	MgO	CaO	Al_2O_3
Glass K-411					
Certified Value	54.30 ± 0.20[a]	14.42 ± 0.20	14.67 ± 0.20	15.47 ± 0.20	
Wet Chemistry					
LAB A[b]	54.24(0.02)	14.49(0.18)	14.64(0.08)	15.53(0.18)	
LAB B	54.36	14.34	14.69	15.41	
EPMA					
LAB C[c]	54.89(0.96)	14.48(0.27)	15.12(0.20)	15.49(0.15)	
Glass K-412					
Certified Value	45.35 ± 0.20	9.96 ± 0.20	19.33 ± 0.20	15.25 ± 0.20	9.27 ± 0.20
Wet Chemistry					
LAB A[b]	45.38(0.04)	10.10(0.20)	19.33(0.02)	15.29(0.10)	9.26(0.12)
LAB B	45.32	9.82	19.32	15.21	9.28
EPMA					
LAB C[c]	45.41(0.77)	9.94(0.18)	19.66(0.25)	15.44(0.15)	9.34(0.29)

[a] The uncertainty of ± 0.20 wt.% assigned to the certified values is the 2-sigma value. This error is a pooled value for all oxides estimated from the ranges between the two laboratories using wet chemical techniques.

[b] The average and (range) of two analyses.

[c] The average and (range) of three analyses.

The technical measurements were performed by C. E. Fiori and R. B. Marinenko under the direction of K.F.J. Heinrich.

The support aspects involved in the certification and issuance of this Standard Reference Material were coordinated through the Office of Standard Reference Materials by R. Keith Kirby.

Washington, D.C. 20234
October 30, 1981
(Revision of Certificate dated 4-26-79)

George A. Uriano, Chief
Office of Standard Reference Materials

(over)

These glasses were prepared in the Ceramics, Glass, and Solid State Science Division of the National Bureau of Standards' Center for Materials Science by D. H. Blackburn and D. A. Kauffman.

The two glasses were tested for microhomogeneity by both random sampling and periodic integrator traces. This work was done at NBS by R. B. Marinenko. No evidence of inhomogeneity was observed in these glasses. An NBS 260 Series Special Publication is being prepared which will describe these microhomogeneity studies and the statistical evaluations.

The wet chemical analyses were performed at the Smithsonian Institution, Washington, D.C. by G. Jarosewich and J. Norberg, and at Pennsylvania State University, University Park, PA, by N. H. Suhr and J. C. Devine.

EPMA was performed at NBS by C. Fiori using different standards where possible. For matrix corrections, the NBS correction procedure, COR (Henoc, J., Henrich, K. F. J., and Myklebust, R. L., National Bureau of Standards Technical Note 769, 1973) was used. While the EPMA results are in good agreement with the wet chemical analyses, they were not included in the determination of the certified values.

A trace of Al_2O_3 ($\leq 0.1\%$) was spectrographically detected in K-411 and a small amount of MnO (approximately 0.1%) was observed in both glasses by atomic absorption.

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4. TITLE AND SUBTITLE

Standard Reference Materials:
Preparation and Characterization of K-411 and K-412
Mineral Glasses for Microanalysis: SRM 470

5. AUTHOR(S)

R. B. Marinenko

6. PERFORMING ORGANIZATION (If joint or other than NBS, see instructions)

NATIONAL BUREAU OF STANDARDS
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☐ Document describes a computer program; SF-185, FIPS Software Summary, is attached.

11. ABSTRACT (A 200-word or less factual summary of most significant information. If document includes a significant bibliography or literature survey, mention it here)

The two mineral glasses in SRM 470, K-411 and K-412, were quantitatively analyzed for major constituents. The results of wet chemical analyses from two independent laboratories were in excellent agreement; therefore, these results were used for certification. Quantitative electron probe microanalysis also agrees favorably with the certified compositions. Specimens were evaluated for micro- and macrohomogeneity with the electron microprobe by using random sampling and periodic integrator homogeneity trace techniques. Statistical analyses as well as the homogeneity traces showed no obvious composition fluctuations either within each specimen or among different specimens. These glasses are therefore excellent standards for microanalytical techniques. They are primarily composed of silicon, iron, magnesium, calcium, and aluminum oxides, none of which is present in less than 9 weight percent nor more than 55 weight percent.

12. KEY WORDS (Six to twelve entries; alphabetical order; capitalize only proper names; and separate key words by semicolons)

chemical analysis; digital periodic integrator; electron probe microanalysis; glass standards; homogeneity testing; microhomogeneity; mineral glasses; Standard Reference Material

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