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The chemical durability of glass: determination of sodium and potassium oxides in durability extract solutions

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In this investigation 21 analysts from 15 laboratories collaborated to determine sodium and potassium oxides in simulated and actual durability extract solutions using atomic absorption spectrophotometry, flame emission spectrophotometry and filter flame photometry. It is shown that in both of the spectrophotometric techniques the values for both alkali metal oxides are enhanced by the presence of other glass constituents but such interference was not experienced with the simple filter flame photometer. Improved results and improved between-laboratory reproducibilities were achieved by the introduction of a flame buffer, in this case a caesium chloride/aluminium nitrate mixture proposed by Schuhknecht and Schinkel [19]. The methods described in the appendices are claimed to be satisfactory for determining both alkalies in durability extract solutions.

La durabilité chimique du verre: dosage des oxydes de sodium et de potassium dans les solutions

21 analystes de 15 laboratoires différents ont participé à cette étude qui avait pour but de doser les oxydes de sodium et de potassium dans des solutions synthétiques et réelles, par spectrophotométrie par absorption atomique, par spectrophotométrie par émission de flamme et par photométrie de flamme à filtre. On montre que pour les deux techniques spectrophotométriques, les valeurs obtenues pour les deux oxydes de métaux alcalins subissent une augmentation due à la présence d'autres constituants du verre. Toutefois, on n'a pas constaté la même interférence dans le cas de la photométrie de flamme à filtre. On a obtenu de meilleurs résultats et une meilleure reproductibilité inter-laboratoire grâce à l'utilisation d'un tampon de flamme, en l'occurrence un mélange de chlorure de césium et de nitrate d'aluminium proposé par Schuhknecht et Schinkel [19]. En annexe, on décrit des méthodes permettant de doser de façon satisfaisante, les deux alcalis dans les solutions.

Chemische Beständigkeit von Glas: Natrium- und Kaliumoxidbestimmung in Auslauglösungen

Bei der vorliegenden Untersuchung arbeiteten 21 Analytiker von 15 Laboratorien zusammen, um Natrium- und Kaliumoxid in Modellösungen und Auslauglösungen zu bestimmen, wobei sie die Atomabsorptions- und die Flammenemissionsspektrofotometrie sowie die Filterflammenfotometrie anwendeten. Es zeigte sich, daß die beiden spektrofotometrischen Verfahren, bedingt durch die anderen vorhandenen Glaskomponenten, erhöhte Werte für die beiden Alkalimetalloxide ergeben; dagegen wurde diese Störung bei der Analyse mit dem Filterflammenfotometer nicht beobachtet. Eine Verbesserung und Reproduzierbarkeit der Ergebnisse wurden durch die Verwendung einer Pufferlösung erzielt, und zwar der Cäsiumchlorid/Aluminiumnitratlösung nach Schuhknecht und Schinkel [19]. Die im Anhang beschriebenen Verfahren genügen den Ansprüchen, die an die Bestimmung von Natrium und Kalium in Auslauglösungen gestellt werden.

Sub Committee A 2 reports on the determinations of boric oxide [1], silica [2], and calcium and magnesium oxides [3] have already been published. The programme of work to produce methods for the analysis of durability extracts is completed in this issue of "Glastechnische Berichte" by further reports on the determinations of the oxides of aluminium [4], iron [5], and lead [6].

1. General considerations

It is well known that the alkali ions in glasses are weakly bonded with oxygen and, consequently, the chemical attack of a glass generally results in the liberation of a measurable amount of these ions. Thus it is not surprising that the first attempts to characterize the chemical durability of glasses were based on the determination of sodium and/or potassium ions released under given conditions.

Tooley and Parmelee [7] studied the action of water on glass grains and used a gravimetric method, precipitation as uranyl zinc sodium acetate, for determining the amount of sodium released.

Whilst the sensitivity of this method is quite satisfactory it has now been superseded by flame photometry. Numerous authors have used this more modern technique for determining the alkalies released from glasses in contact with water [8 to 16] or with acidic solutions [15 to 18]. In flame photometry, a measurement of the intensity of the characteristic lines emitted at 5890 Å (Na) and 7665 Å (K) is made when the solution to be analysed is atomized in the flame of a burner supplied with a suitable gas mixture. Such intensities are compared with those of synthetic solutions of known concentrations atomized under the same conditions. In order to avoid interferences, the addition of substances called "radiation buffers" to the solution is sometimes recommended. Schuhknecht and Schinkel [19] suggest a reagent containing caesium chloride and aluminium nitrate while Jones [20] recommends strontium chloride. Such additions may be particularly useful when the element to be determined co-exists at low concentration with high concentrations of foreign ions.

Atomic absorption spectrophotometry, an analytical technique which appeared more recently, has the sensitivity and selectivity of flame photometry and could also be used. Its principle may be briefly described as follows. The solution of the element to be determined is atomized in the flame of a burner supplied with a suitable gas mixture (air/propane, air/acetylene). The mixture is chosen so that the element to be determined mainly exists as atoms at their ground state in the flame. The emitting source, generally a hollow cathode lamp, consists of a glass envelope with two electrodes: a cathode made of, or covered with, the same element as that to be determined and an anode, which is usually a metallic rod. The envelope contains a filling gas under a pressure of a few millimeters of mercury. When the lamp is supplied with a voltage of 100 to 300 V and a current of 5 to 100 mA, metal atoms are emitted from the cathode. The collisions with the ions of the filling gas lead to the excitation of some of the metal atoms which, when returning to the ground state, emit a characteristic radiation. When a beam of monochromatic light passes through the flame containing the atoms of the element to be determined, these atoms absorb a part of the radiation proportional to their concentration. The comparison of this absorption with that produced under the same conditions by solutions of known concentrations allows the concentration of the unknown solution to be determined. Owing to its very principle, atomic absorption spectrophotometry is highly specific but this does not prevent it from being subject to some minor interferences. Again, in some cases, the addition of "radiation buffers" may prove successful in eliminating these interferences. The choice of a suitable gas mixture is also important.

2. Experimental work

2.1. Determination of sodium oxide

During the experimental stages of the work to develop a test method for measuring the resistance of glass to 6 N hydrochloric acid, a study which produced the procedure eventually adopted by the International Organization for Standardization ISO [21], members of Sub Committee A 2 were able to familiarize themselves with the flame photometric determination of Na_2O in durability extract solutions. In order to prove the suitability of the technique, it was first decided to determine the Na_2O content of a solution resulting from 1 hour autoclave test according to the European Pharmacopoeia¹) applied to flasks made of colourless soda-lime-silica glass referred to as Gl, the composition of which is given in table 1. The autoclave tests were performed by each member with his own equipment and the results obtained are summarized in table 2.

It can be seen from this table that the standard deviation corresponds to 11.4% of the general mean. Such a high ratio might seem disappointing but it should be borne in mind that each member has performed his own autoclave test and that it is probable that the thermal programmes of the different autoclaves used were different. It is probable, therefore, that the scatter of results is mainly due to differences in the test conditions rather than to a lack of accuracy in the flame photometric determination of Na_2O.

Consequently, it was decided to investigate further the method by determining the Na_2O concentrations of durability extract solutions prepared in one laboratory only and, at the same time, study the influence of the acidity of the solution on the sensitivity of the method. Thus flasks made of the same colourless soda-lime-silica glass (Gl) were autoclaved under the conditions described in the European Pharmacopoeia. The contents of the flasks were combined and neutralized with normal hydrochloric acid in the presence of methyl red. The neutralized solution was then divided into two equal parts. One half (solution A) was acidified with 0.5% (v/v) HCl (d = 1.19), the other (solution B) with 5% (v/v) HCl (d = 1.19). After addition of the required volume of HCl, the solutions were diluted to twice the original volume, so that the final Na_2O content was only

Table 1. Chemical composition of the glass Gl

Constituent	Content in %
SiO_2	72.7
Al_2O_3	2.0
Na_2O	13.1
K_2O	0.65
CaO	11.0
MgO	0.1
Fe_2O_3	0.037
TiO_2	0.025
SO_3	0.25
F_2	0.20

Table 2. Results obtained for the determination of the Na_2O content of an extract solution from glass Gl

Laboratory	Na_2O found in µg/ml					
A	11.2	11.2				
B	9.8					
C	9.3	9.1	9.3	9.1	10.1	9.7
D	12.4	12.4				
E	11.02	11.25				
F	10.1	10.7				
G	8.8	8.7				
H	11.5					
J	13.4					
K	9.78 (average of 20 values)					
L	11.0	11.0				
M	9.86	10.02	9.72	10.00		
General mean	10.40					
Standard deviation	1.19					
Coefficient of variation in %	11.4					

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¹) The articles are filled with specially prepared water and autoclaved for 1 hour at 121 °C.

half of the initial value and the final HCl concentrations of the solutions were respectively 0.025 and 0.25 N.

Members were asked to determine sodium oxide in these solutions, either by flame photometry or by atomic absorption spectrophotometry but to use reference solutions with the same strength HCl as test solutions. The results obtained are summarized in table 3.

Mean values for the soda contents of the two extracts were calculated, despite the fact that, due to a slight confusion in the acid content, some members had not used reference solutions having exactly the same acid strength as the test solutions. In addition, the effect of background constituents derived from the autoclaved glass was not taken into account in the preparation of the reference solutions.

The values of the standard deviation and of the coefficient of variation found in both cases show that the between-laboratory reproducibility is quite good, provided that the acidity is controlled and is the same in the test solutions and in the reference solutions. However, the sensitivity of the method is influenced by the acidity, as was demonstrated by Rehm, whose results are shown in table 4. He prepared a series of solutions containing 5 µg Na_2O/ml and with increasing HCl concentrations up to 5 N. He then measured the intensity of the sodium line and calculated the Na_2O value from a calibration graph prepared using aqueous reference solutions.

These results clearly show that increasing the acidity of the solution leads to a decrease in the sensitivity of the method. Similar results have been obtained by Nordberg who, in addition, tested the influence of the kind of acid (hydrochloric, nitric or perchloric); he concluded that nitric acid influenced the sensitivity less than the other two acids in both flame emission and atomic absorption spectrophotometry.

Interference from silica in the determination of sodium had thus so far not been considered important. However, during the concurrent study on the determination of silica [2] it was shown that some low-alkali glasses, such as borosilicate glass, sometimes produced extract solutions which were slightly turbid. This turbidity was shown to be due to the presence of colloidal silica and so, as described in 4. Appendix I, the extract solution is evaporated with a few drops of hydrofluoric acid – to remove the silica – before the alkali is determined.

Possible interferences by other ions in the determination of alkalies had not, so far, been considered because it was thought that their incidence in durability extract solutions would be so small as to present no problems. However, it was decided to investigate this point more thoroughly and so four synthetic solutions numbered 1, 2, 3, and 4 were prepared for distribution to the Committee. Each solution had the same acidity (1/15 N in HNO_3); solutions 1 and 2 had the same Na_2O content (theoretical value: 8.75 µg/ml) but solution 2 contained in addition (in µg/ml): 1 K_2O, 10 CaO, 5 MgO, 1 Al_2O_3, and 0.1 Fe_2O_3. Solution 2, therefore, was considered to be representative of a durability extract from a soda-lime-silica glass. On the other hand, solutions 3 and 4 had the same Na_2O content (theoretical value: 0.5 µg/ml) but solution 4 contained in addition (in µg/ml): 0.5 K_2O, 25 CaO, 0.5 MgO, 15 Al_2O_3, and 0.5 Fe_2O_3 and was considered to be representative of a durability extract from a low-alkali E type glass.

Members were asked to determine Na_2O contents of these solutions, either by flame emission spectrophotometry or by atomic absorption spectrophotometry. Furthermore, in the case of solutions 2 and 4 the determination of Na_2O in the absence and in the presence of the radiation buffer recommended by Schuhknecht and Schinkel [19] was requested. Table 5 summarizes results obtained on solutions 1 and 2 and table 6 those obtained on solutions 3 and 4. In these tables the results are classified according to the experimental technique used for the determination.

Table 3. Results obtained in determining Na_2O in durability extract solutions in the presence of different HCl concentrations

Laboratory	Na_2O found in µg/ml		Analytical technique used
	Solution A	Solution B	
A	5.3	5.5	Flame photometry
B	5.8	5.8	
C	5.0 5.1	5.3 5.2 5.3	Flame photometry
D	5.5	5.8	Flame photometry
E	5.6	5.7	Atomic absorption
F	5.3	5.2	Flame photometry
	5.2	5.2	Atomic absorption
G	5.8 5.5	5.5 5.1	Atomic absorption
H	5.2	5.1	Flame photometry after evaporation of the solution and acidification with $HClO_4$
K	5.3	5.4	Flame photometry
L	5.2 5.2	6.0 6.2	Flame photometry
	5.2 5.2	6.0 6.0	Atomic absorption
M		5.6	Flame photometry
N	5.3	5.2	Flame photometry
P	5.52	5.25	
Mean value	5.35	5.52	
Standard deviation	0.23	0.34	
Coefficient of variation in %	4.3	6.2	

Table 4. Results obtained by Rehm when comparing acidic solutions of NaCl with aqueous reference solutions

HCl concentration	Na_2O concentration	
	theoretical in µg/ml	measured in µg/ml
0.00 N	5.00	5.00
0.01 N	5.00	4.85
0.05 N	5.00	4.50
0.1 N	5.00	4.30
0.5 N	5.00	3.90
1.0 N	5.00	3.60
5.0 N	5.00	2.63

Table 5. Results obtained in determining Na_2O in synthetic solutions 1 and 2

Instrumental technique	Laboratory	µg Na_2O/ml found in solution 1	µg Na_2O/ml found in solution 2	
			in the absence of Schuhknecht and Schinkel reagent	in the presence of Schuhknecht and Schinkel reagent
Atomic absorption spectrophotometry	A	9.04	9.02	8.92
	C	9.1	8.9	9.1
	F	8.37	8.47	8.48
	G	8.64	8.80	8.86
	K	8.51	8.74	8.80
	L	8.76	8.79	9.04
	M	8.84	8.90	8.94
	R	9.03	9.11	9.10
	S	8.95	8.95	–
	Mean value	8.80	8.85	8.91
	Standard deviation	0.25	0.18	0.20
	Coefficient of variation in %	2.8	2.0	2.3
Flame emission	B	9.30		9.00
	C	9.0	8.9	9.0
	D	8.93	9.02	8.92
	F	8.96	8.62	8.55
	H	8.84	8.93	8.58
	J	8.7	8.8	8.8
	K	8.91	9.01	8.95
	M	8.82	8.82	8.88
	S	8.96	9.01	–
	Mean value	8.94	8.89	8.84
	Standard deviation	0.17	0.14	0.18
	Coefficient of variation in %	1.9	1.6	2.0
Overall mean value		8.87	8.87	8.87
Overall standard deviation		0.22	0.16	0.19
Overall coefficient of variation in %		2.5	1.8	2.1

In addition to the results given in tables 5 and 6 Gebhardt determined Na_2O in the same solutions by using the high frequency plasma torch method of excitation and obtained the following results:

Solution 1: 8.1 µg Na_2O/ml;

Solution 2: without Schuhknecht and Schinkel reagent: 9.2 µg Na_2O/ml, with Schuhknecht and Schinkel reagent: 8.8 µg Na_2O/ml;

Solution 3: 0.5 µg Na_2O/ml;

Solution 4: without Schuhknecht and Schinkel reagent: 1.0 µg Na_2O/ml, with Schuhknecht and Schinkel reagent: 0.4 µg Na_2O/ml.

From the foregoing it may be observed that:

a) Both flame emission spectrophotometry and atomic absorption spectrophotometry are quite suitable for determining the small concentrations of Na_2O encountered in durability extract solutions.

b) Other constituents extracted from the glass do not interfere in the sodium determination at the anticipated concentration levels. The addition of a radiation buffer, such as that recommended by Schuhknecht and Schinkel, does not appear to be necessary but its presence does not impair the accuracy of the sodium determination.

c) In some cases, values obtained using the high frequency plasma torch method of excitation were not as good as those reported in tables 5 and 6. However, no definite conclusion can be drawn concerning the suitability of the technique because some difficulties were met during the determination due to the low volume of solution available and the fairly high consumption of the plasma burner. The opinion of the users is that technique could be used with success provided a sufficient volume of solution is available. Unfortunately, in many cases the volume of durability extract solutions available is limited.

The final conclusion from this investigation of the determination of sodium oxide in durability extract solutions is that both flame emission spectrophotometry and atomic absorption spectrophotometry may be recom-

Table 6. Results obtained in determining Na_2O in synthetic solutions 3 and 4

Instrumental technique	Laboratory	µg Na_2O/ml found in solution 3	µg Na_2O/ml found in solution 4	
			in the absence of Schuhknecht and Schinkel reagent	in the presence of Schuhknecht and Schinkel reagent
Atomic absorption spectrophotometry	A	0.52	0.57	0.57
	C	0.5	0.5	0.5
	G	0.50	0.56	0.52
	K	0.51	0.60	0.55
	L	0.48	0.53	0.50
	M	0.51	0.56	0.50
	R	0.53	0.59	0.58
	S	0.54	0.60	–
	Mean value	0.51	0.57	0.53
	Standard deviation	0.016	0.034	0.035
	Coefficient of variation in %	3.1	6.1	6.6
Flame emission	B	0.53	0.59	0.56
	C	0.4	0.5	0.59
	D	0.59	0.62	0.59
	F	0.4	0.6	0.54
	H	0.47	0.56	0.51
	J	0.44	0.52	0.53
	K	0.49	0.54	0.49
	M	0.51	0.58	0.50
	S	0.53	0.58	–
	Mean value	0.48	0.56	0.54
	Standard deviation	0.066	0.041	0.041
	Coefficient of variation in %	13.8	7.3	7.6
Overall mean value		0.49	0.56	0.54
Overall standard deviation		0.050	0.037	0.037
Overall coefficient of variation in %		10.2	6.6	6.9

mended. However, care must be taken to have the same acidity in reference solutions as in the test solutions. The acid concentration should be moderate and nitric acid is preferred to hydrochloric or perchloric acid because of its lower suppressive effect. A detailed procedure is given in 4. Appendix I.

2.2. Determination of potassium oxide

Initially members were invited to determine K_2O in a synthetic solution containing (in µg/ml): 10.2 K_2O and, in addition, 10.2 PbO, 1 Fe_2O_3, and 0.95 Al_2O_3. The solution was 0.1 N in nitric acid. The foreign ions were not introduced with the specific aim of studying interferences but it is obvious that information could be drawn from the results. The choice of the analytical procedure to be adopted (flame emission or atomic absorption spectrophotometry) was left over to each member. The results obtained for that first investigation are given in table 7.

From these results it may be observed that:

a) Both flame emission and atomic absorption spectrophotometry seem to be suitable for determining K_2O in the concentration range which is to be expected in durability extract solutions. In the case of flame emission, three values (9.0; 9.0; 9.0) obtained in laboratory K lie outside the range "mean value $\pm 2\sigma$". If they are omitted, the general mean becomes 10.16 with a standard deviation of $\pm$ 0.37 and a coefficient of variation equal to 3.6%. Values obtained by atomic absorption spectrophotometry are closer together but it is to be noted that only a limited number of results are available.

b) There is no indication of interference from the foreign elements which is particularly interesting in the case of lead oxide, which could be present in significant amounts in durability extract solutions from lead containing glasses.

This first approach may be considered encouraging and the next step consisted in the investigation of the possible interferences from Na_2O, CaO, and MgO. This was justified by the fact that many glasses generally contain much more sodium, calcium and magnesium oxides than potassium oxide. Three solutions, labelled I, II and III, containing the same K_2O concentration were prepared and an aliquot of each of them distributed to each member. All three solutions had the same acidity (1/15 N in HCl, i.e. about 0.25% w/w). Solution I contained K_2O only, solution II contained K_2O and Na_2O in proportions of 1 K_2O for 5 Na_2O (w/w) and solution III contained K_2O, Na_2O, CaO, and 5 MgO (w/w). Solutions II and III may be considered as approximately representative of extracts from borosilicate and soda-lime glasses respectively. Each member was asked to determine K_2O in each solution, either by flame emission and/or by atomic absorption spectrophotometry. Furthermore, the members were asked to proceed in the absence and in the presence of Schuhknecht and Schinkel reagent [19] (10% v/v). Results obtained are summarized in table 8 and are classified according to the instrumental technique used.

As can be seen from these results, the use of the Schuhknecht and Schinkel reagent is highly successful in reducing the interfering effect of sodium (solution II) and of sodium + calcium + magnesium (solution III) when potassium is determined by flame emission photometry or by atomic absorption spectrophotometry. The comparison of the values in table 8 shows an acceptable between-laboratory reproducibility. Just one value (6.60 μg/ml obtained in laboratory N in solution I by atomic absorption spectrophotometry) lies outside the range "mean value ± 2 σ". If this is omitted the atomic

Table 7. Results obtained in determining K_2O in a synthetic solution

Laboratory	K_2O concentration in μg/ml					
	Flame emission				Atomic absorption	
A	10.5	10.5			10.5	10.5
B	10.0	10.05			–	
C	10.2	10.2	10.2	10.2	–	
D	10.75	10.2	9.5	10.4	–	
E	9.85	9.90			–	
F	10.5	10.8			10.3	10.3
G					10.17	10.37
H	10.2				10.2	
J	10.4	10.5	10.2	10.2	–	
K	9.0	9.0	9.0	9.4	–	
	9.4	9.4				
L	10.35				–	
M	10.1	10.3	10.3	10.3	–	
P	10.25				–	
General mean	10.06				10.33	
Standard deviation	0.49				0.16	
Coefficient of variation in %	4.8				1.5	

Table 8. Results obtained in determining K_2O in three synthetic solutions in the absence or in the presence of Schuhknecht and Schinkel reagent

Instrumental technique	Laboratory	μg K_2O/ml found without Schuhknecht and Schinkel reagent			μg K_2O/ml found with Schuhknecht and Schinkel reagent	
		solution I	solution II	solution III	solution II	solution III
Atomic absorption spectrophotometry	A	6.22	6.35	7.21	6.17	6.20
	B	6.25	6.75	7.25	6.17	5.96
	E	6.15	6.41	6.79	6.18	6.20
	F	6.20	6.25	6.52	6.05	6.23
	G	6.22	6.49	6.87	6.12	6.16
	H	6.19	6.53	7.09	6.20	6.18
	K	6.35	7.10	8.15	6.15	6.05
	N	6.60	7.05	8.30	6.15	6.10
	Mean	6.27	6.62	7.27	6.15	6.14
	Standard deviation	0.144	–	–	0.046	0.068
	Coefficient of variation in %	2.3	–	–	0.75	1.1
Flame emission spectrophotometry	H	6.22	7.15	8.50	6.25	6.30
	K	6.15	7.35	9.00	5.95	6.05
	L	6.19	6.47	6.90	6.22	6.17
	N	6.30	6.85	8.07	6.20	6.20
	Mean	6.22	6.96	8.12	6.16	6.18
Filter flame photometry	C	6.23	6.19	6.19	–	–
	D	5.97	6.00	6.00	–	–
	K	6.19	6.45	6.62	6.23	6.20
	M	6.25	6.25	6.35	6.35	6.35
	Mean	6.16	6.22	6.29	6.29	6.28
Overall mean			6.23		6.17	6.17
Overall standard deviation			0.13		0.094	0.099
Overall coefficient of variation in %			2.1		1.5	1.6

Table 9. Results obtained in determining small K_2O concentrations in three synthetic solutions in the absence or in the presence of Schuhknecht and Schinkel reagent

Instrumental technique	Laboratory	μg K_2O/ml found without Schuhknecht and Schinkel reagent			μg K_2O/ml found with Schuhknecht and Schinkel reagent	
		solution A	solution B	solution C	solution B	solution C
Atomic absorption spectrophotometry	A	0.10	0.15	0.17	0.15	0.11
	G	0.12	0.13	0.14	0.13	0.17
	H	0.14	0.15	0.16	0.15	0.15
	M	0.13	0.14	0.17	0.13	0.13
	N	0.15	0.19	0.22	0.16	0.17
	Mean	0.13	0.15	0.17	0.14	0.15
Flame emission spectrophotometry	A	0.11	0.14	0.15	0.16	0.13
	D	0.13	0.13	0.13	0.13	0.13
	H	0.13	0.16	0.20	0.13	0.13
	J	0.11	0.13	0.13	0.10	0.10
	L	0.12	0.19	0.20	0.10	0.10
	M	0.13	0.15	0.19	0.13	0.14
	N	0.12	0.16	0.26	0.12	0.12
	Mean	0.12	0.15	0.18	0.12	0.12
Filter flame photometry	C	0.13	0.15	0.20	–	–
	D	0.13	0.17	0.20	–	–
	R	–	0.15	0.15	0.15	0.15
	Mean	0.13	0.16	0.18	0.18	0.14
Overall mean		0.125	0.153	0.178	0.133	0.129
Overall standard deviation		0.013	0.019	0.037	0.020	0.024
Overall coefficient of variation in %		10.4	12.4	20.8	15.0	18.6

absorption spectrophotometry values show a mean of 6.23 with a standard deviation of ± 0.064 and a coefficient of variation of 1.0%. Furthermore, the overall mean becomes 6.21 with a standard deviation of ± 0.11 and a coefficient of variation of 1.7%.

These figures are considered to be satisfactory and demonstrate the suitability of flame emission or atomic absorption spectrophotometry for determining moderate concentration of K_2O. However, as it is likely that much smaller K_2O concentrations will be met in durability extract solutions, it was decided to investigate further the techniques and to apply them to the determination of concentrations of the order of 0.1 μg K_2O/ml. For that purpose, three solutions respectively labelled A, B, and C, containing the same K_2O concentration were distributed. All had the same acidity (1/15 N in HCl, i.e. about 0.25% w/w). Solution A contained K_2O only, solution B contained K_2O and Na_2O in proportions of 1 K_2O for 250 Na_2O (w/w) and solution C contained K_2O, Na_2O, CaO, and MgO in proportions of 1 K_2O for 1250 Na_2O, 750 CaO, and 250 MgO (w/w). Each member was asked to determine K_2O, by flame emission or by atomic absorption spectrophotometry and, for solutions B and C, both in the absence and in the presence of Schuhknecht and Schinkel reagent. The results obtained are shown in table 9 in which they are classified according to technique.

The final conclusion from this investigation is that when only K_2O is present in the solution (solution A), the mean values obtained by any of the three instruments are virtually the same. They show, also, by the overall standard deviations, that the between-laboratory reproducibility is of a high order. When other ions are present, though, as in solutions B and C, the K_2O value is enhanced with increasing concentrations of other ions and the level of reproducibility also decreases. The addition of the radiation buffer reduces the enhancement effect when atomic absorption or flame emission spectrophotometry are used, but does not produce a reproducibility as good as when pure K_2O solutions are analysed. However, at this low level of concentration of K_2O, < 0.2 ppm, the between-laboratory reproducibility is still considered to be satisfactory. A detailed procedure is given in 5. Appendix II.

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4. Appendix I. A method for the determination of sodium oxide

4.1. Principle

Sodium is determined either by flame photometry or by atomic absorption spectrophotometry.

In the first case, the solution to be analysed is atomized in the flame of a burner and the intensity of the 5890 Å line emitted is measured and compared with that of a series of reference solutions of known Na_2O concentrations atomized under the same conditions. In the second case, the solution to be analysed is atomized in the flame of an air/acetylene burner in which passes the characteristic light emitted by a hollow cathode lamp, the cathode of which is covered with sodium. The portion of the 5890 Å line absorbed by sodium atoms present in the flame is measured and compared with the absorption produced by reference solutions of known Na_2O concentrations atomized under the same conditions.

Two alternative procedures are given: one without the addition of a flame buffer solution and another in which Schuhknecht and Schinkel reagent is added as a flame buffer solution.

4.2. Reagents

Distilled or deionised water and analytical grade reagents shall be used throughout.

Hydrofluoric acid: 40% w/w.

Perchloric acid: 60% w/w.

Nitric acid: approximately N; add 63 ml nitric acid (d = 1.42) to water and dilute to 1000 ml.

Sodium chloride.

Schuhknecht and Schinkel reagent: dissolve 50 g caesium chloride (CsCl) and 250 g aluminium nitrate ($Al(NO_3)_3 \cdot 9\,H_2O$) in water and dilute to 1 litre.

4.3. Standard solutions

4.3.1. Concentrated sodium oxide solution

Accurately weigh 1.8858 g of sodium chloride, previously dried at 250 °C, and dissolve in about 200 ml of water. Transfer to a 1 litre volumetric flask and dilute to the mark. Mix thoroughly and transfer the solution to a plastic bottle for storage.
1 ml ≡ 1 mg Na_2O.

4.3.2. Diluted sodium oxide solution

Transfer a 25.00 ml aliquot of the concentrated sodium oxide solution to a 250 ml volumetric flask, dilute to the mark and mix thoroughly. Transfer to a plastic bottle for storage.
1 ml ≡ 100 µg Na_2O.
Note: This is to be renewed every ten days.

4.3.3. Reference sodium oxide solutions

a) For use without a flame buffer solution

Transfer 2.00; 4.00; 6.00; 8.00, and 10.00 ml aliquots of the diluted sodium oxide solution to separate 100 ml volumetric flasks. Add 6.5 ml of nitric acid solution (approximately N) to each flask, then dilute to the mark and mix thoroughly.

1 ml ≡ 2, 4, 6, 8, 10 µg Na_2O respectively.

Note: These solutions are to be prepared immediately before use.

b) For use with a flame buffer solution

Transfer 2.00; 4.00; 6.00; 8.00, and 10.00 ml aliquots of the diluted sodium oxide solution to separate 100 ml volumetric flasks. Add 6.5 ml of nitric acid solution (approximately N) and 10 ml of Schuhknecht and Schinkel reagent to each flask, then dilute to the mark and mix thoroughly.

1 ml ≡ 2, 4, 6, 8, 10 µg Na_2O respectively.

Note: These solutions are to be prepared immediately before use.

4.4. Preparation of a calibration graph

It is not possible to describe a unique procedure for preparing a calibration graph because the working conditions are largely dependent upon the type of equipment used. Procedures detailed hereafter may only be considered as examples.

The apparatus (filter flame photometer, flame emission spectrophotometer, atomic absorption spectrophotometer) is first adjusted for Na_2O determinations according to the instructions given by the manufacturer. Prepare the calibration graph, using reference solutions of series (a) or of series (b) depending on whether or not the Schuhknecht and Schinkel reagent will be used.

Spray the reference solution containing 10 µg Na_2O/ml into the flame of the burner and adjust the measurement to read the maximum deflection (for instance a 100% transmission for flame emission or an optical density of 1.000 for atomic absorption). Maintain these conditions and spray the series of reference solutions noting the corresponding readings. Repeat the measurements several times for each solution and calculate the mean values. Plot a calibration graph of mean values versus Na_2O concentrations.

4.5. Determination of the Na_2O concentration of the extract solution

Pipette an aliquot of the durability extract solution containing not more than 250 µg of Na_2O into a platinum dish. Add two drops of hydrofluoric acid and one drop of perchloric acid, evaporate just to dryness on a hot plate or a sand bath. Take up the residue with 1.5 ml of nitric acid (approximately N) and digest with 10 ml of hot water. After dissolution and cooling, add 2.5 ml of Schuhknecht and Schinkel reagent, transfer to a 25 ml volumetric flask, and dilute to the mark and mix thoroughly. This solution is called the test solution. Spray the reference solution containing 10 µg Na_2O/ml into the flame of the burner of the equipment used for establishing the calibration graph and operate it in the same conditions as described above. Using the same instrumental conditions spray the test solutions and note the reading. Repeat the adjustment of the equipment and the measurement of the test solution at least three times and calculate the mean value.

From this mean value and by reference to the calibration graph calculate the Na_2O concentration of the test solution.

Note: If the determination is made in the presence of Schuhknecht and Schinkel reagent, the same test solution can also be used for the determination of K_2O according to the procedure given in 5. Appendix II.

5. Appendix II. A method for the determination of potassium oxide

5.1. Principle

Potassium is determined either by flame photometry or by atomic absorption spectrophotometry.

In the first case, the solution to be analysed is atomized in the flame of a burner and the intensity of the 7665 Å line emitted is measured and compared with that of a series of reference solutions of known K_2O concentrations atomized under the same conditions.

In the second case, the test solution is atomized in the flame of an air/acetylene burner through which is passed the characteristic light emitted by a hollow cathode lamp, the cathode of which is covered with potassium. The portion of the 7665 Å line absorbed by potassium atoms present in the flame is measured and compared with the absorption produced by reference solutions of known K_2O concentrations, atomized under the same conditions.

5.2. Reagents

Distilled or deionised water and analytical grade reagents shall be used throughout.

Hydrofluoric acid: 40% w/w.

Perchloric acid: 60% w/w.

Nitric acid: approximately N; add 63 ml nitric acid (d = 1.42) to water and dilute to 1000 ml.

Potassium chloride.

Schuhknecht and Schinkel reagent: dissolve 50 g caesium chloride (CsCl) and 250 g aluminium nitrate ($Al(NO_3)_3 \cdot 9\,H_2O$) in water and dilute to 1 litre.

5.3. Standard solutions

5.3.1. Concentrated potassium oxide solution

Accurately weigh 1.5830 g of potassium chloride, previously dried at 250 °C, and dissolve in about 200 ml of water. Transfer to a 1 litre volumetric flask and dilute to the mark. Mix thoroughly and transfer the solution to a plastic bottle for storage.

1 ml ≡ 1 mg K_2O.

5.3.2. Diluted potassium oxide solution 100 mg K_2O/l

Transfer a 25.00 ml aliquot of the concentrated potassium oxide solution to a 250 ml volumetric flask, dilute to the mark and mix thoroughly. Transfer to a plastic bottle for storage.

1 ml ≡ 100 μg K_2O.

Note: This is to be renewed every ten days.

5.3.3. Diluted potassium oxide solution 10 mg K_2O/l

Transfer a 25.00 ml aliquot of the diluted potassium oxide solution (100 mg K_2O/l) to a 250 ml volumetric flask, dilute to the mark and mix thoroughly. Transfer to a plastic bottle for storage.

1 ml ≡ 10 μg K_2O.

Note: This is to be renewed every ten days.

5.3.4. Reference potassium oxide solutions

a) Concentration range 0 to 10 μg K_2O/ml

Transfer 2.00; 4.00; 6.00; 8.00, and 10.00 ml aliquots of the diluted potassium oxide solution (100 mg K_2O/l) into separate 100 ml volumetric flasks. Add 6.5 ml of nitric acid solution (approximately N) and 10 ml of Schuhknecht and Schinkel reagent in each flask. Dilute to the mark and mix thoroughly.

1 ml ≡ 2, 4, 6, 8, 10 μg K_2O/ml.

b) Concentration range 0 to 1 μg K_2O/ml

Transfer 2.00; 4.00; 6.00; 8.00, and 10.00 ml aliquots of the diluted potassium oxide solution (10 mg K_2O/l) into separate 100 ml volumetric flasks. Add 6.5 ml of nitric acid solution (approximately N) and 10 ml of Schuhknecht and Schinkel reagent in each flask. Dilute to the mark and mix thoroughly.

1 ml ≡ 0.2, 0.4, 0.6, 0.8, 1.0 μg K_2O respectively.

Note: All these reference solutions are to be prepared immediately before use.

5.4. Preparation of calibration graphs

It is not possible to describe a unique procedure for preparing a calibration graph because the working conditions are largely dependent upon the type of equipment used. Procedures detailed hereafter must only be considered as examples.

5.4.1. Concentration range 0 to 10 μg K_2O/ml

The apparatus (filter flame photometer, flame emission spectrophotometer, atomic absorption spectrophotometer) is first adjusted for K_2O determinations according to the instructions given by the manufacturer. The reference solution containing 10 μg K_2O/ml is then aspirated into the flame of the burner and the apparatus operated to read the maximum deflection (for instance a 100% transmission for flame emission or an optical density of 1.000 for atomic absorption). Whilst maintaining these instrument conditions spray the whole series of reference solutions successively and note the corresponding readings. Make several measurements for each solution and calculate the mean values. From these results plot a calibration graph of the readings versus K_2O concentrations.

5.4.2. Concentration range 0 to 1 μg K_2O/ml

The same procedure is applied to the series of reference solutions of concentration 0 to 1 μg K_2O/ml with the apparatus operated to read the maximum deflection when the 1 μg K_2O/ml solution is aspirated into the flame of the burner.

The mean values of the readings are used to plot the second calibration graph (0 to 1 μg K_2O/ml) to be drawn.

5.5. Determination of the K_2O concentration of the extract solution

Pipette an aliquot of the durability extract solution containing not more than 250 μg of K_2O into a platinum dish. Add two drops of hydrofluoric acid and one drop of perchloric acid. Evaporate just to dryness on a hot plate or a sand bath. Take up the residue with 1.5 ml of nitric acid (approximately N) and digest with 10 ml of hot water. After dissolution and cooling, transfer the solution to a 25 ml volumetric flask, add 2.5 ml of Schuhknecht and Schinkel reagent, dilute to the mark and mix thoroughly. The solution so obtained is called the test solution. Aspirate the reference solution containing 10 μg K_2O/ml into the flame of the burner of the equipment used for establishing the calibration graph and operate the equipment in the same conditions as described above. Aspirate the test solution into the flame and note the reading. Repeat the adjustment of the equipment and the measurement of the test solution at least three times and calculate the mean value of the readings. From the calibration graph (concentration range: 0 to 10 μg K_2O/ml), determine the K_2O concentration of the test solution. If this contains less than 1 μg K_2O/ml, it is recommended that the determination should be repeated as follows. Aspirate the reference solution containing 1 μg K_2O/ml into the flame of the burner of the equipment used for establishing the calibration graph and operate the equipment in the same conditions as described above. Aspirate the test solution into the flame and note the reading. Repeat the adjustment of the equipment and the measurement of the test solution at least three times and calculate the mean value of the readings. From the calibration graph (concentration range: 0 to 1 μg K_2O/ml), determine the K_2O concentration of the test solution.

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