BRITISH STANDARD

Sampling and analysis of glass-making sands –

Part 2: Methods for chemical analysis

ICS 81.040.10

British Standards

Publishing and copyright information

The BSI copyright notice displayed in this document indicates when the document was last issued.

ISBN 978 0 580 58104 5

The following BSI references relate to the work on this standard:
Committee reference LBI/36
Draft for comment 08/30159621 DC

Publication history

First published as BS 2975 March 1958

Second edition as BS 2975, February 1988

First published as Part 2 August 2008

Amendments issued since publication

Amd. no.	Date	Text affected

Contents

Annexes

List of tables

Summary of pages

This document comprises a front cover, an inside front cover, pages i and ii, pages 1 to 24, an inside back cover and a back cover.

Foreword

Publishing information

This part of BS 2975 is published by BSI and came into effect on 29 August 2008. It was prepared by Technical Committee LBI/36, *Laboratory glassware and related apparatus*. A list of organizations represented on this committee can be obtained on request to its secretary.

Supersession

This part of BS 2975, along with BS 2975-1:2004, supersedes BS 2975:1988, which is withdrawn.

Relationship with other publications

BS 2975 is published in two parts, as follows:

- Part 1: *Methods for sampling and physical testing of glass-making sands*;
- Part 2: *Methods for chemical analysis*.

Presentational conventions

The provisions of this standard are presented in roman (i.e. upright) type. Its methods are expressed as a set of instructions, a description, or in sentences in which the principal auxiliary verb is “shall”.

Contractual and legal considerations

This publication does not purport to include all the necessary provisions of a contract. Users are responsible for its correct application.

Compliance with a British Standard cannot confer immunity from legal obligations.

1 Scope

This British Standard describes methods suitable for the chemical analysis of glass-making sands, including instrumental methods using X-ray fluorescence spectrometry (XRF), inductively coupled plasma optical emission spectrometry (ICP-OES), ultraviolet-visible spectrometry (UV-VIS) and atomic absorption spectrometry (AAS).

2 Normative references

The following referenced documents are indispensable for the application of this document. For dated references, only the edition cited applies. For undated references, the latest edition of the referenced document (including any amendments) applies.

BS 2975-1, *Sampling and analysis of glass-making sands – Part 1: Methods for sampling and physical testing of glass-making sands*

BS EN ISO 12677:2003, *Chemical analysis of refractory products by XRF – Fused cast bead method*

3 Type of material

The calibration ranges and methods to be used for the chemical analysis of glass-making sands shall be as set out in Table 1.

Table 1 **Calibration ranges and methods**

Oxide	**Method**	**Range % m/m**	
		Min	**Max**
LOI	Gravimetric	0.10	1.0
Fe_2O_3	XRF / UV-VIS / ICP-OES	0.005	1.0
Al_2O_3	XRF / ICP-OES / AAS	0.04	5.0
Cr_2O_3	ICP-OES / AAS	0.000 1	0.03
K_2O	XRF / Flame Photometer / AAS	0.01	3.0
SiO_2	XRF / Gravimetric	94.0	99.8
TiO_2	XRF / UV-VIS	0.016	0.10
CaO	XRF / AAS / Titration	0.006	1.0
MgO	XRF /AAS	0.002	1.0
Mn_3O_4	XRF / AAS	0.0	0.03
S=	XRF / ICP-OES / Combustion	0.0	0.05
Ni	ICP-OES	0.0	0.000 6
Co	ICP-OES	0.0	0.000 1
Cu	ICP-OES	0.0	0.000 35
Na_2O	XRF / AAS / ICP-OES / Flame Photometer	0.05	2.0
Pb_3O_4	XRF	0.0	0.000 5
Carbon	Combustion	0.0	0.1

NOTE The analytes are expressed in the stable oxidation state; correction should be made if other oxidation states are needed.

4 Sample preparation

4.1 General

Control (extraction) systems shall be put in place to reduce exposure to respirable crystalline silica dust to the lowest practicable level.

The specimen or solution to be presented to the instrument shall be prepared from a dry homogeneous finely powdered sample (the procedure for drying silica sand is given in **4.3.3**).

Appropriate bulk sampling methods shall be used to produce a laboratory sample as set out in BS 2975-1. The particle size of the laboratory sample shall be reduced for both wet chemical and XRF techniques.

The accuracy of XRF methods for pressed powder samples is highly dependent on the particle size distribution of the sample; the particle size of material to be used for the preparation of pressed powders shall be less than 75 µm.

NOTE 1 Particle size reduction can be carried out by grinding in a suitable mechanical device or by hand using appropriate grinding media.

NOTE 2 Consistent grain size may be difficult to obtain if the sample is ground by hand. Commercially available mechanical mills for particle size reduction on a laboratory scale include:

- *ball mills, either planetary or centrifugal (3 axes);*
- *disc mills, also called swing mills, ring-and-puck mills or shatterboxes (2 axes);*
- *mortar mills (essentially mechanized pestle-and-mortars).*

The potential for contamination of the sample with elements that are to be determined should be considered when grinding media are chosen. For this reason carbon steel, chrome steel, and zirconia media are not recommended. Suitable media are shown in Table 2.

4.2 Apparatus

4.2.1 *Drying vessel.*

4.2.2 *Drying oven to 110 °C ± 10 °C.*

4.2.3 *Riffle box.*

4.2.4 *Balance,* capable of weighing to 0.01 g.

4.2.5 *Timer.*

4.2.6 *Extraction system.*

4.2.7 *Pestle and mortar or mechanical mill,* type dependent on sample size and intended analysis (see Table 2).

4.2.8 *Desiccator containing dry desiccant.*

4.2.9 *Fine brush.*

Table 2 **Suitable grinding media for silica sands**

Recommended media	Recommended use	Typical analysis	Possible contamination	Notes
Tungsten carbide (normally cemented with Co, but Fe, etc., may be used)	XRF fused cast bead	WC 94%, Co 6%	W, Co or other cementation elements, e.g. Ni	Check specification with supplier
Agate	All XRF techniques, wet chemistry	SiO_2 99.9%	Insignificant	Use with a slow mill speed
Syalon (silicon nitride, silicon aluminium oxynitride)	All XRF techniques, wet chemistry	Si 53.5%, N 35.2%, O 4.8%, Y (or Er) 3.5%, Al 2.5%, Mg 0.5%	Al, Y (or Er)	Can be brittle
Hard porcelain	All XRF techniques, wet chemistry	Al_2O_3 40%, SiO_2 60%	Al	Used in mortar mills

NOTE Samples may be hand ground in any of the above media, to an appropriate particle size. Sample loss should be avoided. Consideration should be given to manufacturer's recommendations regarding appropriate sample size and milling time.

4.3 Procedure

*NOTE This procedure should be carried out with appropriate extraction (**4.2.6**) control measures to reduce exposure to respirable crystalline silica dust.*

4.3.1 Select grinding medium, based on sample size, sample hardness and chemical analysis to be performed (see Table 2). Very small samples can be ground by hand using agate or porcelain pestle and mortar (**4.2.7**). To minimize particle size effects, prepare the sand by grinding to ensure that the fineness is to the tolerance of 10% maximum retained at 75 µm and 0% retained at 150 µm.

4.3.2 If the sample is dry proceed to **4.3.5**. If the sample is moist, use a cone and quartering technique to obtain sufficient sample for the capacity of the grinding vessel to be used.

4.3.3 Dry the moist sand for 1 h or to constant mass in a suitable drying vessel (**4.2.1**) in an oven at 110 °C ± 10 °C (**4.2.2**).

4.3.4 Remove from the oven (**4.2.2**) and cool in a desiccator containing dry desiccant (**4.2.8**).

4.3.5 Riffle dry sample in a riffle box (**4.2.3**).

4.3.6 Clean the mill (**4.2.7**), finishing the process with one of the cleaning agents recommended in **A.12**.

4.3.7 Weigh on a balance (**4.2.4**) the recommended amount of sample for the chosen milling vessel.

4.3.8 Place weighed sample into the mill (**4.2.7**), transfer into the mechanical device and grind for the required time using a timer (**4.2.5**) if one is not fitted to the device.

4.3.9 Empty the mill (**4.2.7**), under extraction (**4.2.6**), onto a clean surface removing as much of the sample as possible using a fine brush (**4.2.9**).

NOTE An appropriate sized sieve and receiver can be used for ease of separating and cleaning spherical grinding media.

4.3.10 Place the ground sample into a clean receptacle or self seal plastic bag and label it appropriately.

4.3.11 Clean the mill (**4.2.7**) and the brush (**4.2.9**).

4.4 Validation of grain size

Contamination of the sample by the grinding media shall be quantified in accordance with Table 2. The grinding performance of the mill shall be monitored to ensure the required fineness of the material is achieved. To combat wear caused to the grinding media over time, which can impact on the grain size of the product, pucks, rings and spheres shall be checked, and pots shall be relined as necessary to maintain particle size distribution.

When using spheres, the number and mass per grinding pot shall be kept constant.

5 Loss on ignition (LOI)

*COMMENTARY ON CLAUSE **5***

LOI is the weight change, expressed as a percentage, caused by heating the sample to a high temperature. It is used to give a measure of the extent of substances that are volatile below the given temperature.

For further details on LOI methodology, see BS EN ISO 21587-1.

5.1 Apparatus

5.1.1 *Platinum boat, or other suitable vessel of sufficient size to contain 2 g of sample at 1 050 °C.*

5.1.2 *Balance*, capable of weighing to 0.000 1 g.

5.1.3 *Desiccator containing dry desiccant*, e.g. silica gel.

5.1.4 *Furnace held at 1 050 °C ± 50 °C.*

5.1.5 *Long handled tongs.*

5.1.6 *Spatula.*

5.1.7 *Drying oven to 110 °C ± 10 °C.*

5.2 Procedure

5.2.1 Dry not less than 10 g of the ground sample in an oven (**5.1.7**) at 110 °C ± 10 °C or to constant mass (**7.8.1.18**) in order to evaluate LOI.

5.2.2 Store over a drying agent in a desiccator (**5.1.3**) whilst cooling.

5.2.3 Weigh boat (**5.1.1**) and record weight W_1.

5.2.4 Using a balance (**5.1.2**) add 2 g ± 0.000 1 g of sample into the boat (**5.1.1**) and record the weight W_2.

5.2.5 Using the tongs (**5.1.5**) place boat (**5.1.1**) and sample in the furnace (**5.1.4**) set at 1 050 °C for 60 minutes.

5.2.6 Remove from furnace (**5.1.4**) with tongs (**5.1.5**) and place in a desiccator (**5.1.3**) to cool.

5.2.7 Once cool, re-weigh boat (**5.1.1**) and sample and record weight W_3.

Calculate the LOI (%) in accordance with the following equation:

$$\text{LOI} = \frac{W_2 - W_3}{W_2 - W_1} \times 100$$

where:

W_1 = weight of boat;

W_2 = weight of boat and sample;

W_3 = weight of ignited boat and sample.

6 X-ray fluorescence (XRF)

6.1 General

The intensities of the fluorescent X-rays from the elements of interest in the sample shall be measured and the chemical composition of the sample shall be analysed by reference to previously determined calibration graphs or equations, applying correction factors for inter-element effects.

NOTE 1 The X-ray intensity might not be directly proportional to the concentration but modified by the concentration of other analytes in the sample (inter-element or matrix effects).

Calibration equations and inter-element corrections shall be established from specimens made from Certified Reference Materials (CRMs) and, where appropriate, synthetic calibrating materials prepared in the same way as the unknowns. Homogeneity, particle size distribution, matrix effects, instrument drift and accuracy of relevant calibration lines shall therefore be taken in to account during specimen measurement.

NOTE 2 Specimens can be prepared for analysis as:

a) fused cast beads;

b) pressed powder pellets;

c) loose powders.

NOTE 3 The use of fused cast beads offers the following advantages and disadvantages:

a) mineralogical and particulate effects are removed;

b) calibration can include beads prepared from mixtures of pure oxides or carbonates in addition to CRMs;

c) dilution with borate flux might significantly affect the sensitivity of analytes present at "trace" level.

NOTE 4 Pressed powder calibration standards should be the same type of matrix as the unknown samples (e.g. same mineralogy). In most cases the mineralogical composition of available reference materials is unknown. Calibration with such materials using pressed pellets is subject to uncertainty.

NOTE 5 The XRF spectrometer software can support a number of models for line overlap and matrix corrections to determine coefficients that describe the shape of the calibration curve. Instrument specific drift correction should be applied if the calibration falls outside acceptable limit values.

6.2 XRF fused cast bead

XRF cast beads shall be generated in accordance with BS EN ISO 12677.

6.3 XRF pressed powder pellet

*COMMENTARY ON **6.3***

Powder calibrations for pressed pellet are specific to the mineralogical and particulate matrix for which they are developed. For example, materials with different particle shapes or different degrees of crystallinity might need separate calibrations. CRMs might not be available in the same matrix as the unknowns.

Guidance on using the XRF pressed pellet method is given in Annex A.

6.3.1 Apparatus

6.3.1.1 *Balance*, capable of weighing to 0.01 g.

6.3.1.2 *Grinding equipment.*

6.3.1.3 *Weighing vessel.*

6.3.1.4 *40 mm stainless steel die set (two pellet dies, holder and plunger).*

6.3.1.5 *Reinforcing metal cup* (optional).

6.3.1.6 *Motorized press*, capable of 25 t pressure.

6.3.1.7 *Tray.*

6.3.1.8 *Oven maintained at 110 °C ± 10 °C.*

6.3.1.9 *Desiccator containing dry desiccant*, e.g. silica gel.

6.3.2 Reagents

6.3.2.1 *Binder* (optional).

6.3.2.2 *Suitable solvent*, e.g. acetone or ethanol (or industrial methylated spirits).

6.3.3 Procedure

6.3.3.1 Weigh the ground sample into a weighing vessel (**6.3.1.3**).

6.3.3.2 Add binder (**6.3.2.1**) if appropriate.

6.3.3.3 Clean the grinding equipment (**6.3.1.2**) with a suitable solvent (**6.3.2.2**).

6.3.3.4 Place the sample into the cleaned grinding vessel (**6.3.1.2**) and mill thoroughly.

6.3.3.5 Transfer mixed sample to the die (**6.3.1.4**), previously cleaned with a suitable solvent (**6.3.2.2**) and with a reinforcing metal cup (**6.3.1.5**) placed in the base.

6.3.3.6 Ensure that the surface of the sample in the die (**6.3.1.4**) is level.

6.3.3.7 Insert the die plunger (**6.3.1.4**) and motorized press (**6.3.1.6**), typically at 20 t pressure for 20 s, however, this is dependent on the sand mineralogy.

6.3.3.8 Release pressure and extract the pellet carefully. It is important that the resulting pellet is flat and uniform on the analytical surface.

6.3.3.9 If a binder (**6.3.2.1**) has been used and needs to be cured, place on a tray (**6.3.1.7**) in an oven (**6.3.1.8**) as per manufacturer's specification.

6.3.3.10 Label after cooling and store in a desiccator (**6.3.1.9**).

6.3.4 Calibration

The XRF spectrometer shall be calibrated using a range of reference samples, CRMs and in-house standards that match the matrix of the unknowns. The analytes of interest in the in-house standards shall be determined by other means, such as wet chemistry and/or fused bead XRF. The concentration values shall be plotted against instrument intensities using the XRF software to obtain a calibration curve.

The calibration range shall encompass the expected values of the unknowns.

NOTE A range of sand CRMs is given in Annex B.

6.4 XRF loose powder

*COMMENTARY ON **6.4***

Powder calibrations for loose powder are specific to the mineralogical and particulate matrix for which they are developed. For example, materials with different particle shapes or different degrees of crystallinity might need separate calibrations. CRMs might not be available in the same matrix as the unknowns.

6.4.1 General

This method shall only be used with an XRF spectrometer that operates under helium or air path. If air path is used then only elements from K (potassium) upwards in the Periodic Table shall be analysed. The sample shall be presented to the XRF spectrometer in a cell fitted with a support film.

NOTE Factors to consider in the selection of sample support films for the analysis of loose powders might include:

a) film thickness and composition;

b) X-ray transmission;

c) strength;

d) film impurities;

e) ease of handling.

6.4.2 Apparatus

6.4.2.1 *Sample cups.*

6.4.2.2 *Demountable cells.*

6.4.2.3 *Support film.*

6.4.3 Procedure

6.4.3.1 Fit the sample cell (**6.4.2.2**) with the support film (**6.4.2.3**) and ensure that it is tight and wrinkle free.

6.4.3.2 Pour approximately 15 g of the ground sample into the cell (**6.4.2.2**) until approximately two-thirds full.

6.4.3.3 Place a lid on the cell (**6.4.2.2**) and tap the side using a soft rod or by hand until the sample forms an even surface at the base. Do not tap the cell (**6.4.2.2**) on hard surfaces as this can cause damage. Insert cell (**6.4.2.2**) in to XRF spectrometer sample cup (**6.4.2.1**).

6.4.3.4 If the XRF spectrometer requires a secondary support film (**6.4.2.3**), ensure that it is clean and wrinkle free. Change if necessary.

6.4.4 Calibration

For pressed pellet calibration procedure the XRF spectrometer shall be calibrated as in **6.3.4**.

7 Wet chemistry

7.1 Apparatus

7.1.1 *Glassware including a range of beakers and volumetric flasks* (Grade B or better).

7.1.2 *General PTFE ware*.

7.1.3 *Balance*, capable of weighing to 0.000 1 g.

7.1.4 *Extraction system*, suitable for hydrofluoric acid and general acids.

7.1.5 *Platinum vessels* (crucibles, dishes and lid(s)).

7.1.6 *Stout wire*.

7.1.7 *Hotplate*, with stirring facilities.

7.1.8 *Sand bath*.

7.1.9 *Bunsen burner*.

7.1.10 *Wash bottle with fine nozzle*.

7.1.11 *Kiln batt*.

7.1.12 *Furnace capable of 1 200 °C ± 50 °C*.

7.1.13 *Long handled tongs*.

7.1.14 *Timer*.

7.1.15 *GF/C filter papers*.

7.1.16 *Buchner filter assembly*.

7.1.17 *Inductively coupled plasma optical emission spectrometer (ICP-OES)*.

7.1.18 *Atomic absorption spectrometer (AAS)*.

7.1.19 *Desiccator*.

7.1.20 *Flame photometer*.

7.1.21 *UV/VIS spectrometer*.

7.1.22 *pH meter.*

7.1.23 *Ashless filter papers.*

7.1.24 *Drying oven 110 °C ± 10°C.*

7.1.25 *Anti bump granules.*

7.1.26 *Steam bath.*

7.1.27 *UV Cells* (10 mm, 20 mm and 40 mm).

7.1.28 *Glass rod.*

7.2 Reagents

7.2.1 Unless stated otherwise all reagents shall be free from such amounts of impurities as might affect the accuracy of the determination.

NOTE Analytical grade will normally be suitable but provision should be made for blank determinations if these are considered essential.

Caution There is an inherent danger in the handling of all chemicals, even by trained personnel. Some chemicals have to be handled with greater care than others (see relevant Materials Safety Data Sheet provided with chemical). It is important that the laboratory safety precautions be observed at all times.

7.2.2 Water deionized (in accordance with BS EN ISO 3696).

7.2.3 Nitric acid, concentrated (S.G. 1.42).

7.2.4 Sulfuric acid, concentrated (S.G. 1.800).

7.2.5 80:20 borate flux (lithium metaborate/tetraborate) w/w.

7.2.6 Sodium carbonate, anhydrous.

7.2.7 Sodium tetraborate.

7.2.8 Hydrochloric acid (SG1.18)

7.2.9 5N hydrochloric acid.

7.2.10 40% hydrofluoric acid v/v.

NOTE Hydrofluoric acid is a particularly aggressive acid and extra care is required when using it and disposing of it.

7.2.11 Perchloric acid 70% v/v (S.G. 1.70).

7.2.12 Ammonia solution (S.G. 0.880).

7.2.13 Caesium sulfate.

7.2.14 Aluminium oxide.

7.3 Standard solutions

7.3.1 Commercially available standard solutions of at least 99.9% purity (FAAS / ICP-OES Grade).

7.3.2 Chromate standard stock solution or if using potassium dichromate: weigh 0.193 6 g ± 0.000 1 g of potassium dichromate ($K_2Cr_2O_7$) and dissolve in 100 ml of water, transfer to a 1 l volumetric flask and make up to the mark with water. Invert several times to mix.

7.3.3 Aluminium standard (1 ml contains 100 ppm of Al_2O_3): weigh 0.930 0 g ± 0.000 1 g of aluminium potassium sulfate, add 50 ml of 5N hydrochloric acid, transfer to 1 l volumetric flask and make up to the mark with water. Invert several times to mix.

7.3.4 1% p-nitrophenol: dissolve 1 g of p-nitrophenol indicator in 75 ml of industrial methylated spirit and make up to the mark with 100 ml with distilled water. Invert several times to mix.

7.3.5 10% tartaric acid: dissolve 100 g of tartaric acid in a beaker containing 1 l of water.

7.3.6 10% hydroxylamine hydrochloride: dissolve 100 g of hydroxylamine hydrochloride in a beaker containing 1 l of water.

7.3.7 Fe_2O_3 standard stock solution: dissolve 0.491 1 g ± 0.000 1 g of ferrous ammonium sulfate in 50 ml to 100 ml of water. Transfer to a 1 l volumetric flask and make up to mark with 1% w/v sulfuric acid. 1 ml of this solution contains 0.1 mg of Fe_2O_3; dilute 10 times to use for the calibration standard.

7.3.8 1,10 o-phenanthroline: weigh 1 g ± 0.000 1 g of 1,10 o-phenanthroline into 800 ml of water. Dissolve by placing on a stirrer hotplate and warming to no more than 80 °C.

NOTE This might take at least 2 h.

Cool and transfer to a 1 l volumetric flask and make up to the mark with water. Invert several times to mix.

7.3.9 5% hydrochloric acid (v/v).

7.3.10 L-ascorbic acid solution 200 g/l (prepared immediately before use).

7.3.11 Saturated sodium acetate solution.

7.3.12 Tiron reagent (5% w/v 1,2-dihydroxybenzene-3,5-disulfonic acid di-sodium salt solution 50 g/l).

7.3.13 Acetate buffer solution, pH = 3.8: dissolve 136 g of sodium acetate tri-hydrate in 1 l of water. Add 390 ml of glacial acetic acid and adjust pH to 3.8 if necessary, using either solid sodium acetate tri-hydrate or glacial acetic acid.

7.3.14 Standard titanium (IV) oxide solution (0.1 mg TiO_2/ml): heat 0.443 g of potassium titanium oxalate di-hydrate with 1 g of ammonium sulfate and 100ml of concentrated H_2SO_4, 1 800 g/l, in a Kjeldahl flask, gradually increasing the temperature until the mixture boils, and maintain at boiling point for 10 min. Cool, pour the solution slowly into 750 ml of cold water, stirring well. Dilute the cold solution to the mark in a 1 l volumetric flask. Invert several times to mix. Prepare a dilute standard titanium (IV) oxide solution containing 10 μg/ml TiO_2 immediately before use.

7.3.15 Silver nitrate solution, 25 g/l (prepared immediately before use).

7.3.16 Standard silica solution (0.1 mg SiO_2/ml): weigh 0.100 g of silica (SiO_2), i.e. sand containing not less than 99.8% by mass of SiO_2, heated to 1 000 °C for 1 h and stirred with a stout platinum wire at 20 min intervals. Fuse with 1 g of anhydrous sodium carbonate in a platinum crucible. Dissolve the cold melt in water, transfer to a 1 000 ml volumetric flask, dilute to the mark with water and invert several times to mix. Store the solution in a polyethylene bottle.

7.3.17 Caesium chloride (10% w/v).

7.3.18 Ammonium molybdate solution, 80 g/L: dissolve 80 g of ammonium molybdate tetrahydrate in water, filter if necessary, and dilute to 1 l. Store in a polyethylene bottle. Discard after four weeks or earlier if any appreciable deposit is observed.

7.3.19 Sulfuric-nitric acid mixture: to 650 ml water add 100 ml sulfuric acid and 250 ml of nitric acid.

7.3.20 1:1 sulfuric acid v/v: pour one part of H_2SO_4 (**7.2.4**) (S.G. 1.800) into one part of water slowly and carefully while stirring, as much heat is evolved.

7.3.21 1:1 hydrochloric acid v/v: pour one part of HCl (**7.2.8**) into one part of water.

7.3.22 1:4 hydrochloric acid v/v: pour one part of HCl (**7.2.8**) into four parts of water.

7.3.23 1:99 hydrochloric acid v/v: pour one part of HCl (**7.2.8**) into 99 parts of water.

7.3.24 1:1 ammonia: pour one part of ammonia solution (**7.2.12**) into one part of water.

7.3.25 1:19 nitric acid: pour one part of nitric acid (**7.2.3**) into 19 parts of water.

7.4 ICP-OES

7.4.1 Determine elements in solution by ICP-OES (see Table 1).

7.4.2 A reagent blank is run with this method.

7.4.3 Weigh 2 g ± 0.000 5 g of finely ground sample into a platinum vessel (**7.1.5**).

7.4.4 Add sufficient water to the vessel (**7.1.5**) to just cover the sample (about 5 ml).

7.4.5 Add 10 ml of concentrated HNO_3 (**7.2.3**) followed by 10 ml of HF.

7.4.6 Place the vessel on a sand bath (**7.1.8**) (or hot plate (**7.1.7**)) to effect digestion.

7.4.7 Upon digestion add a further 10 ml aliquot of HF (**7.2.10**) to just cover the residue.

7.4.8 Return to sand bath (**7.1.8**) (or hot plate (**7.1.7**)) to complete digestion.

7.4.9 When dry, ignite the crucible (**7.1.5**) over a Bunsen flame (**7.1.9**) to remove any remaining HF.

7.4.10 Sprinkle the residue with 1 g of borate flux and place in a furnace (**7.1.12**) at 1 050 °C ± 50 °C for 10 min.

7.4.11 Remove and allow to cool.

7.4.12 Add 10 ml of water followed by 10 ml of concentrated HNO_3 (**7.2.3**).

7.4.13 Cover vessel (**7.1.5**) with a platinum lid (**7.1.5**) and place on a hotplate (**7.1.7**) to aid dissolution.

7.4.14 Transfer quantitatively to a 100 ml volumetric flask and make up to the mark with water, mixing well.

7.4.15 The required analytes are determined using a suitable ICP-OES and the results recorded.

7.4.16 Calibration

The ICP-OES shall be set up and calibrated using standard solutions to give the required concentration range according to the manufacturer's instructions.

7.4.17 Calculation of result

$$C = \frac{D}{S}$$

where:

C = Sample concentration (ppm)

D = Dilution factor X ICP-OES reading (ppm)

S = Sample weight (g)

7.5 Atomic absorption spectroscopy

NOTE For a list of analytes see Table 1.

7.5.1 Determination of Cr_2O_3

7.5.1.1 A reagent blank is run with this procedure.

7.5.1.2 Weigh 2 g ± 0.000 1 g of finely ground sample into a platinum vessel (**7.1.5**).

7.5.1.3 Add 15 ml of HF (**7.2.10**) and 15 drops of concentrated H_2SO_4 (**7.2.4**).

7.5.1.4 Place the crucible (**7.1.5**) on a sand bath (**7.1.8**) and evaporate to dryness.

7.5.1.5 Cool and add a further 10 ml aliquot of HF (**7.2.10**), ensuring all undigested residue is covered with HF (**7.2.10**).

7.5.1.6 Return vessel (**7.1.5**) to sand bath (**7.1.8**) and evaporate to dryness.

7.5.1.7 When dry, ignite vessel over a Bunsen flame (**7.1.9**) to remove any excess HF fumes.

7.5.1.8 Cool.

7.5.1.9 Add 1 g of sodium carbonate (**7.2.6**), 0.25 g ± 0.01 g of sodium tetraborate (**7.2.7**) and place in a furnace (**7.1.12**) at 1 200 °C ± 50 °C for 10 min.

7.5.1.10 Remove and allow to cool.

7.5.1.11 Add 20 ml of hot water and two anti bump granules (**7.1.25**).

7.5.1.12 Place on a hotplate (**7.1.7**) and warm gently to aid dissolution (approx. 10 min).

7.5.1.13 Cool and wash vessel (**7.1.5**) contents into a 250 ml beaker (**7.1.1**) with hot water.

NOTE Hydrochloric acid might need to be added here to aid dissolution of the borate.

7.5.1.14 Repeat until all the melt has been transferred into the beaker (**7.1.1**).

7.5.1.15 When transfer is complete, place the beaker (**7.1.1**) on a hot plate (**7.1.7**) and gently boil to reduce the volume to less than 25 ml.

7.5.1.16 Filter the solution through a Buchner filter (**7.1.16**) containing a 5.5 cm ∅GF/C filter paper (**7.1.15**).

7.5.1.17 Wash with hot water ensuring that the final volume is no more than 20 ml.

7.5.1.18 Cool and transfer to a 25 ml volumetric flask (**7.1.1**).

7.5.1.19 Make up to the mark with water and mix well.

7.5.2 Calibration of atomic absorption spectrometer (AAS)

7.5.2.1 General

The AAS (**7.1.18**) shall be set up and calibrated using standard solutions to give the required concentration range according to the manufacturer's instructions.

7.5.2.2 Determination by atomic absorption

Analytes shall be determined in accordance with standard AAS (**7.1.18**) procedures. Solutions shall be aspirated into a flame and the sample response compared against a calibration curve covering the concentration range of interest in accordance with the instrument provider's instructions (see **7.5.4.9** and **7.5.4.10**).

7.5.3 Determination of Al_2O_3

7.5.3.1 A reagent blank is run with this procedure.

7.5.3.2 Weigh 0.1 g ± 0.000 1 g of finely ground sample into a platinum vessel (**7.1.5**).

7.5.3.3 Add 5 ml of HF (**7.2.10**) and five drops of concentrated H_2SO_4 (**7.2.4**) and place on a sand bath (**7.1.8**).

7.5.3.4 Evaporate to dryness.

7.5.3.5 When dry, remove the crucible (**7.1.5**) and ignite over a Bunsen flame (**7.1.9**) to remove any excess HF fumes.

7.5.3.6 Add 0.25 g ± 0.01 g of sodium tetraborate (**7.2.7**) and place in a furnace (**7.1.12**) at 1 050 °C ± 50 °C for 10 min.

7.5.3.7 Remove and cool.

7.5.3.8 Add 10 ml of 1:1 HCl (**7.3.21**) followed by 10 ml of water.

7.5.3.9 Warm on a hotplate (**7.1.7**) to effect dissolution.

7.5.3.10 Transfer to a 250 ml beaker (**7.1.1**) with hot water.

7.5.3.11 When transfer is complete, place beaker (**7.1.1**) on a hot plate (**7.1.7**) and boil gently to reduce the final volume to less than 50 ml.

7.5.3.12 Cool and transfer to a 100 ml volumetric flask (**7.1.1**).

7.5.3.13 Make up to the mark with water and mix well.

7.5.3.14 Run solution on AAS (**7.1.18**) against a suitable concentration graph and determine the Al_2O_3 concentration.

7.5.4 Determination of CaO, MgO, Mn_3O_4, Na_2O and K_2O

7.5.4.1 A reagent blank is run with this procedure.

7.5.4.2 Weigh 1.0 g ± 0.000 1 g of finely ground sample into a platinum vessel (**7.1.5**).

7.5.4.3 Moisten with water and add 15 ml of HF (**7.2.10**), 1 ml of concentrated HNO_3 (**7.2.3**) and 2 ml of $HClO_4$ (**7.2.11**) (perchloric acid) and place on a sand bath (**7.1.8**) or steam bath (**7.1.26**) to digest until solution is complete.

7.5.4.4 Transfer the vessel (**7.1.5**) to a hotplate (**7.1.7**) and increase the temperature gradually and evaporate until perchloric acid fumes cease.

7.5.4.5 Cool the vessel (**7.1.5**), add a further 2 ml of $HClO_4$ (**7.2.11**) (perchloric acid) and then repeat the evaporation until the residue is almost dry.

7.5.4.6 Allow the solution to cool, add 10 ml of 1:4 HCl (**7.3.22**) and warm the mixture to produce a clear solution.

7.5.4.7 Cool, transfer to a suitable volumetric flask (**7.1.1**), dilute to the mark with water and invert several times to mix.

7.5.4.8 If recommended in the manufacturer's instructions, add a suitable ionization buffer (e.g. Caesium chloride (10% v/v)) before diluting to the mark to produce 10% in the final solution used for measurement.

7.5.4.9 Analyse solution on AAS (**7.1.18**). Determine analyte concentration by comparing sample response against that generated for a series of standards covering the required concentration range.

NOTE 1 Further dilutions of the sample solution might be necessary for measurement at the required concentration range for each individual oxide.

NOTE 2 1 g of sample in a final volume of 100 ml will produce a solution containing 1 µg/ml at the 0.01% level, 10 µg/ml at the 0.1% level, or 100 µg/ml at the 1.0% level of the oxides.

7.5.4.10 The AAS (**7.1.18**) is set up and calibrated using standard solutions to give the required concentration range according to the manufacturer's instructions.

7.6 Colorimetric, UV-VIS spectrometer

NOTE Many glass sands have a small but significant carbon content, particularly geologically recent sands. This might be in the form of lignite or soft proto-coal particles. During acid digestions these materials form a dark colloidal dispersion which might significantly interfere with determinations carried out using UV-VIS spectrometry. The colloidal meshwork of carbon compounds might be removed by adding a few spots of nitric acid during the final stages of evaporations, at the point where sulfuric acid fumes are evolved, then allowing the mixture to reflux for a few minutes before allowing the remaining sulfuric acid to evaporate.

7.6.1 Fe_2O_3

7.6.1.1 Principle

Fe_2O_3 is determined using a UV-VIS spectrometer. 1,10 o-phenanthroline forms a red complex with ferrous ions, the depth of colour being dependent on the pH of the solution, as well as on the concentration of ferrous ions. The pH is adjusted to approximately 5.5.

7.6.1.2 Procedure

7.6.1.2.1 A reagent blank is run with this procedure.

7.6.1.2.2 Weigh 0.5 g ± 0.000 1 g of finely ground sample into a platinum vessel (**7.1.5**).

7.6.1.2.3 Add 15 ml of HF (**7.2.10**) and 10 drops of concentrated H_2SO_4 (**7.2.4**).

7.6.1.2.4 Place vessel (**7.1.5**) on a sand bath (**7.1.8**) and evaporate to dryness.

7.6.1.2.5 Add 10 ml of 1:4 HCl (**7.3.22**) to dissolve any residual salts.

7.6.1.2.6 Transfer quantitatively to a 100 ml volumetric flask (**7.1.1**).

7.6.1.2.7 Add 10 ml of 10% tartaric acid (**7.3.5**) and one drop of 1% p-nitrophenol indicator (**7.3.4**).

7.6.1.2.8 Add 1:1 ammonia solution (**7.3.24**) drop-wise until the solution just changes to yellow.

7.6.1.2.9 After rinsing the inner walls of the volumetric flask (**7.1.1**) with water, add 1:4 HCl (**7.3.22**) drop-wise until the yellow colour is just discharged.

7.6.1.2.10 Add three drops in excess.

7.6.1.2.11 Add 2 ml of 10% hydroxylamine hydrochloride (**7.3.6**) and 10 ml 1,10 o-phenanthroline (**7.3.8**).

7.6.1.2.12 Dilute to the mark with water and mix well.

7.6.1.2.13 Leave the solution for 30 min to develop the colour.

7.6.1.2.14 Measure the absorbance of each solution at 510 nm using 10 mm, 20 mm or 40 mm cells (**7.1.27**), with water as reference.

7.6.1.2.15 Subtract the blank from the sample reading and calculate Fe_2O_3 content by comparing sample response against a calibration curve covering range of interest.

7.6.1.3 Calibration

7.6.1.3.1 The UV-VIS spectrometer shall be set up and calibrated using standard solutions covering the required concentration range, at a wavelength of 510 nm, according to the manufacturer's instructions.

7.6.1.3.2 Pipette 10 ml of the standard iron stock solution (containing 0.1 mg Fe_2O_3/ml) into a 100 ml volumetric flask (**7.1.1**), dilute to the mark with water and mix well. Label as 0.01 mg Fe_2O_3/ml.

7.6.1.3.3 Prepare a suitable calibration graph by taking aliquots of the diluted iron standard solution, prepared as in **7.6.1.2.2**. Fully label each aliquot. Measure the absorbance of each solution at 510 nm using suitable cells, with water as reference. Subtract the blank from the sample reading and plot the absorbance against mg Fe_2O_3.

7.6.2 TiO_2

7.6.2.1 Principle

TiO_2 is determined using a UV-VIS spectrometer. Tiron forms a yellow complex, the depth of the colour being proportional to the concentration of the TiO_2 concentration. The pH is adjusted to 3.8.

7.6.2.2 Procedure

7.6.2.2.1 A reagent blank is run with this procedure.

7.6.2.2.2 Weigh 0.3 g ± 0.000 1 g of finely ground samples into a platinum vessel (**7.1.5**).

7.6.2.2.3 Add 15 ml of HF (**7.2.10**) and 10 drops of concentrated H_2SO_4 (**7.2.4**) and place on a sand bath (**7.1.8**).

7.6.2.2.4 Evaporate to near dryness, i.e. 1 ml to 2 ml.

7.6.2.2.5 Add 0.25 g ± 0.1 g sodium carbonate (**7.2.6**) and fuse at 1 050 °C ± 50 °C for 10 min with swirling to ensure exposure of the dried salts to liquid carbonate. Allow to cool, then add 15 ml water and heat gently to digest the cake.

7.6.2.2.6 Allow to cool, then transfer the residue to a 100 ml beaker (**7.1.1**) using the minimum quantity of water, ensuring that the volume does not exceed 25 ml.

7.6.2.2.7 Add 1 ml of L-ascorbic acid solution (**7.3.10**) and 5 ml of tiron reagent (**7.3.12**) to the beaker (**7.1.1**).

7.6.2.2.8 Using a calibrated pH meter (**7.1.22**), adjust the pH to 3.8 ± 0.1 by the drop-wise addition of saturated sodium acetate (**7.3.11**) solution, stirring throughout.

NOTE A yellow colour should develop as the pH nears 3.8.

7.6.2.2.9 Rinse electrode of pH meter (**7.1.22**) with minimum amount of water.

7.6.2.2.10 Transfer the solution to a 50 ml volumetric flask (**7.1.1**).

7.6.2.2.11 Add 10 ml of acetate buffer solution (**7.3.13**) and make up to the mark with water. Invert several times to mix.

7.6.2.2.12 Allow the solution to stand for 15 min, then measure at a wavelength of 380 nm using a 10 mm cell (**7.1.27**), with water as reference.

7.6.2.2.13 Subtract the blank from the sample reading and calculate TiO_2 content by comparing sample response against a suitable calibration curve covering the analytical range of interest (**7.6.2.3**).

7.6.2.3 Calibration

The UV/VIS spectrometer shall be set up according to the manufacturer's instructions.

Establish a calibration curve by taking several aliquots of the diluted standard titanium (IV) oxide solution (containing 10 µg/ml TiO_2 (**7.3.14**)) into separate 100 ml beakers using the standard solutions to cover the expected concentration range. Also prepare a zero solution with no standard added. Ensure that each aliquot is fully labelled. Add to each beaker 0.25 g ± 0.1 g sodium carbonate and use the minimum quantity of water necessary to dissolve, with gentle heating if required. Allow to cool. Ensure the volume does not exceed 25 ml. Develop the colour as described from the point in the procedure where 1 ml of L-ascorbic acid solution is added (**7.6.2.2.7**).

NOTE The drop-wise addition of dilute H_2SO_4 *might be necessary when adjusting the pH of the solutions.*

Measure the absorbance of each solution at 380 nm using 10 mm cells with water as reference. Subtract the blank from the sample reading and plot the absorbance against µg TiO_2 (**7.3.14**).

7.7 Alkali metals by emission techniques

COMMENTARY ON 7.7

*A flame photometer (**7.1.20**) or an AAS unit (**7.1.18**) in emission mode or ICP-OES (**7.1.17**) may be used to determine* K_2O *and* Na_2O*.*

*Flame photometer (**7.1.20**) techniques are subject to significant molecular interferences. These may be attenuated by precipitation of "*R_2O_3*" elements prior to aspiration.*

Molecular interferences may be reduced by treating the aspirant solution spot by spot with concentrated ammonia solution until R_2O_3 *metals precipitate. Normally these form an open meshwork of solids which settle quickly to the bottom of the volumetric flask. Aspirant can be taken from the top of the liquid if sufficient care is taken to avoid the precipitate. Otherwise, an aliquot of the aspirant can be centrifuged to ensure settlement of the solids, prior to aspiration.*

*ICP-OES (**7.1.17**) is not subject to these molecular interferences if the solutions are buffered prior to aspiration. If ICP-OES equipment is available, these should be preferred over flame photometric techniques for precision and accuracy of alkali metals determinations.*

7.7.1 Procedure

7.7.1.1 Weigh 1 g of the finely ground material sample, dried as in **4.3.3**, in to a small platinum vessel (**7.1.5**).

7.7.1.2 Ignite gently to remove any organic matter over a Bunsen flame (**7.1.9**).

7.7.1.3 Cool the dish (**7.1.5**) and add 10 ml of sulfuric-nitric acid mixture and 10 ml of hydrofluoric acid (**7.2.10**) (40% w/w).

7.7.1.4 Transfer to a sand bath (**7.1.8**) and evaporate to dryness using a suitable extraction system (**7.1.4**).

7.7.1.5 On reaching dryness add a further 10 ml of sulfuric-nitric acid mixture and rinse vessel (**7.1.5**) walls with water.

7.7.1.6 Re-evaporate to dryness.

7.7.1.7 Add 20 ml of diluted nitric acid (1:19) (**7.3.25**) to the cool, dry material and digest on a steam bath (**7.1.26**) until completely dissolved.

7.7.1.8 Cool, filter if necessary and dilute to 250 ml in a volumetric flask (**7.1.1**) with water (Solution A).

7.7.1.9 Transfer 25 ml of Solution A to a 50 ml volumetric flask (**7.1.1**) containing 5 ml each of caesium sulfate solution (300 ppm Cs) and aluminium sulfate solution (2 000 ppm Al_2O_3).

7.7.1.10 Dilute to 50 ml with water (Solution B).

7.7.1.11 Determine alkali content using flame photometer in accordance with manufacturer's instructions.

NOTE If the alkali content is in excess of the normal range, readings might be brought into range either by dilution of Solution B or by appropriate dilution of Solution A before the addition of caesium and aluminium sulfate. It is essential to maintain in the solutions presented to the instrument concentrations equivalent to 300 ppm Cs and 2 000 ppm Al_2O_3 *in 50 ml of solution.*

7.7.2 Calibration

The instrument shall be set up according to the manufacturer's instructions, using the following standard solutions.

- Potassium/sodium top standard (K_2O 20 ppm, Na_2O 5 ppm): to a 1 l volumetric flask (**7.1.1**) add 40 ml of dilute nitric acid (1:19) (**7.3.25**), 100 ml of caesium sulfate solution (300 ppm), 30 ml aluminium sulfate solution (10 mg Al_2O_3/ml) and 50 ml of potassium/sodium concentrated standard Solution A. Dilute with water to the mark and mix well.
- Potassium/sodium zero standard: to a 1 l volumetric flask (**7.1.1**) add 40 ml of dilute nitric acid (1:19) (**7.3.25**), 100 ml caesium sulfate solution (300 ppm Cs) and 30 ml of aluminium sulfate (10 mg/Al_2O_3/ml). Dilute to 1 l with water and mix well.
- Potassium/sodium intermediate standards: to seven 200 ml volumetric flasks (**7.1.1**) add 8 ml of dilute nitric acid (1:19) (**7.3.25**), 20 ml caesium sulfate solution (300 ppm Cs), 6 ml aluminium sulfate solution (10 mg/ml Al_2O_3/ml) and 5, 10, 20, 40, 50, 60 and 80 ml respectively of the potassium/sodium standard Solution B to yield 1, 2, 4, 8, 10, 12 and 16 ppm K_2O and 0.25, 0.5, 1, 2, 2.5, 3 and 4 ppm Na_2O.

7.8 SiO_2

7.8.1 Procedure

7.8.1.1 Weigh 1.0 g ± 0.000 1 g (M) of finely ground sample into a large platinum dish (**7.1.5**).

7.8.1.2 Add 1.5 g of anhydrous sodium carbonate and mix the contents intimately using a glass rod (**7.1.28**). Concentrate the mixture in the centre of the dish (**7.1.5**), and then flatten it to cover an area about 30 mm in diameter. Cover the mixture uniformly with an additional 0.5 g of anhydrous sodium carbonate, cleaning the rod with some of it and brushing the last traces into the dish (**7.1.5**).

7.8.1.3 Cover the dish (**7.1.5**) with a platinum lid (**7.1.5**) and heat the mixture in a muffle furnace (**7.1.12**) and maintain at a temperature of 1 000 °C ± 20 °C for 10 min.

7.8.1.4 Remove the dish (**7.1.5**) from the muffle furnace (**7.1.12**) and allow to cool.

7.8.1.5 Add 20 ml of hot water, rinsing the platinum lid (**7.1.5**) into the dish (**7.1.5**).

7.8.1.6 Carefully add 20 ml of 1:1 hydrochloric acid solution to the dish (**7.1.5**), cover it and allow the mixture to digest on a steam bath (**7.1.26**) until disintegration of the melt is complete.

NOTE The action of the acid can be hastened by occasionally detaching the layers of insoluble matter which cover the surface and protect the unattacked portion of the fused mass.

7.8.1.7 Crush all flakes of solid matter with a glass rod (**7.1.28**), then evaporate to dryness on a steam bath (**7.1.26**).

7.8.1.8 Cool, drench the residue with 10 ml of concentrated hydrochloric acid (**7.2.8**) and add 30 ml to 50 ml of hot water.

7.8.1.9 Digest on a steam bath (**7.1.26**) for 10 min, then filter through a double acid washed medium grade ashless filter paper (**7.1.23**).

7.8.1.10 Wash the dish (**7.1.5**), residue and filter paper (**7.1.23**) with small volumes of hot dilute (1:99) hydrochloric acid solution (**7.3.23**), transferring the residue from the dish (**7.1.5**) to the filter paper (**7.1.23**).

7.8.1.11 Wash the residue with hot water until free from chloride when tested with the silver nitrate solution. Retain the filtrate (A).

7.8.1.12 Transfer the filter paper (**7.1.23**) to a previously heated and weighed platinum crucible (**7.1.5**) (with lid) and heat gently until the carbon has been burned away.

7.8.1.13 Cover the crucible with a platinum lid (**7.1.5**), heat the precipitate for 1 h in a muffle furnace (**7.1.12**) at 1 220 °C ± 20 °C, allow the crucible and contents to cool in a desiccator (**7.1.19**) and weigh on a balance (**7.1.3**).

7.8.1.14 Repeat the procedure of heating, cooling and weighing to constant weight (until the difference in mass between two successive weighings does not exceed 0.5 mg). Record the mass of the residue obtained from the last weighing as M_1.

7.8.1.15 Treat the heated silica residue with 10 ml of HF (**7.2.10**) and 6 drops of sulfuric acid solution (1:1) (**7.3.20**)

7.8.1.16 Place on a hotplate (**7.1.7**) and heat gently to obtain a solution of the silica. Evaporate, then raise the temperature to volatilize the sulfuric acid.

7.8.1.17 Heat the residue for 5 min in a furnace (**7.1.12**) at 1 220 °C ± 20 °C, allow the crucible (**7.1.5**) and contents to cool in a desiccator (**7.1.19**) and weigh on a balance (**7.1.3**).

7.8.1.18 Repeat the procedure of heating, cooling and weighing to constant weight (until the difference in mass between two successive weighings does not exceed 0.5 mg). Record the mass of the residue obtained from the last weighing as M_2.

7.8.1.19 Take the difference in mass between M_1 and M_2 to represent the mass of silica.

7.8.1.20 Fuse the residue with the minimum quantity of anhydrous sodium carbonate (**7.2.6**), allow to cool, dissolve in hydrochloric acid solution (1:4) (**7.3.22**) and add to filtrate A.

7.8.1.21 Transfer to a 500 ml volumetric flask (**7.1.1**), dilute to the mark with water and mix well (Solution A).

7.8.1.22 Transfer 50 ml aliquot portions from Solution A, using a pipette, to each of two 100 ml volumetric flasks (**7.1.1**). To one flask (**7.1.1**) add 5 ml of hydrochloric acid solution (1:1) (**7.3.21**) and 10 ml of the ammonium molybdate solution (**7.3.18**), dilute to the mark with water and mix well.

7.8.1.23 To the other flask (**7.1.1**) add 5 ml of hydrochloric acid solution (1:4) (**7.3.22**), dilute to the mark with water and mix well.

7.8.1.24 Allow the solutions to stand for 5 min, then measure the absorbance at 420 nm in 4 mm cells (**7.1.27**) using the solution without molybdate as reference. Complete the measurement within 15 min of the addition of the molybdate.

7.8.1.25 Subtract the absorbance of the colorimetric blank from the observed absorbance and calculate the mass in grams (M_3) of silica present in the original sample using the calibration graph.

7.8.1.26 Calculate the percentage silica content of the sample from the following expression:

$$\frac{M_1 - M_2 + M_3}{M} \times 100$$

7.8.2 Colorimetric blank

7.8.2.1 Determine the absorbance of the blank for each fresh preparation of the ammonium molybdate solution as follows.

- Add 10 ml of hydrochloric acid solution (1:4) (**7.3.22**) to a 100 ml volumetric flask (**7.1.1**), dilute to about 50 ml and add 10 ml of the ammonium molybdate solution (**7.3.18**). Dilute to the mark with water, mix well and then allow to stand for 5 min.
- Measure the absorbance of the solution at 420 nm using 40 mm cells, with water as reference, within 15 min of the addition of the molybdate.

7.8.3 Calibration

7.8.3.1 Transfer to separate 100 ml volumetric flasks (**7.1.1**) measured volumes of the standard silica solution (**7.3.16**) to cover the range 0 mg to 1.0 mg and dilute each to 50 ml.

7.8.3.2 To each flask (**7.1.1**) add 10 ml of the hydrochloric acid solution (1:4) (**7.3.22**) and 10 ml of the ammonium molybdate solution (**7.3.18**). Dilute to the mark with water and invert several times to mix. Allow to stand for 5 min.

7.8.3.3 Measure the absorbance of the solutions at 420 nm using 40 mm cells and with the solution which contains no added silica as reference.

7.8.3.4 Plot the observed absorbance against the mass of silica.

7.8.4 Procedure for determination of silica by “loss on HF or apparent silica” (suitable for high purity sands), where the SiO_2 content is above 99.5%

NOTE The simple technique described is subject to error due to the weight of metal sulfates present at the end of the process. In glass sands the most obvious error is due to the presence of aluminium sulfate. A correction can be made for this assuming that the Al_2O_3 *content is known.*

The mathematical correction is given by:

Real SiO_2 *(%) = Apparent* SiO_2 *(%) + 1.536 1 (*Al_2O_3 *(%))*

Similar corrections can be derived for residual potassium and sodium sulfates.

7.8.4.1 Add 15 ml of HF (**7.2.10**) and 10 ml of 1:1 sulfuric acid solution (**7.3.20**) to the residue obtained from the loss-on-ignition determination (see **5.2.7**).

7.8.4.2 Place the crucible (**7.1.5**) (with lid) on a hotplate (**7.1.7**).

7.8.4.3 Evaporate to a syrup, taking care to avoid loss by spitting.

7.8.4.4 Cool, wash down the sides of the crucible (**7.1.5**) with water, add a further 5 ml of HF (**7.2.10**) and repeat the evaporation to dryness.

7.8.4.5 Heat the residue on a hotplate (**7.1.7**) until fumes of sulfuric acid are no longer evolved.

7.8.4.6 Heat in a muffle furnace (**7.1.12**) at 1 220 °C ± 20 °C for 15 min.

7.8.4.7 Allow to cool in a desiccator (**7.1.19**) and weigh using a balance (**7.1.3**).

7.8.4.8 Repeat the operations of heating, cooling and weighing to constant weight (until the difference in mass between two successive weighings does not exceed 0.5 mg).

7.8.4.9 Calculate the difference between this mass and that of the original sample as a percentage of the mass taken.

8 Combustion

8.1 Principle

The sample is ignited at high temperature in an oxygen rich environment and the carbon and sulfur content determined quantitatively by comparison to standards of known concentration.

NOTE Combustion of the samples in an induction furnace releases sulfur and carbon, which are oxidized and measured by infrared absorption in accordance with the manufacturer's instructions.

8.2 Apparatus

8.2.1 *Balance*, capable of weighing to 0.010 0 g.

8.2.2 *Combustion crucible*.

8.2.3 *Combustion instrument*.

8.3 Procedure

8.3.1 Weigh on a balance (**8.2.1**) 0.500 0 g ± 0.010 0 g of the dried sample into a conditioned sample combustion crucible (**8.2.2**).

8.3.2 To the sample combustion crucible (**8.2.2**), add any specific additional requirements as defined by the combustion instrument (**8.2.3**) manufacturer to effect combustion.

8.3.3 Present and analyse the sample to the combustion instrument (**8.2.3**) as per the manufacturer's instruction.

8.3.4 Perform the analysis in triplicate and determine the mean concentration value.

Annex A (informative) Guidance on using the XRF pressed powder method (see 6.3)

A.1 Grinding aids are not necessary when grinding silica sand.

A.2 X-ray intensity from a sample will increase as the particle size decreases, due to the reduction of voids in the sample.

A.3 Although powder pellets are a standard method of determining heavier (atomic number) major and trace elements, reliable data cannot normally be obtained for these elements unless meticulous precautions are taken to achieve consistent powder preparation and calibration.

A.4 Where powdered sand does not readily form a robust pressed pellet, a suitable binder can be blended with the sample before pressing to assist in the formation of a stable pellet that can be introduced into the XRF spectrometer without adversely affecting the vacuum.

A.5 The addition of a binder will assist in the pellet forming process by flowing under pressure and caking when the pressure is relieved.

A.6 Binders can be powder or liquid and range from common laboratory reagents such as waxes, cellulose, boric acid, thermosetting resins or polymers in solvents, to commercial brand-name products and proprietary tablets. The objective is to produce a robust, homogeneous pellet with minimum sample dilution and contamination. Powdered binders can be mixed with the sample before comminution, however, care should be taken to ensure that the binder does not cake in the mill. Alternatively, the binder can be added to a weighing bottle with a ground sample and shaken for sufficient time to ensure homogeneity. Similarly, liquid binders should be blended with the sample before pellet forming.

A.7 Boric acid is hygroscopic and should be used in granular form.

A.8 Pressing the sample/binder mixture in a collapsible cup will reduce the surface area of the pellet and reduce the effect on the XRF spectrometer vacuum.

A.9 Sample dilution can reduce the sensitivity of low atomic number analytes and those expected at trace concentrations.

A.10 Thermosetting resin binders should be allowed an additional curing stage.

A.11 Pellets should be stored in a desiccator.

A.12 Mills should be cleaned using any of the following:

- water;
- suitable solvents such as acetone or ethanol (or industrial methylated spirits);
- silica of at least 99% purity.

Annex B (informative) Compositions of sand CRMs

The CRMs in Table B.1 are currently available to assist in the calibration process.

Table B.1 **Composition of sand CRMs**

Analyte	**SGT 6** A) % m/m	**SGT 8** % m/m	**SGT 9** % m/m	**SGT 10** % m/m	**BCS 313/1** B) % m/m	**SRM 165a** % m/m	**SRM 1413** C) % m/m	**IPT 61** D) % m/m	**IPT 62** % m/m
SiO_2	98.66	95.63	97.24	98.73	99.78	—	82.77	99.79	99.62
Al_2O_3	0.60	2.07	1.35	0.513	0.036	0.059	9.90	0.054	0.11
Fe_2O_3 E)	0.032	0.26	0.103	0.059 6	0.012	0.012	0.24	0.014	0.072
TiO_2	0.024	0.073	0.044	0.172	0.017	0.011	0.11	0.026	0.036
CaO	<0.02	0.06	0.02	0.024 3	0.006	—	0.74	(0.004)	(0.004)
MgO	<0.02	0.12	0.06	0.038 7	0.001 3	—	0.06	(0.003)	(0.004)
Na_2O	<0.02	0.20	0.10	0.019 5	0.003	—	1.75	(0.002)	(0.002)
K_2O	0.40	1.06	0.82	0.127	0.005	—	3.94	(0.007)	(0.007)
Cr_2O_3 F)	(0.000 3)	(0.001 1)	(0.000 3)	0.008 1	—	0.000 11	—	—	—
BaO	—	—	—	0.004 0	—	—	0.12	—	—
MnO	—	—	—	0.001 2	0.000 13	—	—	—	—
ZrO_2	—	—	—	—	(0.002)	0.006	—	0.010	0.010
LOI	0.14	0.48	0.24	0.24	(0.1)	—	—	(0.06)	0.10

NOTE Figures in brackets are only approximate.

A) SGT – Society of Glass Technology

B) BCS – Bureau of Analysed Samples Ltd

C) SRM – National Institute of Standards and Technology (NIST), USA

D) IPT – Instituto de Pesquisas Tecnologicas, Brazil

E) Total iron expressed as Fe_2O_3

F) Total chromium expressed as Cr_2O_3

Bibliography

For dated references, only the edition cited applies. For undated references, the latest edition of the referenced document (including any amendments) applies.

BS EN ISO 21587-1, *Chemical analysis of aluminosilicate refractory products (alternative to the X-ray fluorescence method) – Part 1: Apparatus, reagents, dissolution and gravimetric silica*

BS EN ISO 3696, *Water for analytical laboratory use – Specification and test methods*

BSI – British Standards Institution

BSI is the independent national body responsible for preparing British Standards. It presents the UK view on standards in Europe and at the international level. It is incorporated by Royal Charter.

Revisions

British Standards are updated by amendment or revision. Users of British Standards should make sure that they possess the latest amendments or editions.

It is the constant aim of BSI to improve the quality of our products and services. We would be grateful if anyone finding an inaccuracy or ambiguity while using this British Standard would inform the Secretary of the technical committee responsible, the identity of which can be found on the inside front cover.
Tel: +44 (0)20 8996 9000 Fax: +44 (0)20 8996 7400

BSI offers members an individual updating service called PLUS which ensures that subscribers automatically receive the latest editions of standards.

Buying standards

Orders for all BSI, international and foreign standards publications should be addressed to Customer Services. Tel: +44 (0)20 8996 9001
Fax: +44 (0)20 8996 7001 Email: orders@bsigroup.com

You may also buy directly using a debit/credit card from the BSI Shop on the Website http://www.bsigroup.com/shop.

In response to orders for international standards, it is BSI policy to supply the BSI implementation of those that have been published as British Standards, unless otherwise requested.

Information on standards

BSI provides a wide range of information on national, European and international standards through its Library and its Technical Help to Exporters Service. Various BSI electronic information services are also available which give details on all its products and services. Contact the Information Centre. Tel: +44 (0)20 8996 7111
Fax: +44 (0)20 8996 7048 Email: info@bsigroup.com

Subscribing members of BSI are kept up to date with standards developments and receive substantial discounts on the purchase price of standards. For details of these and other benefits contact Membership Administration. Tel: +44 (0)20 8996 7002
Fax: +44 (0)20 8996 7001 Email: membership@bsigroup.com

Information regarding online access to British Standards via British Standards Online can be found at http://www.bsigroup.com/BSOL.

Further information about BSI is available on the BSI website at http://www.bsigroup.com.

Copyright

British Standards

BSI Group Headquarters
389 Chiswick High Road,
London W4 4AL, UK
Tel +44 (0)20 8996 9001
Fax +44 (0)20 8996 7001
www.bsigroup.com/standards