



Standard Test Methods for Chemical Analysis of Ceramic Whiteware Materials Using Wavelength Dispersive X-Ray Fluorescence Spectrometry¹

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1. Scope

1.1 These test methods cover the determination of ten major elements (SiO_2 , Al_2O_3 , Fe_2O_3 , MgO , CaO , Na_2O , K_2O , TiO_2 , P_2O_5 , MnO , and LOI) in ceramic whitewares clays and minerals using wavelength dispersive X-ray fluorescence spectrometry (WDXRF). The sample is first ignited, then fused with lithium tetraborate and the resultant glass disc is introduced into a wavelength dispersive X-ray spectrometer. The disc is irradiated with X-rays from an X-ray tube. X-ray photons emitted by the elements in the samples are counted and concentrations determined using previously prepared calibration standards. (1)² In addition to 10 major elements, the method provides a gravimetric loss-on-ignition.

NOTE 1—Much of the text of this test method is derived directly from *Major element analysis by wavelength dispersive X-ray fluorescence spectrometry*, included in Ref (1).

1.2 Interferences, with analysis by WDXRF, may result from mineralogical or other structural effects, line overlaps, and matrix effects. The structure of the sample, mineralogical or otherwise, is eliminated through fusion with a suitable flux. Fusion of the sample diminishes matrix effects and produces a stable, flat, homogeneous sample for presentation to the spectrometer. Selecting certain types of crystal monochromators eliminates many of the line overlaps and multiorder line interferences. A mathematical correction procedure (2) is used to correct for the absorption and enhancement matrix effects.

1.3 Concentrations of the elements in clays and minerals are determined independent of the oxidation state and are reported in the oxidation state in which they most commonly occur in the earth's crust.

1.4 Concentration ranges:

Element	Concentration range (percent)	
SiO_2	0.10	99.0
Al_2O_3	0.10	58.0
Fe_2O_3	0.04	28.0
MgO	0.10	60.0

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² The boldface numbers in parentheses refer to the list of references at the end of this standard.

Element	Concentration range (percent)	
CaO	0.02	60.0
Na_2O	0.15	30.0
K_2O	0.02	30.0
TiO_2	0.02	10.0
P_2O_5	0.05	50.0
MnO	0.01	15.0
LOI (925°C)	0.01	100.0

1.5 This standard does not purport to address all of the safety concerns, if any, associated with its use. It is the responsibility of the user of this standard to establish appropriate safety and health practices and determine the applicability of regulatory limitations prior to use.

2. Referenced Documents

2.1 ASTM Standards:³

- C 242 Terminology of Ceramic Whitewares and Related Products
- C 322 Test Method for Sampling Ceramic Whiteware Clays
- C 323 Test Methods for Chemical Analysis of Ceramic Whiteware Clays

3. Apparatus

3.1 *Simultaneous X-ray Spectrometer*, for example, Philips PW1606 or equivalent.

3.2 *Pt-Au Alloy Crucibles and Molds*, (3).

3.3 *Fluxer*, ((4) or equivalent).

3.4 *Two Muffle Furnaces with Rocker Attachments*—A muffle furnace is not required if the fluxer has automatic operation with its own heat source.

3.5 *Hot Plate and Muffle Furnace*.

4. Reagents

4.1 Digest the samples in Johnson Matthey Spectroflux 100⁴ or equivalent brand (lithium tetraborate). A blend of lithium tetraborate (Spectroflux 100⁴) and lithium metaborate (Spectroflux 100A⁴) can be used if a lower fusion point is desired.

³ For referenced ASTM standards, visit the ASTM website, www.astm.org, or contact ASTM Customer Service at service@astm.org. For *Annual Book of ASTM Standards* volume information, refer to the standard's Document Summary page on the ASTM website.

⁴ Spectroflux is a registered trademark of Johnson Matthey, Johnson Matthey Plc 2-4 Cockspur Street, Trafalgar Square, London, SW1Y 5BQ, United Kingdom.

The flux is ordered in powdered form, lot size as appropriate, and identified by number and date.

4.2 Dry the minus 60-mesh material for the lot 2 days at 300°C and keep in sealed Mason jars.

4.3 After drying, perform a loss-on-fusion for each lot of flux from the manufacturer so that an appropriate amount of flux can be weighed out to yield 8.0000 g of lithium tetraborate after fusion.

4.4 Weigh the charges of flux using a Zymark⁵ robot to ± 0.0035 g (± 0.04 % precision). If the Zymark⁵ robot is not available the samples can be weighed by hand.

4.5 Clean the platinum ware in 50 percent reagent grade HCl, rinse in deionized water and dry at 140°C. Other acids may be used instead of HCl, depending on the preference of the laboratory.

4.6 Prepare the LiBr used as a nonwetting agent by neutralizing reagent grade concentrated HBr (48 %) with LiCO₃.

4.7 Filter the LiBr solution and dilute 1:1 with deionized water.

5. Safety Precautions

5.1 Fusions and ignitions of samples in a muffle furnace must be performed under a high velocity canopy hood. Boiling of the HCl cleaning solution is performed in a chemical fume hood with a safety sash. Safety glasses and special nonflammable, nonasbestos, heat resistant gloves must be worn when removing the fluxer from the muffle furnace. Glass discs are sharp on the rear edge and should be handled with care. Dust from the flux must not be inhaled, so pouring of the powdered flux must be done in a chemical hood. Preparation of the LiBr solution must be done by slowly adding LiCO₃ to the HBr so the generation of CO₂ does not cause the acid to spill over the edge of the beaker. The specific Chemical Hygiene Plan (CHP) for the laboratory, or laboratories if the corporation has more than one, gives the first-aid treatment and disposal procedures for chemical products used in this method.

6. Procedure

6.1 Ignite a 0.8000 g portion of minus 80-mesh sample in a tared 95 percent Pt/5 percent Au crucible at 925°C for 40 minutes. Report the weight loss as percent loss on ignition (LOI).

6.2 Add a charge of lithium tetraborate (or a blend of lithium tetraborate/lithium metaborate) that will contribute 8.0000 g after fusion to the sample and thoroughly mix the powders.

6.3 The combined weights of the sample and the flux will result in an “infinitely thick” sample disc to the instrument.

6.4 Add a 0.250 mL aliquot of the 1:1 LiBr solution, serving as a nonwetting agent, to the sample.

6.5 Load whatever number of crucibles (with samples) and molds the fluxer is equipped to hold and the same number of empty molds onto the fluxer.

6.6 Following the instructions of the fluxer, allow it to reach a temperature of 1120°C for ten minutes, and then rock for 5

TABLE 1 Operating Conditions for Determination of Elements by WDXRF

Element	Line	Crystal	Detector Gas	Window
Na	K α	PX-1	Flow, P-10	2 μ m, polypropylene
Mg	K α	TLAP	Flow, P-10	2 μ m, polypropylene
Al	K α	PET	Sealed neon	25 μ m, beryllium
Si	K α	InSb	Sealed neon	25 μ m, beryllium
P	K α	Ge	Sealed neon	50 μ m, beryllium
K	K α	LiF 200	Sealed krypton	100 μ m, beryllium
Ca	K α	LiF 200	Sealed krypton	100 μ m, beryllium
Ti	K α	LiF 200	Sealed krypton	100 μ m, beryllium
Mn	K α	LiF 200	Sealed krypton	100 μ m, beryllium
Fe	K α	LiF 200	Sealed krypton	100 μ m, beryllium

PX-1 = Tungsten carbide layered; TLAP = thallium hydrogen phthalate; PET = pentaerythritol tetrakis (hydroxymethyl) methane; InSb = indium antimonide; GE = Germanium 111; LiF 200 = lithium fluoride (200 lattice orientation); P-10 gas = 90 percent argon + 10 percent methane.

minutes to stir and homogenize the samples. If sulfur is to be determined, fusion temperature must be 1050°C or less and the blend of lithium tetraborate/lithium metaborate must be used.

6.7 Remove the fluxer from the furnace, pour the molten mixtures into their respective molds, and cool to near room temperature. An essential feature of this mold is the mold design (3).

6.8 Samples with high concentrations of Cu, Cr, Ni, Fe, Mn and high organic content require various special sample preparation techniques, and, in some cases, cannot be prepared at all.

6.9 Samples with arsenic or lead with concentrations in excess of 2000 ppm, or with combined As/Pb concentration in excess of 3000 ppm cannot be prepared because of risk of damage of the Pt/Au crucibles.

6.10 Using the wavelength dispersive X-ray spectrometer, the major element concentrations are determined by comparing the intensities obtained from standards with those obtained from the sample (5,6). For example, the following instrumental conditions are for the Phillips PW1606 spectrometer. These conditions will be different for other models of x-ray spectrophotometers:

Tube	Rhodium, end window
Power	35 Kv and 60 ma
Time	100 s
Atmosphere	Vacuum

7. Operating Conditions for Determination of Elements by WDXRF

7.1 Recalibrate the spectrophotometer every two weeks or as required for the particular model of spectrophotometer being used. The computerized recalibration is performed using discs from the original calibration which are used to set the slope of the calibration curve. The U.S. Geographical Survey reference materials used include AGV-2 (Andesite), DTS-1 (Dunite), BHVO-1 (Basalt), STM-1 (Syenite), NOD-P-1 (Manganese Nodule), MRG-1, BX-N, FK-N, GS-N, MICA-FE, NIM-D, NIM-P, GSR-4, GFS-401, and NBS-120C.⁶

⁶ Refer to the U. S. Geological Survey listing of their reference materials, ([HTTP://minerals.cr.usgs.gov/geo_chem_stand/](http://minerals.cr.usgs.gov/geo_chem_stand/)) or contact U.S. Geological Survey, Box 25046, MS 973 Denver, CO 80225 for complete details of the reference materials used in this procedure.

⁵ Zymark is a registered trademark of Zymark Corporation, Hopkinton Massachusetts.

7.2 Prepare six blanks from the current batch of flux and LiBr to use for recalibration of the curve's intercept. This allows the original calibration to be maintained while compensating for minor changes in the reagents, P-10⁶ gas, or instrument parameters due to equipment maintenance. Following a recalibration, prepare and count a new disc of the quality control check standard TB-1⁶ to verify the calibration.

7.3 Correct long-term instrument drift by using drift monitor analyses. Compare monitor intensity values obtained during the analyses with monitor intensity values from the original calibration. Calculate the corrections using the spectrometer's software. Long-term drift monitoring cannot correct for short-term or significant changes in the operating parameters.

7.4 In order to keep track of instrumental short-term drift, use every twelfth disc as an instrument check standard: AGV-2 (Andesite), DTS-1 (Dunite), BCS 381, or BX-N⁶. These standards represent the average, high and low for the 10 analyzed elements. If the analyzed disc exceeds three times the standard deviation of the counting statistics, halt the analysis and check the instrument using other discs. If the disc is corrupt, remove it and make another one. Perform a recalibration if the instrument shows signs of drift.

7.5 In addition to the instrument standards, prepare a sample preparation check standard, TB-1⁶ for every 20 samples which is produced and analyzed long with the samples. If this disc shows a deviation of 3 standard deviations or more, and the instrument standards show no deviation, then prepare another

sample of TB-1⁶. If it again shows deviation, then halt the sample preparation and locate the problem. Instrument recalibration is performed if both the sample preparation standard and the instrument standard exceed controls.

8. Report

8.1 Report the following information:

8.1.1 Identification of the material tested, and

8.1.2 A table listing oxides and LOI by their percentage in the sample.

9. Precision and Bias

9.1 *Precision*—The WDXRF method for major element analysis is unique among analytical method packages in that it takes advantage of the summation of the determined elements. This summation acts as a measure of quality control. If an analysis includes the principal elements in a sample, then the total of their determinations should approach 100 percent. This check is the main reason that a LOI was initially incorporated in the package. If an analysis yields a total major element oxide determination of less than 97 percent or greater than 101 percent, then it is automatically repeated. Precision in the WDXRF method depends on the stability of the instrument, the orientation of this sample disc as it is presented to the instrument, and the homogeneity of the sample preparation.

9.2 *Bias*—No data, regarding the reference samples, as supplied by the National Institute of Standards and Technology, is available to determine bias.

APPENDIX

(Nonmandatory Information)

X1. TABLES

TABLE X1.1 Element to Oxide Conversion Factors

Ag ₂ O	1.0741	CuO	1.2518	Lu ₂ O ₃	1.1371	PtO	1.0820	ThO ₂	1.1379
Al ₂ O ₃	1.8895	Dy ₂ O ₃	1.1477	MgO	1.6582	Rb ₂ O	1.0936	TiO ₂	1.6681
As ₂ O ₃	1.3203	Er ₂ O ₃	1.1435	MnO	1.2912	ReO	1.0859	Tl ₂ O ₃	1.1174
As ₂ O ₅	1.5339	Eu ₂ O ₃	1.1579	MnO ₂	1.5825	RhO	1.5555	Tm ₂ O ₃	1.1421
Au ₂ O	1.0406	FeO	1.2865	MoO ₃	1.5003	RuO	1.1583	UO ₂	1.1344
B ₂ O ₃	3.2202	Fe ₂ O ₃	1.4197	NO ₃	4.4267	SO ₃	2.4972	UO ₃	1.2017
BaO	1.1165	Ga ₂ O ₃	1.3442	Na ₂ O	1.4305	Sb ₂ O ₅	1.3284	U ₃ O ₈	1.1792
BeO	2.7758	Gd ₂ O ₃	1.1526	Nb ₂ O ₅	1.4305	Sc ₂ O ₃	1.5338	V ₂ O ₅	1.7852
Bi ₂ O ₅	1.1914	GeO ₂	1.4408	Nd ₂ O ₃	1.1664	SeO ₃	1.6079	WO ₃	1.2610
CO ₂	3.6644	HfO ₂	1.1793	NiO	1.2725	SiO ₂	2.1392	Y ₂ O ₃	1.2699
CaO	1.3992	HgO	1.0798	OsO	1.0841	Sm ₂ O ₃	1.1596	Yb ₂ O ₃	1.1387
CdO	1.1423	Ho ₂ O ₃	1.1455	P ₂ O ₅	2.2916	SnO ₂	1.2696	ZnO	1.2448
Ce ₂ O ₃	1.1713	In ₂ O ₃	1.2091	PbO	1.0772	SrO	1.1826	ZrO ₂	1.3508
CeO ₂	1.2284	IrO	1.0832	PbO ₂	1.1544	Ta ₂ O ₅	1.2211		
CoO	1.2715	K ₂ O	1.2046	PdO	1.1504	Tb ₂ O ₃	1.1510		
Cr ₂ O ₃	1.4615	La ₂ O ₃	1.718	Pr ₂ O ₃	1.1703	Tb ₄ O ₇	1.1762		
Ca ₂ O	1.0602	Li ₂ O	2.1527	Pr ₆ O ₁₁	1.2082	TeO ₃	1.3762		

TABLE X1.2 Weight-to-ppm-to-ppb Equivalents

Weight Percent	ppm	ppb	ppt	
1.0	10000			
0.1	1000			
0.01	100			
0.001	10			
0.0001	1	1000		1 µg/g or 1 mg/L
0.00001	0.1	100		
0.000001	0.01	10		
0.0000001	0.001	1	1000	1 ng/g or 1 µg/L
0.00000001	0.0001	0.1	100	
0.000000001	0.00001	0.01	10	
0.0000000001	0.000001	0.001	1	1 pg/g or 1 ng/L

TABLE X1.3 Grain Size and Sieve Equivalents

Mesh Opening		U.S. Standard Mesh No.	Tyler Mesh Equivalent
Micrometers	Inches		
850	0.0331	20	20
710	0.0278	25	24
600	0.0234	30	28
500	0.0197	35	32
425	0.0165	40	35
355	0.0139	45	42
300	0.0117	50	48
250	0.0098	60	60
212	0.0083	70	65
180	0.0070	80	80
150	0.0059	100	100
125	0.0049	120	115
106	0.0041	140	150
90	0.0035	170	170
75	0.0029	200	200
63	0.0025	230	250
53	0.0021	270	270
45	0.0017	325	325
38	0.0015	400	400

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