Original Paper

Microwave-assisted digestion of ceramic frits for boron and lithium determination by inductively coupled plasma spectrometry (ICP-OES)

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Boron and lithium are two elements commonly found in the chemical composition of ceramic frits. They are usually determined by volumetric titration and atomic absorption spectrometry, respectively, after melting the ceramic frit by high-temperature alkaline fusion and dissolving the melt in acid medium. This dissolution procedure is long and tedious, and does not enable determining both elements simultaneously. An alternative ceramic frit dissolution procedure based on microwave-assisted digestion in acid medium has been proposed, which allows jointly determining boron and lithium by inductively coupled plasma-optical emission spectrometry. This procedure is rapid and reproducible, and the results are independent of frit chemical composition.

1. Introduction

Ceramic frits are semi-finished, intermediate products used in preparing glaze suspensions for manufacturing glazed ceramic tiles. Technical and aesthetic properties of ceramic tiles are highly dependent on glaze characteristics.

Frits are glassy materials made by melting different natural or synthetic crystalline raw materials (quartz, feldspars, zinc oxide, borates, carbonates, zircon, oxide, etc.) at high temperatures.

Most of the elements found in frits (Si, Al, Fe, Ca, Mg, Na, K, Ti, Zr, Ba, Pb, Zn, Hf, and P) are analysed by the X-ray fluorescence (XRF) spectrometry technique [1], which requires preparing fused disks of the sample. However, ceramic frits also contain other light elements, such as boron and lithium, which cannot be analysed by XRF, since this technique is not very sensitive to these two elements: detection limits are high and measurement reproducibility is low. Boron and lithium are usually determined by volumetric titration [2] and by atomic absorption spectrometry [3 and 4] (AAS) respectively. Both determinations require dissolving boron and lithium. One way of dissolving a frit sample consists of disaggregating it by high-temperature alkaline fusion (1000 °C) and then dissolving the melt in acid medium. Though effective, this process is long and tedious. Nor does it enable simultaneous determination of boron and lithium with suitable accuracy by techniques such as inductively coupled plasma – optical emission spectrometry (ICP-OES) [5 to 7] owing to the high concentration of salts as a result of the alkaline fusion.

In this paper an alternative ceramic frit dissolution procedure has been fine-tuned, involving microwave-assisted digestion in acid medium, which enables simultaneously determining boron and lithium by ICP-OES.

2. Experimental procedures

2.1 Materials

Two series of frits have been used. Table 1 details the chemical composition of each frit. The first series consists of five frits (F-1, F-2, F-3, F-4 and F-5) that contain boron and the second series comprises three frits (F-6, F-7 and F-8) that contain lithium. Each series covers the typical range of values found in industrial frits. It can be observed that the quantity of lithium is always very small, never exceeding 1 %(m/m) Li_2O.

Sodium and potassium carbonate were used to disaggregate the frit samples by alkaline fusion. HCl, HNO_3 and HF concentrates or mixtures of these were used to dissolve the frit samples; a solution of $AlCl_3 \cdot 6H_2O$ (c = 100 g/l) was also used to complex the excess HF (hydrofluoric acid can attack measuring equipment, causing measurement errors) [8 to 10].

Boric acid was used to calibrate the ICP-OES equipment for measuring boron content. Lithium chloride was used to calibrate the AAS equipment and lithium carbonate was used to calibrate the ICP-OES equipment

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Table 1. Chemical composition (in % (m/m)) of the frits F-1 to F-8 used

oxide	F-1	F-2	F-3	F-4	F-5	F-6	F-7	F-8
SiO_2	61.4	57.2	53.5	50.7	61.6	54.2	68.9	64.1
Al_2O_3	6.9	9.8	11.8	7.8	7.4	6.2	5.6	6.6
B_2O_3	2.92	8.42	7.65	5.92	2.32	3.89	9.34	6.71
Fe_2O_3	0.12	0.21	0.15	0.14	0.15	0.08	0.05	0.08
CaO	14.7	9.54	10.2	8.90	13.0	28.6	3.10	15.3
MgO	1.49	0.66	0.83	4.32	0.89	0.82	0.35	0.40
Na_2O	0.43	1.70	1.25	1.51	0.40	0.20	5.60	3.49
K_2O	4.4	6.71	7.27	3.67	4.78	0.36	1.27	0.85
TiO_2	0.03	0.03	0.06	<0.1	0.04	0.02	0.03	0.03
ZrO_2	<0.01	0.02	0.16	8.00	0.02	3.42	0.04	1.63
BaO	0.02	0.08	0.59	0.05	0.04	0.01	0.69	0.72
Li_2O	<0.01	<0.01	<0.01	<0.01	<0.01	0.94	0.05	0.50
PbO	0.05	<0.01	0.70	<0.1	<0.01	0.19	2.15	0.04
ZnO	7.14	4.83	4.63	8.02	9.36	0.21	2.32	0.09

Table 2. Reference materials used to validate the digestion procedure in acid medium

lithium standards		boron standards	
SRM 181	SRM 98b	SRM OPAL 91	SRM 3107
GBW 07404 SOIL		GBW 07404 SOIL	

for measuring lithium content. The three reactants were supplied by Merck, Darmstadt (Germany).

Five reference materials (shown in table 2) were also used to test the validity of the proposed procedure of microwave-assisted frit sample digestion in acid medium.

2.2 Equipment

Frit sample digestion was performed using an Anton Paar, Model Paar Physica (Anton Paar GmbH, Graz (Austria)), microwave apparatus, equipped with two types of digestion tubes: six quartz tubes with 50 ml capacity, which enable working at a maximum pressure of 75 bar and six Teflon tubes with 100 ml capacity, whose maximum working pressure is 35 bar. The apparatus is fitted with an infrared sensor for continuous monitoring of pressure and temperature in each tube. A laboratory muffle kiln and platinum crucibles were used in disaggregating the samples by fusion.

The joint determination of boron and lithium was performed on a Leeman, Model DRE (Direct Reading Echelle) ICP-OES instrument (Leeman Labs, Inc., Lowell, MA (USA)). Lithium was furthermore analysed on a Perkin Elmer, Model 1100B, atomic absorption spectrophotometer, while boron was also analysed by volumetric titration with an automatic Metrohm titrator fitted with a pH electrode, with a micropipette having a resolution of 0.01 ml for proportioning the 0.1 mol/l NaOH solution and a mannitol solution doser.

2.3 Procedure

In each of the eight frits (table 1), two ways of processing the samples were studied. One involved disaggregating the samples by the traditional alkaline fusion procedure (sample fusion in platinum crucibles in a laboratory muffle kiln at 1000 °C for 20 min), followed by dissolution in acid medium (HCl solution) [2]. The other consisted of digesting the samples by an alternative procedure based on sample attack by acid medium, while simultaneously subjecting the samples to microwave radiation. In both cases a dissolution is produced that enables determining boron and lithium content by the most suitable analytical technique: boron and lithium were respectively determined by volumetric titration and atomic absorption spectrometry in the dissolution obtained by the traditional procedure (these two analytical techniques are the standard techniques for analysing these elements [2], and they were simultaneously determined by ICP-OES in the dissolution produced by the proposed alternative procedure.

To design the new frit sample digestion procedure, three variables were studied in accordance with the literature [11 to 18]: the quantity of frit sample to be digested, the acids or mixtures of acids used and digestion process time.

Table 3 details the eight methods used to digest each of the eight frits. The table lists the quantity of sample taken, nature and volume of the acid or mixture of acids added, quantity of 100 g/l aluminium chloride hexahydrate solution added on ending the digestion process, maximum working power of the microwave apparatus (1000 W in every case) and sample residence time in the microwave apparatus at maximum power. Each of the eight methods was tested on at least three samples of every frit and their corresponding blank solutions, which contained all the reactants used except the sample.

Lithium measurement by atomic absorption spectrometry (AAS) was run at 670.8 nm in an air-acetylene

Table 3. Parameters of the methods for sample digestion with maximum working power of the microwave apparatus of 1000 W

parameter	method 1	method 2	method 3	method 4	method 5	method 6	method 7	method 8
sample quantity in mg	200	200	200	200	200	200	200	200
acid solution in ml	HNO_3 (9)	HNO_3 (2) + HCl (4)	HNO_3 (3) + HCl (9)	HNO_3 (3) + HCl (9) + HF (10)	HNO_3 (3) + HCl (9) + HF (10)	HNO_3 (3) + HCl (9) + HF (10)	HNO_3 (3) + HCl (9) + HF (5)	HNO_3 (3) + HCl (9) + HF (5)
$AlCl_3{\cdot}6H_2O$ solution in ml	0	0	0	40	40	40	20	20
time in min	10	10	10	15	15	10	10	5

Table 4. B_2O_3 concentrations (in % (mm)) determined in the frit samples

frits	sample prepared by digestion and analysed by ICP-OES								sample prepared by disaggregation and analysed by the standard method (volumetric titration)
	method 1	method 2	method 3	method 4	method 5	method 6	method 7	method 8	
F1	1.14	1.41	1.43	3.02	3.07	3.01	3.06	3.02	2.96 ± 0.10
F2	3.59	3.68	3.74	8.35	8.44	8.33	8.30	8.36	8.42 ± 0.15
F3	–	–	–	7.73	7.66	7.74	7.50	7.66	7.65 ± 0.15
F4	–	–	–	5.72	5.79	6.02	5.87	5.97	5.92 ± 0.12
F5	–	–	–	2.30	2.24	2.17	2.35	2.28	2.20 ± 0.10

flame, with burner diagonal to the beam and slot of 0.7 nm. The calibration curve was prepared with lithium chloride in ≈ 0.2 mol/l HCl medium (the standards used were 0.5, 1, 2 and 2.5 mg/l lithium) and validated using reference material SRM 3179-II, which contains 100.0±0.5 mg/l lithium.

To measure boron, as the frit compositions contain cations that can interfere with the potentiometric determination of boron, these cations were precipitated by adding $CaCO_3$ to the dissolution resulting from the disaggregation as a preliminary step to boron titration. Boron, in the form of boric acid, was determined by volumetric titration. Titration was carried out by previously neutralizing the hydrochloric acid used in dissolving the sample. Mannitol was then added, which complexes the boric acid, subsequently titrating with a standard NaOH solution. The end point of the titration is clearly detected, despite boric acid being an excessively weak acid, owing to the addition of mannitol which forms more acid complexes.

To measure lithium by ICP-OES, the line 670.784 nm was selected. Measurement was conducted radially at a power of 1.1 kW. Cooling gas flow rate was 15 l/min and that of the auxiliary gas was 0.3 l/min, using argon in both cases. Sample capture rate was 1.5 ml/min. The calibration curve was prepared with lithium carbonate (Li_2CO_3) (using 0, 1 and 10 mg/l lithium standards) and validated using reference material SRM 3179-II of (100±0.5) mg/l lithium.

To measure boron by ICP-OES, the line 249.678 nm was selected. Measurement was conducted radially at a power of 1.2 kW. Cooling gas flow rate was 17 l/min and that of the auxiliary gas was 0.3 l/min, using argon in both cases. Sample capture rate was 1.5 ml/min. The calibration curve was prepared with boric acid (H_3BO_3) (using 0, 1, 10 and 50 mg/l boron standards) and validated with different standards: a standard boron solution of 1000 mg/l boron supplied by Fluka, and reference material SRM 3107 Boron Spectrometric Solution of (5000±30) mg/l boron.

The proposed alternative procedure of microwave-assisted frit sample digestion in acid medium was also validated, besides using the standard methods to determine each element, by using the reference materials listed in table 2.

3. Results and discussion

The values found in the determination of the boron and lithium content in the frits listed in table 1 are set out below for each sample preparation procedure used: traditional disaggregation procedure and alternative digestion procedure. In this last case, every frit sample was subjected to eight different methods with a view to determining the most suitable conditions for conducting the digestion process.

3.1 Results of the boron determination

Table 4 gives the results of the determination of boron content in frits F-1 to F-5, using two sample preparation procedures: disaggregation and digestion. It can be observed that in methods 1, 2 and 3 (based on recommendations of the EPA methods for digestion of siliceous samples) only nitric and hydrochloric acids were used. Nitric acid is an oxidizing acid, which dissolves many metals, whose oxidizing power rises considerably with temperature. Hydrochloric acid is a non-oxidizing acid, which on mixing with other acids such as nitric acid accelerates metal dissolution. However in none of the three cases good sample digestion was achieved, so that a quantity of boron was measured far below that actually present in the sample (found by frit sample disaggregation and volumetric titration).

Since no satisfactory results were yielded in the digestion process, it was decided to add hydrofluoric acid to break up the vitreous structure of the frits and make the digestion process more effective (method 4). In this case a solution of $AlCl_3 \cdot 6H_2O$ (100 g/l) also needs to be added. By forming very stable complexes between the Al^{3+} cation and the F^- anion, this solution keeps the excess hydrofluoric acid from forming volatile compounds with boron and interfering with boron measurement, and from attacking the glass surfaces of the measuring equipment. Method 4 yields a boron content measurement that does not differ significantly from the value found by sample disaggregation and determination by volumetric titration. The variables involved in the frit sample digestion process were then adjusted: reagent quantity was minimized (to reduce reagent consumption) as was digestion time (to expedite the test), while sample quantity was increased (to improve data reproducibility). Methods 5, 6, 7 and 8 correspond to the adjustment of the foregoing variables. It can be observed (table 4) that good results are obtained in every case, with no significant differences compared with the results of method 4.

In view of the outcomes, it can be concluded that method 8 enables conducting good sample digestion (with minimum microwave treatment time and reagent quantity), yielding a boron concentration measurement that is practically identical to the value found by frit sample disaggregation and volumetric titration.

Besides using the standard method (volumetric titration) to analyse the boron present in a frit, the proposed procedure (microwave-assisted frit sample digestion in acid medium) was also validated by using reference materials. Thus, reference materials OPAL 91 and GBW 07404 were subjected to a digestion process in accordance with method 8, though it is to be noted that the boron concentration in these reference materials is very low compared with the boron concentration found in most frits. Table 5 sets out the results. No significant difference is observed between the measured value and the certified value.

Table 5. Results of the determination of B_2O_3 concentration (in % (mm)) in the certified reference materials

reference material	experimental	theoretical
SRM OPAL 91	0.105 ± 0.009	0.097
GBW 07404	0.039 ± 0.009	0.031

Table 6. Results of the determination of Li_2O concentration (in % (m/m)) in the frit samples

frits	sample prepared by digestion (method 8) and analysed by ICP-OES	sample prepared by disaggregation and analysed by the standard method (AAS)
F6	0.97	0.94 ± 0.05
F7	0.05	0.05 ± 0.01
F8	0.51	0.50 ± 0.03

Table 7. Results of the determination of Li_2O concentration (in % (m/m)) in the reference materials

reference material	measured	certified
SRM 181	6.31 ± 0.01	6.39
SRM 98b	0.049 ± 0.009	0.0463
GBW 07404	0.010 ± 0.005	0.0119

3.2 Results of the lithium determination

Table 6 details the results of the determination of lithium content in frits F-6 to F-8, using two sample preparation procedures: disaggregation and digestion in accordance with method 8. In view of the outcomes it can be concluded that method 8 provides good sample digestion, yielding a lithium content measurement that is practically identical to the value found by frit sample disaggregation and atomic absorption spectrometry (AAS).

Besides using the standard method (atomic absorption spectrometry) to analyse the lithium present in a frit, the proposed procedure (microwave-assisted frit sample digestion in acid medium) was also validated by using reference materials. Thus, reference materials SRM 181, SRM 98b and GBW-07404 were subjected to a digestion process in accordance with method 8. Table 7 gives the results. No significant difference is observed between the measured value and the certified value.

4. Conclusions

In this study a new procedure has been fine-tuned for preparing a frit sample for the determination of its boron and lithium content. The procedure consists of microwave-assisted frit sample digestion in acid medium, which yields complete dissolution of the sample and enables simultaneous determination of the boron and lithium content by the ICP-OES analytical technique. Furthermore, this new procedure has been compared with the one used traditionally, involving disaggregation of the frit sample by alkaline fusion and dissolution in acid medium, determining boron by volumetric titration and lithium by atomic absorption spectrometry. The following conclusions can be drawn from the results obtained:

a) Frit sample preparation by microwave-assisted digestion in acid medium is rapid, reproducible and avoids using platinum material in the laboratory.

b) The mixture of hydrochloric acid and nitric acid is unsuitable for producing microwave-assisted frit digestion. To achieve complete dissolution of the boron and lithium present in the frits it is necessary to add hydrofluoric acid and aluminium chloride (the latter to keep excess hydrofluoric acid from attacking the measuring equipment and forming volatile boron compounds).

c) The optimum way of conducting frit sample digestion is by taking 200 mg sample and mixing this with 3 ml HNO_3, 9 ml HCl, 5 ml HF and 20 ml $AlCl_3 \cdot 6H_2O$ solution (at 100 g/l), and then subjecting the mixture to microwave radiation with a 5 min residence at 1000 W.

d) The new frit sample preparation procedure enables simultaneous determination of the boron and lithium content in a frit by the ICP-OES technique. This provides a great saving in time due to both sample preparation and the analytical technique used.

e) The proposed procedure is valid for all the tested frits, demonstrating that the result of the treatment is independent of frit chemical composition. Detection limits of 0.002 and 0.001 % were reached respectively for lithium and boron. This accuracy far exceeds the requirements for ceramic frit analysis.

5. References

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