Chemical Analysis of Impurities in Zirconia and Aluminium Nitride Ceramics by Inductively Coupled Plasma Atomic Emission Spectrometry

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Inductively coupled plasma atomic emission spectrometry (ICP-AES) has been used for the determination of the most significant impurities (Al, Ca, Fe, Mg, P, Si and Ti) in zirconia and aluminium nitride ceramics according to the following procedure: (i) development of two decomposition methods for each material; (ii) study of spectral interferences, matrix and interelemental effects; and (iii) determination of the detection limits. Good precision and accuracy were attained. The procedures developed in this work can be applied to zirconia partially stabilised by the addition of CaO, MgO or Y₂O₃, tetragonal zirconia polycrystals with the addition of Y₂O₃, pure aluminium nitride or aluminium nitride with additions of alkaline earth oxides, Y₂O₃ or CeO₂.

Keywords: Inductively coupled plasma atomic emission spectrometry; aluminium nitride ceramic; zirconia ceramic

Few materials show as much potential as advanced ceramics. They are suitable for high-temperature engineering, electric and electronic applications.^{1,2} The purity requirements for advanced ceramics are increasingly exacting owing to the dramatic effect of impurities on the physical properties of the resultant products.³ The impurities tend to form a glassy grain boundary phase at high temperatures which results in poor mechanical performance and low creep resistance in structural ceramics. In electronic ceramics the effect of impurities is even more drastic, *e.g.*, d.c. conductivity, resistivity *versus* temperature and dielectric constant can be affected by the impurities.

For this reason, there is an increasing demand for more accurate and rapid methods of analysis. However, in the literature there is very little data available on the analysis of these materials. Flame-excited atomic absorption spectrometry was used for the analysis of zirconias,⁴ however, owing to the purity of these materials this technique is not suitable. The colorimetric determination reported by Kruidhof⁵ presents a lot of difficulties. A high-resolution inductively coupled plasma atomic emission spectrometric method was developed by Ishii and Satoh.⁶ They only determined hafnium in high-purity zirconium oxide, the dissolution of the sample was achieved with mixtures of ammonium sulphate and concentrated sulphuric acid. This dissolution method is only appropriate for less resistant zirconia materials.

In the present work a procedure involving inductively coupled plasma atomic emission spectrometry (ICP-AES) has been developed for the determination of impurities (Al, Ca, Fe, Mg, P, Si and Ti) in the following types of advanced ceramics: (i) oxide ceramics (zirconia stabilised with Y₂O₃, CaO or MgO) and (ii) non-oxide ceramics (pure aluminium nitride or with additions of alkaline earth oxides, Y₂O₃ or CeO₂).

Experimental

Apparatus and Operating Conditions

A Jobin-Yvon Model JY-38 VHR sequential spectrometer with a high-resolution monochromator was used (Table 1). The specifications of the ICP source and operating conditions are reported in Table 2.

Chemicals

The stock standard solutions were prepared by dissolving the pure metals, oxides or salts (99.9–99.99%). The oxides Fe₂O₃,

Table 1. Specification of the atomic emission spectrometer

Mounting	1 m crossed Czerny - Turner
Grating	3600 grooves mm ⁻¹
Wavelength range	175–490 nm
Entrance slit	30 µm
Exit slit	30 µm
Photomultiplier	Hamamatsu R446

Table 2. Specification of ICP source and operating conditions

Radiofrequency generator	Durr-JY 3832
Frequency	56 MHz (+ 0.05%)
Output power	2.2 kW
Induced power	1.6 kW
Reflected power	<5 W
Pump	Peristaltic P.S. Analytical (2.1 ml min ⁻¹)
Nebuliser	Meinhard, TR-C2-30, pneumatic
<i>Operating conditions—</i>	
Outer argon flow-rate	16 l min ⁻¹
Carrier argon flow-rate	0.5 l min ⁻¹
Coating argon flow-rate	0.4 l min ⁻¹

MgO, Y₂O₃, CaCO₃ and TiO₂ were dissolved in hydrochloric acid; Al₂O₃ was decomposed by fusion with Na₂CO₃ + Na₂B₄O₇ and dissolved in hydrochloric acid; SiO₂ was decomposed by fusion with Na₂CO₃ and dissolved in distilled water; and (NH₄)₂Ce(NO₃)₆ and ZrOCl₂ were dissolved in distilled water.

Samples

An oxide ceramic [zirconia stabilised with Y₂O₃ (Y-TZP)] and a non-oxide ceramic (aluminium nitride) were chosen for this work.

Sample Preparation

Two types of decomposition methods (acid attack and alkali fusion) were used to achieve complete dissolution of the samples.⁷

Method A

The sample (200.0 mg) is fused with 2.00 g of a mixture of Na₂CO₃ + Na₂B₄O₇ (11 + 5 moles = 53.68 + 46.32% m/m) in

a platinum crucible, and subsequently heated on a Meker burner for 15 min at 1100 °C. The cooled melt is dissolved in 50 ml of (1 + 1) hydrochloric acid and the solution diluted to 100 ml with distilled water.

Method B

This method is based on the work of Ishii and Satoh.⁶ In a 100-ml beaker 200.0 mg of sample are weighed and 10 ml of concentrated H₂SO₄ and 3.5 g of (NH₄)₂SO₄ are added. After covering the beaker with a watchglass, the mixture is heated until SO₃ fumes appear. After cooling, the solution is diluted with distilled water in a 100-ml calibrated flask.

Method C

The sample (200.0 mg) is heated with 5 ml of concentrated HCl in a polytetrafluoroethylene (PTFE) pressure vessel⁸ at 160 °C for 12 h. After cooling, the solution is diluted with distilled water and transferred carefully into a 100-ml calibrated flask.

Preparation of Standards and Calibration

Pure aqueous solutions were used for the determination of detection limits at the five wavelengths selected for each element (Table 3).

The standards used to obtain the detection limits (of the impurities in the samples) contained the reagents and the macroconstituents (ZrO₂, 2000 µg ml⁻¹ or Al, 1200 µg ml⁻¹).

The calibration graphs for the analytes were obtained using a blank solution and a standard of appropriate concentration

Table 3. Spectral lines, ratio of the net signal to background signal (S/B) and detection limits in pure aqueous solutions

Oxide*	λ/nm	S/B	DL/ng ml ⁻¹
Al ₂ O ₃ (10)	396.152	39.1	10
	309.278	43.5	12
	394.401	21.5	21
	308.215	17.6	28
	237.324	9.9	100
CaO (0.5)	396.847	105.9	0.3
	393.366	208.1	0.8
	422.673	1.8	0.9
	315.887	1.9	33
	317.933	0.8	70
Fe ₂ O ₃ (10)	259.940	85.8	7.4
	238.204	66.8	7.6
	239.562	48.1	12
	240.488	25.2	27
	261.187	37.2	45
MgO (1)	280.270	60.7	0.5
	279.553	110.1	1.8
	285.213	11.5	13
	383.826	0.8	57
	279.806	0.9	114
P ₂ O ₅ (100)	213.618	38.7	97
	213.547	5.3	114
	214.914	24.1	178
	253.565	10.2	433
	255.388	4.5	745
SiO ₂ (100)	251.611	316.1	24
	252.851	119.8	26
	251.432	104.9	26
	250.690	141.6	47
	228.158	167.2	60
TiO ₂ (10)	334.941	499.1	0.5
	337.280	285.4	0.9
	323.452	323.6	1.2
	336.121	268.4	1.9
	368.520	206.2	1.9

* The concentration of aqueous solutions (µg ml⁻¹) is indicated in parentheses.

Table 4. Spectral interferences on the selected lines for impurities

Element	λ/nm	Interferences
Al	396.152	Interference from the Zr II 396.16-nm line and increase in emission background with Ca
	309.278	OH band
	394.401	Little interference from the Zr II 394.34-nm and Zr II 394.38-nm lines and an increase in emission background with Ca
	308.215	OH band
	237.324	Zr II 237.30-nm line interference
Fe	259.940	Increase in emission background with Zr
P	213.618	Increase in the background with Zr II 213.56 and 213.68-nm lines and Al

Fig. 1. Spectral scans in the vicinity of wavelengths (a) Al I 396.152 nm, (b) Al I 394.401 nm, and (c) Al I 237.324 nm; A, 0.2 µg ml⁻¹ Al₂O₃; B, 2000 µg ml⁻¹ ZrO₂; C, 200 µg ml⁻¹ ZrO₂; D, 200 µg ml⁻¹ CaO; E, 20 µg ml⁻¹ CaO; and F, 1 µg ml⁻¹ CaO

with the exception of Al₂O₃ where two standard solutions were used. These solutions were prepared matrix-matched with the decomposition reagents.

Results and Discussion

Evaluation of Sample Decomposition Methods

The fusion method with Na₂CO₃ + Na₂B₄O₇ is effective for both samples (zirconia and AlN).

Decomposition with (NH₄)₂SO₄ is useful because of its rapidity and the purity of the reagents required. Following this method, only the Y-TZP is completely dissolved.

Acid attack with HCl in a PTFE reaction vessel introduces the lowest salt content. However, this procedure can only be applied to AlN materials.

Selection of Analytical Lines

Five wavelengths were selected for each element on the basis of their sensitivity.^{9,10} The ratio of net analyte intensity to background intensity and the detection limits under operating conditions, defined previously, were determined. In Table 3 the wavelengths are indicated in order of increasing detection limit. These data are very useful because this order of wavelengths does not agree with the literature.

Spectral Interferences

A study of spectral interferences was carried out. This study started on the lowest detection limit (DL) line of each analyte until one free from spectral interferences or with easily controlled interferences was found.

Spectral scans were performed in the vicinity of each wavelength with analyte solutions close to ten times the detection limits, 20 µg ml⁻¹ solutions of each impurity, 200 µg ml⁻¹ solutions of additive (CaO, CeO₂, MgO, HfO₂ and Y₂O₃) and 2000 µg ml⁻¹ solutions of ZrO₂ and Al₂O₃. The interferences detected are given in Table 4 and in Figs. 1, 2 and 3.

It has been found that, at Al I 396.152 nm and 394.401 nm; Fe II 259.940 nm; and P I 213.618 nm, where an increase in emission background occurs, the net intensity of the analyte remains constant with and without the interferent element. The background correction was obtained at a point where the emission background remains constant in practice.

The Al I 394.401-nm line had to be used for the determination of aluminium in zirconia materials because it is subject to little spectral interference.

Table 5. Spectral lines suitable for analysis of impurities and detection limits. Values represent concentration (µg g⁻¹ and µg ml⁻¹) in the samples

Impurity (wavelength)	Y-TZP				AlN			
	Method A		Method B		Method A		Method C	
	µg g ⁻¹	µg ml ⁻¹	µg g ⁻¹	µg ml ⁻¹	µg g ⁻¹	µg ml ⁻¹	µg g ⁻¹	µg ml ⁻¹
Al ₂ O ₃ (394.401 nm)	3	6 × 10 ⁻³	3	6 × 10 ⁻³	—	—	—	—
CaO (396.847 nm)	0.15	3 × 10 ⁻⁴	0.04	8 × 10 ⁻⁵	0.05	1 × 10 ⁻⁴	0.03	7 × 10 ⁻⁵
Fe ₂ O ₃ (259.940 nm)	2	4 × 10 ⁻³	1.5	3 × 10 ⁻³	2	4 × 10 ⁻³	1	2 × 10 ⁻³
MgO (280.270 nm)	0.15	3 × 10 ⁻⁴	0.2	4 × 10 ⁻⁴	0.05	1 × 10 ⁻⁴	0.05	1 × 10 ⁻⁴
P ₂ O ₅ (213.618 nm)	355	71 × 10 ⁻²	195	29 × 10 ⁻²	310	62 × 10 ⁻²	125	25 × 10 ⁻²
SiO ₂ (251.611 nm)	6.5	13 × 10 ⁻³	6	12 × 10 ⁻³	6.5	13 × 10 ⁻³	5.5	11 × 10 ⁻³
TiO ₂ (334.941 nm)	1.9	38 × 10 ⁻⁴	1.65	33 × 10 ⁻⁴	0.5	10 × 10 ⁻⁴	0.25	5 × 10 ⁻⁴

The inter-element correction factor for Zr on the Al I 394.401-nm line was determined. The real concentration of Al₂O₃ was obtained according to the equation

$$c_{rAl} = c_{appAl} - \alpha c_{Zr}$$

where c_{rAl} is the real concentration of alumina, c_{appAl} the apparent concentration of alumina, c_{Zr} the concentration of zirconia and α the inter-element correction factor.

In order to determine this factor a series of standard solutions (0, 500, 1000, 1500 and 2000 µg ml⁻¹ of ZrO₂) with 0.2 µg ml⁻¹ of Al₂O₃ were prepared. The concentration of Al₂O₃ ($c_{appAl} - c_{rAl}$) versus the concentration of ZrO₂ is a straight line graph with slope $\alpha = 1.4 \times 10^{-5}$ (inter-element correction factor), Fig. 4.

The valid spectral lines used to perform the chemical analyses in these materials are listed in Table 5.

Fig. 2. Spectral scans in the vicinity of the Fe II 259.940-nm line. A, 0.2 µg ml⁻¹ Fe₂O₃; and B, 2000 µg ml⁻¹ ZrO₂

Fig. 3. Spectral scans in the vicinity of the P I 213.618-nm line. A, 1 µg ml⁻¹ P₂O₅; B, 2000 µg ml⁻¹ Al₂O₃; and C, 2000 µg ml⁻¹ ZrO₂

Fig. 4. Graph for the determination of the zirconium inter-element correction factor on the Al 1394.401-nm line. Slope, $\alpha = 1.4 \times 10^{-5}$

Matrix Effect

It was found that the use of hydrochloric acid in the dissolution of the aluminium nitride gives rise to a decrease in signal. This effect is more important when the mixtures $(NH_4)_2SO_4 - H_2SO_4$ or $Na_2CO_3 - Na_2B_4O_7$ are used. The effect of macroconstituents is negligible compared with the effect of decomposition reactants in the determination of trace impurities, hence the standard solutions were prepared as above.

Detection Limits

The detection limits were calculated as the concentration equivalent to 3σ of that measured on the background signal.

The results obtained by the different decomposition methods are given in Table 5.

The results obtained with the acid attack (methods B and C) are slightly lower than those obtained with the fusion method. The values for the AlN sample, decomposed with HCl (method C), are the lowest because of the reagent employed.

The results indicate that the determination of Al_2O_3 , CaO, MgO, Fe_2O_3 , SiO_2 and TiO_2 is feasible using ICP-AES. The detection of P_2O_5 is only possible when it is present in significant amounts.

Chemical Analysis

Five Y-TZP and AlN samples were analysed. The average of the results using the decomposition methods defined above and the standard deviation are summarised in Table 6.

There is good agreement between the results of the chemical determination obtained with the two decomposition methods for each sample.

The standard deviation values indicate good precision. Phosphorus pentoxide can not be detected in AlN material.

Accuracy

Unfortunately, standard reference materials are not available and it is difficult to compare the results obtained using different methods because of the reasons indicated in the introduction.

In this work the accuracy was obtained by adding known amounts of each element (approximately the same amount that would naturally be present) at the sample dissolution stage.

Table 6. Determination of the most significant impurities in Y-TZP and AlN. Values represent concentration (as %) and standard deviation in parentheses

Impurity	Y-TZP		AlN	
	Method A	Method B	Method A	Method C
Al_2O_3	0.56 (0.01)	0.53 (0.02)	—	—
CaO	0.0012 (0.0007)	0.0010 (0.0005)	0.021 (0.003)	0.019 (0.005)
Fe_2O_3	0.017 (0.001)	0.014 (0.001)	0.037 (0.007)	0.040 (0.008)
MgO	0.0021 (0.0003)	0.0017 (0.0006)	0.004 (0.006)	0.004 (0.005)
P_2O_5	0.053 (0.008)	0.052 (0.006)	ND*	ND*
SiO_2	0.12 (0.05)	0.11 (0.03)	0.052 (0.006)	0.057 (0.008)
TiO_2	0.075 (0.001)	0.075 (0.002)	0.011 (0.005)	0.013 (0.007)

* ND: not detected.

The accuracy of the results for the elements is between 95 and 105% for decomposition by Method A and between 97 and 103% for decomposition by Methods B and C, i.e., the accuracy of the results obtained by the different decomposition methods for the samples is similar.

Conclusion

The results obtained in the present investigation support ICP-AES as an appropriate technique for the determination of the most important impurities (Al_2O_3 , CaO, Fe_2O_3 , MgO, SiO_2 and TiO_2) in zirconia and aluminium nitride ceramics. The determination of P_2O_5 is only possible when a significant concentration is present.

The procedures developed are rapid and present good precision and accuracy. Application to zirconia partially stabilised by CaO, MgO and Y_2O_3 , tetragonal zirconia polycrystals with the addition of Y_2O_3 to pure aluminium nitride or to aluminium nitride with additions of alkaline earth oxides, Y_2O_3 or CeO_2 is possible.

References

- Billy, M., and Mexmain, J., *World Ceramics*, 1985, 2.
- Clough, D. J., *Ceram. Eng. Sci. Proc.*, 1985, 6, 1244.
- Keler, E. K., and Andreeva, A. B., *Ogneupory*, 1958, 23, 552.
- Bastius, H., *Ceram. Forum. Int.*, 1984, 61, 3, 140.
- Kruidhof, H., *Anal. Chim. Acta*, 1978, 99, 193.
- Ishii, H., and Satoh, K., *Talanta*, 1982, 29, 243.
- Fariñas, J. C., Martínez, M. R., and Barba, M. F., "Actas del II Congreso Iberoamericano de Cerámica, Vidrio y refractarios," Buenos Aires (Argentina), 1988, in the press.
- Bernas, B., *Anal. Chem.*, 1968, 40, 1682.
- Boumans, P. W. J. M., *Spectrochim. Acta, Part B*, 1981, 36, 169.
- Brenner, I. B., Eldad, H., *ICP Inf. Newsl.*, 1984, 10, 6, 451.

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Analysis of Organic Residues of Archaeological Origin by High-temperature Gas Chromatography and Gas Chromatography - Mass Spectrometry

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Organic residues are extracted from materials of archaeological interest by solvent extraction and subjected directly to high-temperature gas chromatography (GC) and gas chromatography - mass spectrometry (GC - MS). The use of high-temperature GC allows intact acyl lipids, e.g., triacylglycerols, diacylglycerols, monoacylglycerols and wax esters, to be analysed without prior degradation (e.g., saponification) to release constituent fatty acids and alcohols. Trimethylsilylation is employed to block protic sites in free fatty acids and hydroxylated components. The data obtained from temperature programmed GC and GC - MS analyses, employing immobilised apolar (dimethyl polysiloxane type) stationary phases, provide essential compositional information that would be lost if the more conventional degradative approach to acyl lipid analysis was adopted.

Keywords: High-temperature gas chromatography; mass spectrometry; lipid; archaeology; sherd

There is an increasing amount of evidence to show that chemical analyses of the organic constituents from a wide variety of materials of archaeological interest can yield important information concerning past cultural and economic activities. Analysis has covered a broad spectrum of remains, including soils,^{1,2} midden dumps,³ human remains,⁴⁻⁷ and other artefacts, particularly pottery containers.⁸⁻¹⁰

Ceramics are the major loci for the survival of residual organic matter either absorbed into the porous micro-structure of the fired clay wall or preserved in visible surface deposits. A recent investigation has shown that possible post-depositional diagenetic effects, such as contamination arising from migration of soil components, or compositional alterations through microbial activity, are minimal for lipids absorbed in potsherds.¹¹ Hence, these lipid residues are a direct reflection of the original contents and usage of ceramic vessels. Positive identification provides an important research area for the classification of artefact use, determined by food preparation and consumption, and by other economic, manufacturing and technological activities. The realisation of these opportunities necessitates a rapid, but informative means of study of a large number of pottery vessels.¹²

Lipids in particular are well preserved in favourable environments and have potential for use in the classification of biogenic organic matter on chemotaxonomic and biosystematic grounds. Until now, investigations of lipid constituents of archaeological materials have relied on methodologies that either do not make best use of the compositional information available, or are too time consuming to be applied to the processing of the large number of samples necessary to afford information of use to archaeologists.

We describe herein the use of high-temperature gas chromatography (GC) and gas chromatography - mass spectrometry (GC - MS) techniques in the analysis of total lipid extracts from archaeological materials. These techniques have been employed in the investigation of extracts of archaeological materials from widely varying contexts, e.g., soils, peat bogs and hominid remains. However, for the purposes of this paper we will illustrate the use of these techniques in assessing the composition of lipids extracted from ceramic pot sherds.

Experimental

Materials

All solvents used were of AnalaR or HPLC grade and distilled before use. Disposable screw-topped glass vials (15 ml) were

used for extractions to eliminate the possibility of cross-contamination. All other glassware was rinsed with concentrated nitric acid, de-ionised water and organic solvent before use.

Samples

Freshly excavated ceramic potsherds were obtained from the Raunds Area Project (RAP), an extensive archaeological study of a multi-period landscape in the Nene Valley, Northamptonshire, UK.¹³ Sherds (5-200 g) were stored in brown paper envelopes in a deep freeze (-20°C) until required for investigation.

Lipid Extraction

Fragments of sherd (2 g) were freed from adhering soil by scraping with a scalpel blade. The sherd was then ground to a fine powder in a de-greased pestle and mortar. Following transfer into a 15-ml glass vial and addition of a known amount of internal standard (10 or 50 μg of heptadecane), the powdered sherd was extracted by ultrasonication (2×15 min) with a mixture of chloroform and methanol ($2 + 1; 2 \times 10$ ml). After each extraction, the solvent extract was freed from suspended particulate matter by centrifugation, decanted into a round-bottomed flask and reduced to a small volume by rotary evaporation. After decanting into a small, pre-weighed screw-topped vial (0.5 dram) the remaining extraction solvent was removed under a gently blown stream of dry nitrogen. The dried extracts were stored in a deep freeze (-20°C) until required for GC and GC - MS analysis.

Trimethylsilylation

Trimethylsilyl (TMS) ether and ester derivatives were prepared by treating (60°C , 10 min) aliquots (ca. 50 μg) of the total lipid extracts with an excess of *N,O*-bis(trimethylsilyl)-trifluoroacetamide.

Gas Chromatography

The GC analyses were performed on a Hewlett-Packard 5890A gas chromatograph connected to a Hewlett-Packard 3396A computing integrator/plotter. Samples were introduced by on-column injection into a 60 cm $\times$ 0.32 mm i.d. retention gap (de-activated polyimide clad fused silica, Phase Separations) connected to the analytical column via a light-weight glass-lined stainless-steel union of 0.8 mm i.d. (S.G.E.). The