Application of radiofrequency glow discharge-optical emission spectrometry for direct analysis of main components of glass samples

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An internal standard calibration methodology for radiofrequency glow discharge optical emission spectrometry (rf-GD-OES) has been evaluated for the quantitative analysis of glass samples. Glasses of very different composition and thickness (from 2.8 to 5.8 mm thick) were used for calibration. The absence of spectral interferences from sputtered oxygen was first investigated. For calibration, Si was selected as the internal standard and, when plotting intensity ratios (I_x/I_{Si}) versus concentration ratios (C_x/C_{Si}), linear graphs over the entire range of tested concentrations were obtained. In all cases, concentrations of the oxides of different elements have been used instead of elemental concentrations as is habitually done for the analysis of conductors. Thus, the proposed methodology allows us to quantify the oxygen indirectly without measuring its emission intensity. In addition, the internal standard calibration procedure was applied for the determination of the glass major components (SiO_2, Na_2O, CaO, MgO, Al_2O_3 and K_2O) by rf-GD-OES in two glass samples and results showed good agreement with the certified values.

Introduction

Nowadays, there are many industries (steel, ceramic, glass, electronics, etc.) demanding an analytical technique that allows for bulk and in-depth profile rapid analysis, both in conductive and non-conductive samples, with little or no sample preparation, good sensitivity ($\mu g\ g^{-1}$ concentration range) and wide elemental coverage (from light to heavy elements). In this regard, radiofrequency glow discharge optical emission spectrometry (rf-GD-OES) can be considered a powerful technique for the characterization of solid samples, with a potential for bulk and in-depth profile analysis of metals and semiconductors which is today well documented.[1] This unique combination of attributes makes rf-GD-OES an attractive alternative to established solid analysis techniques such as arc/spark-OES, Auger electron spectroscopy, X-ray fluorescence and secondary-ion mass spectrometry.[2,3]

Unfortunately, the application of rf-GD-OES to the direct analysis of non-conductive samples (such as glasses or ceramics) has been limited to date[4,5] and much work remains still to be done in the area of accurate quantification in this kind of sample. The influence of sample thickness in the analytical signals,[4,6] the difficulties of measuring or estimating the electrical parameters which control the discharge[7,8] and the presence of light elements (as oxides or nitrides in most cases) in the samples could be invoked to explain the very few reports published so far dealing with quantitative elemental analyses in insulators. On the other hand, the quantification of sample

light elements, such as carbon, nitrogen, oxygen and hydrogen, is complicated due to the presence of these elements in the atmosphere, usually leading to overestimations of their solid sample concentration.[9] Furthermore, in the determination of non-metals by OES, it has to be taken into account that these elements mainly emit in the vacuum ultraviolet region of the spectrum. Thus, detection of such emission lines is made more difficult owing to their absorption by air present in the optical path.

A few approaches have been successfully evaluated so far for quantitative analysis of non-conductive materials using rf-GD-OES. Concerning homogeneous glass samples, Anfone et al.[4] investigated the analytical characteristics of rf-GD-OES for the elemental analysis of bulk glasses. In that work, the same matrix composition was used throughout the experiments, thus restricting the applicability of the proposed methodology to the use of matrix-matched standards. On the other hand, the capability of rf-GD-OES for the chemical quantification of glasses of different thicknesses and varied matrix composition has been recently investigated in our group.[10] In this latter case, the proposed quantification scheme was based on the "constant emission yield" concept[11,12] and the measured analytical signals were normalized to a thickness selected as "standard thickness" while discharge argon emissions were used as reference signal.

The aim of the present work is to investigate a simpler quantification scheme to carry out the determination of the elemental composition of homogeneous non-conductive materials. Although the internal standard calibration methodology has been widely employed for bulk calibrations addressed to the analysis of conductors with GD-OES,[13] to our knowledge it has not been investigated yet for the quantification of non-conductors by direct solid analysis. In this paper, the

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capabilities of rf-GD-OES for the chemical quantification of bulk glass specimens of different thicknesses and matrix compositions have been investigated by resorting to internal standard calibration.

As a first stage of this study, in order to discard spectral interferences coming from the sputtered oxygen (*e.g.*, molecular bands) present in the glass samples, the spectra in the surroundings of the selected atomic line were investigated for each analyte.

Experimental

The analytical experiments were carried out with a JY 5000RF instrument manufactured by Jobin–Yvon Emission, Horiba Group (Longjumeau Cedex, France). Furthermore, a home-made GD-OES system equipped with a charge-coupled detector (CCD) was also used for some optical emission studies.

The JY 5000RF instrument is made up of a standard JY glow discharge source with an anode of 4 mm internal diameter, two optical spectrometers (a polychromator and a monochromator) and the Quantum IQ V2.22 software. One of the spectrometers consists of a 0.5 m Paschen–Runge polychromator (119–777 nm of wavelength range and a concave grating of 2400 lines mm^{-1}) with the optical path purged with nitrogen. Also, the system is equipped with a Czerny–Turner monochromator (0.64 m focal length and a planar holographic grating of 2400 lines mm^{-1}) which allows an increase in the instrument's capabilities to any desired wavelength within its spectral range (160–900 nm).

The home-made GD-OES system had been developed in our laboratory previously.[14,15] Some modifications have been recently introduced to achieve a better coupling of the radio-frequency energy. The GD chamber, made of stainless steel, was constructed according to the design of Marcus *et al.*[16] A limiting copper disc acting as grounded anode, with a central orifice of 4 mm internal diameter, was used to restrict the area of the cathode (sample) being sputtered. The rf power was supplied by a 13.56 MHz generator (RFX600, Advanced Energy Industries, Fort Collins, CO, USA), the impedance being matched by an automatic matching network (Advanced Energy ATX Tuner). The optical emission is viewed axially through a fused-silica window and collected by a lens at the entrance slit of a 0.5 m Czerny–Turner Spectrograph (SpectraProR-500, EG&G Princeton Applied Research, Princeton, NJ, USA) with flat gratings of 1200 and 2400 lines mm^{-1}. The detector was a CCD with 1024 × 256 pixels (LN/CCD-1100-PF/UV, Princeton Applied Research) cooled by liquid nitrogen.

The full width at half maximum (FWHM) using the home-made system was 0.067 nm at the selected Si line (grating of 2400 lines mm^{-1}), while for the commercial JY 5000RF the FWHM was 0.040 nm at the Si line with the polychromator and 0.020 nm at the Mg line with the monochromator.

The emission lines selected (corresponding to atomic transitions, except for Ca) were 130.21 nm for oxygen, 285.21 nm for magnesium, 288.15 nm for silicon, 393.36 nm for calcium, 396.16 nm for aluminium, 589.59 nm for sodium and 766.49 nm for potassium. For the experiments, net analytical signals (*i.e.* background subtracted) were considered. The background

intensity was measured as an average in the interval 0.2–0.1 nm beside the corresponding analytical emission wavelength.

The rf forward power was the electrical parameter measured in the rf-GD-OES instruments used. The operational mode "constant pressure–constant forward power"[10] was selected throughout the experiments. The pressure was kept fixed at 450 Pa and the forward power employed with the JY 5000RF was in the 25–35 W range,[10] depending on the thickness of the glasses (forward powers higher than 35 W were not used in order to avoid problems related to the breakdown of the samples). The forward power employed with the home-made GD-OES system was 55 W. The reflected power was, in all cases, lower than 1 W.

The calibration curves to quantify the elements present in two glass samples were obtained by using homogeneous glasses of known composition (Table 1). Moreover, for some optical studies a homogeneous glass sample (HG) 1.8 mm thick from Saint-Gobain Cristaleria (Aviles, Spain)[17] and a ceramic disc (ref. CC650A) from the Swedish Institutet för Metallforskning (Stockholm, Sweden) were investigated. The silica content in the HG and SG glasses was determined by gravimetric analysis; sodium by atomic absorption spectrometry and calcium, magnesium, aluminium and potassium by X-ray fluorescence. All concentrations are given as mass%. The ceramic CC650A sample has a high oxygen content (32.0% O, 0.15% N, 4.9% C, 22.0% Ti, 0.01% Zr, 37.0% Al, 3.1% W and 0.3% Co) rather similar to the glass specimens employed in our experiments (in the 38.9–47.0% concentration range). In some experiments the Vaw 3035 aluminium alloy (GAZ GmbH, Düsseldorf) containing 84.9% Al, 10.47% Si, 1.98% Cu, 0.65% Fe, and 0.59% Mg as major elements was investigated.

For rf-GD-OES analysis, the solid materials were polished to a mirror-finish using different grinding papers and then cleaned with ethanol. SiC grinding paper (120, 600 and 1200 grit) was used for the CC650A and Vaw 3035 reference materials, and CeO_2 (300 and 100 grit) and Al_2O_3 for the homogeneous glasses. Samples were cooled at 0 °C by a cold liquid circulating between the sample and the rf power input.

Table 1 Chemical composition and thickness of calibration standards (concentrations are expressed as mass percentages and thickness as millimetres)

Standard	Thickness	SiO$_2$	Na$_2$O	CaO	MgO	Al$_2$O$_3$	K$_2$O
A2[a]	3.1	37.0	0.30	0.70	3.50	12.0	2.50
B1[a]	2.8	51.0	0.00	25.0	0.00	0.00	0.00
C3[a]	3.0	9.90	7.90	0.03	0.00	27.1	6.90
F1[a]	2.8	59.0	1.00	3.00	1.00	2.00	20.0
N-621[b]	5.0	71.1	12.7	10.7	0.27	2.76	2.01
SG-1[c]	4.1	71.2	12.8	1.50	0.03	7.78	0.02
SG-2[c]	5.8	71.2	13.9	9.00	4.70	0.55	0.10
SG-3[c]	2.9	67.7	4.34	10.1	0.22	0.99	5.38
SG-4[c]	4.0	70.0	14.3	11.1	2.70	0.85	0.04
SG-5[c]	3.2	70.6	14.2	8.80	3.80	1.10	0.50
SG-6[c]	3.1	70.1	14.2	8.80	3.80	1.20	0.50
SG-7[c]	3.9	70.7	14.0	8.70	3.70	0.60	0.15
SG-8[c]	3.8	70.7	14.0	8.70	3.70	0.60	0.15
SG-9[c]	3.5	70.1	14.0	8.70	3.70	0.60	0.15

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High-purity argon (99.999% minimum purity) from Air Liquide (Oviedo, Spain) was employed as discharge gas.

Results and discussion

Investigation of molecular emission and possible spectral interferences

Studies of the discharge mechanisms taking place in GDs have attracted great interest for many years.[18,19] One topic of current attention is the effect of traces of molecular gases (*e.g.*, hydrogen, nitrogen and oxygen) in the noble plasma gas.[20–22] These traces may arise from the sample itself or from contaminations in the source (*e.g.*, impurities from the discharge gas, residual gases or by air leakage). The presence of

molecular gases can affect the analytical quantification procedures and become particularly important in thin film analysis by GD-OES.[23,24] Several works have studied the behaviour of the analytical emission lines and other analytical properties of GDs in the presence of hydrogen,[25] nitrogen[26] or oxygen.[27] In the case of oxygen it has been observed that, even at low concentrations, the addition of this gas gives rise to important decreases in analytical emission lines and sample sputtering rates.[21,27]

One of the main problems commonly associated with the quantification of non-conductive materials, such as glasses, by rf-GD-OES is the presence of a high oxygen content in these solid samples (about 40% as oxide of the different elements). This oxygen could give rise to interferences in the selected analytical atomic emission lines. In this vein, a critical previous
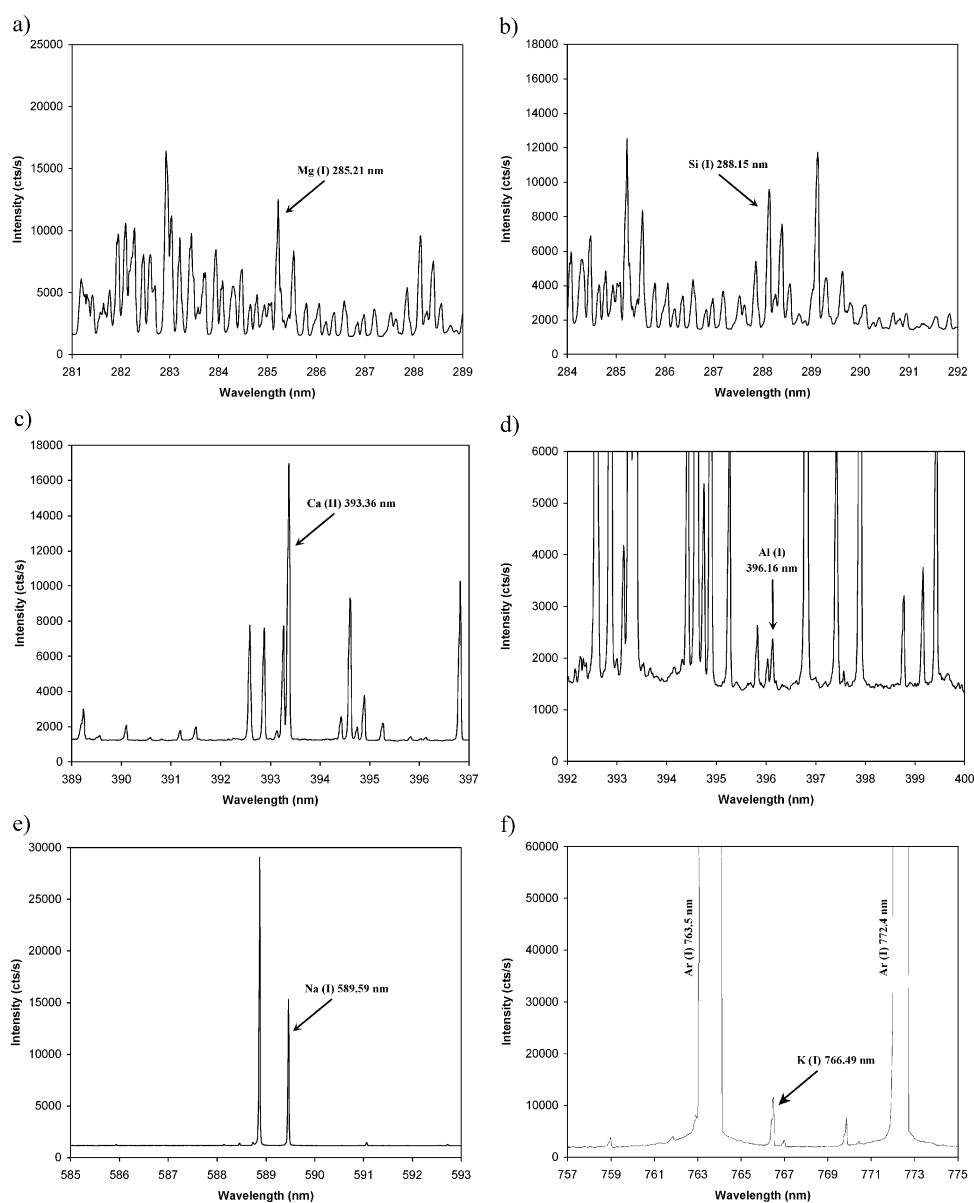
Fig. 1 Rf-GD-OES spectra obtained with the home-made glow discharge system at 55 W of forward power using a homogeneous glass sample HG 1.8 mm thick. The 2400 lines mm^{-1} grating was used for the spectra in (a)–(e). The 1200 lines mm^{-1} grating was used for (f). (a) Mg(I) 285.21 nm. (b) Si(I) 288.15 nm. (c) Ca(II) 393.36 nm. (d) Al(I) 396.16 nm. (e) Na(I) 589.59 nm. (f) K(I) 766.49 nm.

step in the search for a quantification procedure for glasses would be to ensure the absence of molecular bands or oxygen lines, interfering with the selected atomic lines of the analytes of the glass specimens.

For that purpose, the emission spectra around the selected analytical emission lines for magnesium, silicon, calcium, aluminium, sodium and potassium were measured in the 1.8 mm thick HG sample using our home-made rf-GD-OES system coupled to a CCD. The observed results are shown in Fig. 1 for the six elements studied. Fig. 1e and f show the emission spectra obtained in the surroundings of sodium and potassium emission wavelengths, respectively. As can be observed, neither spectrum exhibits any molecular band or atomic line of oxygen overlapping with the selected analytical wavelengths. On the other hand, the emission spectra obtained for magnesium, silicon, calcium and aluminium (Fig. 1a–d, respectively) show more complicated profiles at the selected analytical wavelength interval for each element. This complexity is particularly noteworthy for Mg and Si in the wavelength range between 281 and 292 nm.

The spectral window between 278 and 292 nm is depicted in Fig. 2 for two reference materials (Vaw 3035 and CC650A), the chemical composition of which is given in the Experimental section (the CC650A contains oxygen while the other does not). As can be seen, the spectra for both samples are very different due to the oxygen present in the CC650A material. It is known that the neutral oxygen molecule does not readily show an emission spectrum in discharge tubes at low pressure.[28] However, there are three systems for $O_2{}^+$ the Second Negative System (A $^2\Pi_u$-X $^2\Pi_g$) being the only one emitting in the spectral region shown in Fig. 2(b). It has been reported that the bands of this system occur in discharge tubes containing oxygen at low pressure, especially in the negative glow.[28]

In order to ensure that the selected wavelengths for each element of the glass specimens are not actually interfered, the analytical line profiles of Mg, Si, Ca and Al emissions were measured in the 1.8 mm thick HG sample using the JY 5000RF instrument at 30 W of forward power. The line profile scans (spectral windows of 1 nm) for Mg and Al were measured with the monochromator, whereas the Si and Ca profiles were obtained by using the polychromator. In both cases the optical spectrometers (*i.e.*, the monochromator and polychromator) have a better spectral resolution than the CCD used above. As can be seen in Fig. 3, selected wavelengths for each analyte can be isolated from close potential spectral interferences with the JY 5000RF. Moreover, several standard glasses (B1, C3 and F1) and a ceramic disc (CC650A) were investigated in order to ensure that every selected analytical wavelength is interference free (as shown in Fig. 3, signals are not observed at the corresponding analytical wavelength in the absence of analyte and presence of sputtered oxygen).

Internal standard calibration

In GD-OES the intensity of a specific emission line of an element x may be given by the following equation:

$$I_x = K_x \times C_x \times Q_m \quad (1)$$

a)

b)
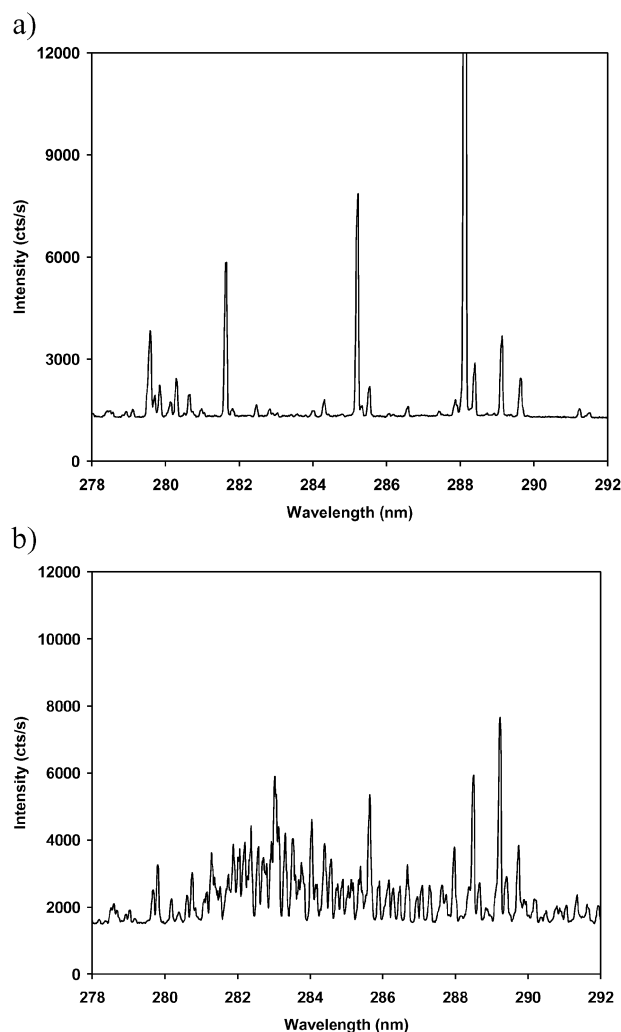
Fig. 2 Rf-GD-OES spectra in the interval 278–292 nm obtained with the home-made glow discharge system. (a) Vaw 3035 ceramic material (0% oxygen content). (b) CC650A aluminium alloy (32% oxygen content).

where K_x is a constant characteristic of the atomic species x, C_x is the concentration of element x and Q_m is the effective sputtering rate of sample m.[29] Since the intensity is sputtering rate dependent, one possible method of correcting for sample-to-sample sputtering rate differences is to ratio the intensity of the analyte to that of an internal standard.

Any constituent of the sample which is present at a constant or at a known amount in each of the analyzed samples could be used as an internal standard (IS), providing that its intensity signal is reasonable high.[30] If an IS at a constant amount in all the samples is used (as is the case when using Fe as IS for analyzing any constituent in carbon steel samples, where the Fe content is >99%) the calibration curves are plotted as intensity ratios of the analyte to the IS *versus* the analyte concentration.

On the other hand, if the selected IS is not present at a constant amount (as happens in our case with the constituents of the glass specimens) its concentration must be exactly
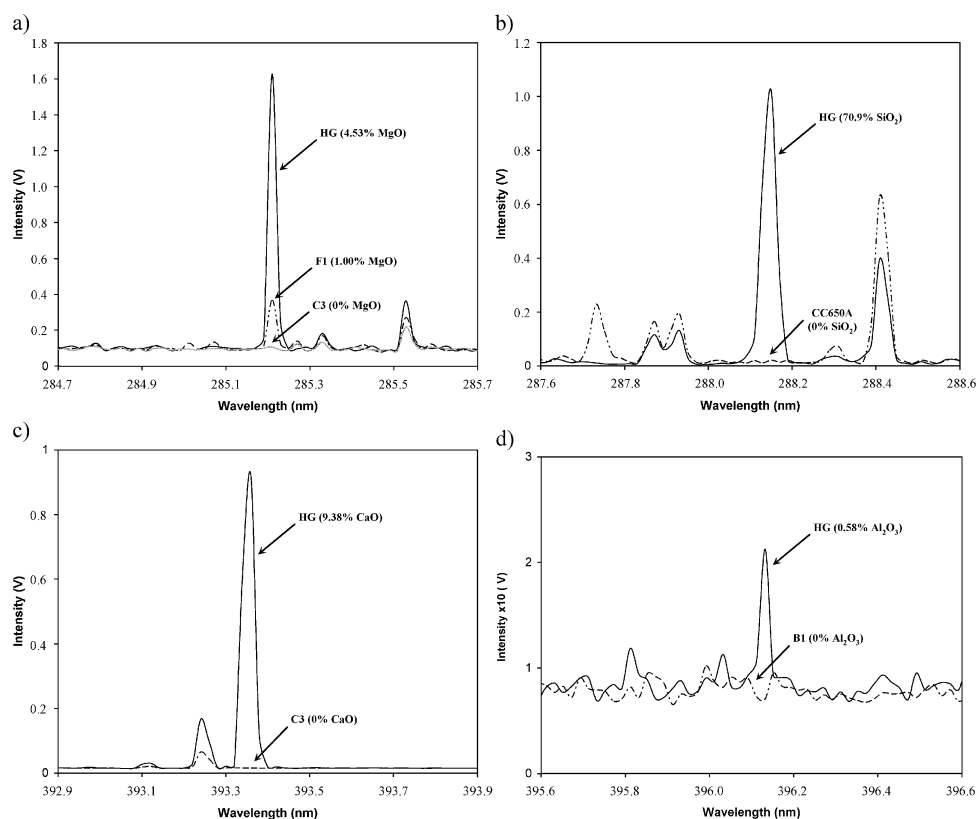
Fig. 3 Rf-GD-OES line profile scans obtained with the JY 5000RF instrument at 30 W of forward power. Si and Ca were detected with the polychromator, while Al and Mg were measured with the monochromator. (a) Mg(I) 285.21 nm. (b) Si(I) 288.15 nm. (c) Ca(II) 393.36 nm. (d) Al(I) 396.16 nm.

known in each standard and the calibration curves must be plotted according to the following function:

$$(I_x/I_{IS}) = K_x \times (C_x/C_{IS}) \qquad (2)$$

where I_x is the intensity of the analyte x, I_{IS} the intensity of the internal standard, C_x the concentration of the analyte x and C_{IS} the concentration of the internal standard. Even if the measured intensities are highly sputtering rate dependent, the use of this equation eliminates the dependency assuming that for homogeneous materials both the analyte and reference element sputter at the same rate.[31] If the concentration of the IS is not known, all elements contained in a given sample must be analyzed (or at least the amount of non-analyzed elements must be known). Thus, the absolute concentrations can be calculated by a sum normalization to 100% and the IS element is calculated as the difference 100% − sum (all analytes):

$$C_{IS} = (100 - C_{na}) \Big/ \left(1 + \sum_x Y_x\right) \qquad (3)$$

where C_{na} is the concentration of non-analyzed elements and Y_x are the relative concentrations (C_x/C_{IS}) obtained from the calibration curves of each analyte. Subsequently, it is possible to employ the calculated concentration of the internal standard element to deduce the absolute concentration of each element (i.e., by multiplying the relative concentration by C_{IS}).
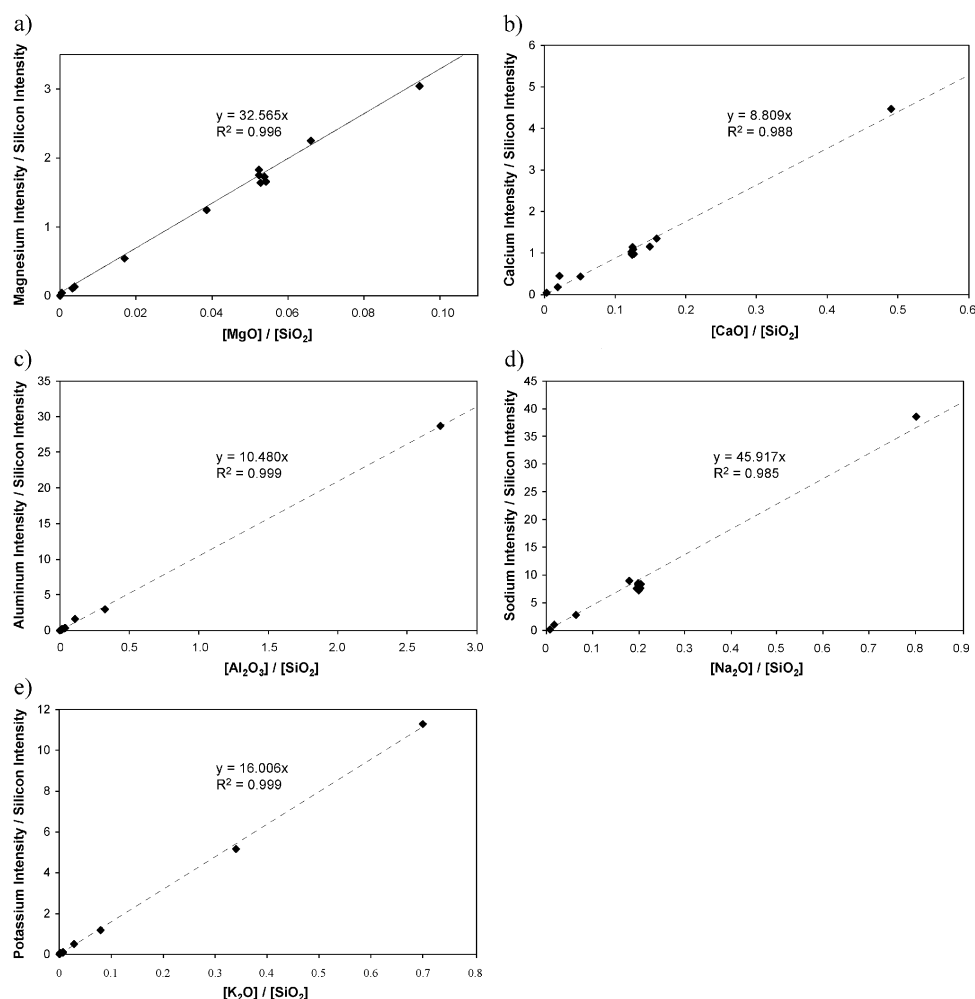
In this work, Si was selected as IS because it is always present in glass samples, generally as the major matrix element. For the evaluation of the proposed methodology,

calibration curves including all the selected calibration standard glasses, given in Table 1, were performed by applying eqn (2). As the selected glasses have different thickness and matrix compositions, the forward power employed was varied in the 25–35 W range depending on the glass thickness (25 W for B1 and F1, 30 W for A2, C3, N-621, SG-1, SG-3, SG-4, SG-5, SG-6, SG-7, SG-8 and SG-9, and 35 W for SG-2). On the other hand, two additional calibration glasses (D1 and E1) were eventually discarded from the calibration curves due to their high thickness (6.0 and 6.5 mm thick, respectively), which gave rise to very low emission intensities (i.e., the precisions of I_x/I_{IS} were too poor).

Fig. 4 shows the calibration curves obtained for Mg, Ca, Al, Na and K using the Si-based internal standard calibration methodology suggested by eqn (2). In all cases, instead of plotting elemental concentrations as is usually done, the concentrations of the different elements have been expressed as their corresponding oxides. As can be seen in Fig. 4, the data fit rather well to straight lines in all cases. Therefore, it is possible to conclude that this IS calibration methodology corrects for changes due to the forward power differences in the interval assayed (from 25 to 35 W), the insulator thickness (as can be seen in Table 1, standards from 2.8 to 5.8 mm were used in the same calibration curves) and the sample matrix.

On the other hand, the calibration curve obtained at 130.21 nm for oxygen using the calibration standards given in Table 1 does not fit a linear function (see Fig. 5) and therefore its use

a)

$y = 32.565x$
$R^2 = 0.996$

[MgO] / [SiO$_2$]

Magnesium Intensity / Silicon Intensity

b)

$y = 8.809x$
$R^2 = 0.988$

[CaO] / [SiO$_2$]

Calcium Intensity / Silicon Intensity

c)

$y = 10.480x$
$R^2 = 0.999$

[Al$_2$O$_3$] / [SiO$_2$]

Aluminum Intensity / Silicon Intensity

d)

$y = 45.917x$
$R^2 = 0.985$

[Na$_2$O] / [SiO$_2$]

Sodium Intensity / Silicon Intensity

e)

$y = 16.006x$
$R^2 = 0.999$

[K$_2$O] / [SiO$_2$]

Potassium Intensity / Silicon Intensity

Fig. 4 Calibration graphs obtained with rf-GD-OES at the selected operating conditions (450 Pa and 25–35 W forward power) using the internal standard calibration methodology. (a) Mg(I) 285.21 nm. (b) Ca(II) 393.36 nm. (c) Al(I) 396.16 nm. (d) Na(I) 589.59 nm. (e) K(I) 766.49 nm.

was discarded for oxygen quantification. This lack of linearity can be attributed to problems such as poor instrument sensitivity, formation of molecular oxygen through plasma reactions, presence of air bubbles in the samples, *etc*.

Oxygen Intensity / Silicon Intensity

[Oxygen] / [Silicon]
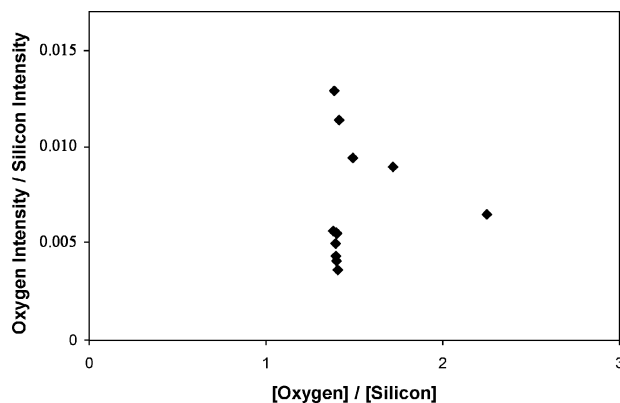
Fig. 5 Calibration curve obtained at the 130.21 nm oxygen(I) emission line by rf-GD-OES at the selected operating conditions (450 Pa of pressure and 25–35 W forward power) using the proposed internal standard calibration methodology.

Quantification of glass samples

The IS calibration methodology was applied to the quantification by rf-GD-OES of the major components (SiO$_2$, Na$_2$O, CaO, MgO, Al$_2$O$_3$ and K$_2$O) in two glass samples, 2.8 and 3.0 mm thick. In order to avoid the use of the oxygen calibration curve, the normalisation to 100% was carried out by summing the oxide concentrations instead of individual elements. Therefore, this proposed quantification methodology would allow the determination of the glass components without measuring the emission intensities of the oxygen atomic line.

The concentration of non-analyzed trace elements (less than 0.5% as total) in the two selected samples was taken into account in the sum normalisation (0.015% TiO$_2$, 0.092% Fe$_2$O$_3$ and 0.33% SO$_3$ for HG glass sample, and 0.018% TiO$_2$, 0.043% Fe$_2$O$_3$, 0.056% As$_2$O$_3$ and 0.28% SO$_3$ for N-620 glass). In both cases, the forward power used for the sputtering of samples was 25 W. The quantitative results obtained are collected in Table 2 for both glass specimens tested and, as can be seen, the concentrations are in good agreement with the accepted values. Therefore, these results demonstrate that the use of silicon as an internal stan-

Table 2 Quantitative analyses of two homogeneous glasses (concentrations are expressed as mass percentages). Uncertainties correspond to the standard deviation of three independent replicates

	Known composition		RF-GD-OES	
	HG[a]	N-620[b]	HG[a]	N-620[b]
SiO_2	70.9 ± 0.2	72.1 ± 0.08	70.7 ± 2.0	71.9 ± 1.2
Na_2O	13.9 ± 0.1	14.4 ± 0.06	14.2 ± 1.3	14.3 ± 0.5
CaO	9.38 ± 0.05	7.11 ± 0.05	9.24 ± 1.0	6.90 ± 0.5
MgO	4.53 ± 0.04	3.69 ± 0.05	4.21 ± 0.1	4.18 ± 0.09
Al_2O_3	0.58 ± 0.02	1.80 ± 0.03	0.75 ± 0.2	1.90 ± 0.1
K_2O	0.28 ± 0.01	0.41 ± 0.03	0.38 ± 0.1	0.37 ± 0.04

[a] The sample HG was 2.8 mm thick (Saint-Gobain Cristalería S.A, Avilés, Spain). [b] The sample N-620 was 3.0 mm thick (NIST, Gaithersburg, MD).

dard seems effective in normalizing the discharge changes occurring in the bulk analysis of non-conductive materials by rf-GD-OES.

Conclusions

The rf-GD-OES technique has been evaluated for quantitative bulk analysis of silicate glasses by resorting to an internal standard quantification methodology. Results demonstrated that the use of Si as internal standard is robust enough to obtain linear calibration graphs using standards of varied composition and different thickness. So far, the methodology has just been investigated for main components of glasses. The low sputtering rates obtained with non-conductors constitutes a serious impediment to achieving good sensitivity in the analysis of traces.

The changes in the rf forward power employed (in the interval from 25 to 35 W) were also effectively corrected by such an approach. Therefore, this quantification methodology can be of interest for the analysis of a large variety of samples and particular case applications (e.g., it could be applied using low forward power in order to avoid the cracking of fragile samples, or high forward power in order to achieve proper sputtering rates in thick samples). Besides, it has to be stressed that the methodology proposed here is comparatively simple and fast. In fact, the measurement of sputtering rates of all the calibration standards, as required using previously reported procedures for glasses with rf-GD-OES,[10] is not needed.

Finally, it should be highlighted that in comparison with the XRF technique, which provides accurate and precise results and is commonly established in the glass industries, the methodology proposed here offers interesting perspectives, since no sample preparation is required for quantitative analysis and it offers a bigger application field when considering that, in principle, it allows the analysis of light elements and the in-depth profiling of layered samples.

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