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Energy-dispersive x-ray fluorescence analysis of modern coloured glasses from Marinha Grande (Portugal)

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The elemental composition (K, Ca, Ti, Cr, Mn, Fe, Co, Ni, Cu, Zn, As, Se, Sr, Ba, Nd and Pb) of modern coloured glasses was obtained by energy-dispersive x-ray fluorescence (EDXRF) spectrometry. This non-destructive technique is frequently used in the analysis of historical glass objects. Two reference glasses were also measured to assess the overall accuracy of the EDXRF method. Reference and unknown glasses were analysed without any preparation. The coloured glass samples studied belong to the Glass Museum of Marinha Grande and were chosen from two distinct collections, which were characterized by the different concentrations of some elements (K, Ti, Cr, Mn, Fe, Ba and Pb). The determined major elements allowed the identification of two raw materials used in glass manufacture, sand and lime. Multivariate statistical analysis, namely principal component extraction, simplified the identification of some of the colouring chemical elements, associating them with the different colours of the glass objects. Copyright © 2003 John Wiley & Sons, Ltd.

INTRODUCTION

The manufacture of coloured glasses has been known for several millennia.[1] Throughout the years, colour was always one of the most interesting and fascinating themes in glass production. Colour in glasses is due to the addition of polyvalent transition metals (e.g. Cr, Co and Cu) or rare earth ions with unpaired electrons in 3d or 4f orbitals, respectively. Other sources of colour include the formation of metal (e.g. Cu, Ag and Au) or semiconductor colloidal particles[2] [e.g. CdS, CdSe and $Cd_{(x+y)}Se_yS_x$]. In spite of the extensive knowledge in glass science, even at the present time the only way of obtaining the exact colour and tonality required is through experimental trials. In these experiments both the technological features of glass manufacture (melting and redox conditions) and the use of different compounds (e.g. colorants, decolorants and opacifiers), as well as their relative concentrations, are studied.

The glass objects analysed in this work were two experimental sample sets of coloured glass from a well-known glass factory, the former 'Fábrica de Vidros da Marinha Grande', which started manufacturing in 1748. Since the beginning of the 20th century it was under direct administration of the Government, changing its name in 1954 to 'Fábrica Escola Irmão Stephens', having in mind to act also as a school for glass masters. The factory was also famous for manufacturing lead glass. Marinha Grande (Portugal) is a city with one of the highest concentrations of glass industries in Europe.

Both glass sets were manufactured from the 1980s to the beginning of the 1990s. The factory closed in 1994 and these samples now belong to the Glass Museum of Marinha Grande. It is known that the types of coloured glasses were sodium silicate based and that among the raw materials two types of silica sand were used. One was from Rio Maior (Portugal) containing iron and alumina and the other, more pure (98.8% silica), was imported from Belgium.

In the elemental analysis of historical glass objects, one must use non-destructive methods. In our study, although dealing with modern glasses, the objects are fairly valuable from a historical point of view. The selected technique, energy-dispersive x-ray fluorescence (EDXRF) spectrometry, has recently been used in this type of studies.[3,4] This non-destructive technique is capable of quantifying chemical elements from Na to U, within the concentration range from parts per million to percentages. EDXRF is also a multielemental technique with short measuring times, which allows the relatively fast analysis of each sample.

In this work, we intended to identify the major and minor chemical elements present in these coloured glass samples. The major elements allow the classification of the type of glassware with which we are dealing and possibly the identification of the original raw materials used in the glass

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manufacture. A comparison of the elemental compositions from both sets can give us some hints about the differences of the manufacturing processes. Furthermore, an important issue is to check if EDXRF is able to identify the different colouring elements, i.e. major or minor chemical elements or combination of chemical elements responsible for the different colours of the analysed glasses.

EXPERIMENTAL

Measuring conditions

Samples were analysed with an EDXRF spectrometer at the Instrumentation Unit of the International Atomic Energy Agency's Laboratories at Seibersdorf (Austria). The spectrometer was equipped with a water-cooled 3 kW molybdenum x-ray tube as the primary excitation source and a Canberra-based spectrometric track. The continuum radiation from the x-ray tube excited the molybdenum secondary target and the fluorescent K lines obtained were used to excite the elements present in a sample. This experimental set-up provided a reduced background, which improved the peak to background ratio and consequently improved the detection limit. Samples were measured at 55 kV and a current between 10 and 40 mA, depending on the dead time obtained. The measurements were made under vacuum even though the low-Z elements could not be accurately determined owing to the characteristics of the excitation beam. The angles between the sample plane and the incident and emerging beams were both 45°. Fluorescent lines from the sample were measured with a cryogenically cooled Si(Li) detector, with a resolution of 180 eV at 5.9 keV (Mn Kα line).

All samples and standards were analysed without any previous preparation. Spectra were collected by a multi-channel analyser and net peak intensities were calculated with Quantitative X-ray Analysis System (QXAS)[5] software. Elemental concentrations were obtained with the Scatman Fundamental Parameters program[6].

Statistical analysis of the elemental concentrations obtained was carried out with Statistica software (v.5.1).

Fundamental parameters calibration

The fundamental parameters method[7] requires a calibration with only one standard sample. This calibration consists in the calculation of the instrumental constant (G), which is related to the geometric arrangement and is given theoretically by the equation

$$G = \frac{d\Omega_1 d\Omega_2}{4\pi \cos\theta_1} \tag{1}$$

where θ_1 = incident angle relative to the normal of the sample surface, Ω_1 = incident solid angle of x-ray beam and Ω_2 = emerging solid angle of x-ray beam. However for higher accuracy, the use of more standards is recommended and several foils of pure chemical elements (Ti, Cr, Fe, Co, Ni, Cu, Zn and Ge) were analysed. Two pressed pellets, a carbonate (SrCO$_3$) and an oxide (Y$_2$O$_3$), were also measured.
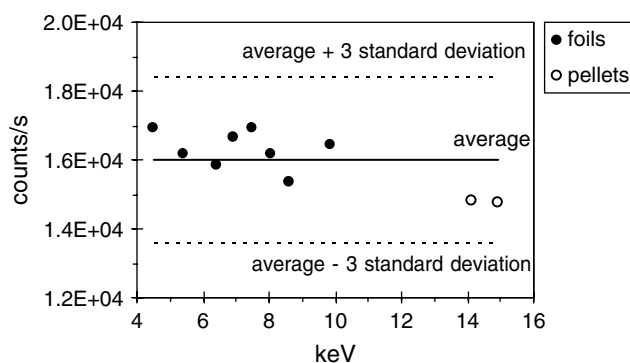

Figure 1. Instrumental constants (G) obtained experimentally for foils of pure chemical elements (Ti, Cr, Fe, Co, Ni, Cu, Zn and Ge) and pressed pellets (SrCO$_3$ and Y$_2$O$_3$).

The instrumental constants obtained from the measurements of the above-mentioned standards are plotted in Fig. 1.

The values obtained for the pressed pellets were slightly smaller, probably owing to the different structures of the pure element foils and pressed powder pellets. However, they were also included to cover all the energy range of interest (from K to Y Kα lines). The average instrumental constant was $(1.60 \pm 0.08) \times 10^4$ counts s^{-1}.

Sample absorption from the dark matrix was corrected with the coherent and incoherent scattered radiation obtained from the Mo secondary target. The incoherent scatter dominates for the low-Z elements whereas the coherent scatter dominates for the high-Z elements. Therefore, the instrumental constant for incoherent scattering (G_{inc}) is more reliable when obtained from the measurement of low-Z standards, while the instrumental constant for coherent scattering (G_{coh}) is more reliable for high-Z standards. In the present work, the instrumental constants for scattering (G_{inc} and G_{coh}) were determined from measurements of standard foils (Al, Ti, Fe, Co, Zn and Ge) and pellets (SiO$_2$ and S) (Fig. 2). The average values for coherent and incoherent scattered radiation were $(8.1 \pm 0.4) \times 10^4$ and $(4.8 \pm 0.2) \times 10^4$ counts s^{-1}, respectively.

The relative standard deviations for the three calculated average instrumental calibration constants were close to 5%.
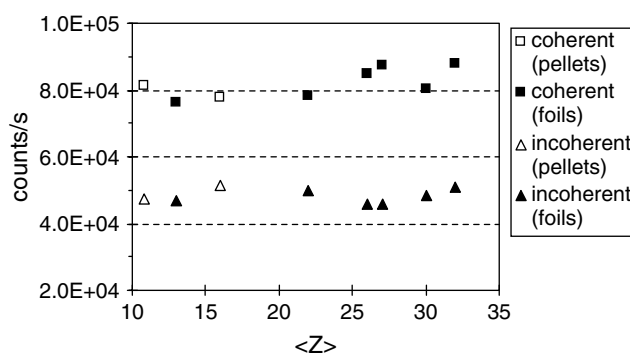

Figure 2. Instrumental scatter constants (G_{coh} and G_{inc}) obtained experimentally for foils of pure chemical elements (Al, Ti, Fe, Co, Zn and Ge) and pellets (SiO$_2$ and S).

Table 1. Recommended and obtained concentrations (%) for reference soda-lime glass (glass B) and potash glass with high lime content (glass D)

Element	Reference glass B		Reference glass D	
	Recommended[8]	Obtained	Recommended[8]	Obtained
K	0.83	0.89	9.4	10.6
Ca	6.1	6.9	10.6	11.5
Ti	0.053	0.077	0.23	0.29
Mn	0.19	0.24	0.43	0.52
Fe	0.24	0.30	0.36	0.41
Co	0.036	0.038	0.018	0.013
Ni	0.078	0.091	0.039	0.040
Cu	2.1	3.2	0.30	0.35
Zn	0.15	0.20	0.080	0.088
Sr	0.016	0.020	0.048	0.060
Pb	0.57	0.46	0.19[a]	0.20

[a] Theoretical value.

Reference glasses

The accuracy of the overall method was tested by the analysis of two reference glasses, provided by Dr Robert H. Brill of the Corning Museum of Glass (New York). One was a soda-lime glass and the second a potash glass with high lime content.[8] These glasses were measured and the net peak intensities calculated, using exactly the same procedure as used for the unknown samples. Throughout the quantification the reference glasses were considered as unknown samples, i.e. no assumption was made about the composition of the dark matrix and no form of normalization was applied. The results obtained for reference glasses B and D (Table 1) differ from the expected values by less than 25%, which is typical for the XRF analysis without any previous sample preparation.[9]

Coloured glasses

The unknown coloured glasses included two sets of large and small disks. The first collection consisted of eight samples 8 cm in diameter and 1 cm thick, and the second set 14 small disks 3 cm in diameter and 0.5 cm thick. These glass samples can roughly be grouped into five different colours (nine blue, six purple, five green, one brown and one pale yellow). Within each colour group several tones and opacities were observed, but no additional separation was made.

Since all glasses were analysed without any sample preparation, particular care was taken in order to choose the region for the analysis, which should be as flat and smooth as possible. As modern glasses were analysed, no surface corrosion was detected in the samples. Since at least one side of all the objects was flat, or had a sufficiently large flat region (the x-ray beam on measurement plane was $\sim$1 cm^2), the XRF analysis of these coloured glasses was fairly simple.

RESULTS

Elemental concentrations (%) obtained by EDXRF for Marinha Grande glass samples are displayed in Tables 2 and 3.

From the results obtained only Si, Ca, Fe, As, Sr and Pb are present in all samples (Si was identified in all glasses, but it was not quantified owing to the difficulties in correction for the enhancement effect caused by the excitation of Si by Mo secondary target L-line series). The glass matrix should be composed of sand (mainly SiO_2 with Fe_2O_3 as an impurity), lime (CaO) and soda (Na was not identified owing to the low efficiency of the experimental setup in the detection of low-Z elements, but it is known that soda was used in the glass production). Strontium concentrations are always below 0.020% and its source is probably the sand used in the glass manufacture[10] (the mean Sr concentration in sandstone

Table 2. Concentrations (%) obtained by EDXRF for modern coloured glasses of the first collection (large disks)

Element	I blue	II purple	III purple	IV purple	V blue	VI blue	VII blue	VIII blue
K	0.16	0.43	0.11	n.d.[a]	n.d.	n.d.	n.d.	n.d.
Ca	5.1	4.4	4.5	4.7	5.6	4.9	4.5	4.6
Ti	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Cr	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Mn	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Fe	0.017	<0.01	0.011	0.019	0.025	0.019	0.026	0.018
Co	n.d.	n.d.	n.d.	n.d.	n.d.	0.19	0.17	n.d.
Ni	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	0.013
Cu	0.87	n.d.	n.d.	<0.01	0.92	n.d.	n.d.	0.014
Zn	<0.01	n.d.	n.d.	<0.01	0.012	n.d.	<0.01	<0.01
As	0.73	0.66	0.74	0.78	0.83	0.73	0.72	0.80
Se	n.d.	0.036	<0.01	0.046	n.d.	n.d.	n.d.	n.d.
Sr	<0.01	0.012	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
Ba	n.d.	0.4	0.08	n.d.	n.d.	n.d.	n.d.	n.d.
Nd	n.d.	2.1	1.0	n.d.	n.d.	n.d.	n.d.	n.d.
Pb	<0.01	0.011	<0.01	0.016	<0.01	<0.01	<0.01	0.013

[a] n.d., not detected.

Table 3. Concentrations (%) obtained by EDXRF for modern coloured glasses of the second collection (small disks)

Element	IX blue	X blue	XI blue	XII blue	XIII green	XIV green	XV green	XVI green	XVII purple	XVIII brown	XIX purple	XX purple	XXI yellow	XXII green
K	0.59	0.46	1.2	0.64	0.38	0.82	0.51	0.42	0.25	0.33	0.47	0.78	n.d.[a]	0.96
Ca	4.4	4.2	4.1	4.3	4.3	4.5	4.4	4.8	4.8	3.8	4.5	4.5	5.5	4.5
Ti	0.20	0.062	n.d.	0.11	0.15	0.12	0.088	0.18	0.041	n.d.	n.d.	n.d.	n.d.	0.12
Cr	0.11	0.10	n.d.	0.087	0.12	0.13	0.15	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	0.12
Mn	0.057	0.022	0.045	0.078	0.039	0.047	0.051	0.037	0.021	4.3	1.6	n.d.	n.d.	0.098
Fe	0.17	0.041	0.060	0.13	0.13	0.10	0.13	0.24	0.081	3.6	0.073	0.042	0.024	0.17
Co	0.047	0.042	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	0.011	n.d.	n.d.	n.d.	n.d.
Ni	n.d.	n.d.	0.029	n.d.	n.d.	n.d.	n.d.	0.016	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Cu	0.18	0.15	0.030	0.29	0.26	0.045	0.15	0.018	<0.01	0.018	<0.01	n.d.	n.d.	0.044
Zn	0.031	<0.01	0.011	0.024	0.015	<0.01	0.030	<0.01	0.010	<0.01	<0.01	0.019	0.019	0.019
As	0.51	0.83	0.56	0.52	0.60	0.54	0.63	0.60	0.30	0.32	0.62	0.39	<0.01	0.39
Se	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	0.048	n.d.	n.d.	n.d.	n.d.	n.d.
Sr	<0.01	<0.01	0.020	0.012	<0.01	0.015	0.011	<0.01	<0.01	0.015	<0.01	0.019	<0.01	0.014
Ba	0.2	n.d.	1.0	0.7	0.5	0.5	0.7	0.1	0.3	0.4	0.3	1.5	n.d.	0.5
Nd	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	1.4	n.d.	n.d.
Pb	0.079	0.10	0.69	0.26	0.12	0.38	0.32	0.048	0.072	0.14	0.091	0.86	0.029	0.22

[a] n.d., not detected.

is 0.032%).[11] The analysed glasses also have a low content of Pb (<0.86%), an element usually added to the glass matrix to decrease the melting temperature and/or to increase the solubility of the colouring compounds.[12] However, in our samples the Pb content may be due to careless selection of glass cullets, which are usually added to the raw materials. As mentioned above, the factory production also included lead crystal objects.

A comparison of the elemental concentrations obtained for both glass sets revealed that in the first collection (Table 2) the number of detected elements was less, i.e. elements such as K, Ti, Cr, Mn and Ba were identified only in a small number of samples or were not present at all. A more impure sand was certainly used in the manufacturing of the glasses from the second collection, responsible also for the higher Fe content in those samples (Table 3).

Furthermore, elements such as Co, Ni, Se and Nd were detected only in a small number of samples in both sets, which might indicate that they do not belong to the major glass raw materials and were probably added for a specific purpose.

Statistical analysis

Owing to the large number of the results obtained in this work (16 elements × 22 samples), we applied factor analysis, as often used in this type of study.[13–15] The extraction of principal components from the normalized data (concentrations marked as not detected and <0.01% were replaced by 0.005%), allow us to reduce the number of variables (elements) by grouping them into principal components. To simplify the interpretation of the data, the number of extracted principal components should be as small as possible. However, they should also account for the maximum variance of the initial data. The extracted components were rotated, also to simplify the interpretation of the results.

In the present work, the extracted five principal components account for 77% of the total variance and their loadings after varimax rotation[16] are displayed in Table 4.

Factor 1 is related to Pb, Sr, Ba, K and Ni (in decreasing order of factor loadings), and factor 2 with Cr, Ti and Zn. Owing to the lower content of most of these elements in the glass samples from the first set, these first two principal components allows us to distinguish between the two sets of glasses analysed (Fig. 3).

Owing to the absence or low concentrations of Cr, Ti and Zn (factor 2), samples XVII, XVIII, XIX and XXI from the second set are closer to the first collection of glasses.

Table 4. Factor loadings obtained by principal component analysis applied to the elemental concentrations of coloured glasses and variance explained by each individual factor

| Element	Factor 1	Factor 2	Factor 3	Factor 4	Factor 5
K	0.84	−0.41	−0.03	0.09	0.00
Ca	−0.52	0.32	0.52	0.37	0.27
Ti	0.06	−0.87	0.05	0.01	0.12
Cr	0.11	−0.92	0.05	0.02	0.11
Mn	0.01	0.15	−0.96	0.08	0.06
Fe	0.03	0.08	−0.96	0.11	0.07
Co	−0.25	0.01	0.01	−0.62	−0.02
Ni	0.62	0.27	0.10	−0.29	0.28
Cu	−0.24	0.13	0.28	0.33	0.67
Zn	0.17	−0.65	0.15	0.49	0.10
As	−0.14	0.19	0.35	−0.63	0.19
Se	−0.23	0.21	0.12	0.13	−0.69
Sr	0.88	−0.04	−0.23	0.22	−0.11
Ba	0.86	−0.13	−0.03	0.33	−0.19
Nd	0.25	0.29	0.18	0.17	−0.65
Pb	0.91	−0.08	0.04	0.21	−0.02
Variance (%)	30	17	13	9	8
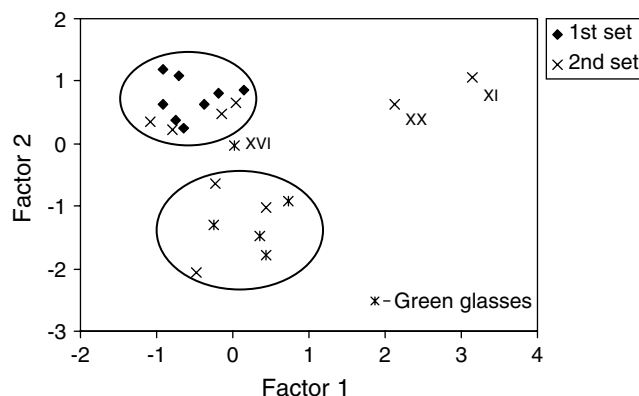
Figure 3. Factor 1 scores versus factor 2 scores obtained by principal components analysis applied to the elemental concentrations of coloured glasses.

Green glasses proved to have higher Cr contents (lower factor 2 scores), which is the green colour element of modern glasses. Glass XVI is an exception, since it is the only green sample without Cr. However, this is also one of a few samples in which Ni was identified.

Samples XI and XX show higher percentages of Ba and Pb (high factor 1 scores) and therefore in Fig. 3 they are separated from the others.

Mn and Fe are correlated in factor 3 (Fig. 4). These elements are both present at high concentrations in sample XVIII (brown) and Mn is also present at a high concentration in sample XIX (purple). The contribution of each element is strongly dependent on its concentration and also on the relative concentrations of other colouring elements and modifiers also present in the glass. The addition of manganese oxide (MnO_2) to the glass will produce purple–brown or shades of violet, depending on the other modifiers present.[17] Concerning the brown sample XVIII, owing to its high Fe content (3.6%) this glass should be darker. However, the relatively low colour intensity observed for this sample is due to a high concentration of Mn (4.3%), which was added as a decolorizing agent to promote the oxidation of Fe^{2+} to Fe^{3+} (the optical absorption due to the ferric
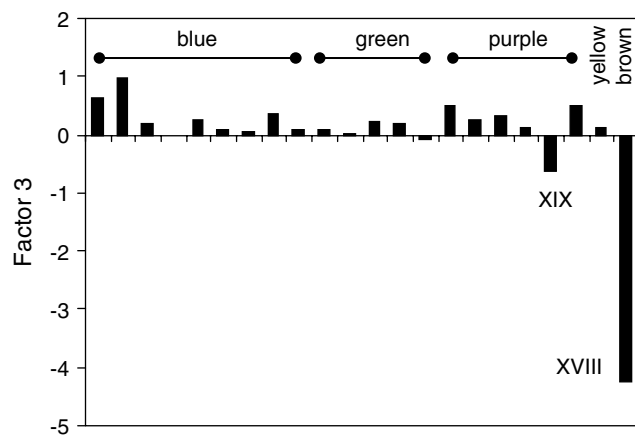
species is about 15 times less intense than to the reduced ferrous state[2]). Manganese should be responsible for the purple colour of sample XIX as it is the usual colour element in historical purple glasses[18] (note that in this sample the concentration of Fe is very low).

Concentrations of As and Co control factor 4 (negatively correlated with these elements), while factor 5 is positively related with Cu and negatively with Se and Nd. A plot of the scores of these two factors associates them with some particular colours (Fig. 5).

The majority of the blue glasses analysed in this study are characterized by the presence of Co (low factor 4 scores) and/or high Cu content (high factor 5 scores). These samples constitute the copper blues (samples I, V and XII) and the dark or cobalt blues (samples VI and VII). Sometimes, Cu is also present in cobalt blues (samples IX and X). In this work, some other copper blue glasses appear between these two main groups, due to the presence of Ni (samples VIII and XI). A more careful examination of sample VIII, by optical absorption spectroscopy, showed that the blue colour is due to cobalt. As it is known that cobalt is a very effective colouring agent, even a very low concentration, in this case not detected by EDXRF, is responsible for the colour obtained.

In silicate glasses there is equilibrium between the two iron oxide states (Fe^{2+}, blue colour; Fe^{3+}, yellow) and a wide range of tonalities will be provided by this mixture of blue and yellow colours, depending on the more or less oxidizing conditions in the furnace and the oxidizing or reducing agents used. Therefore, in certain glasses the difference between blue and green colours cannot be explained only by the elemental compositions (e.g. blue sample XI and green sample XVI).

The purple glasses are clearly distinguished by the presence of Se and/or Nd (low factor 5 scores). The exception is sample XIX where, as mentioned above, the purple colour can be attributed to the high Mn content (1.6%).

In the pale yellow glass (sample XXI), the only colouring element present is Fe and the low colour intensity is due to its small concentration (0.024%). Mn was not detected, indicating that no MnO_2 was added to the batch as a decolorizing agent.

Figure 4. Factor 3 scores obtained by principal components analysis applied to the elemental concentrations of coloured glasses.
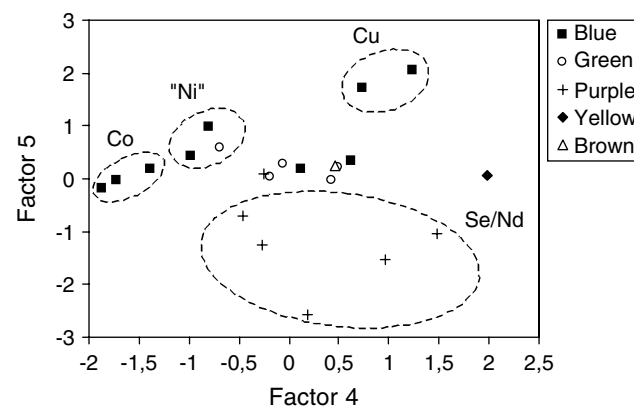

Figure 5. Factor 4 scores versus factor 5 scores obtained by principal components analysis applied to the elemental concentrations of coloured glasses.

The second set has higher concentrations of Pb and Ba. No explanation was found for this observation except that a careless choice of cullet as raw material was made, as mentioned earlier.

CONCLUSIONS

EDXRF was found to be a very powerful tool in the non-destructive analysis of valuable glass samples, which need not undergo any kind of preparation or surface treatment. The results of EDXRF measurements on the two collections of modern coloured glasses from Marinha Grande revealed the use of sand (mainly SiO_2 and Fe_2O_3 as an impurity) and lime (CaO) as the major glass raw materials.

Some elements (K, Ti, Cr, Mn, Fe, Ba and Pb) can be used to distinguish between the two glass collections. The lower content or even the absence of these elements in the samples belonging to the first set is probably due to the use of superior raw materials in the glass production (e.g. use of more pure sand imported from Belgium). Based on the elemental concentrations obtained, four samples from the second set (samples XVII, XVIII, XIX and XXI) seem to be similar to those in the first collection.

All glasses from the second set contain higher percentages of Pb. Nevertheless, even in those samples the concentration is relatively low and the presence of Pb is probably due to careless choice of cullet added to the raw materials.

The statistical analysis of the EDXRF results based on principal components extraction simplified both the interpretation and presentation of the results. Green glasses have a higher Cr content, even though this element is also present in some blue samples of the second collection, certainly added to obtain different tonalities.

Based on the results obtained, the blue glasses were divided in two main groups: Co blues and Cu blues. The first group is sometimes characterized by a combination of Co and Cu and in the second group some of the glasses also include Ni.

Some of the blue and green colours are due to different $FeO-Fe_2O_3$ equilibria in the glasses and so in certain glasses these colours cannot be distinguished only by the elemental compositions.

In the majority of the purple glasses the colour could be related to the elements Se and Nd. However, in one of these samples the purple colour was due to the high Mn content, which is a common association observed in historical coloured glasses.

The brown glass analysed contained high Fe and Mn contents. In the pale yellow glass the only colouring element present is Fe (at a low concentration), responsible for its low colour intensity.

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