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*Abstract*

This paper presents the potential of Raman spectroscopy, a non-destructive technique which can be applied *in situ*, for the analyses of glass and its alteration. Recent analytical developments are summarised for different glass compositions and practical examples are given. The paper describes how to extract compositional information from the glass, first based on the spectrum profile to rapidly distinguish alkali silicate from alkaline-earth alkali silicate and lead alkali silicate glass, then using the spectral decomposition and correlations to extract quantitative data. For alkali silicate glasses, which are most prone to alteration, the spectral characteristics of the different alteration processes (selective leaching or dissolution) in the Raman spectra of the altered glass are described. These new developments have greatly widened the potential of the technique and supplement well its previously documented ability to measure the thickness of the altered layer and identify crystalline deposits.

*Résumé*

Cet article présente le potentiel de la spectroscopie de Raman, une technique non destructive qui peut être appliquée *in situ* pour les analyses du verre et de ses altérations. Les développements analytiques récents ont été récapitulés pour chaque différente composition du verre et des exemples pratiques sont donnés. L'article décrit comment extraire du verre les informations sur sa composition, d'abord basé sur le profil du spectre pour distinguer rapidement le silicate alcalin du silicate alcalin de terre alcaline et du verre de silicate plombo-alcalin, ensuite en utilisant la décomposition du spectre et les corrélations pour extraire les données quantitatives. Pour les verres de silicate alcalin, qui sont les plus sujets à l'altération, sont décrites les caractéristiques spectrales des différents processus d'altération (infiltration sélective ou dissolution) dans les spectres de Raman sur les verres altérés. Ces nouveaux développements ont grandement élargi le potentiel de la technique et complètent bien sa capacité documentée précédemment, à mesurer l'épaisseur d'une couche altérée et identifier les dépôts cristallins.

## Raman spectrometry, a non-destructive solution to the study of glass and its alteration

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**Introduction**

Alkali silicate has always been the main man-made glass composition. However, other compositions can be found for historic glasses, in particular lead silicate, including so-called 'crystal', as well as calcium alkali silicate and calcium aluminium silicate glass. The composition influences the visual appearance of the glass and many of its physical properties, as well as controlling its stability towards alteration.

The problem of glass alteration is widespread in museum collections. For remedial and preventive conservation of glass objects, knowledge about their stability as well as the thickness and structure of the altered surface compared to the bulk is essential. This information is generally gained after sampling the glass, an approach which is unacceptable for most historic objects. For that reason interest in the development of non-destructive techniques for glass analysis has been growing. Among those available, Raman spectroscopy is the most complete, as it can provide information on the glass composition, structure and alteration.

*Synopsis*

Este documento presenta la capacidad de la espectroscopia de Raman, una técnica no destructiva que puede aplicarse *in situ* para el análisis del vidrio y su alteración. Se resumen desarrollos analíticos recientes para distintas composiciones de vidrio y se ofrecen ejemplos prácticos. El documento describe cómo obtener información de la composición del vidrio, basado en primer lugar en el perfil espectral para distinguir rápidamente los silicatos álcali de los silicatos álcali alcalinotérreos y cristal de silicato álcali de plomo, y empleando después la descomposición y correlaciones espectrales para obtener datos cuantitativos. Se describen las características espectrales de los diferentes procesos de alteración (lixiviación o disolución selectiva) en los espectros de Raman de cristales alterados, para los cristales de silicato álcali, con más tendencia a alterarse. Estos nuevos progresos han ampliado en gran medida la capacidad de la técnica y complementan esa capacidad previamente documentada para calcular el grosor de la capa alterada e identificar depósitos cristalinos.

This paper presents new analytical methodology developed for the study of glass and its alteration using Raman spectrometry, focussing on recent developments and some practical examples. It aims to inform conservators and conservation scientists of the potentials and limitations of the technique for the analyses of glasses based on different studies.

**Experimental***Samples*

Glasses from different origins and compositional groups were examined, including:

- Alkali silicate glasses: (i) historic glasses from the National Museums of Scotland (NMS) collections, mainly soda silicate, a few potash silicate and calcium alkali silicate glasses. Part of this glass collection suffered from alteration accelerated by the environmental and storage conditions (Robinet 2006c); (ii) Soda glass replicas aged artificially in different pollution environments (Robinet 2007); (iii) deteriorated smalt pigments (cobalt coloured potash glass) from 16th–18th century oil paintings; (iv) a fragment of a Roman archaeological glass block from the shipwreck of the Embiez exposed to sea water for 1800 years; and (v) stained glass windows from Saint-Denis cathedral in France.
- Lead silicate glasses: (i) Palissy lead glazed ceramics deteriorated in archaeological contexts; and (ii) ancient and modern crystal glasses.
- Calcium silicate glass rich in iron and aluminium: (i) glassy archaeological slags produced as by-products of the iron smelting process from Glinet, France, dating from the 16th century.

Only selected examples from each group are presented, together with their elemental compositions obtained by either electron microprobe (EPMA), SEM-EDS or PIXE (Table 1).

*Raman spectroscopy*

Raman spectra were recorded on a LabRam Infinity micro-spectrometer (Jobin-Yvon-Horiba, France) equipped with a Peltier-cooled CCD. The 532 nm line of a frequency doubled Nd:YAG laser was used as the exciting radiation and the power of illumination at the sample surface ranged between 5 and 9 mW. The backscattered light was collected through the 100× objective of an Olympus microscope. A confocal hole of 200 μm, or 70 μm for altered layer, was used, so the size of the analysed laser spot was respectively ~9 or 3 μm diameter at the waist and ~6 or 4 μm along the vertical axis.

Table 1. Elemental composition of glass measured by EPMA<sup>a</sup>, SEM-EDS<sup>b</sup>, PIXE<sup>c</sup>

Object	Ref	Mol%												
		SiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>	Na <sub>2</sub> O	K <sub>2</sub> O	CaO	MgO	PbO	CuO	MnO	FeO/ Fe <sub>2</sub> O <sub>3</sub>	P <sub>2</sub> O <sub>5</sub>	As <sub>2</sub> O <sub>3</sub>	NiO
<sup>a</sup> Islamic glass 19th c	1895.270	65.2	1.0	0.2	3.4	26.54	2.8	–	–	0.3	0.4	–	–	–
<sup>a</sup> Islamic glass 19th c	1975.145	67.7	0.6	13.9	1.3	10.95	5.0	–	–	–	0.4	–	–	–
<sup>a</sup> Venetian glass 18th c	1956.1233	75.3	0.4	0.7	11.3	9.84	2.8	–	–	0.2	0.1	–	–	–
<sup>a</sup> Roman glass	Embiez	72.7	1.1	18.8	0.2	5.65	0.8	–	–	–	0.3	–	–	–
<sup>b</sup> Smalt	2720	74.9	0.3	0.5	11.4	–	–	–	–	–	1.0	–	5.0	0.7 6.2
<sup>c</sup> Stained glass	yellow ancient	53.9	1.1	0.9	10.5	22.27	6.4	–	–	0.6	0.3	3.5	0.5	–
<sup>c</sup> Stained glass	green modern	72.2	0.7	9.5	1.4	13.65	0.3	–	1.3	–	0.5	–	0.6	–
<sup>a</sup> Napoleonic crystal	A.1998.492	78.4	0.1	0.7	8.1	–	–	12.5	–	–	0.1	–	–	–
<sup>c</sup> Palissy's ceramic glaze	EP 2278	56.2	8.0	–	0.2	1.55	1.4	27.5	3.3	0.2	0.8	–	0.4	–
<sup>a</sup> Glass slag	GL 07 16	62.7	3.7	0.2	1.0	22.87	1.6	–	–	0.6	7.1	–	–	–

The Raman spectra were recorded between 150 and 1350  $\text{cm}^{-1}$  for the silicate structure and between 2800 and 3800  $\text{cm}^{-1}$  for the OH vibration, with a spectral resolution of 2–3  $\text{cm}^{-1}$ . The acquisition time ranged between 1 to 10 min depending on the quality of the spectrum required and the presence of a fluorescence background. The baseline was subtracted from the spectra by Labspec software using the line type correction. Great care should be taken when subtracting the baseline as it may affect the information extracted from the spectra (Robinet *in press*). The corrected Raman spectra were curve-fitted with Gaussian functions using Origin microcal software.

### Analytical methodology

Raman spectrometry is a non-destructive vibrational technique which provides information about the chemical structure *in situ*, on a micron scale (Figure 1). The technique relies on the Raman scattering produced by the interaction of focussed laser light with a sample. Raman spectrometry has the potential to examine transparent materials at various depths using the confocal system of the spectrometer (Robinet 2005).

For glass, the Raman spectrum is associated with the vibration of the Si-O network, with mostly bending vibrations in the region 300–600  $\text{cm}^{-1}$  and stretching vibrations in the region 900–1200  $\text{cm}^{-1}$  (Furukawa 1981, McMillan 1984). The vibration of these silicates, and therefore the Raman spectra profiles, are modified by the type and concentration of cations in the structure. Raman spectra of glasses generally display broad peaks owing to the distribution of local environments in the structure arising from the non-crystalline nature of these materials. Since there is no unique glass composition, identification cannot be made by comparison with the spectrum of a reference, as for crystalline materials. For these reasons the interpretation of the Raman spectra of glasses is not straightforward.

The recent developments presented herein aim to facilitate the interpretation and the extraction of information from the Raman spectra of glasses. The potential of the technique was widened by the complementary use of elemental analytical techniques. From this combination and the use of a large range of glass samples, correlations were established for each compositional group between the spectral components, obtained through decomposition of the Raman spectra, and the elemental composition in the glass.

### Elemental composition

#### *Raman spectrum profile*

The examination of a large range of glasses of different compositions revealed that some information can be gained simply on the basis of the spectra profiles. Thus, we can distinguish rapidly between alkali silicate, alkaline-earth alkali silicate (mostly calcium), and lead alkali silicate glasses (Figure 2). The differences are explained by the differences in the type and concentration of cations present in the glass.

High concentration of alkali is generally marked in the spectrum by the presence of an intense peak centred at 1100  $\text{cm}^{-1}$ , resulting from the Si-O stretching vibration of silicate species with one non-bridging oxygen (1 NBO). Since alkalis are preferentially coordinated to these silicate species, the peak at 1100  $\text{cm}^{-1}$  dominates at high alkali content. In contrast, doubly charged cations, such as alkaline-earth ( $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ ) or lead cations, are preferentially coordinated to silicate species with 2 NBOs. The peaks associated with the vibration of these species appear around 950–1050  $\text{cm}^{-1}$  (Furukawa 1981, McMillan 1984). For these reasons, the spectra of glasses containing high alkali and low calcium will differ from those with high alkaline-earth or high lead content. This effect is useful, for example, in distinguishing the two main compositions encountered in historic stained glass windows – glasses with high calcium and high potassium versus those with high soda and low calcium (Figure 3). Better

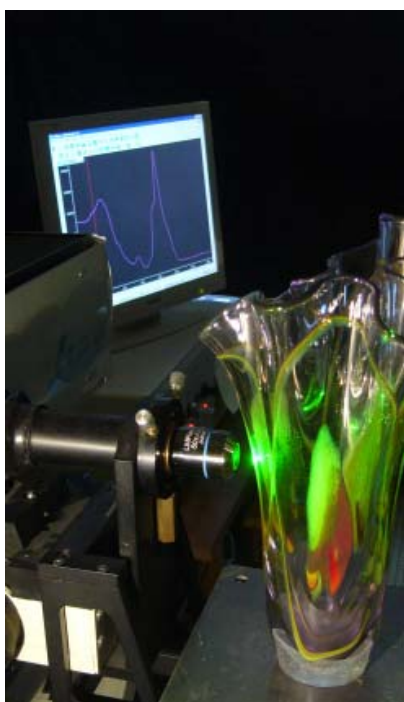


Figure 1. *In situ* Raman measurement on glass

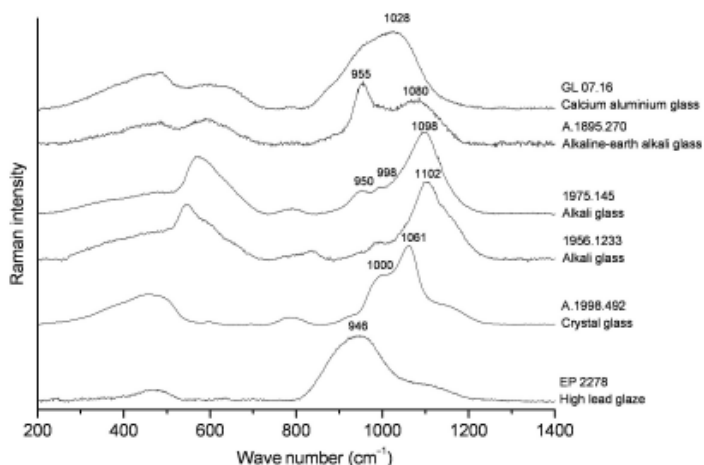


Figure 2. Comparison of Raman spectra of glass from different compositional groups

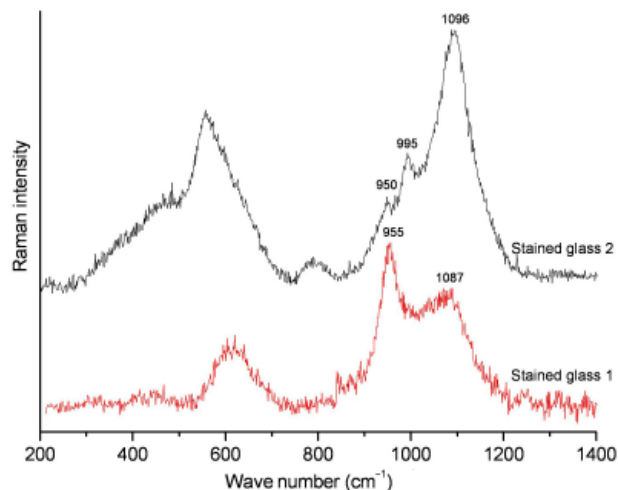


Figure 3. Raman spectra of stained glass from the cathedral of Saint-Denis

knowledge of the recipes used in historic stained glass may help in the future to correlate these spectra directly to a historical period or a restoration phase. However, because potassium and sodium – both alkali ions – are similar chemically, these ions affect the glass structure in a similar way. Therefore it is not possible to distinguish potash (1956, 1233) from soda glasses (1975, 145) by Raman spectroscopy as in Figure 2. When mostly poly-charged cations and little or no alkali is present in the glass, the stretching band is very broad without a characteristic profile. Although the stretching band of calcium silicate glass slags and high lead silicate glazes are centred at different frequencies (1050 and 1000  $\text{cm}^{-1}$  respectively), it is not possible to associate these spectral differences with certainty to their composition (Figure 2). Work is in progress to examine the structure of these glasses and interpret their Raman spectra.

#### *Spectral decomposition and correlations*

To extract further information from the Raman spectra of glasses, it is essential to correlate the subtle changes in the spectra with the elemental composition. For this reason, spectral decomposition is used to separate the different vibrational components of a spectrum. Because there are always a large number of possibilities to decompose a spectrum, it was necessary to find a simple and uniform method that would allow comparison among any Raman spectra. Therefore we developed a unique decomposition model for each compositional group which could be applied to any spectrum within that group. Details of these methods are presented elsewhere for alkali silicate glasses (Robinet 2006a) and lead alkali silicate glasses (Robinet *in press*) and will be published subsequently for calcium silicate glasses. An example of spectral decomposition of an alkali silicate glass is presented in Figure 4. Details about the assignment of the different components are given in Robinet 2006a.

Correlations could be established between the spectral components and the elemental compositions which allowed to link the spectral region to the selected elements in the glass. As a result, it is now possible to extract quantitative compositional information from the Raman spectra. Thus, in alkali silicate glasses the silica content can be estimated from the position of the intense peak around 550  $\text{cm}^{-1}$  and the total cation content from the peak areas ratio  $A_{950}/A_{1040}$ , both of which contribute to the general stability of the glass. The correlation between the position of the intense peak around 550  $\text{cm}^{-1}$  ( $B_{550}$ ) and the silica content is presented in Figure 5. It has been noted that alteration increases rapidly for glasses with a silica content below 66 mol% (El-Shamy 1973), consequently this correlation may help rapidly identify these unstable glasses. In lead silicate glasses, we can determine the lead content from the position of the intense peak around 1070  $\text{cm}^{-1}$ , and the

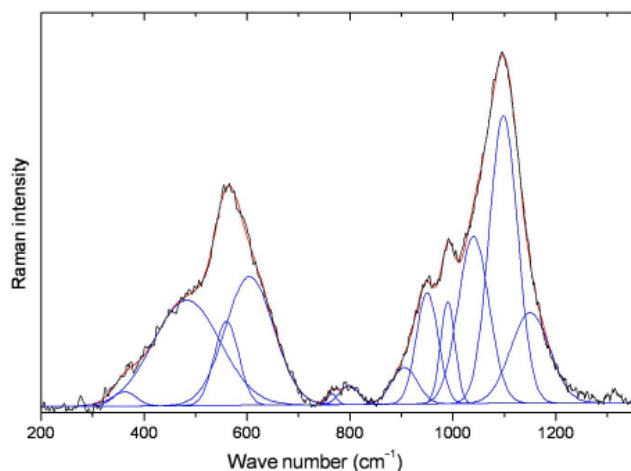


Figure 4. Spectral decomposition of an alkali silicate glass

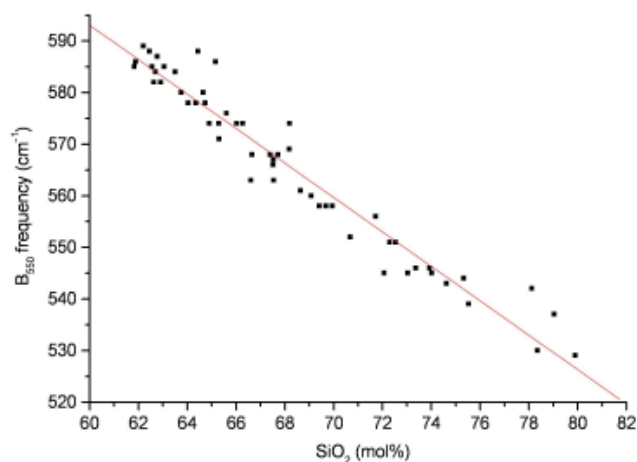


Figure 5. Correlation between the position of the  $B_{530}$  summit and the silica content for alkali silicate glass

alkali + alkaline-earth content and silica content from the area ratios of the peaks at  $1100$  and  $1150\text{ cm}^{-1}$  over the stretching band, respectively. In the case of calcium silicate glass slags, band intensity variations with the composition are observed in the spectra around  $600\text{ cm}^{-1}$  and  $950\text{ cm}^{-1}$  (Figure 6). The initial results suggest that these spectral modifications are linked to the calcium and iron content, respectively.

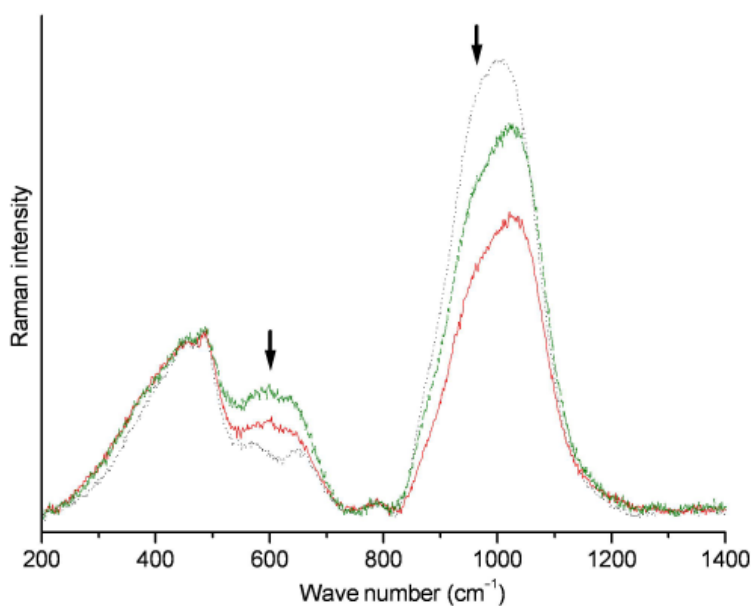


Figure 6. Spectral variations observed in the Raman spectra of calcium silicate glass slags

### Glass alteration

The main factors affecting the alteration of a glass are its composition and environmental conditions, in particular the presence of water/humidity and pollutants. Alteration will first affect glasses with the most unstable compositions, that is glass with low silica, high alkali and low stabilisers, such as calcium or lead.

In the presence of water, different reactions may take place, including ion-exchange or leaching (causing depletion of alkali, the most mobile ions) and hydration, hydrolysis, or dissolution of the silicate network. In acidic environments selective leaching of alkali dominates while at high pH the dissolution process predominates (Clark 1979, Newton and Davison 1989). The alteration leads to the formation of a modified highly hydrated layer at the glass surface, the thickness of which may vary depending on the glass

composition, environmental corrosiveness, time of exposure and other parameters. Because this hydrated layer is sensitive to RH and temperature fluctuations, cracks may develop and the object may become very fragile. In this situation sampling of the object is often prohibited and only non-destructive techniques are acceptable.

### *Spectral characteristics*

Raman spectrometry proved perfectly adapted to the examination of the modification of the glass structure induced by alteration, providing that an altered layer with a minimum thickness of 2  $\mu\text{m}$  is present (Robinet 2006b). Study of the glass replicas aged artificially in different environments revealed characteristic changes in the Raman spectra, as well as in the visual appearance of the glass surface. These modifications could be linked to the two known alteration processes – leaching or dissolution. Details of this study and the interpretation of these modifications are presented in Robinet 2007, and a description of the main features follows:

- The selective leaching of alkali in a glass is revealed in the spectra by the decrease or disappearance of the intense peak at  $1100\text{ cm}^{-1}$  associated with the vibration of species with 1 NBO mostly coordinated with alkali. After exposure to an acidic environment, where the leaching reaction is maintained, the glass retains visually its transparency and only develops fine cracks. However as soon as it is exposed to a drier environment, the modified layer dehydrates and develops large cracks and scales.
- The dissolution reaction, which involves the breakage of the Si-O bonds, is more complex to characterise by Raman spectroscopy. Because the glass structure is completely destroyed, the Raman signal produced by the remaining network is very weak; consequently the use of a long acquisition time with a small confocal hole to avoid interference from the bulk glass is essential. Following exposure to a very humid and therefore rapidly alkaline environment, the modified layer displays a new peak around  $670\text{ cm}^{-1}$  in its spectrum. The structural origin for this has not yet been determined. We believe this peak is characteristic of the dissolution reaction which dominates at high pH. In addition, if the modified layer containing all the dissolved elements (known as the gel layer) remains on the glass surface and is not diluted in solution, it polymerises to form a new amorphous material (mostly dependent on changes in RH). Visually the modified layer develops iridescence due to the presence of one or more micrometric layers. The layer(s) may become opaque, often white, due to the crystallisation of salts, such as carbonates or sulfates, within the gel which are formed after reaction with air. The gel may also incorporate new elements from the external environment (particles/ions from the air, ground or water) which may modify the colour and structure of this layer.
- The hydration of the glass is observed in the spectra by the presence of a broad band centred around  $3400\text{ cm}^{-1}$ . This band corresponds to the superimposition of several components associated with the vibration of O-H bonds from molecular water below  $3500\text{ cm}^{-1}$  and from silanols, Si-OH, above  $3500\text{ cm}^{-1}$ .
- Finally, Raman spectroscopy can be used to identify the crystalline deposits on the glass, such as carbonates, sulfates, formates, etc., providing information about the possible cause of the alteration.

### *Application to historic and archaeological glasses*

The spectral characteristics defined for each alteration process were used to interpret the alteration of alkali glass exposed to very different environments.

The alteration affecting the NMS collections was caused by the combination of an unstable glass composition, fluctuating RH, and a high concentration of organic pollutants (Robinet 2006c). White crystalline deposits and thick modified layers developed, generally combined with cracking of the surface. The

spectral modification observed in all the altered glasses from the NMS collection was associated with the leaching of alkali and the hydration of the structure, which suggested alteration due to an acidic environment (Robinet 2006b). The crystalline deposits were identified by Raman spectroscopy as sodium formates, confirming that formic acid was responsible for the accelerated alteration (Robinet 2004).

With smalt pigments present in oil paintings, the alteration causes discoloration of the strong blue particles. The Raman spectrum profile of the bulk confirmed an alkali-rich silicate glass (Figure 7). The decrease of the intense peak around  $1100\text{ cm}^{-1}$  in the spectrum of the altered region indicates that the alkali has been selectively leached out of the glass structure. This result is consistent with previous studies reporting an acidification of the oil with time, causing the alteration of smalt pigments in painting (Spring 2005).

The Roman glass exposed to sea water developed alteration of the glass adjacent to the cracks in the bulk. The Raman spectrum of the bulk is characteristic of an alkali silicate glass (Figure 8), and the correlations for the  $B_{550}$  peak (Figure 5) indicates that it contains around  $73 \pm 1\text{ mol}\% \text{ SiO}_2$ , which is consistent with the measurements made by electron microprobe (Table 1). The Raman spectrum of the altered region (Figure 8) indicates that selective leaching of the alkali has taken place with hydration of the glass. The broad peak at  $660\text{ cm}^{-1}$  in the spectrum of the altered glass is reminiscent of the peak observed in glass exposed to an alkaline environment and, therefore, suggests that a dissolution reaction has also occurred. Sharp peaks in the spectrum indicate the formation of crystalline compounds, with carbonate, based on the peak around  $1079\text{ cm}^{-1}$  and an organic compound, possibly acetate from the peaks at  $933$ ,  $1359$  and  $2946\text{ cm}^{-1}$ . These results provide new information about the glass structure and work is in progress to understand the alteration processes and the structural modifications associated with this environment.

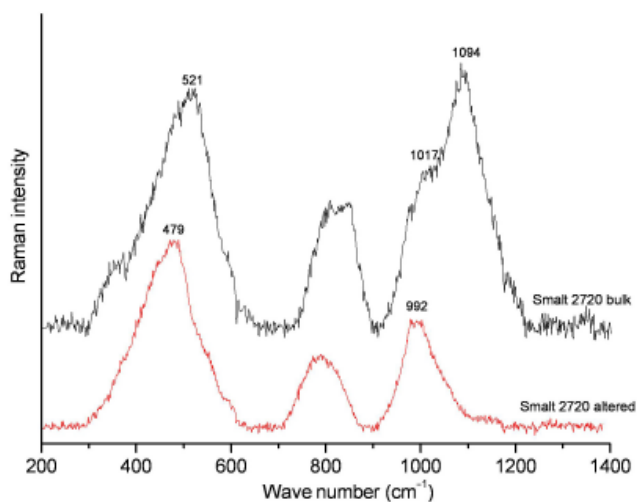


Figure 7. Raman spectra of the bulk and altered regions of smalt pigment in oil painting

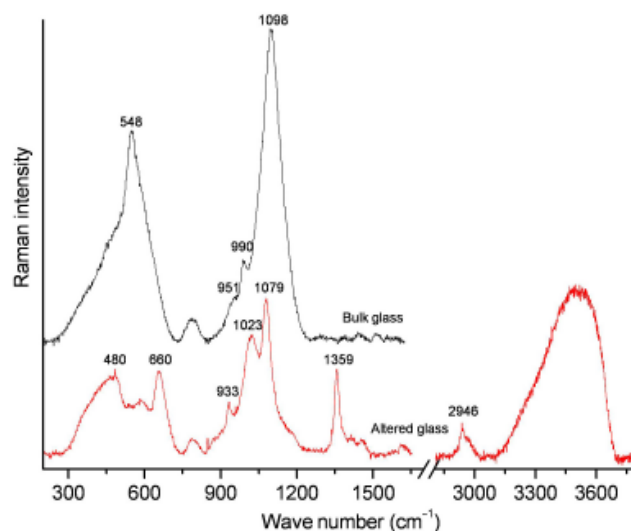


Figure 8. Raman spectra of the bulk and altered regions of Roman glass aged 1800 years in sea water

## Conclusion

The paper demonstrated the potentials and limitations of Raman spectroscopy for the study of glasses and their alteration and summarised recent developments in the analyses of glass spectra. The ability of the technique to non-destructively acquire information about the glass composition, as well as on the type, degree and, perhaps, cause of its alteration will make Raman spectroscopy an essential technique for the study of the condition and the conservation of glasses. Further applications are expected in this field, in particular the use spectral mapping to study the heterogeneity of altered layers.



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