

## PROBLEMS OF ANALYSIS BY FTIR OF CALCIUM SULPHATE-BASED PREPARATORY LAYERS: THE CASE OF A GROUP OF 16TH-CENTURY PORTUGUESE PAINTINGS\*

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*This paper provides a contribution to FTIR analysis of calcium sulphate-based grounds of paintings when a mixture of compounds with different degrees of hydration is present. The study is based on the analysis with that technique, electron microscopy coupled with energy-dispersive X-ray spectrometry and X-ray diffraction of both the grounds of 16th-century Portuguese paintings and reference samples prepared with anhydrite and calcium sulphate dihydrate bound in an animal glue solution. It is shown that the interpretation of the degree of hydration of calcium sulphate ground samples using FTIR cannot be based solely on the study of the hydroxyl bands, as is usual in routine work, but that small deviations of the S–O vibration bands are an important indicator of the presence of anhydrite in the grounds.*

KEYWORDS: FTIR, CALCIUM SULPHATE, GYPSUM, ANHYDRITE, PAINTING, GROUND

### INTRODUCTION

Calcium sulphate mixed with animal glue and applied in one or several superimposed layers remained the more frequently used material in Southern Europe, including Portugal, for the priming of panel paintings, altarpieces and sculptures, from medieval times until the end of the 16th century at least (Gettens and Mrose 1954; Martin *et al.* 1992; Gómez *et al.* 1998; Ribeiro and Santamaria 1999; Ledesma *et al.* 2000; Mendes 2004; Nadolny 2008). In works from the same period executed in Northern Europe, namely in Flanders, chalk—that is, calcium carbonate—was used instead (Billinge *et al.* 1997). Analytical studies on paintings from this period confirm this general trend, although calcium carbonate has sometimes been reported in the ground layers of Southern European—notably Portuguese—paintings, in a single layer or mixed with calcium sulphate (Martin *et al.* 1992; Benquerença *et al.* 2009; Martínez 2010).

In the case of calcium sulphate-based grounds, the degree of hydration of the material is an important feature to consider when investigating the working practices of a given period or region, because it can be present in the form of gypsum—that is, calcium sulphate dihydrate ( $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ )—in the form of calcium sulphate hemihydrate ( $\text{CaSO}_4 \cdot \frac{1}{2}\text{H}_2\text{O}$ ) and in the form of anhydrite ( $\text{CaSO}_4$ ) (Gómez *et al.* 2008; Seufert *et al.* 2009).

Calcium sulphate was regularly mentioned in medieval and later Italian art technical treatises, such as the well-known Cennino Cennini book (Déroche 1991), and in Iberian treatises from the

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16th and 17th centuries (Ventura 1982; Veliz 1986; Cruz and Afonso 2008). According to these sources, *gesso grosso* mixed with animal glue was to be spread in more than one layer over the sized wooden panel, followed by the application of several layers of *gesso sottile*—also known, in the Iberian countries, as *gesso mate* (Ventura 1982). The first material is roasted gypsum, which—due to poor lack of control of the calcination process—was mainly composed of anhydrite, although it may contain more than 50% of gypsum (Martin *et al.* 1992). *Gesso mate* is made by soaking roasted gypsum in an excess of water until dissolution and precipitation of calcium sulphate dihydrate (Woudhuysen-Keller 2008). Although bearing the same chemical composition and crystalline structure as natural gypsum, the processed gypsum has a needle-like morphology that increases its mechanical resistance (Gómez *et al.* 1998).

Fourier transform infrared spectroscopy (FTIR) is commonly used to characterize the grounds of paintings (Federspiel 1995; Souza and Derrick 1995; Genestar 2002). This technique enables us to easily identify the characteristic vibration bands of sulphates or carbonates, while the presence, intensity and shape of the hydroxyl bands due to water can give some information on the degree of hydration of calcium sulphates (Derrick *et al.* 1999; Mandal and Mandal 2002). However, FTIR analytical techniques are limited when a mixture of calcium sulphates with different degrees of hydration is present (Genestar 2002). In fact, strong hydroxyl bands due to the hydrated material would mask the absence or low intensity of these bands in the anhydrous compound, making it difficult to ascertain its presence.

In the context of a scientific programme that aims at identifying the materials and techniques of the workshop of Francisco João, the most productive artist working in the region of Évora, southern Portugal, between 1562 and 1595, the grounds of a group of six panel paintings were investigated with  $\mu$ -FTIR and using scanning electron microscopy coupled with energy-dispersive X-ray spectrometry (SEM–EDX). These techniques were used to characterize the analytical composition, degree of hydration, morphology and number of layers of the grounds. Some of the samples analysed showed medium to strong hydroxyl stretching and bending bands typical of gypsum, but SEM backscattered images (SEM–BSE) of the same samples showed the presence of a coarse material usually associated with *gesso grosso*, a material mainly composed of anhydrite. This led to further analysis of the degree of hydration of the material with X-ray diffraction (XRD). On the basis of studies on the structure and coordination behaviour of water molecules in calcium sulphate (Mandal and Mandal 2002), a deeper analysis of the  $\mu$ -FTIR spectra was performed. For this, reference samples prepared with varying proportions of anhydrite and calcium sulphate dihydrate bound in an animal glue solution were analysed using  $\mu$ -FTIR and XRD, and compared with the results obtained from the original samples.

This paper presents the results of the study of the grounds of this group of Portuguese paintings, with particular focus on the relevance of the water bound to the sulphate ion of calcium sulphate, its influence in the position of the S–O vibration bands in the FTIR spectra, and the possibility of recognizing mixtures of anhydrite and calcium sulphate dihydrate in the grounds of paintings with infrared spectroscopic techniques.

## EXPERIMENTAL

### *Samples*

Paint samples with a maximum surface dimension of 1 mm<sup>2</sup> and a depth of about 500  $\mu$ m were collected from six paintings (Table 1). Part of each sample was embedded in resin and

Table 1 *The paintings analysed*

ID	Painting	Height × width (cm × cm)	Church of origin
P1	<i>Saint Helen and the discovery of the Holy Cross</i>	251.7 × 170.1	Church of S. Helena do Monte Calvário, Évora
P2	<i>Deposition</i>	132.4 × 113.0	Church of S. Helena do Monte Calvário, Évora
P3	<i>Descent from the Cross</i>	123.2 × 50.7	Church of S. Francisco, Évora
P4	<i>Christ carrying the Cross</i>	95.0 × 80.2	Church of S. Miguel de Machede, Évora
P5	<i>Resurrection of Christ</i>	166.2 × 106.2	Church of S. Neutel, Alvito
P6	<i>Descent from the Cross</i>	174.7 × 171.4	Church of S. Maria, Beja

Table 2 *The composition of dry material in the reference samples*

Sample	Gypsum (v/v %)	Anhydrite (v/v %)
G100	100	0
G75A25	75	25
G50A50	50	50
G25A75	25	75
A100	0	100

its cross-section studied with microscopic techniques, while the rest of the same sample, unmounted, was separated in different fragments for  $\mu$ -FTIR and XRD analysis of the ground layer.

Reference samples were prepared with commercial plaster used in building construction, from Sival (Portugal). The material was soaked in water (1 part of plaster to 10 parts of water, v/v) and stirred regularly for 3 weeks to obtain calcium sulphate dihydrate. It was then strained through a cloth and left to dry. Anhydrite was acquired from Kremer Pigmente (Germany). Multiplex panels were given a sizing layer of warm animal glue diluted at 10% in water (w/w). Different proportions of anhydrite and gypsum (v/v) were mixed together as a dry powder (Table 2). These formulations were each bound in the 10% animal glue solution and made into a paste that was spread with a spatula over the sized test panels. The proportion of two parts dry powder and one part animal glue solution (v/v) was used in order to minimize the influence of the organic material in the FTIR spectra, which would happen if the gesso had been applied in a more liquid, glue-rich, suspension.

### *Analytical methods*

The embedded samples were analysed by optical microscopy in reflection mode, under incident light (OM-Vis) and ultraviolet radiation (OM-UV), using an Axioplan polarization microscope (Carl Zeiss) with magnifications up to 1000×. Some of them were also analysed, after deposition of a gold and palladium film, using a variable-pressure scanning electron microscope Hitachi 3700N, operated at 20 kV, in BSE mode and with a Bruker Contact 200 EDS detector.

All reference samples and a minimum of two samples of the ground layer per painting were analysed by  $\mu$ -FTIR. The spectra were obtained using a Nexus 670 FTIR spectrometer coupled to a Nicolet Continuum microscope by Thermo Nicolet, in the range between 4000 and 600  $\text{cm}^{-1}$ , with a KBr beam splitter, an Ever-Glo infrared source and a Nicolet mercury–cadmium–telluride detector (MCT-A) for MIR measurements. The samples were compressed in a Spectra-Tech  $\mu$ Sample Plan microcompression diamond cell and analysed in transmission mode over an area of 100  $\mu\text{m}$  in diameter. For each sample, 256 scans were recorded with a spectral resolution of 4  $\text{cm}^{-1}$ .

XRD analysis was performed on four different samples collected from each reference test panel and on one single original sample of each painting previously analysed by  $\mu$ -FTIR. X-ray diffractograms of the ground layers of non-embedded paint samples were obtained using a Bruker AXS D8 Discover XRD system with a GADDS detector by scanning from 12.4° to 77.5° ( $2\theta$ ), with a step resolution of 0.02° and an acquisition time of 900 s. Cu radiation ( $\lambda = 1.5406 \text{ \AA}$ ) as incident beam, generated by a voltage of 40 kV and a current of 40 mA, and a 1 mm diameter collimator were used.

## RESULTS AND DISCUSSION

### Microscopy

A white ground, with a maximum thickness in excess of 350  $\mu\text{m}$ , was applied on all panels (OM). The detection of Ca and S by SEM–EDX identified calcium sulphate as the main inorganic component of the grounds. SEM–EDX mapping of areas of the ground layers occasionally detected residual amounts of Al, Si and K in P1, P2 and P4, and Mg in P4 and P5. A large particle (60  $\mu\text{m} \times 150 \mu\text{m}$ ) of celestite ( $\text{SrSO}_4$ ), exhibiting a higher density in the SEM–BSE image, was observed in a single sample from P4. This mineral is present in sedimentary rocks such as gypsum deposits and has already been mentioned in the grounds of paintings (Gómez *et al.* 1998). Besides celestite, other minerals such as dolomite, aluminosilicates, calcite or clay are frequently associated with gypsum and could account for the elements detected by EDX analysis.

SEM–BSE images of paint cross-sections revealed the coarse texture of the ground, with particles of different shape and size and the frequent presence of large fibrous rectangular particles, of about 100  $\mu\text{m}$  in width by 230  $\mu\text{m}$  long, that were also clearly visible under OM (Figs 1 and 2). This coarse morphology has been associated with the *gesso grosso* which, in

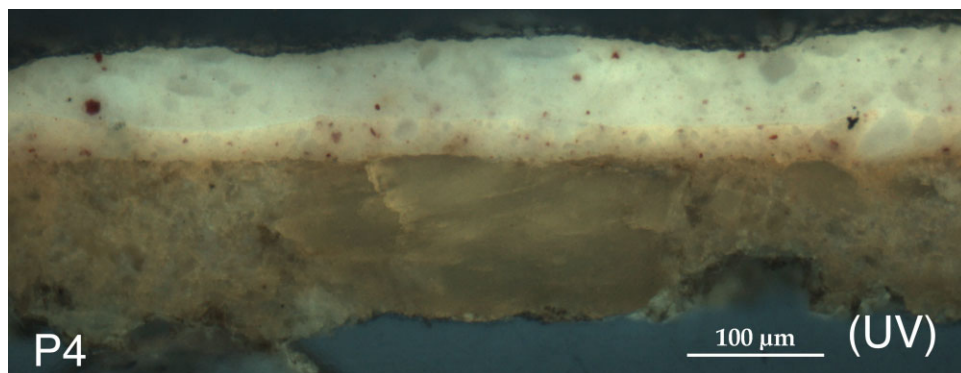


Figure 1 A large fibrous particle visible in a sample from painting P4 (OM–UV).

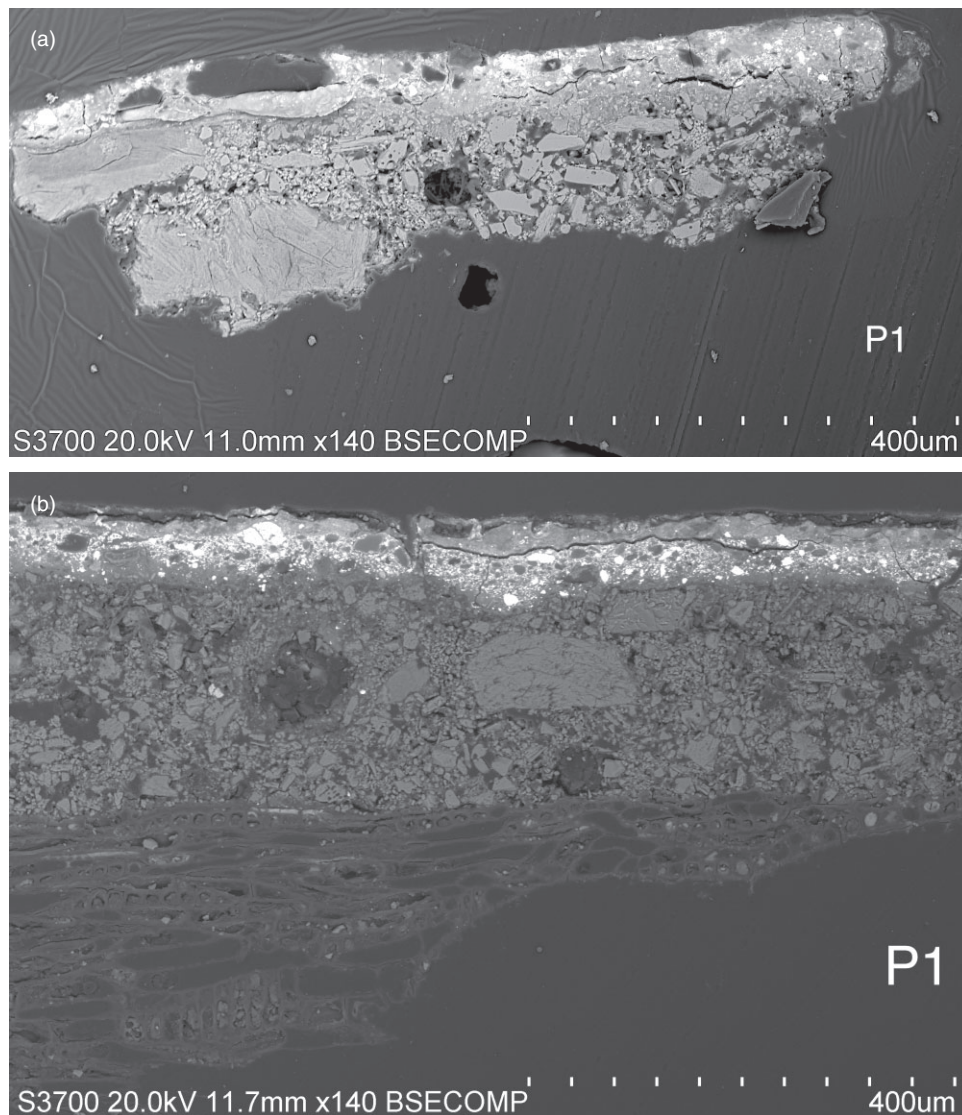


Figure 2 SEM-BSE images of two samples from painting P1, where the heterogeneity of the ground is visible all across the layer.

general, is mainly composed of the soluble anhydrous form of calcium sulphate (Martin *et al.* 1992). The heterogeneity of the ground was the same across the thickness of the layer and no different strata could be distinguished in the SEM-BSE images, suggesting that only one type of material was used (Fig. 2). To avoid erroneous conclusions based on incomplete samples, the absence of more than one stratum was confirmed by the analysis of at least one sample that reached the support, collected from each group of paintings.

*FTIR analysis and its problems*

Regarding organic materials, the FTIR spectra exhibited two absorption bands near  $1650\text{ cm}^{-1}$  and  $1545\text{ cm}^{-1}$  that could be attributed to C=O stretching and N–H bending vibrations, respectively, of the amide groups characteristic of proteins (Derrick *et al.* 1999). The weak amide III absorption band resulting from C–H bending vibrations of the amide groups around  $1460\text{ cm}^{-1}$  was not always visible due to overlapping features of carbonates, present in small quantities in the grounds. Even though the N–H stretching band near  $3350\text{ cm}^{-1}$  typical of proteins could not be resolved due to overlapping spectral features with the calcium sulphate hydroxyl stretching vibrations, the amide II overtone, also known as amide B, was clearly visible in all  $\mu$ -FTIR spectra, creating a weak shoulder around  $3080\text{ cm}^{-1}$  and further confirming the presence of proteins (Meilunas *et al.* 1990; Barth 2007; Manzano *et al.* 2009). According to historical sources and published analytical data on paintings of this period, this proteic material would probably be animal glue.

An absorption carbonyl band around  $1710\text{ cm}^{-1}$  along with two sharp bands around  $2920$ – $2930\text{ cm}^{-1}$  and  $2850\text{ cm}^{-1}$ , due respectively to stretching  $\text{CH}_3$  and  $\text{CH}_2$  vibrations, indicated the presence of free fatty acids formed during the ageing process of oil (Van der Weerd *et al.* 2005; Mazzeo *et al.* 2008). This fatty material probably resulted from the binding medium of the layers applied on top of the ground or from materials used in old restorations that would be prone to impregnate a layer whose porosity, as displayed by SEM–BSE images, is clearly evident.

Regarding inorganic materials, the characteristic vibration bands of sulphates in the range  $1200$ – $1130\text{ cm}^{-1}$  ( $\nu\text{S}=\text{O}$ ),  $673$ – $675\text{ cm}^{-1}$  ( $\delta\text{S}-\text{O}$ ) and between  $1016\text{ cm}^{-1}$  and  $1005\text{ cm}^{-1}$  ( $\nu\text{S}-\text{O}$ ), confirmed the presence of calcium sulphate on all samples (Table 3) (Derrick *et al.* 1999). A weak absorption band between  $876\text{ cm}^{-1}$  and  $890\text{ cm}^{-1}$ , together with a weak double absorption at  $\sim 1410\text{ cm}^{-1}$  and  $\sim 1446\text{ cm}^{-1}$ , was found on samples from all the paintings and could be attributed to the C–O stretching vibrations of carbonates (Derrick *et al.* 1999). These are present in small quantities on the grounds of all the paintings. The band at  $1410\text{ cm}^{-1}$  is typical of calcite, whereas the band at  $1446\text{ cm}^{-1}$  suggests that dolomite is also present (Gunasekaran *et al.* 2006). This result is in agreement with the EDX detection of Mg in paintings P4 and P5. The limited number of samples analysed appears to be responsible for the non-detection of Mg by EDX on the grounds of the other paintings.

The bands centred at  $\sim 3400\text{ cm}^{-1}$ , sometimes exhibiting a shape similar to the gypsum spectrum, with absorptions at  $\sim 3545\text{ cm}^{-1}$ ,  $\sim 3490\text{ cm}^{-1}$ ,  $\sim 3400\text{ cm}^{-1}$  and  $\sim 3240\text{ cm}^{-1}$  (Table 3, Fig. 3), can be assigned to stretching hydroxyl vibrations and denote the hydration of the used materials. The lack of the hydroxyl band near  $3609\text{ cm}^{-1}$  ( $\nu\text{O}-\text{H}$ ), characteristic of calcium sulphate hemihydrate, excluded the presence of this material in the ground samples.

The  $1620\text{ cm}^{-1}$  band ( $\delta\text{O}-\text{H}$ ) relates to strongly held water molecules and is evident in all forms of hydrated calcium sulphate, whereas the  $1680\text{ cm}^{-1}$  band ( $\delta\text{O}-\text{H}$ ) indicates the presence of loosely held water molecules in gypsum and is therefore absent from the hemi- and anhydrous form of calcium sulphate (Mandal and Mandal 2002). This is confirmed by many published spectra of calcium sulphate with different degrees of hydration (Federspiel 1995; Genestar 2002). The bending hydroxyl band located at  $\sim 1620\text{ cm}^{-1}$  was observed on all spectra, except when it was overlapped by the broader envelope caused by the amide I band ( $\sim 1650\text{ cm}^{-1}$ ) derived from the organic binding medium (Fig. 3). Furthermore, a weak  $\sim 1680\text{ cm}^{-1}$  band ( $\delta\text{O}-\text{H}$ ), sometimes appearing in the form of a shoulder in the broader absorption band of amide I, was detected in the grounds of all paintings except for P3 and P4. Different samples collected from the same ground often did not exhibit this band (Table 3 and Fig. 3).

Table 3 The FTIR wavenumbers of the calcium sulphate compounds from the ground samples of the paintings ( $\text{cm}^{-1}$ )

Sample	$\nu\text{S}=\text{O}$	$\delta\text{S}-\text{O}$	$\nu\text{S}-\text{O}$	$\nu\text{OH}$	$\delta\text{OH}$
P1/A	1126 vs	673 vs	1015 sh	3546–3490 ms 3408 s 3237 sh	1684 m 1621 s
P1/B	1147 vs	674 vs	1015 sh	3399 w	–
P2/A	1140 vs	673 vs	1015 sh	3544–3491 mw 3407 mw 3240 sh	1684 sh 1621 mw
P2/B	1132 vs	673 vs	1015 sh	3544–3492 w 3407 w 3244 sh	1621 m
P3/A	1155 vs	674 vs	1015 sh	3398 m	–
P3/B	1161 vs	673 vs	1016 sh	3400 m	–
P4/A	1163 vs	675 vs	1005 m	3411 mw	–
P4/B	1161 vs	673 vs	1016 sh	3531 wsh 3404 w 3253 wsh	– 1622 sh
P5/A	1201 vs	673 vs	1016 sh	3543–3491 m 3406 ms 3244 sh	1685 w 1622 ms
P5/B	1149 vs	673 vs	–	3549–3481 sh 3405 s 3244 sh	1681 wsh 1622 ms
P6/A	1132 vs	674 vs	1014 sh	3544 w 3406 w 3246 sh	1683 w 1621 mw
P6/B	1188 vs	673 vs	1014 sh	3541–3494 m 3408 ms 3246 sh	1685 mw 1622 m

From these results, it appears that the ground of paintings P3 and P4 are solely composed of anhydrite, while the grounds of all other paintings must contain anhydrite and gypsum. Excluding samples from paintings P3 and P4, the similarity between the FTIR spectra of the ground samples and the reference spectrum of gypsum suggests that this is the major constituent of these ground layers (Fig. 3). However, these results seem to contradict the SEM–EDX images, where the presence of *gesso grosso*—that is, mainly anhydrite—is suggested instead. In order to clarify this issue, XRD analysis was performed.

#### XRD analysis

All XRD spectra obtained for painting samples are dominated by anhydrite, as would be expected from the observations done by microscopy (Fig. 4). In all spectra, with the exception of that obtained for sample P3/A, gypsum is present, but the peak at  $3.06 \text{ \AA}$ , the major peak that can be attributed to gypsum, has a much lower intensity than the peak at  $3.50 \text{ \AA}$  due to anhydrite. The ratio between its areas (gypsum/anhydrite; that is, G/A) is lower than 0.05 with the exception of sample P5/B, for which the ratio is 0.3 (Table 4).

On the basis of the relationship between the anhydrite concentration and the ratio of the areas of peaks at  $3.50 \text{ \AA}$  and  $3.06 \text{ \AA}$  (ratio A/G) that was determined with four reference samples

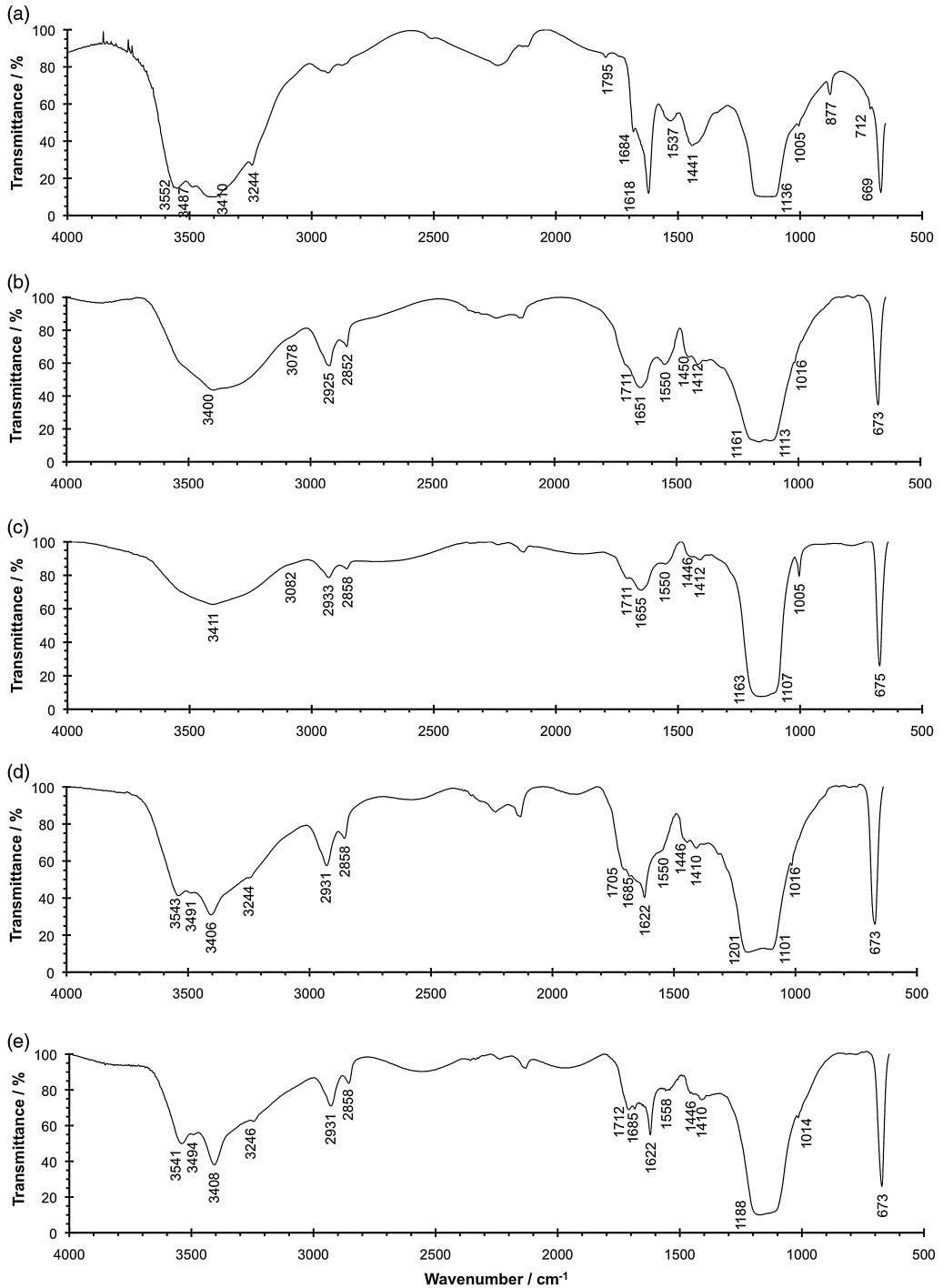


Figure 3 FTIR spectra of (a) gypsum mixed with animal glue and ground samples (b) P3/B, (c) P4/A, (d) P5/A and (e) P6/B.



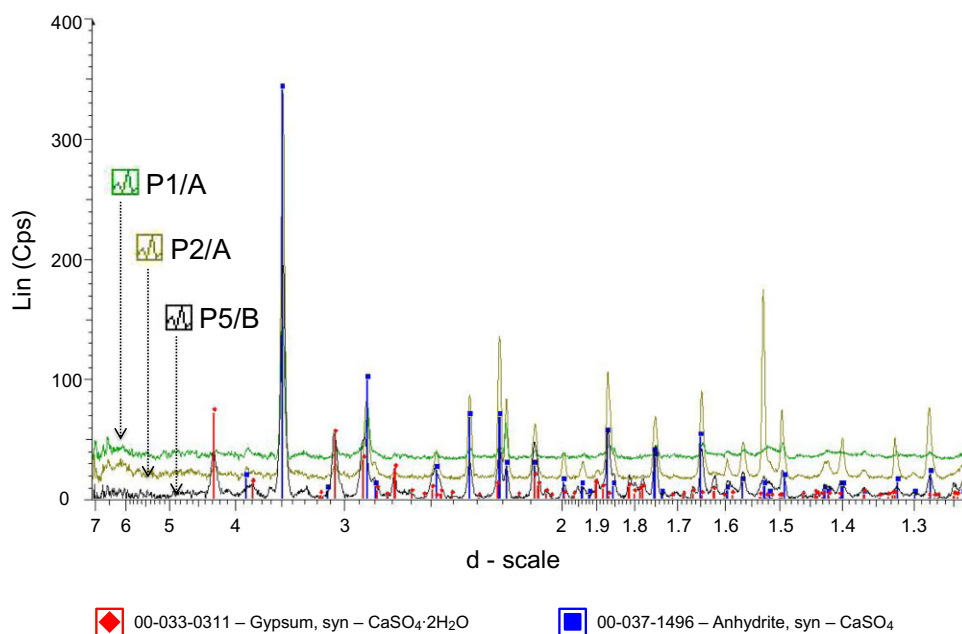


Figure 4 X-ray diffraction patterns of samples P1/A, P2/A and P5/B (see online for a colour version of this figure).

Table 4 The ratio between the areas of the XRD peaks attributed to gypsum (G) and anhydrite (A) at 3.06 and 3.50 Å, respectively, for samples taken from paintings P1–P6

Sample	G/A	A/G
P1/A	0.040	24.8
P2/A	0.028	35.2
P3/A	0.000	
P4/B	0.028	36.2
P5/B	0.305	3.3
P6/A	0.031	32.5

(Fig. 5), it is possible to estimate that sample P5/B is composed of about 43% anhydrite and 57% gypsum, while the other samples are essentially composed of anhydrite.

These results confirm the limits of FTIR in identifying mixtures of calcium sulphate with different degrees of hydration, in particular, when the characteristic vibration bands of gypsum, notably the  $1680\text{ cm}^{-1}$  band ( $\delta\text{O-H}$ ), frequently hidden by amide absorptions, are not visible.

#### FTIR analysis of the reference samples and its implications

Besides calcium sulphate, the dihydrated material produced from Portuguese commercial plaster used in the reference samples also contains calcite, detected through the characteristic absorption bands at  $1795\text{ cm}^{-1}$ ,  $1441\text{ cm}^{-1}$ ,  $877\text{ cm}^{-1}$  and  $712\text{ cm}^{-1}$  (Fig. 3).

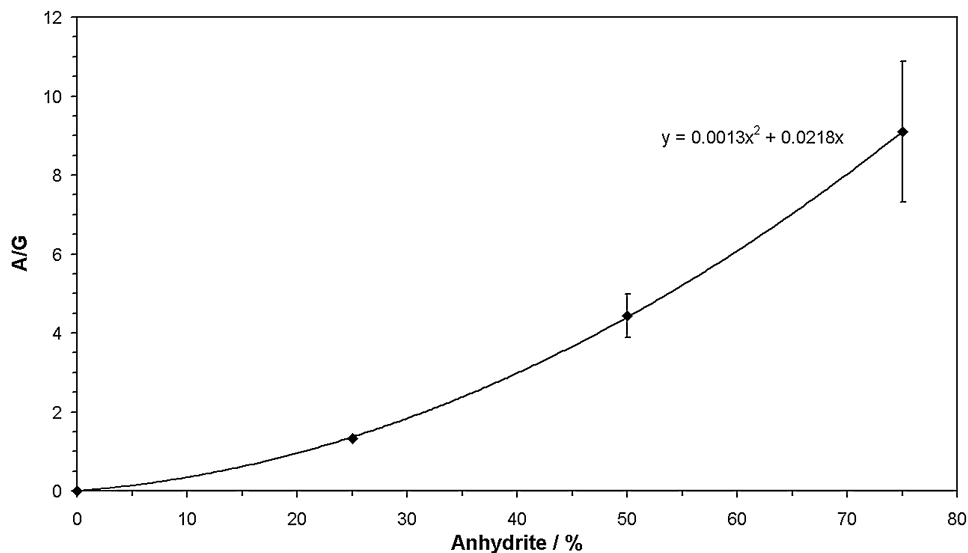


Figure 5 The ratio between the areas of the XRD major peaks attributed to anhydrite and gypsum (A/G) as a function of the volume concentration of anhydrite in the reference samples. For each point, the uncertainty is given by the standard deviation obtained by analysis of four samples.

FTIR analysis clearly showed that the hydroxyl bending and stretching bands remained visible, although with decreasing intensity, as the amount of gypsum was reduced in the mixture (Fig. 6). The presence of anhydrite caused the gradual deviation of the S–O bending and stretching vibrations from  $669\text{ cm}^{-1}$  to  $673\text{ cm}^{-1}$  and from  $1005\text{ cm}^{-1}$  to  $1014\text{ cm}^{-1}$ , respectively (Table 5, Fig. 6). When the mixture contains up to 50% of anhydrite, the S–O stretching vibration appears as a double absorption at  $1005\text{ cm}^{-1}$  and  $1014\text{ cm}^{-1}$ . It took a minimum of 75% of anhydrite in the mixture for the deviation to be complete, with the FTIR spectra showing a single band at  $1014\text{ cm}^{-1}$ .

These deviations can be explained by the collapse of the calcium sulphate structure near the atom of sulphur that occurs when the strongly held water molecules are released during the process of anhydrite formation, when hydrated calcium sulphate is heated above  $350^\circ\text{C}$  (Mandal and Mandal 2002). This causes crystal structure and symmetry modifications that give rise to a deviation in the absorption bands in the FTIR spectrum in sulphur vibrations and not in the hydroxyl region (Mandal and Mandal 2002). The samples taken from the paintings in general show these deviations from the gypsum spectrum. The S–O bending band appears at  $673\text{--}675\text{ cm}^{-1}$  instead of  $669\text{--}670\text{ cm}^{-1}$ , and the S–O stretching band is shifted from  $1005\text{ cm}^{-1}$  to  $1014\text{--}1016\text{ cm}^{-1}$  on all spectra, except for sample P4/A, where it remained at  $1005\text{ cm}^{-1}$  (Table 3, Fig. 3). Considering the spectra obtained for the reference samples (Table 5), the deviations of the S–O bending and stretching bands suggest that the grounds of all paintings were mainly composed of anhydrite and not of gypsum, as indicated by the general shape of the FTIR spectra. The comparison of the FTIR spectra of reference sample G25A75 and original sample P5/A clearly illustrates the correspondence between them (Fig. 6). This result is in agreement with the coarse texture observed in the SEM–BSE images of cross-sections and the XRD spectra. The frequent detection of the  $1680\text{ cm}^{-1}$  band ( $\delta\text{O–H}$ ) and the XRD patterns show that gypsum is also present,

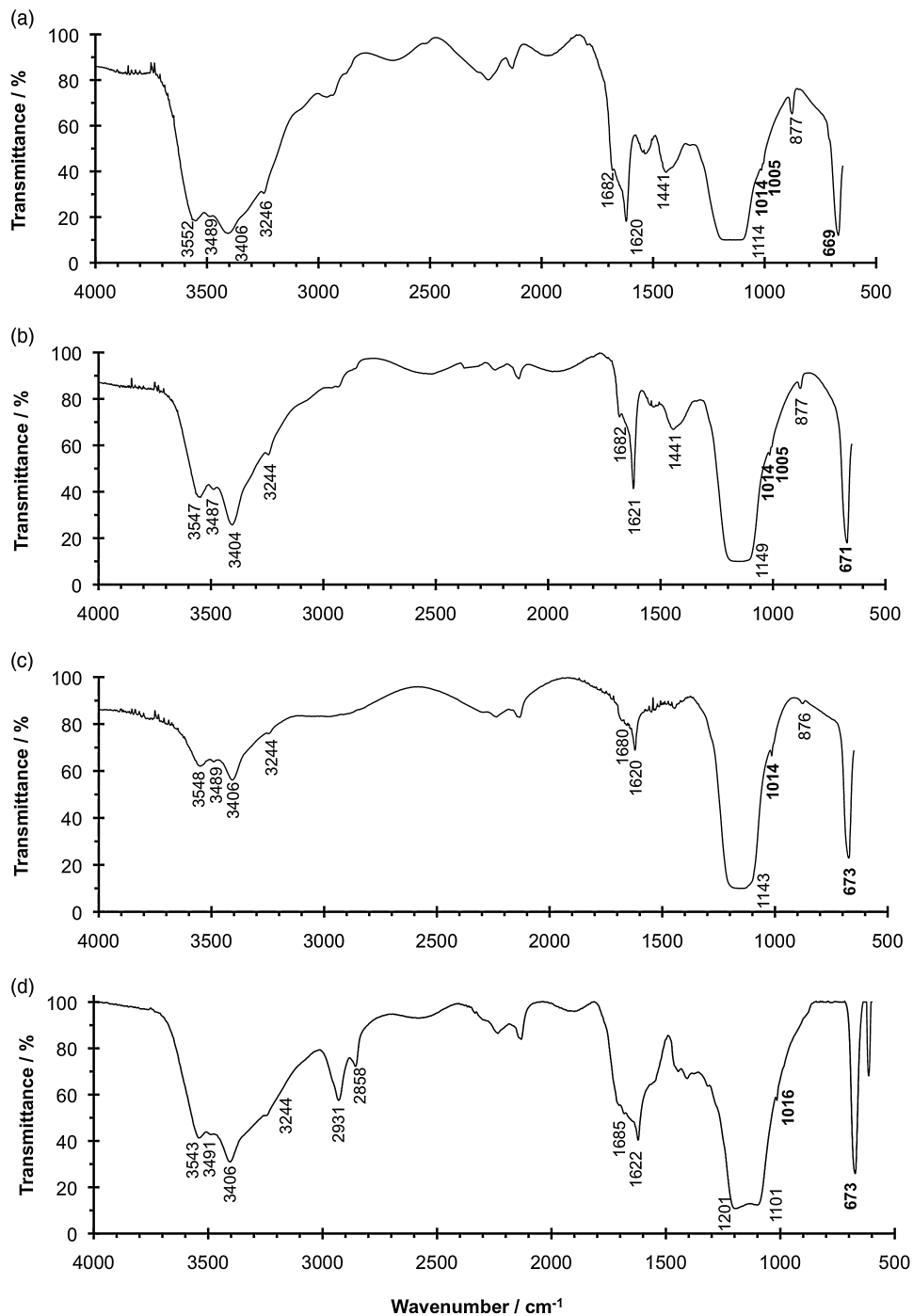


Figure 6 FTIR spectra of the reference samples and their comparison with original painting sample P5/A: (a) G75A25; (b) G50A50; (c) G25A75; (d) P5/A.

Table 5 The FTIR wavenumbers of calcium sulphate compounds from the reference samples ( $\text{cm}^{-1}$ )

Sample	$\nu\text{S}=\text{O}$	$\delta\text{S}-\text{O}$	$\nu\text{S}-\text{O}$	$\nu\text{OH}$	$\delta\text{OH}$
G100	1136	669	1005	3552	1618
				3487	1684
				3410	
				3244	
G75A25	1144	669	1014 1005 sh	3552	1620
				3489	1682
				3406	
				3246	
G50A50	1149	671	1014 1005 sh	3547	1621
				3487	1682
				3404	
				3244	
G25A75	1143	673	1014	3548	1620
				3489	1680
				3406	
				3244	
A100	1148	675	1015	3548 w	1623
				3407 mw	

although not in a sufficient quantity as to be detected in the SEM–BSE images. The dihydrated calcium sulphate found in the grounds most probably originated from an incomplete roasting of the gypsum.

Regarding the FTIR and XRD spectra obtained for the painting samples that show some significant differences compared with one another, these differences can be interpreted as due to the heterogeneity of the material constituent of the ground layer, which is observed in the SEM–BSE images.

#### CONCLUSION

The assignment of the bands presented in FTIR spectra obtained for samples of the grounds of six 16th-century Portuguese paintings and the general form of these spectra suggested that the grounds were mainly composed of gypsum, the *gesso sottile* or the *gesso mate* mentioned in historical treatises, although mixed with some anhydrite. This would be the final conclusion if the characterization of the grounds was done solely with FTIR, as usual, and no other structural method was employed. However, the SEM–BSE observations, first, and subsequently the XRD spectra clearly showed that, in fact, the samples were mainly composed of anhydrite—that is, *gesso grosso*—although gypsum was also present. The subsequent re-evaluation of FTIR spectra, on the basis of the spectra obtained for reference samples, led to the conclusion that the small deviations of the S–O vibration bands are an important indicator of the presence of anhydrite as the major component or, at least, in significant concentration. That is, the interpretation of FTIR spectra of painting samples such as those studied here cannot be based solely on the hydroxyl bands present, as is usual in routine work, but small deviations of S–O bands must be taken into account.

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