

Provided for non-commercial research and education use.
Not for reproduction, distribution or commercial use.



This article appeared in a journal published by Elsevier. The attached copy is furnished to the author for internal non-commercial research and education use, including for instruction at the authors institution and sharing with colleagues.

Other uses, including reproduction and distribution, or selling or licensing copies, or posting to personal, institutional or third party websites are prohibited.

In most cases authors are permitted to post their version of the article (e.g. in Word or Tex form) to their personal website or institutional repository. Authors requiring further information regarding Elsevier's archiving and manuscript policies are encouraged to visit:

<http://www.elsevier.com/copyright>

Contents lists available at [SciVerse ScienceDirect](#)

Microchemical Journal

journal homepage: www.elsevier.com/locate/microc

Spectroscopic, morphological and chemical characterization of historic pigments based on carbon. Paths for the identification of an artistic pigment

E. Tomasini^a, G. Siracusano^b, M.S. Maier^{a,*}^a UMYMFOR and Departamento de Química Orgánica, Facultad de Ciencias Exactas y Naturales, Universidad de Buenos Aires, Pabellón 2, Ciudad Universitaria, (1428) Ciudad Autónoma de Buenos Aires, Argentina^b CONICET, Universidad Nacional de San Martín, B. Quinquela Martín 1784 (1296) Ciudad Autónoma de Buenos Aires, Argentina

ARTICLE INFO

Article history:

Received 12 October 2011

Accepted 12 November 2011

Available online 18 November 2011

Keywords:

Carbon-based pigments

Carbon black

FTIR

ATR

SEM-EDS

Colonial art

ABSTRACT

Analytical characterization of reference carbon-based black pigments has been performed using Fourier transform infrared spectroscopy (FTIR) with attenuated total reflectance (ATR) and scanning electron microscopy (SEM) coupled to an energy-dispersive X-ray spectrometer (EDS). The unambiguous identification of these pigments, which are found in paintings, rock art and archeological artifacts, still remains a big challenge due to the variety of sources and manufacturing processes used in their preparation. The analytical results achieved in this study allowed us to discriminate between carbon-based pigments from different sources and detect adulterations. The methodological approach was successfully applied to the identification of vegetable charcoal and bone black in two colonial paintings dated from the eighteenth century. Conclusions regarding the pictorial techniques were drawn from FTIR data.

© 2011 Elsevier B.V. All rights reserved.

1. Introduction

Carbon-based black pigments are a group of dark-colored materials composed by some form of elemental carbon [1]. According to Winter [2] they may be classified taking into account the source material and the manufacturing process. Four groups may be distinguished: graphite (either natural or artificial), flame carbons, chars, and cokes. Flame carbons comprise any carbon produced in the gas phase that originates from the incomplete combustion of hydrocarbon precursors such as oil and resins. Lampblack is soot collected from burning oil, while bistre is obtained from the burning of resinous wood. Chars are carbons formed from solid precursors such as wood, bark and stone fruits that remain solid through the carbonization process. Thus, the end products retain much of the morphology of the starting material. Coke is defined as any carbonized product for which the precursor was in a liquid or plastic state immediately before carbonization. This group includes the carbonization product of collagen, the organic component from animal bones.

Other pigments containing amorphous carbonaceous material comprise bitumen, the organic component of asphalt [3], and humic-earth materials, such as Vandyke brown and Cassel earth [4]. These pigments are composed of complex mixtures of natural organic substances derived from animal and vegetable sources.

* Corresponding author at: UMYMFOR and Departamento de Química Orgánica, Facultad de Ciencias Exactas y Naturales, Universidad de Buenos Aires, Pabellón 2, Ciudad Universitaria, (C1428EGA), Ciudad Autónoma de Buenos Aires, Argentina. Tel./fax: + 54 11 4576 3385.

E-mail address: maier@qo.fcen.uba.ar (M.S. Maier).

Carbon-based pigments have been identified in archeological artifacts [5], rock art [6,7], and in easel and wall paintings [1,3,4,8]. Generally, the presence of a carbon-based pigment was inferred from the absence of black iron and manganese oxides. In most cases the pigment was assumed to be charcoal or simply “carbon black”, a term generally used to mean any pigment based on carbon [9,10]. As the precise identification of pigments is important for understanding the technology employed in the manufacture of an artwork as well as the resources available, the unambiguous characterization of carbon-based pigments remains a big challenge.

Scanning electron microscopy (SEM) coupled to an energy-dispersive X-ray spectrometer (EDS) and powder X-ray diffraction (XRD) have traditionally been applied to the analysis of carbon-based pigments, in particular for the identification of mineral phases such as hydroxyapatite in charred ivory and bone or when black oxides were used in combination with carbon-based pigments [2,9].

Raman and Fourier-transformed infrared spectroscopy (FTIR) have the advantage of being molecular techniques that are able to characterize both organic and inorganic components [11,12]. The identification of carbonaceous material can be easily accomplished by Raman spectroscopy based on characteristic bands of carbon at $\sim 1580\text{ cm}^{-1}$ (G band) and $\sim 1350\text{ cm}^{-1}$ (D band) [13]. Nevertheless, it is very difficult to discriminate the source of carbon-based pigments because their Raman spectra are very similar, although differences in band positions, intensities, and bandwidths may be observed after a detailed study of the spectra [14,15].

FTIR is a well established technique that has been extensively applied to the investigation of painted surfaces containing organic and inorganic materials such as pigments and binding media [11]. It has

the advantage of being available in many museums and archeometry laboratories. In particular, attenuated total reflectance (ATR) technique allows the analysis of small samples and requires no previous preparation. Recently, FTIR has been successfully applied to the characterization of black printing inks [16] and to the differentiation of earth pigments [17].

In this work ten carbon-based black pigments used in art and as references for archeometric studies, together with a sample of commercial vegetable charcoal, have been studied in detail by a combination of FTIR-ATR and SEM-EDS microscopy. XRD was useful for characterizing crystalline inorganic materials related to a particular pigment, helping in the assignment of bands in IR spectra. The aim of this study was to establish discriminative criteria to distinguish between carbon-based pigments and extend this approach to the identification of black pigments in two paintings dated from the early eighteenth century and housed in two churches in Bolivia.

2. Materials and methods

2.1. Reference samples

Ten pigments based on carbon were analyzed (supplied by Kremer Pigmente, Germany, and Zecchi, Italy). For comparison purposes we included a sample of algarrobo (*Prosopis sp.*) charcoal. Table 1 lists sources and characteristics of the samples studied.

2.2. Painting samples

Two microsamples were extracted from black areas of the figure of Leviathan in a wall painting (A) and an easel painting (C) from two churches of Bolivia, Copacabana de Andamarca and Caquiaviri, respectively. Both paintings, dated from the eighteenth century, depict the eschatological subjects of Death, Judgment, Glory and Hell. The pictures of the Last Four Things were vital for the Catholic believe, since they had as purpose to recall the believer the finitude of life and the eternal bliss that awaited those who pursued God's path and the endless punishments reserved for sinners. Both samples were analyzed by SEM, EDS, and FTIR in the transmission mode. For sample A, the pigment layer was carefully separated from the preparation layer under a Leica MZ6 stereomicroscope and each layer was analyzed separately by FTIR.

2.3. Analytical instrumentation and methods

2.3.1. Fourier-transformed infrared spectroscopy

IR spectra were obtained on a Nicolet i510 FTIR spectrometer with the "Smart iTR" single-bounce ATR accessory with ZnSe crystal. For each reference sample 32 scans were recorded in the 4000–650 cm^{-1} spectral range in the transmittance mode with a resolution of 4 cm^{-1} .

Spectral data were collected with Omnic v8.0 (Thermo Electron Corp.) software without post-run processing. The spectrum of air was used as background.

Infrared spectra of painting samples were obtained on a Nicolet Magna 550 Fourier transform spectrometer. For each sample 32 scans were recorded in the 4000–400 cm^{-1} spectral range in the transmittance mode with a resolution of 4 cm^{-1} . Spectral data were collected with OMNIC 7.3 (Thermo Electron Corp.) software. The KBr pressed disk technique (1% sample in KBr) was used.

2.3.2. Scanning electron microscopy

Information on surface morphology of the samples was obtained by using a Field Environmental scanning electron microscope (FE-SEM) Zeiss:Supra 40 coupled with an energy-dispersive X-ray spectrometer (SEM-EDS) INCA X Sight, Oxford Instrument, for the elemental chemical analyses.

2.3.3. X-ray diffraction

X-ray diffraction (XRD) patterns were recorded on a Siemens D-5000 powder diffractometer with $\text{CuK}\alpha$ radiation at a wavelength of 1.54056 Å, a diffracted beam graphite monochromator, and a scintillator counter. Experiments were performed at steps of (2θ) 0.02° and a counting time of 1.0 s/step.

3. Results and discussion

In this section we describe the results of the analytical characterization of reference carbon-based pigments and the discriminative criteria established to distinguish between them. The methodological approach was applied to the identification of black pigments in two colonial artworks from the eighteenth century.

3.1. Reference pigments

3.1.1. Graphite

SEM micrograph of sample GRZ (Fig. 1a) showed an amorphous morphology compared to that expected for graphite. The elemental composition of the sample as obtained by EDS (Table 2) indicated a high concentration of oxygen in addition to carbon and minor amounts of silicon, iron, aluminum, and magnesium, which can be part of a mixture of oxides or clays.

The infrared spectrum (Fig. 2a) showed very few bands; the weak band at $\sim 1580 \text{ cm}^{-1}$ can be assigned to graphite in its transition state E2g [18]. The abundant amount of oxygen (41.53%) and the low crystallinity of the sample were indicative of oxidized graphite. As fully oxidized graphite shows pronounced bands at 1700 and 1070 cm^{-1} [19], sample GRZ is suggested to be partially oxidized. On the other hand, the band at 992 cm^{-1} and those at lower wavenumbers were assigned to quartz and magnesium and iron aluminosilicates, as was evident from its elemental composition.

3.1.2. Lampblack

Sample LPZ showed a typical SEM image (Fig. 1b) of carbon soot [20]. Spherical structures of 80–200 nm, apparently homogeneous with smooth surfaces, were observed. EDS analysis (Table 2) clearly showed carbon as the most abundant element. As expected, the infrared spectrum (Fig. 2b) did not show any significant bands. A very weak staggering around 1650 cm^{-1} suggested the presence of C=C bonds of polycyclic aromatic compounds present in the amorphous domains [21].

3.1.3. Vine Black

Vine black pigments originate from charred vine (*Vitis sp.*) wood but the pigment name has historically been applied to char and coke from a wide variety of other materials [3,10].

Sample VBZ, at a micrometer level showed crystals of 1–2 μm in size and small globular particles with a rough surface. At a nanometer level,

Table 1
Reference pigments.

Reference samples name	Type	Commercial name and reference number	Manufacturer
GRZ	Crystalline carbon	Graphite – 1300	Zecchi
LBZ	Flame carbon	Lampblack – 0998	Zecchi
BSZ	Flame carbon	Bistre – 1200	Zecchi
VBZ	Char	Vine Black – 0941	Zecchi
VBK	Char	Vine Black – 47000	Kremer
CWC	Char	<i>Prosopis sp.</i> Wood Charcoal	Local supplier
IBZ	Coke	Ivory Black – 0979	Zecchi
BTZ	Coke	Asphaltum (Bitumen) – 0098	Zecchi
VDK	Earth	Van Dyck Brown – 41000	Kremer
EKZ	Earth	Cassel Earth – 0796	Zecchi
VDZ	Earth	Van Dyck Brown – 0011	Zecchi

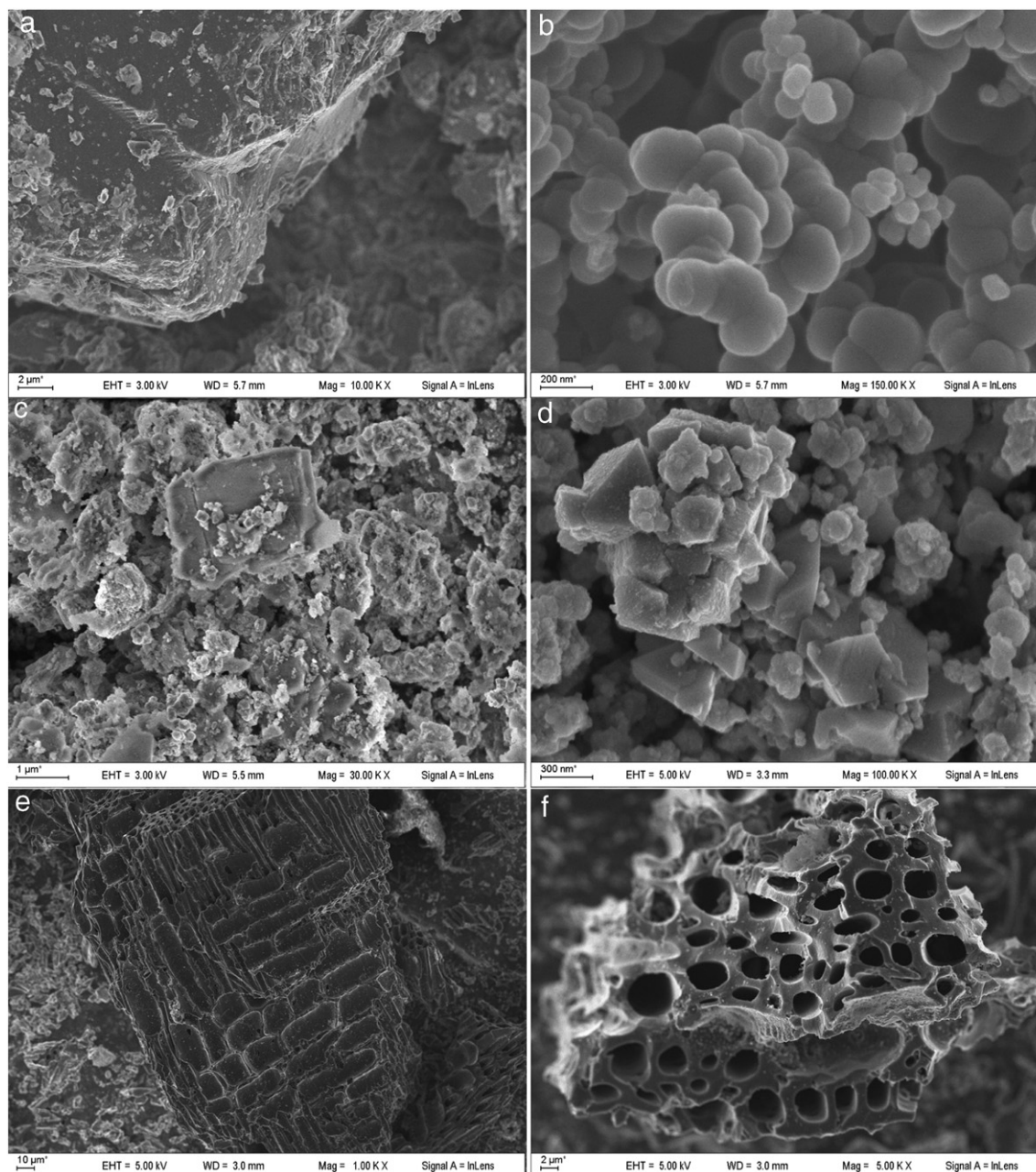


Fig. 1. SEM micrographs of carbon-based pigments: (a) Graphite (GRZ); (b) Lampblack (LBZ); (c) Zecchi vine black (VBZ); (d) Kremer vine black (VBK); (e) and (f) *Prosopis* sp. charcoal.

globular particles of ~ 50 nm and needle-like particles of ~ 500 nm and ~ 100 nm were observed (Fig. 1c). Chemical analysis by EDS showed an elemental composition indicative for the presence of oxides and clays (Table 2).

The FTIR spectrum (Fig. 2c) showed bands at 989 , 870 , 793 , and 667 cm^{-1} related to clay minerals, aluminosilicates based on structures such as 2(Si,Al)-O tetrahedral sheets enclosing one (Mg, Al, Fe)-OH octahedral sheet [22]. The band at 1631 cm^{-1} may correspond to H_2O trapped between crystals. Although the mineral components predominate, the presence of weak bands at 2902 and 2841 cm^{-1} due to C–H vibration frequencies as well as EDS results suggested the presence of minor organic components.

Analysis by XRD confirmed the presence of pyrolusite (MnO_2) and magnetite (Fe_3O_4), which are probably the components responsible for the black color of the pigment.

Sample VBK presented triangular and rhombic crystals of 100 to 300 nm and pseudocubic particles of ~ 100 nm (Fig. 1d). The results

of EDS analysis (Table 2) suggested the presence of barium sulfate, probably used as a filler due to its low cost [23]. The amount of carbon in the pigment was too low for a carbonization plant product and the presence of iron may be related to the addition of iron oxides to obtain a dark-colored material. Finally, the presence of strontium was not surprising considering that it can replace barium in nature.

The IR spectrum (Fig. 2d) clearly showed characteristic bands of barium sulfate at 1161 , 1066 and 982 cm^{-1} . No bands of organic compounds were observed. Analysis by XRD confirmed the presence of barium sulfate and magnetite (Fe_3O_4).Z

These results indicate that pigments VBZ and VBK are not original vine black pigments but adulterated products.

3.1.4. Charcoal

Sample CWC, a commercial wood charcoal (*Prosopis* sp.), was analyzed in order to compare it with the reference samples of charcoals VBZ and VBK.

Table 2
Results from elemental microanalysis (SEM-EDS) of carbon-based pigments.

ELEMENT	Graphite (GRZ)	Lampblack (LBZ)	Bistre (BSZ)	Vine B. (VBZ)	Vine B. (VBK)	Charcoal (CWC)	Ivory Black (IBZ)	Bitumen (BTZ)	Vandyke (VDK)	Cassel E. (EKZ)	Vandyke (VDZ)
C	47.46	97.55	65.3	42.44	8.56	89.8	29.69	95.85	77.54	71.01	8.84
O	41.53	2.35	28.64	43.23	59.33	8.52	47.22	4.15	21.02	27.86	60.63
Si	7.98		0.13	5.66			0.43				0.93
Fe	1.57		0.14	4.04	1.44	0.14	0.24		0.12	0.33	27.26
Al	1.52			1.73							
Mg	0.23			1.29		0.13	0.37		0.30		
S	–	0.30	0.18	0.33	14.41				0.36	0.22	
K			5.37			0.27					
Ca			0.24	0.30		1.00	13.42		0.66	0.57	
Na				0.54			0.66				
Cl						0.13					
Mn				0.44							1.57
Ba					15.39						
Sr					0.96						
P							7.97				
Ti											0.76

Results expressed as percentages of total content (%)

SEM micrographs (Fig. 1e and f) showed cell wall structures, channels and holes due to the dehydration process of wood. This observation is coincident with the fact that the wood structure of algarrobo suffers significant qualitative changes because of the temperature effect [24].

The elemental composition of CWC (Table 2) showed carbon as the most abundant element. The presence of oxygen was indicative of oxidized compounds arising from incomplete degradation of lignin, cellulose and hemicellulose in the wood. Minor elements as calcium, potassium and chloride are expected to derive from plant material.

The infrared spectrum of CWC (Fig. 2e) showed weak stretching vibrations of calcium carbonate (CaCO_3) at 1420, 873.7, and 711.8 cm^{-1} [17]. XRD confirmed the presence of CaCO_3 and showed broad peaks at 24.1° and 43.8° (2θ) corresponding to graphitic peaks (002) and (100), respectively due to short-range order of graphenes [25].

3.1.5. Ivory Black

SEM analysis of sample IBZ (Fig. 3a) at a micrometric level showed amorphous crystals tending to be angular with a wide range of sizes. At a nanometric level, layered structures with spherical particles around 50 nm were observed on the surface of the crystals.

According to EDS analysis (Table 2), the presence of calcium and phosphorous was indicative of hydroxyapatite. The carbon content may be ascribed to carbonized remains of bone tissue whose main component is collagen; this carbonaceous material is responsible for the deep black color of the pigment.

Fig. 2f showed the IR spectrum of pigment IBZ. The stretching vibrations of calcium carbonate at 1456, 1411 and 872 cm^{-1} are characteristic of carbonated hydroxyapatite, as expected for bone samples [26]. The strong band at 1018 cm^{-1} , with a shoulder at 1086 cm^{-1} , together with bands at 559 and 600 cm^{-1} of the phosphate group coincide with a poorly crystalline non-stoichiometric apatite [27]. The IR spectrum also showed bands due to remains of collagen, the main bioorganic part of bone, after calcination [28,29]. A broad band at 1589 cm^{-1} was assigned to the C=O stretching of amides, while the sharp band at 2013 cm^{-1} is characteristic of isocyanate (RNCO), thiocyanate (RSCN), and isothiocyanate (RNCS) groups related to degradation products of proteins.

This pigment is generally identified by its inorganic composition, either by the presence of phosphorous in SEM-EDS analysis or by the characteristic bands of hydroxyapatite in the IR spectrum.

3.1.6. Bitumen

Sample BTZ showed an amorphous morphology by SEM (Fig. 3b). EDS microanalysis (Table 2), indicated the presence of C (95.85%) as the major component together with minor amounts of oxygen (4.15%). The IR spectrum of the sample (Fig. 4a) showed characteristic absorptions of

hydrocarbons. Strong bands at 2950, 2922, and 2853 cm^{-1} are due to asymmetric and symmetric stretchings of C–H of methylene and methyl groups. The two bands at 1456 and 1375 cm^{-1} are characteristic of asymmetric and symmetric bending of the methyl group. The broad band centered at 1600 cm^{-1} can be assigned to C=C vibration in olefins and aromatic rings, while bands at 868, 810 and 722 cm^{-1} can be ascribed to the deformation mode of aromatic C–H bonds. These observations are in accordance with the presence of complex mixtures of aliphatic and aromatic compounds, as described previously [30].

3.1.7. Bistre

According to the manufacturer this pigment is prepared from wood soot. Analysis by SEM of sample BSZ (Fig. 3c) showed an amorphous structure and a few irregular-shaped crystals. The overall composition obtained by EDS is shown in Table 2. Besides carbon, a high percentage of oxygen was observed. The presence of potassium is typical for the carbonization of wood and it can be found as an oxide or carbonate. Minor components (<1%) may correspond to ashes resulting from the carbonized wood.

The IR spectrum (Fig. 4b) showed a broad band in the region of 3500–3000 cm^{-1} that was assigned to O–H stretching of alcohols. Weak bands at 2951 and 2838 cm^{-1} were assigned to aliphatic C–H stretching while the broad band at 1568 cm^{-1} was indicative for aromatic ring vibrations. Bands occurring at 1400–1370 cm^{-1} corresponded to aliphatic methylene and methyl groups. The band centered at 1110 cm^{-1} was assigned to C–O stretching of aryl ether structures and phenol groups. In the region from 872 to 745 cm^{-1} , sharp bands due to benzene ring substitution were observed. Finally, the bands between 701 and 576 cm^{-1} were assigned to C–C stretching of phenolic and polycyclic aromatic hydrocarbons (PAH) typically found in tarry residues [31].

3.1.8. Vandyke and Cassel earth

Pigments VDK and EKZ are described together since they show the same characteristics, despite having been provided by different manufacturers. Both pigments showed lamellar and irregular morphologies by SEM (Fig. 3d and e). The carbon content was significant in both samples (71–77%), with a low percentage of iron (Table 2). The presence of calcium and magnesium may be related to components of plant origin.

The infrared spectra of samples VDK and EKZ (Fig. 4c) showed typical bands of humic substances, which are the main components of organic matter in soils and are responsible for their dark color [32]. Bands at 3600–2900, 1700–1600, 1430–1410, and 1275–1260 cm^{-1} may be attributed to carboxylic, aromatic and phenolic groups responsible for the acid character of the humic substances. The bands at 2919 and

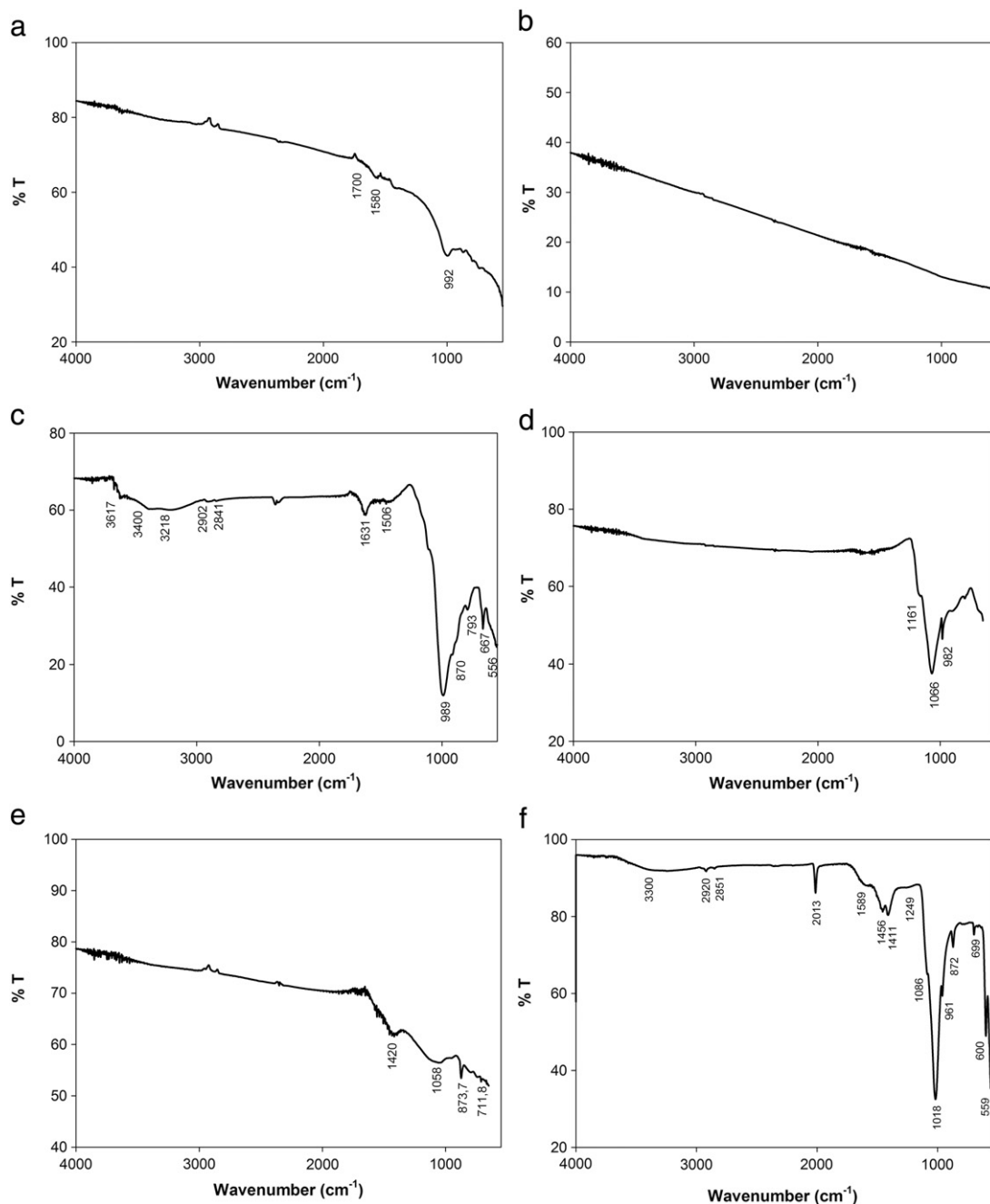


Fig. 2. FT-IR ATR spectra of carbon-based pigments: (a) Graphite (GRZ); (b) Lampblack (LBZ); (c) Zecchi vine black (VBZ); (d) Kremer vine black (VBK); (e) *Prosopis* sp. Charcoal; (f) Ivory black (IBZ).

2850 cm^{-1} due to C–H stretchings of methylene and methyl groups were indicative of the presence of aliphatic chains in the macromolecule structure. The absence of characteristic bands due to aromatic C–H stretching ($3000\text{--}3100\text{ cm}^{-1}$) may indicate a high degree of substitution in the aromatic systems.

The SEM micrograph of VDZ (Fig. 3f) showed particles of 50–100 nm with pseudocubic shape. EDS microanalysis (Table 2) indicated the presence of oxygen (60.63%) and iron (27.26%) as the major elements together with a low carbon content (8.84%).

The infrared spectrum (Fig. 2j) showed weak bands at $1073\text{--}1020$, 899 , and 819 cm^{-1} common to several clay minerals and iron oxides, together with a strong band at 695 cm^{-1} attributable to magnetite [22]. XRD analysis confirmed the presence of magnetite and hematite in coincidence with the observation of pseudocubic crystals by SEM [33]. The absence of pyrolusite (MnO_2) intense peaks in the XRD

pattern suggests that manganese is part of clays minerals like those of the Neotocite group, which may contain titanium, an element detected by EDS microanalysis of VDZ.

Pigment VDZ consists mainly of iron oxides and is completely different from VDK and EKZ.

3.2. Criteria for discrimination of carbon-based black pigments

The application of quantitative microanalysis (SEM-EDS) and FTIR, two of the techniques most commonly used to examine works of art, allowed the characterization of reference carbon-based pigments. The information obtained by both techniques was organized in two flow charts in order to help in the discrimination of the pigments studied. In Fig. 5, pigments are grouped on the basis of the atomic percentage of carbon in each sample, as determined by EDS microanalysis.

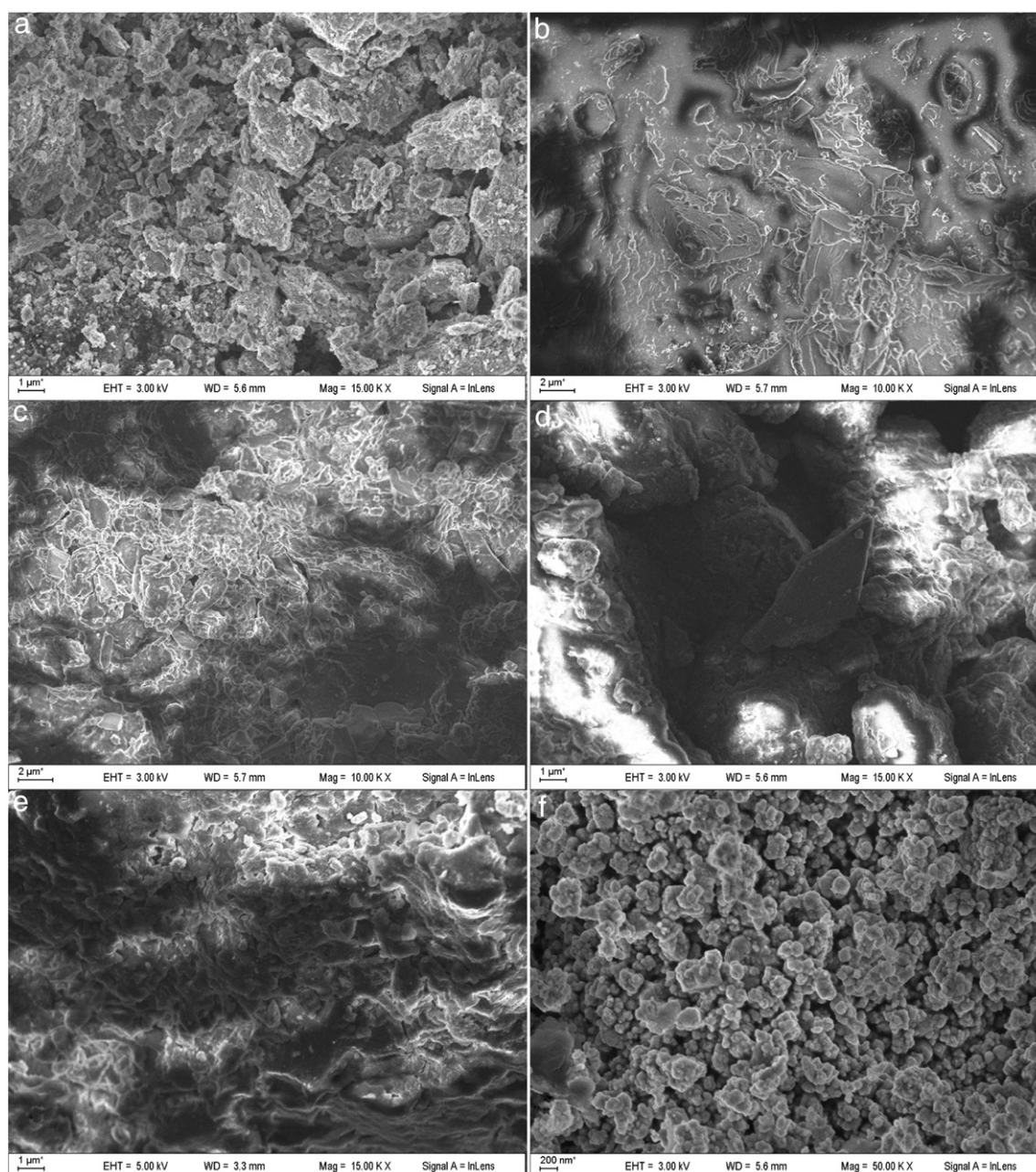


Fig. 3. SEM micrographs of carbon-based pigments: (a) Ivory black (IBZ); (b) Bitumen (BTZ); (c) Bistre (BSZ); (d) Zecchi Cassel earth (EKZ); (e) Kremer Vandyke (VDK); (f) Zecchi Vandyke (VDZ).

Further differentiation between the pigments in each group is based on the presence of elements, which may be characteristic for each pigment.

Lampblack (LBZ), commercial charcoal (CWC), and bitumen (BTZ) are characterized by their high content of carbon (>85%). LBZ is distinguished from BTZ and CWC by the presence of sulfur, presumably from heterocyclic aromatic hydrocarbons, while WCW is distinguished from BTZ by the presence of potassium, among other minor elements derived from plant material. Bistre (BSZ), Vandyke (VDK) and Cassel earth (EKZ) are pigments, which contain a high amount of organic matter together with variable amounts of inorganic matter. BSZ can be easily differentiated from VDK and EKZ due to the high content of potassium, while VDK and EKZ differ only in the presence of magnesium in VDK.

Grafite (GRZ), Vine Black (VBZ) and Ivory Black (IBZ) from Zecchi contain 20–50% of carbon. IBZ can be easily distinguished from GRZ

and VBZ by the presence of phosphorous and the high content of calcium derived from hydroxyapatite. VBZ differs from GRZ in the presence of calcium and sodium, minor elements present in plant cells.

The last group comprises pigments VBK and VDZ, which are characterized by a low content of carbon (<10%) and a high content of oxygen (ca. 60%) due to the presence of inorganic components. VBK can be easily distinguished from VDZ by the presence of high amounts of barium and sulfur, while VDZ is rich in iron (27%).

Fig. 6 shows the discrimination of the reference pigments by FTIR-ATR taking into account the presence of certain characteristic bands. As Lampblack (LBZ) shows no bands in the IR spectrum, it will not be included in the discrimination analysis. Pigments BTZ, BSZ, VDK, and EKZ show typical C–H bands at 3000–2800 cm^{-1} . The FTIR spectra of VDK, EKZ and BSZ are quite different from that of bitumen (BTZ) and the presence of sharp bands at 1375 and 1455 cm^{-1} due to aliphatic C–H methyl groups allows the discrimination of BTZ from

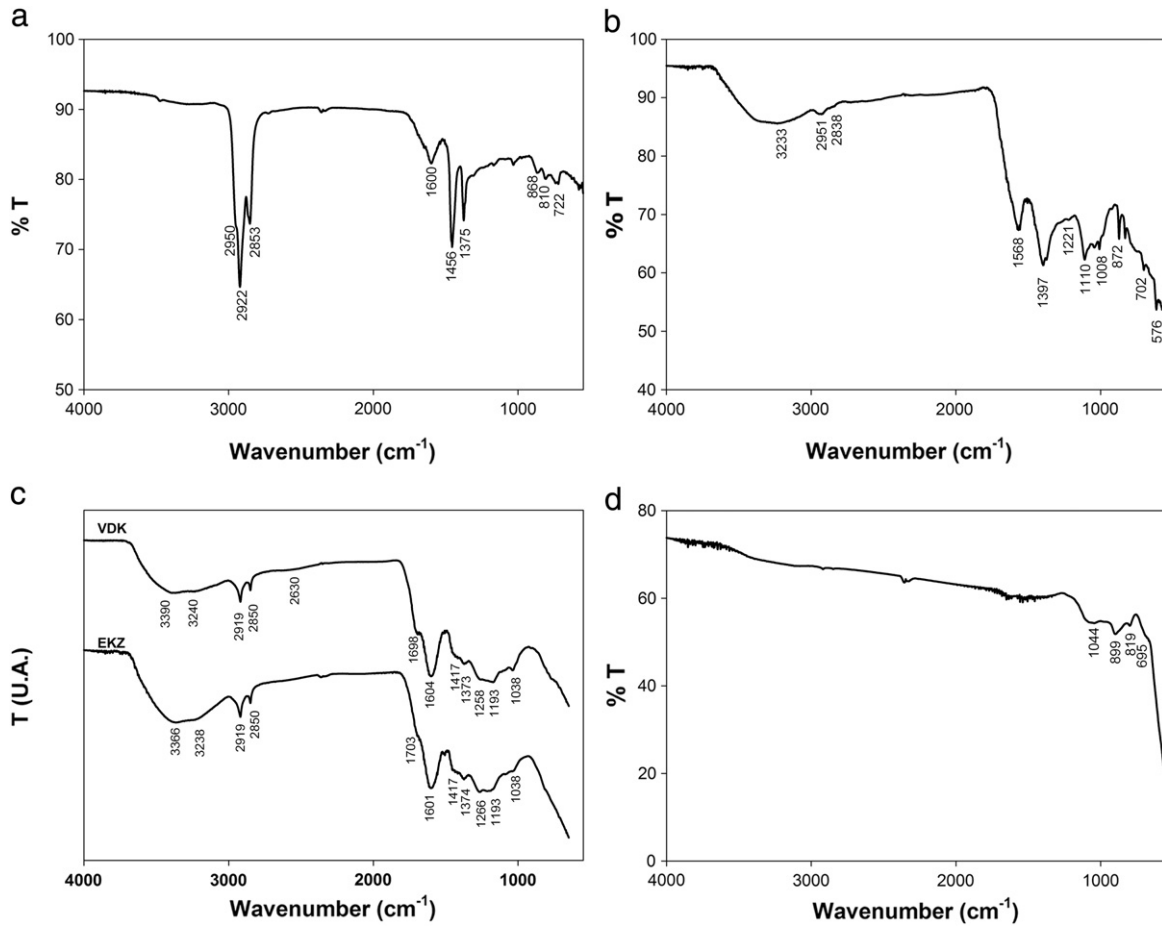


Fig. 4. FTIR-ATR spectra of carbon-based pigments: (a) Bitumen (BTZ); (b) Bistre (BSZ); (c) Kremer Vandyke (VDK) and Zecchi Cassel earth (EKZ); (d) Zecchi Vandyke (VDZ).

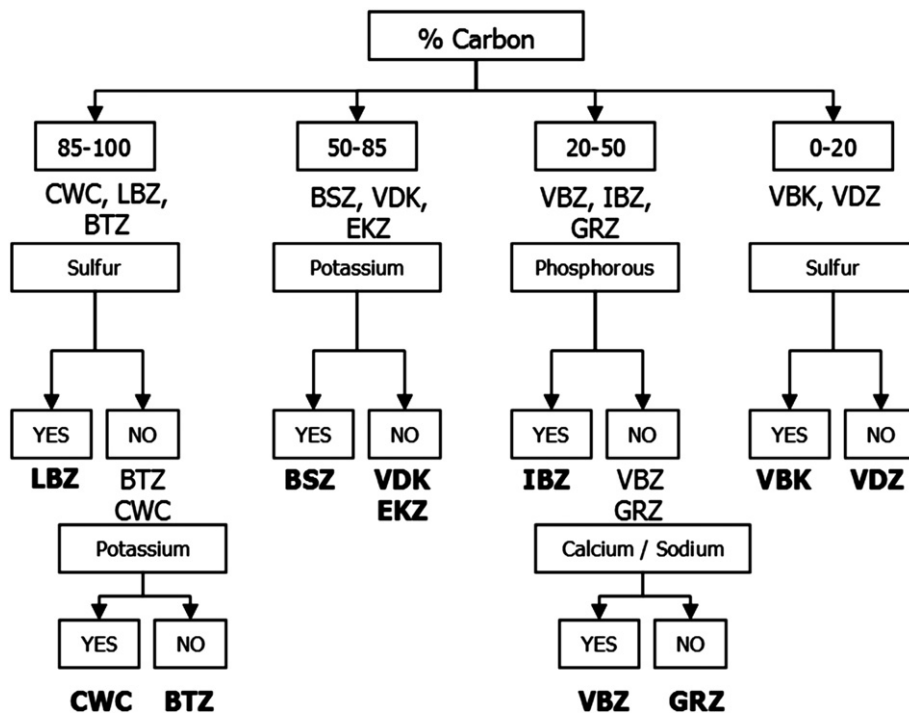


Fig. 5. Flow chart for carbon-based pigments discrimination by EDS analysis.

BSZ, VDK, and EKZ. The latter three pigments show similar FTIR spectra but VDK and EKZ can be distinguished from BSZ by a broad band at $1350\text{--}1200\text{ cm}^{-1}$ characteristic of C–O and C–N stretchings of humic substances.

The FTIR spectrum of Ivory Black (IBZ) shows a distinctive band at 2013 cm^{-1} associated with collagen degradation products, together with strong bands at $1018, 600$ and 559 cm^{-1} due to the phosphate group. The presence of weak bands at $1700\text{--}1400\text{ cm}^{-1}$ characteristic of organic compounds makes it possible to separate CWC, GRZ and VBZ from the oxide-based pigments VBK and VDZ. These two pigments can be distinguished by the sharp band at 1066 cm^{-1} for the barium sulfate group in VBK.

Finally, the broad band at $1250\text{--}1000\text{ cm}^{-1}$ makes it possible to separate CWC from VBZ and GRZ, which can be distinguished on the basis of the broad band at $1000\text{--}800\text{ cm}^{-1}$ characteristic of an aluminosilicate based pigment as VBZ.

3.3. Identification of carbon-based black pigments in paintings

Analysis of microsample A by optical microscopy (Fig. 7a) and SEM (Fig. 7b) showed the presence of a heterogeneous pigment layer consisting of irregular black particles. Further analysis of one of these particles by SEM (Fig. 7c) showed a structure resembling that of charred wood and suggested the use of charcoal as the black pigment. EDS microanalysis indicated the presence of carbon (84.04%) and oxygen (15.14%) as the major elements together with minor amounts of sulfur (0.27%), calcium (0.48%), and potassium (0.06%). This elemental composition discarded bone black and oxide-based pigments. The presence of potassium indicated the vegetable origin of the pigment. White particles observed in the micrograph (Fig. x) were consistent with calcium sulfate, as determined by EDS analysis.

The FTIR spectrum of the black pigment layer (Fig. 7d) showed no bands except a weak band centered at 1157 cm^{-1} , which might correspond to calcium sulfate hydrate (gypsum) [11]. Indeed, structurally

disordered graphitic materials do not present strong resolved IR bands, as samples GRZ and CWC. The absence of any strong spectral features due to organic groups such as methyl and methylene, carbonyl and hydroxyl groups related to the use of an organic binder and the presence of small particles of calcium sulfate in the micrograph of the sample suggested that the pigment might have been mixed with gypsum and applied using water as the vehicle. The FTIR spectrum of the preparation layer (Fig. 7d) was dominated by characteristic peaks of sulfate ($601\text{ cm}^{-1}, 668\text{ cm}^{-1}, 1144\text{ cm}^{-1}, 1624\text{ cm}^{-1}, 1682\text{ cm}^{-1}, 3405\text{ cm}^{-1}, 3549\text{ cm}^{-1}$), which are indicative for the presence of calcium sulfate hydrate [11].

Microsample C showed an intense black color under the stereomicroscope (Fig. 8a). Analysis by SEM-EDS of the black layer indicated the presence of carbon (77.3%) and oxygen (22.3%) as the major elements together with phosphorous (0.03%), aluminum (0.10%), silicon (0.16%), sulfur (0.04%), potassium (0.02%), and calcium (0.06%). The presence of phosphorous and calcium was indicative of a bone black pigment. EDS microanalysis of the preparation layer revealed the presence of aluminum, silicon, iron, and calcium, characteristic of an earth.

The FTIR spectrum of sample C (Fig. 8b) depicted bands at $2012, 599$ and 559 cm^{-1} , characteristic of a hydroxyapatite based black. The broad band at 1066 cm^{-1} due to Si–O–Si and Si–O–Al stretchings of silicate minerals from the preparation layer may be superimposed to the band around 1020 cm^{-1} related to the phosphate group. Bands at 2931 and 2863 cm^{-1} of C–H bonds and a broad band at $1750\text{--}1715\text{ cm}^{-1}$ of C=O were indicative of triacylglycerides and fatty acids as degradation products of a siccative oil used as a binder of the bone black pigment. The presence of bands at 1645 and 1557 cm^{-1} suggested the use of a proteinaceous binder for the preparation layer.

4. Conclusions

Identification of the sources of carbon-based black pigments in works of art and archeology is a challenging goal. In this study, a

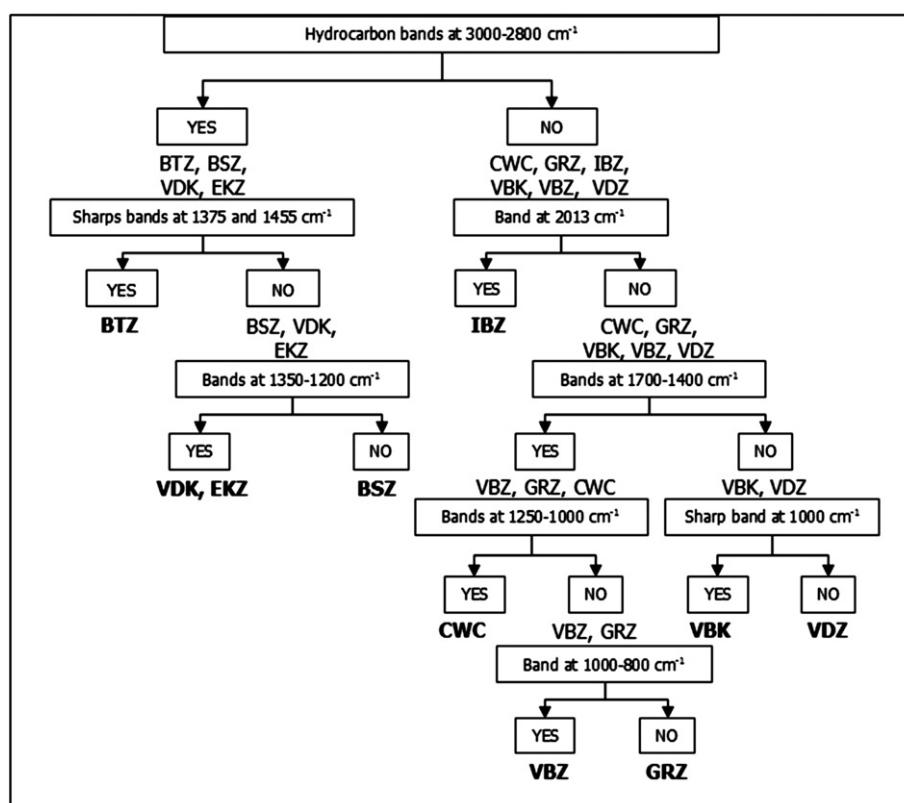


Fig. 6. Flow chart for carbon-based pigments discrimination by FTIR-ATR analysis.

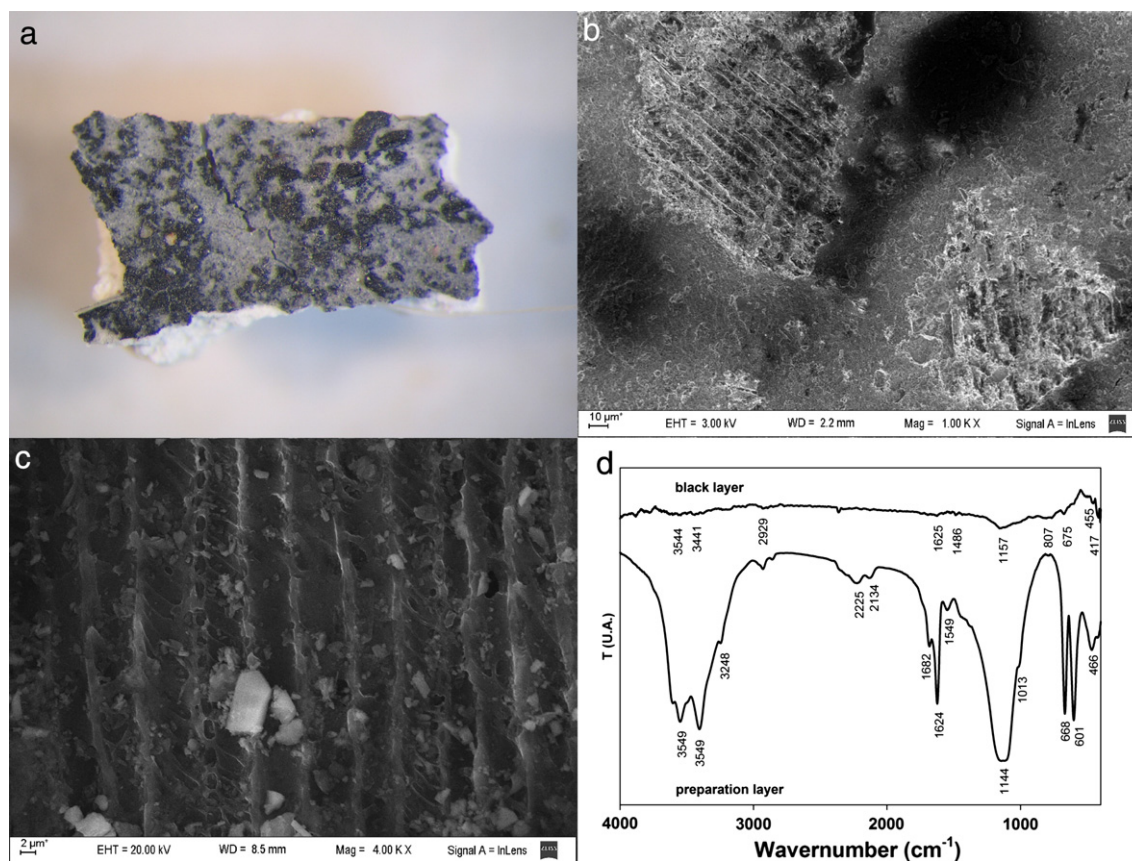


Fig. 7. (a) Sample of the black pigment (A) taken from a mural painting of the church of Copacabana de Andamarca; (b) SEM micrograph of the black pigment layer; (c) SEM micrograph of the black pigment layer with calcium sulfate particles; (d) FTIR spectra of the black layer and the preparation layer.

methodological approach to discriminate between reference carbon-based pigments is described. The procedure is based on the combined application of SEM, EDS microanalysis and FTIR-ATR spectroscopy. These techniques are widely used in the fields of art and art conservation and require a minimum amount of sample.

Morphology and semiquantitative microanalysis, as determined by SEM and EDS, permitted a rapid differentiation between pigments with high content of carbon and those containing inorganic matter as major components. Further identification of minor elements such as sulfur, phosphorous, potassium and calcium enabled a conclusion regarding the type of carbon-based pigment. FTIR was helpful in the differentiation of those pigments with high content of organic compounds, such as

bitumen, bister, and the humic-earth materials, Vandyke and Cassel earth, as well as in the characterization of the mineral-based pigments. The proposed analytical approach allowed the detection of adulteration in the reference vine black pigments by addition of black mineral pigments and barite as an extender.

The paths proposed for the characterization of carbon-based black pigments are easy to follow and are strongly recommended when the presence of a carbon-based black pigment has been previously detected by Raman spectroscopy.

We have successfully applied our methodological approach to the identification of black pigments in two colonial artworks from the eighteenth century. Although micro-sampling was necessary, the

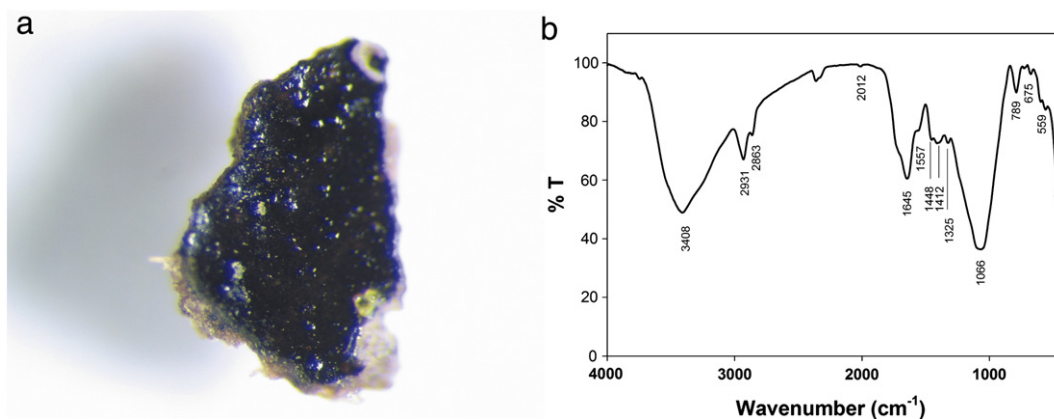


Fig. 8. (a) Sample of the black pigment (C) taken from a painting of the church of Caquiaviri; (b) FTIR spectrum of sample C.

amount of sample required did not affect the integrity of the paintings, which were further restored. The chemical information obtained on the materials and technology used in the manufacture of the paintings contributed to increase our knowledge on Andean colonial art.

Acknowledgments

We thank the following for financial support: Consejo Nacional de Investigaciones Científicas y Técnicas (CONICET) and Agencia Nacional de Promoción Científica y Tecnológica (ANPCyT); for painting samples: Carlos Rúa (Centro Nacional de Restauración, La Paz, Bolivia); and for preliminary analysis: Blanca Gómez and Sara D. Parera. E. T. thanks CONICET for a postdoctoral fellowship. M. S. M. and G. S. are Research Members of CONICET.

Appendix A. Supplementary data

Supplementary data to this article can be found online at doi:10.1016/j.microc.2011.11.005.

References

- [1] J. Winter, E. West FitzHugh, Pigments based on carbon, in: B.H. Berrie (Ed.), *Artists' pigments*, vol. 4, Archetype, London, 2007, pp. 1–37.
- [2] J. Winter, The characterization of pigments based on carbon, *Stud. Conserv.* 28 (1983) 49–66.
- [3] C. Bothe, Asphalt, in: B.H. Berrie (Ed.), *Artists' pigments*, vol. 4, Archetype, London, 2007, pp. 111–149.
- [4] R.L. Feller, R.M. Johnston-Feller, Vandyke brown, in: E. West FitzHugh (Ed.), *Artists' pigments*, vol. 3, Oxford University Press, New York, 1997, pp. 157–190.
- [5] A.S. Cavalheri, A.M.O.A. Balan, R. Künzli, C.J.L. Constantino, Vibrational spectroscopy applied to the study of archaeological ceramic artifacts from Guarani culture in Brazil, *Vib. Spectrosc.* 54 (2010) 164–168.
- [6] E. Chalmin, M. Menu, C. Vignaud, Analysis of rock art painting and technology of Palaeolithic painters, *Meas. Sci. Technol.* 14 (2003) 1590–1597.
- [7] M. Menu, L'analyse de l'art préhistorique, *l'Anthropologie* 113 (2009) 547–558.
- [8] O. Hein, I. Karatasios, D. Mourelatos, Byzantine wall paintings from Mani (Greece): microanalytical investigation of pigments and plasters, *Anal. Bioanal. Chem.* 395 (2009) 2061–2071.
- [9] J.D. Stewart, K.R. Adams, Evaluating visual criteria for identifying carbon- and iron-based pottery paints from the four corners region using SEM-EDS, *Am. Antiquity* 64 (1999) 675–696.
- [10] N. Eastaugh, V. Walsh, T. Chaplin, R. Siddall, *Pigment Compendium, A Dictionary and Optical Microscopy of Historical Pigments*, Elsevier, Burlington, 2008.
- [11] M.R. Derrick, D. Stulik, J.M. Landry, *Infrared Spectroscopy in Conservation Science*, The Getty Conservation Institute, Los Angeles, 1999.
- [12] H.G.M. Edwards, J.M. Chalmers, *Raman Spectroscopy in Archaeology and Art History*, The Royal Society of Chemistry, Cambridge, 2005.
- [13] J. van der Weerd, G.D. Smith, S. Firth, R.J.H. Clark, Identification of black pigments on prehistoric Southwest American potsherds by infrared and Raman microscopy, *J. Archaeol. Sci.* 31 (2004) 1429–1437.
- [14] A. Sadezky, H. Muckenhuber, H. Grothe, R. Niessner, U. Pöschl, Raman microscopy of soot and related carbonaceous materials: spectral analysis and structural information, *Carbon* 43 (2005) 1731–1742.
- [15] J. Jehlička, O. Urban, J. Pokorný, Raman spectroscopy of carbon and solid bitumens in sedimentary and metamorphic rocks, *Spectrochim. Acta, Part A* 59 (2003) 2341–2352.
- [16] A. Vila, N. Ferrer, J.F. García, Chemical composition of contemporary black printing inks based on infrared spectroscopy: basic information for the characterization and discrimination of artistic prints, *Anal. Chim. Acta* 591 (2007) 97–105.
- [17] C. Genestar, C. Pons, Earth pigments in painting: characterization and differentiation by means of FTIR spectroscopy and SEM-EDS microanalysis, *Anal. Bioanal. Chem.* 382 (2005) 269–274.
- [18] A.R. Friedel, G.L. Carson, Infrared spectrum of ground graphite, *J. Phys. Chem.* 75 (1973) 1149–1151.
- [19] H.K. Jeong, Y.P. Lee, M.H. Jin, E.S. Kim, J.J. Bae, Y.H. Lee Thermal, stability of graphite oxide, *Chem. Phys. Lett.* 470 (2009) 255–258.
- [20] Y.Z.J. Jin, C. Gao, W.L. Hsu, Y. Zhu, A. Huczko, M. Bystrzejewski, M. Roe, C.Y. Lee, S. Acquah, H. Kroto, D.R.M. Walton, Large-scale synthesis and characterization of carbon spheres prepared by direct pyrolysis of hydrocarbons, *Carbon* 43 (2005) 1944–1953.
- [21] R. Selvan, R. Unnikrishnan, S. Ganapathy, T. Pradeep, Macroscopic synthesis and characterization of giant fullerenes, *Chem. Phys. Lett.* 316 (2000) 205–210.
- [22] H.W. van der Marel, H. Beutelspacher, *Atlas of Infrared Spectroscopy of Clay Minerals and their Admixtures*, Elsevier, Amsterdam, 1976.
- [23] R.L. Feller, Barium sulfate – natural and synthetic, in: R.L. Feller (Ed.), *Artists' pigments*, vol. 1, Oxford University Press, New York, 1986.
- [24] R.K. Sharma, J.B. Wooten, V.L. Baliga, X. Lin, W.G. Chan, M.R. Hajaligol, Characterization of chars from pyrolysis of lignin, *Fuel* 83 (2004) 1469–1482.
- [25] L. Lu, V. Sahajwalla, C. Kong, D. Harris, Quantitative X-ray diffraction analysis and its application to various coals, *Carbon* 39 (2001) 1821–1833.
- [26] M.E. Fleet, Infrared spectra of carbonate apatites: ν_2 -region bands, *Biomaterials* 30 (2009) 1473–1481.
- [27] N.P. Camacho, S. Rinnenthaler, E.P. Paschalis, R. Mendelsohn, A.L. Boskey, P. Fratzl, Complementary information on bone ultrastructure from scanning small angle x-ray scattering and fourier-transform infrared microspectroscopy, *Bone* 25 (1999) 287–293.
- [28] A. Kamińska, A. Sionkowska, Effect of UV radiation on the infrared spectra of collagen, *Polym. Degrad. Stab.* 51 (1996) 19–26.
- [29] L.F. Sukhodub, C. Moseke, L.B. Sukhodub, B. Sulkio-Cleff, V.Ya. Maleev, M.A. Semenov, E.G. Bereznyak, T.V. Bolbukh, Collagen-hydroxyapatite-water interactions investigated by XRD, piezogravimetry, infrared and Raman spectroscopy, *J. Mol. Struct.* 704 (2004) 53–58.
- [30] G.M. Languri, Molecular studies of asphalt, mummy and kassel earth pigments: their characterization, identification and effect on the drying of traditional oil paint, Archetype Publications, London, 2004.
- [31] C.S. Ku, S.P. Mun, Characterization of pyrolysis tar derived from lignocellulosic biomass, *J. Ind. Eng. Chem.* 12 (2006) 853–861.
- [32] A. Vergnoux, M. Guiliano, R. Di Rocco, M. Domeizel, F. Théraulaz, P. Doumenq, Quantitative and mid-infra-red changes of humic substances from burned soils, *Environ. Res.* 111 (2011) 205–214.
- [33] M.A. Legodi, D. de Waal, The preparation of magnetite, goethite, hematite and maghemite of pigment quality from mill scale iron waste, *Dye. Pigment.* 74 (2007) 161–168.