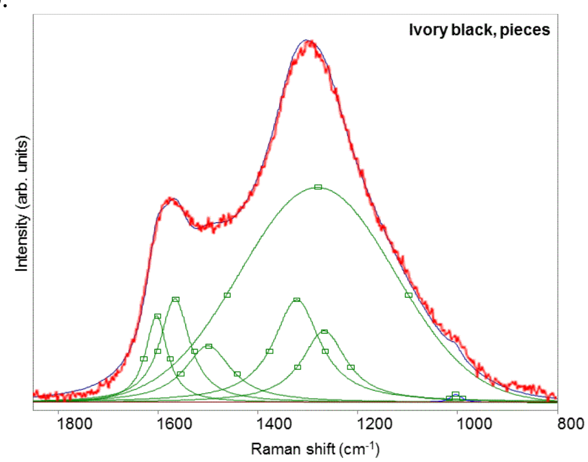
RAMAN SPECTROSCOPY FOR THE INVESTIGATION OF CARBON BASED BLACK PIGMENTS. A. Coccato[1], J. Jehlicka[2], L. Moens[3] and P. Vandenabeele[1], [1]Ghent University, Department of Archaeology, Sint-Pietersnieuwstraat 35 B-9000 Ghent, Belgium, Raman@ugent.be, [2]Charles University, Prague, Institute of Geochemistry, Mineralogy and Mineral Resources, Albertov 6, 128 43 Prague 2, Czech Republic, jehlicka@natur.cuni.cz, [3]Ghent University, Department of Analytical Chemistry, Krijgslaan 281 B-9000 Ghent, Belgium, Raman@ugent.be.

Introduction: A series of commercially available carbon based black pigments was analyzed by means of Raman spectroscopy. The purpose of this study is archaeometrical, although strongly overlapping with geology and materials science. Anyway, the geological definitions are not applicable in a straightforward way [1]. Moreover, the nomenclature of pigments is strongly ambiguous: often ancient treatises (as Pliny the Elder, Cennini, etc.) use obscure terms and non-univocal definitions in their recipes [2]. Some definitions for carbonaceous materials and carbon based black pigments are given in the table in order to try to minimize misunderstandings and misinterpretations.

The in plane stretching of carbon rings (G band, [3]) is always present in the Raman spectrum of carbonaceous material. Additional bands are visible in spectra of disordered materials (D, [4-7]). These disorder bands contain information about the carbonaceous materials structure [4, 6, 7] but their assignment is not yet clear [8-12]. The traceability of disorder in carbon based materials, that is achievable by means of Raman spectroscopy, can be of help in better defining the artists' pigment "carbon black", according to its production process.

	Definition, general [1, 3]	Correspondence with artists' materials [1]
Graphite	Crystalline hexagonal form of carbon.	Present in **black earths** and **black chalk**. **Graphite** pencils since XVI century.
Coke	Man-made material and fuel produced by carbonization of precursor bituminous coals or petroleum.	Main fraction of **ivory** and **bone blacks** (coked collagen + hydroxyapatite)
Coal	Lithified plant remains. Allochtonous materials are present.	**Asphaltum**, **bitumen**, **Van Dyck** and **Cassel brown** are natural bituminous coals.
Char	Residue of pyrolysis of wood. The morphology and structure depends on the precursors (non-graphitizable carbons).	Main component of **fruitstone chars**, **cork black**, **vine black** and **wood charcoal** in general.
Soot	Any carbon produced in the gas phase.	Main constituent of **lamp-black**, **soot** and **bister**.

Experimental: Carbon based black pigments were purchased from Kremer Pigmente (Aichstetten, Germany). They cover different origins (mineral, vegetal, animal) and different carbon types (graphitic well-ordered carbons; cokes, coals, chars and soots) – see table for the geological definitions and for some information about related black pigments. Raman spectra were obtained with both the red (785 nm) and green (532 nm) lasers of a Bruker Senterra Raman spectrometer. The laser power at the sample was kept as low as possible, to avoid thermal modifications in the carbonaceous structure. A linear baseline was subtracted in the region between ca. 850 and 1800 cm^{-1} [6, 13]. Spectral deconvolution was performed in GRAMS/AI 8.0.



Results and discussion: The determination of the structure of carbonaceous materials is of primary importance in the fields of geology and materials science. Important factors influence the metamorphic transformation in rocks: pressure as part of metamorphism and duration of the processes. On the contrary, man-made carbon based black pigments are mainly produced at atmospheric pressure. For archaeometrical purposes, it is indeed important to understand the materials that were used, in terms of technological know-how of the artist as well as his own preferences in painting practice.

Different methods are proposed in literature to correlate the Raman signature of a carbonaceous material with its structure.

Spectral parameters ratios are used to quantify the disordered carbon in respect to the ordered structure [5, 6]. A major problem when trying to calculate these ratios is the difficulty in identifying the D1 band. This band shifts with the laser wavelength [6, 9, 15, 16] and can be found in the range from 1280 [14] to 1400 cm^{-1}

[17, 18]. This wide range overlaps with the D4 band [4] and diamondlike carbon features [17, 18].

This method based on D1 and G bands spectral parameters is known to have weaknesses [5], and when it is applied to carbon based black pigments, it is less reliable, since the inhomogeneity among and within the studied samples is much wider than for geological samples. R1 and R2 ratios are successfully used to monitor trends in samples from homogeneous series [5], which is not the case here.

Something more applicable for the use of Raman spectroscopy on carbon based black pigments seems to be the evaluation of the fine structure of the spectrum, especially the carbon disorder bands (number and characteristics). This is published for coal geological materials [7] and wood charcoal [4]. Moreover, a band at 1190 cm^{-1} has been found in soot materials and in wood charcoal. A shoulder or band appearing in the region 1100-1250 cm^{-1} has been either identified as the D4 band [12] either as diamondlike sp^3 carbon band [4], but no agreement is obtained yet (for example [8]). Special attention was thus taken when dealing with the range 1000 to 1250 cm^{-1}, since almost every studied sample has features in this region (one or two bands are observed for both excitations). The assignment of these bands is not among the purposes of this study, but their presence is likely to be linked to disordered carbons and thus important for carbon based black pigments.

Conclusions: The applicability of Raman spectroscopy to study carbon based black pigments is here explored. In addition to the commonly investigated G and D1 bands [5, 6, 19], attention is drawn to the other disorder bands [4, 7, 8], in terms of number and band position, for better understanding the disorder features of the investigated material. The study of reference materials helps in the identification of disorder specificities of carbon based black pigments that will give a deeper insight in the type of “carbon black” that was used.

The potentialities of this disorder-focused approach can be applied for a deeper comprehension of the materials used in works of art, even if the quantification of the disorder respect to the ordered carbon doesn’t seem accessible with this purely qualitative method. The investigation of the bands below 1300 cm^{-1} seems promising as well, being related to specific disorder features possibly related to the raw materials used for producing carbon black.

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