Crystallite size of the graphitic phase in soot ink based on historic recipe: A potential dating tool for old manuscripts

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Physical Sciences - Article

Keywords: Soot ink, Ottoman manuscript, lamp black, Raman spectroscopy, carbon-based pigments, dating

Posted Date: December 29th, 2021

DOI: https://doi.org/10.21203/rs.3.rs-1211962/v1

Abstract

In this paper, we report the crystallite size of the graphitic phase observed in a soot ink sample prepared based on an original Ottoman recipe in the 18th century for the first time. Intensity ratio of the D and G bands that were observed at 1384 and 1609 cm^{-1} respectively, revealed that the crystallite size is 24.33 nm. This corresponds to a carbon phase between graphitic and well graphitic stage. We strongly believe that this could be further used particularly for dating purposes by investigating carbon-black pigments which we have not encountered its consideration in the literature for mainly manuscripts. Here, we especially propose using the Tuinstra-Koenig relationship together with the consideration of D and G band profiles to derive the crystallite size of the graphitic phase observed in soot ink and other various carbon-black inks for the purpose of manuscript dating.

Full Text

Since the first time it was employed, writing has had a special significance for every civilisation. It has been employed as an aesthetic feature as well as a technique for recording information in Islamic civilizations. Although oral culture was popular in the early years of Islam, with the growth of the Islamic world, writing and creating copies of the Qur'an has become increasingly important for diverse nations to understand it accurately. Muslims enhanced the beauty of inscriptions by incorporating spiritual sentiments and religious endeavours. For this reason, various writing styles appeared during ages [1,2]. Calligraphy has become an alternative to painting, and surfaces in architectural and other fields are embellished with calligraphic inscriptions. In some cases, the aesthetics of the inscription have grown more popular than the content of the text. Beautiful calligraphy places were built in the realms of architecture and art, particularly in the Ottoman culture, and beautiful inscriptions were inscribed on these regions by prominent calligraphists [2,3]. The Ottoman civilisation saw the apex of ink manufacturing in terms of colour and quality. Even after centuries, writings in books and treatises from the Ottoman Empire have retained their colour and life. To address the need of calligraphers who practice the art of calligraphy, a foundation for ink manufacturing has been formed [2,4].

Soot cannot be acquired in the city since it causes problems owing to the smoke emitted during manufacture. As a result, throughout the Ottoman Empire, individuals who produced soot and those who produced ink from this substance were two distinct groups. Ink manufacturing facilities were erected in the city core, while soot manufacturing facilities were established around the city. These individuals processed soot to make ink at industrial facilities erected near Tekfur Palace in Istanbul's Egrikapi neighbourhood [2,4]. In certain mosques, the soot produced by oil lamps was utilized to make ink by putting it in a system at a specific location. The air flow was designed to produce soot, which was collected in a specific entryway. The most stunning example of this approach is the Suleymaniye Mosque. The doors to the mosque are located at the top of the north gate. The soot from the mosque's oil lamps is gathered through these vents with the air circulation in the soot chambers. Calligraphers, who require ink for writing, utilized soot to create ink [2,5].

Regarding the studies encountered in previous works on black pigments and inks/soot inks, Autran et al. investigated the nature of the black pigments used on ancient Egyptian papyri from Champollion collection and they found that the carbon-black pigment found in the ink was identified as flame carbon (lampblack or soot). They used X-ray diffraction tomography and confirmed the existence of carbon-based pigment [6]. In another recent research by Idjouadiene and co-workers, Algerian heritage manuscripts were investigated by Raman spectroscopy for the first time and iron gall ink and ivory/bone black was detected successfully. Also black ink used in the Kabylia region was reported to be made from burned sheep wool [7]. Raman spectroscopy also helped dating the Egyptian papyri and that work allowed scientists to distinguish the periods and authors suggested that the black pigments used for Egyptian Book of the Dead fragment of the early Hellenistic period are distinct from the carbon pigments used in writing inks of other ancient manuscripts [8]. Kantoğlu et al. identified the inks used in Ottoman diplomatic documents dating from the 13th to the 20th century by Raman and FTIR spectroscopy. They found that those manuscripts were written in iron-gall and carbon-based ink (carbon black/soot), cochineal (red) ink and gold [9]. Many other research efforts on determination of black inks and its alternatives with different techniques like Scanning Electron Microscopy were also performed on black inks so far [10–12]. Lamp black as a black pigment which was determined by Raman spectroscopy was also reported in many previous studies such as decoration of the main frame of Ms Pers 1 (UCL) “Anatomy of the Body” [13,14].

Raman spectrum of the black ink used in our study was presented in Fig. 1 together with the spot where the spectrum was collected. Our findings demonstrated that black paint (denoted in blue colour in the matching database results in Fig. 2) prepared based on the ancient recipe which was previously reported [2,4,15–17] was consistent with the database-matched [18] lamp black by 82.27% hit score. Second best hit was the ivory black with the hit score of 61.30% which is relatively lower score compared to lamp black. This difference and matching scores are due to the search algorithm by the software and full width at half maximum (FWHM) and the relative intensities of the D and G bands of the spectrum. We observed sp^3 and sp^2 hybridised amorphous carbon FWHM at D and G bands at 1384 and 1609 cm^{-1}, respectively. The absence of the band which is unique to phosphate at 960 cm^{-1} is a clear indication of absence of bone black and burned ivory origin [19]. Broad bands appeared in our soot ink sample imply the low degree of crystallinity of the black pigment (soot ink we used here) [20]. The broad bands for amorphous carbon observed at 1590 and 1320 cm^{-1} for research on wall paintings at Sala Vaccarini in Catania (Sicily) are also in line with our findings. Moreover, to the best of our knowledge it is also noteworthy to state that we have not found many papers focus particularly on the FWHM data in neither painting used already in artifacts nor soot ink samples prepared based on the ancient recipes. Coccato and co-workers also emphasized the lack of archaeometric literature on the distinguishing among various carbon-based black pigments in their work in 2014 [21]. Thus, we believe that our findings are of importance in terms of filling this gap and contributing the determination of carbon-based materials in near future.

As stated in previous publications, we also suggest that the G band (1609 cm^{-1}) is associated with in-plane stretching vibration of the aromatic ring C-C bond (E_2g_2 mode), whereas the D band (1384 cm^{-1}) is

a result of in-plane defects and the presence of heteroatoms (A_{1g} mode) [21,22]. Besides, FWHM data was also presented in Table 1 together with the D and G band positions. According to Table 1, FWHM of D and G bands observed in our study were 101.01 and 213.95 cm^{-1}, respectively. Here, we should emphasize that the position of the D band shifts based on the used laser's excitation wavelength [23–25]. Based on these works and an investigation on Raman spectroscopy of carbon materials published in 1990 by Wang et al. [26], the carbon in our soot ink sample prepared based on an Ottoman era recipe was glassy carbon [26]. Besides, G band is expected whenever the D band is observed and this band occurs (and rises in intensity) in disordered materials [21,27].

Tuinstra and Koenig (1970) developed a relationship between the graphite peak parameters and the "amount of crystal boundary" of the graphitic sample based on artificial carbon samples based on the intensity ratio of the D and G bands [28]. They used equation below to find the crystallite size (L_a). (In the equation, λ corresponds to the laser excitation wavelength (532 nm here)). According to the equation here, we found this intensity ratio (I_D/I_G) as 0.79. This data corresponds to a crystallite size of 24.33 nm which is somewhere between graphitic and well-graphitic-carbon [28]. This relationship is also known as "TK relation".

$$L_a\ (nm) = 2.4x10^{-10}\ \lambda^4\ (I_D/I_G)^{-1}$$

This paper highlighted the importance of the usage of the D and G bands of the carbon signals in Raman spectrum and their FWHM data to interpret the carbon phase (and crystallite size) of the soot ink prepared according to the Ottoman era recipe that was used in manuscripts. This analogous black ink (soot ink) and its multi-analytical investigation would pave the way for understanding how such inks were prepared in previous ages and how the resultant ink was effective on the paper used. We were able to determine the crystallite size of the carbonaceous phase in soot ink to be 24.37 nm based on TK relationship. We observed D and G bands at 1304 and 1609 cm^{-1}, respectively which are in line with previous reported data.

However, our work clearly has some limitations because it is extremely rare and almost impossible to access cultural heritage artifacts (manuscripts etc.) in museums and exhibitions due to regulations. Despite this, it is quite crucial to access such original recipes in ancient resources thus, at least the scientists have opportunity to prepare such samples according to the original recipe and comparison is possible with the original product and the prepared one. Moreover, this study has only investigated only one sample of soot ink based on the original recipe. There must be many black ink preparation recipes from many nations' archives. It would be very interesting to prepare those samples with an international and multidisciplinary effort with multi analytical techniques to see the differences between the samples. In this way, it would be even possible to suggest technology/art/knowledge/know-how transfer between continents during ages. Finally, there is a strong need in research on such historical ink samples using different laser excitation wavelengths in a systematic way with the support of multi-analytical approach

to see the differences in band profiles (position, intensity and FWHM) of D and G bands to distinguish the phases of the carbonaceous materials thus, proposing the dates.

Table 1. Raman shift, intensity, and FWHM data on the D and G carbon bands.

Raman shift (cm^{-1})	Intensity	FWHM (cm^{-1})
1384 (D band)	25246 (D band)	101.01 (D band)
1609 (G band)	31797 (G band)	213.95 (G band)

Our paper highlighted the importance of the usage of the D and G bands of the carbon signals in Raman spectrum and their FWHM data to interpret the carbon phase (and crystallite size) of the soot ink prepared according to the Ottoman era recipe that was used in manuscripts. This analogous black ink (soot ink) and its multi-analytical investigation would pave the way for understanding how such inks were prepared in previous ages and how the resultant ink was effective on the paper used. We were able to determine the crystallite size of the carbonaceous phase in soot ink to be 24.37 nm based on TK relationship. We observed D and G bands at 1304 and 1609 cm^{-1}, respectively which are in line with previous reported data. However, our work clearly has some limitations because it is extremely rare and almost impossible to access cultural heritage artifacts (manuscripts etc.) in museums and exhibitions due to regulations. Despite this, it is quite crucial to access such original recipes in ancient resources thus, at least the scientists have opportunity to prepare such samples according to the original recipe and comparison is possible with the original product and the prepared one. Moreover, this study has only investigated only one sample of soot ink based on the original recipe. There must be many black ink preparation recipes from many nations' archives. It would be very interesting to prepare those samples with an international and multidisciplinary effort with multi analytical techniques to see the differences between the samples. In this way, it would be even possible to suggest technology/art/knowledge/know-how transfer between continents during ages.

Finally, there is a strong need in research on such historical ink samples using different laser excitation wavelengths in a systematic way with the support of multi-analytical approach to see the differences in band profiles (position, intensity and FWHM) of D and G bands to distinguish the phases of the carbonaceous materials thus, proposing the dates. Here, we propose using Tuinstra-Koenig relationship (by crystallite size of graphitic phases) to estimate the production dates by utilizing the Raman band profiles of carbon phases for the first time for ancient manuscripts.

Methods

Historical soot ink samples were prepared as previously described in historical records and publications based on those records[2,15,16]. As stated in those publications we translated the preparation quote as follows: We used one fifth of the substances s listed below: *"3.2 g soot, 6.4 g bile, 1.6 g crystallized sugar, 1.6 g of iron sulfate, 10 g Arabic gum, 75 g rosewater, Soot and bile are mixed and dried and then 2 g of water is added, and the mixture was crushed. Then, it was dried under sun light. Crystallized sugar and*

iron sulfate were melted in 1.6 g of water separately. The melted crystallized sugar, iron sulfate and Arabic gum with a consistency of honey is added to the dried soot and crushed with finger again. The mixture was dried again. Then, rosewater was added to the mixture and 81 g of ink was produced". (Here, one "dirham" corresponds to 3.2075 g particularly in Ottoman measurement standards for weight). Raman spectrum of the black soot ink was recorded between 145-3104 cm−1 by Renishaw İnVia Raman spectrometer equipped with a diode-pumped solid state (DPSS) 532 nm (class 1) laser excitation line. Reference silicon wafer (520.7 ± 0.5 cm^{-1}) was used for the calibration of the Raman spectrometer. The spectrometer was attached to a Research Grade Leica DM2700 microscope with better than 2 μm depth resolution. Spectral and spatial resolution were 2 cm^{-1} and 1 μm, respectively. Detector was cooled to −70 °C thermoelectrically by Peltier module. Integrated detector was Renishaw Centrus 2945K7 (1040×256 pixels). The power of the incident laser applied on the sample's surface requires to be low enough to avoid heating, degradation and even burning of the sample. Approximately 5% (~1 mW corresponding to a laser power density of ~0.625 mW/$μm^2$) power of laser was applied on the sample. This amount of laser exposure on the sample is not enough to trigger any type of thermal alteration or damage on the sample. Laser exposure time was 20 s with 1 accumulation and fixed laser spot size was 2 μm. 2400 lines/mm of grating was used. Raman spectral image was collected by Renishaw confocal İnVia Raman Microscope with 20× magnification. Raman spectrum (Fig. 1) was collected from the spot (Figure 1b) under 20× microscope objective (scale bar in the image is 50 μm).

Declarations

Acknowledgements. O.U. and A.O. acknowledge to B.Y. for supplying the recipe-based soot ink for this study. B.Y. acknowledges Scientific and Technological Research Council of Turkey (Project number: 114K288)

Author contributions. O.U. planned the study, performed the Raman spectroscopy experiment, analysed, and interpreted the data and wrote the paper. A.O. and B.Y. helped to write the draft of the paper by contributing supplying the resources (references). B.Y. supplied the soot sample ink by preparing it based on the original ancient recipe. All authors were given the opportunity to review the results and comment on the manuscript.

Competing interests. The authors declare no competing interests.

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Figures

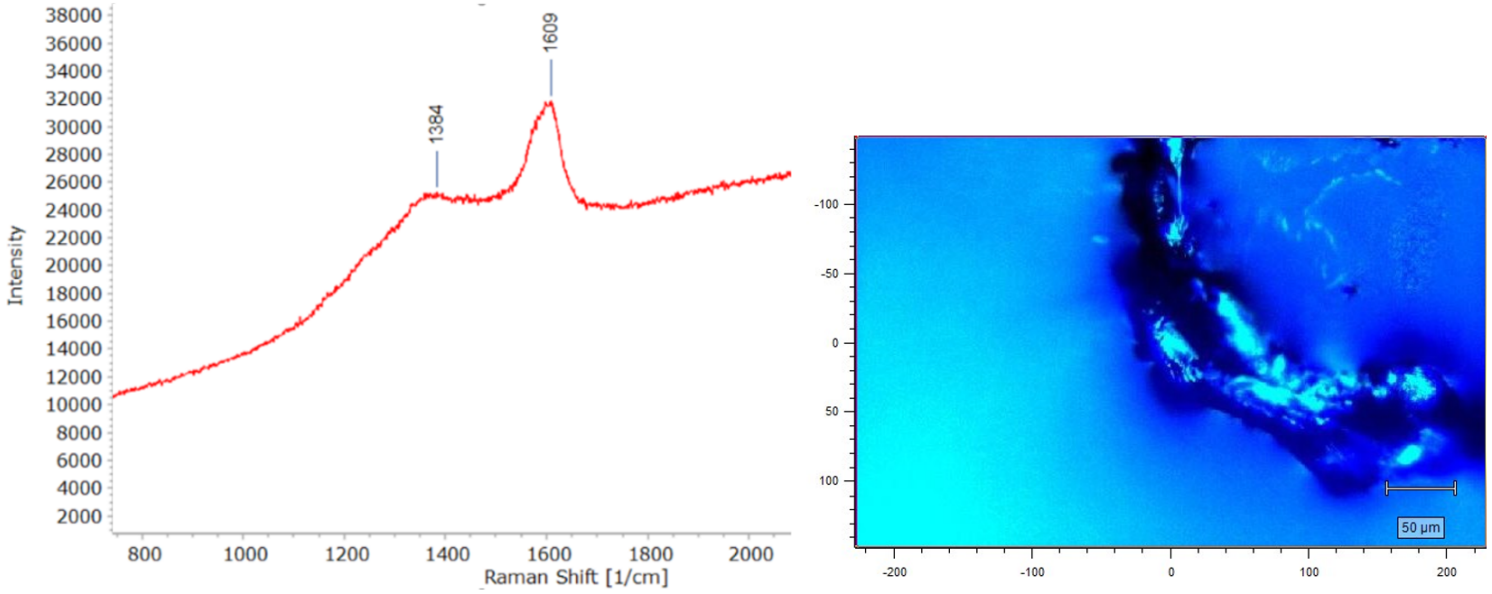

Figure 1

The Raman spectrum showing D and G bands (left panel) and the spot (center of the image at 0:0 coordinate) where the spectrum of the soot ink collected (right panel).

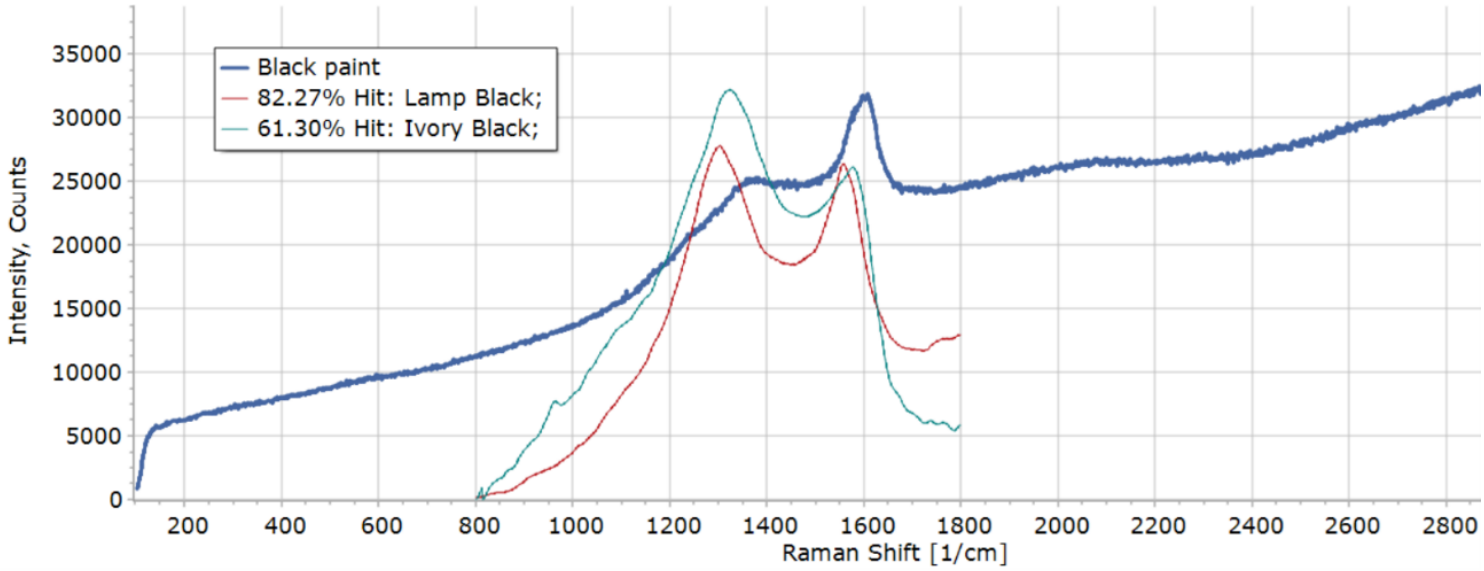

Figure 2

Matching hits for the Raman spectrum of the soot ink.