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Characterization of sepia ink in ancient graphic documents by capillary electrophoresis

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ABSTRACT

A simple and rapid capillary electrophoresis with diode array detection method was developed for sepia ink identification in ancient graphic documents.
Separation was performed in a fused-silica capillary (64.5 cm length, 50 μm i.d.). The running buffer was 20 mM sodium tetraborate solution, pH 9.2. The applied potential was 25 kV, temperature 25 °C and detection was at 220 nm. An appropriate extraction procedure was applied for the take and treatment of sample from the reference substances and ancient graphic documents. This method was successfully applied to the collection of drawings and maps from the Royal Chancellery Archives of Granada (Spain).

1. Introduction

Writing ink was invented in China and Egypt ca. 2500 B.C. using soot as main component. From the Middle Ages, Arabic gum, copper sulphate and tannins were used. The most common colours were black, red, blue, and later sepia, as they had to be saturated colours and dark enough to make reading easy. They were applied with a quill or a reed [1].

"Sepia" ink, of a reddish-brown tone, is drawn directly from the ink pouch of the *Sepia officinalis* (cuttlefish). It is a dark and semitransparent colour, which can be used as ink for writing or watercolour. It has a great tonal range that depends on the dissolution used. Sepia ink use is known since the 17th century, but it is not until the 19th century that it became really common, especially among artists and painters [2]. At present, it is still very common in arts, although the term "sepia" is now applied to any ink which has this reddish tone, regardless of its origin [3].

Processing sepia ink for writing is quiet simple: first, the ink is extracted straight from the pouch of the *Sepia officinalis* (cuttlefish), this process needs to be done quickly since the contact of the ink with the air has to be minimal. Then, a medium is added, generally Arabic gum and water, being the quantitative relation 1 part of water for every 1000 parts of ink, approximately. At this moment, the sepia ink can be used for writing, generally applied with quill or reed [4].

Sepia ink is mainly composed of melanin, the substance that gives sepia its colour and acts as a pigment, and of mucus, that gives sepia its glutinous texture. Sepia ink has little resistance to sunlight [5].

Melanin is found in a diverse array of biological structures. While melanin is commonly associated with skin and hair colour in humans, various melanin types are also present in the inner ear, eyes, bird feathers, insect cuticles and the ink sac of *Sepia* cuttlefish. Degradation studies on sepia melanin show that it is a copolymer of 5,6-dihydroxyindole (DHI) and 5,6-dihydroxyindole-2-carboxylic acid (DHICA) (Fig. 1) [6].

Further oxidation of these units indicates that pyrrole mono-, di- and tri-carboxylic acids could be present in the polymeric chain of the pigment. As an example, it was recently reported that *Sepia* melanin is a mixture of oligomeric structures incorporating over 75% of DHICA-derived units and 20% of DHI-derived units, occurring for most part in the pyrrole carboxylic acid degraded form. Three types of linkages for 5,6-dihydroxyindole units are found within the melanin structures: (*a*) cross-linkages between pyrrole rings; (*b*) chain linkages through benzene-type rings alone, propagating a chain; and (*c*) branching linkages between benzene and pyrrole rings, creating a branch from the main chain [7].

Analytical methods are used for melanin determination in biological materials. Ito and Jimbow [8] proposed a method based on the chemical degradation of the melanin polymer followed by high performance liquid cromatography (HPLC) identification and quantification of specific degradation products by electrochemical detection. Also, recently, Yang et al. [9] proposed a new HPLC method with fluorescence detection for melanin determination in biological materials. On the other hand, there are no examples for sepia melanin determination in graphic document samples, they have not been found in the reviewed bibliography.

From the point of view of conservation and restoration of Documental Heritage, knowledge of the manufactured materials and techniques used is essential to determine the best restoration

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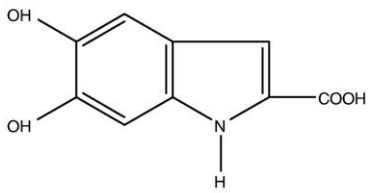
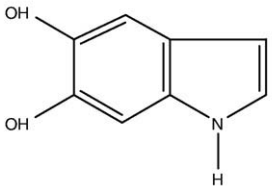


5,6-dihydroxyindole-2-carboxilic acid



5,6-dihydroxyindole

Fig. 1. Chemical structure of sepia melanin principal constituents.

treatments. In order to do so, it becomes very important to identify sepia ink components and to differentiate sepia from other inks similar in colour such as metal gall inks [10]. Although sepia ink use was very common before the 19th century, for a long time there was no effective method to differentiate it from metal gall inks. However, metal gall inks can be identified when visible paper degradation has occurred due to ink corrosion.

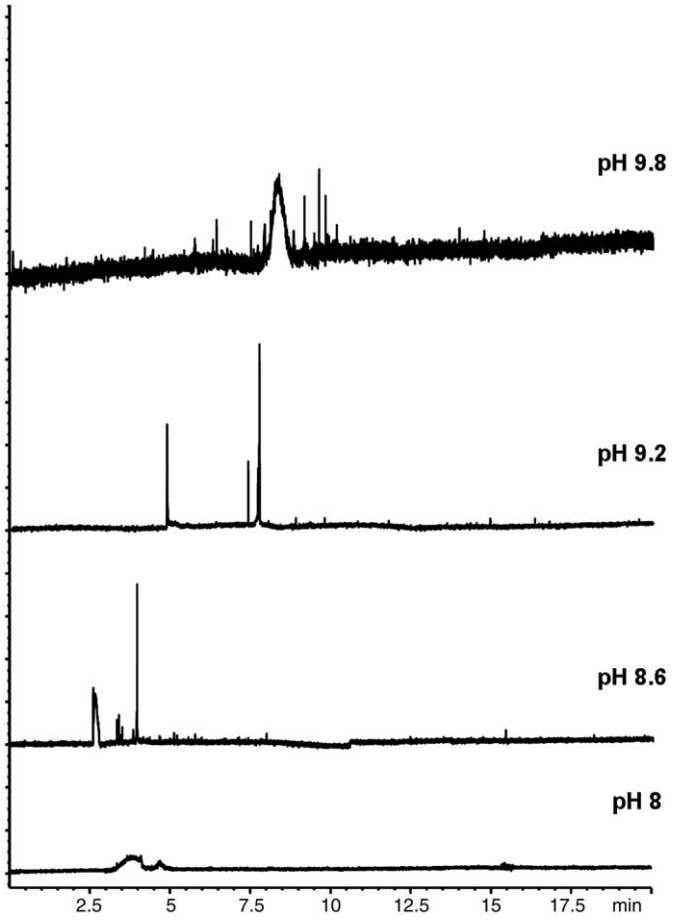


Fig. 2. Electropherograms of sepia ink at different pH values.

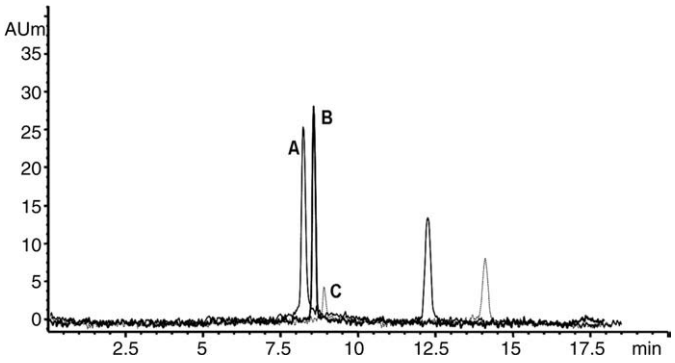


Fig. 3. Sepia ink electropherograms from different cuttlefish: A, B and C.

Colouring agent identification in the paint layers of artworks is a complex task due to the simultaneous presence of dyes, pigments, minerals, polysaccharides, proteins, oils and/or resins. The rich matrix composition implies the necessity for preliminary separation of the components of the sample prior to identification.

Capillary electrophoresis (CE) has proven to be a very powerful tool for characterization of inorganic and organic compounds since its introduction by Jorgeson and Lukacs in the early 80s [11]. CE has been applied to solve analytical problems related to forensic chemistry, food chemistry, clinical chemistry, biochemistry, pharmaceutical science, neuroscience, molecular biology and environmental science.

However, few studies have used CE in order to identify art materials on graphic documents. This technique has only been applied on textile dyes [12,13], on graphic documents [14] and to identify colouring materials on paintings [15].

This is a rapid technique that allows short analysis times and high separation efficiency. CE has proved to be an excellent alternative to HPLC [16]. CE resolution is greater than that of HPLC and precision is of the same order. Moreover, CE is less costly than HPLC and requires only modest quantities of sample. Concentration sensitivity of diodo array detection in CE is, however, relatively poor compared with that of HPLC.

The methods of analysis for ink identification must be highly selective and sensitive because of the complexity of the matrixes and the limited quantity of sample available, particularly in the case of graphic documents and archive materials [17]. For these reasons, CE is the technique selected for developing a new method to identify inks in ancient graphic documents.

Sample taking process is really an essential step since the reliability of an analytical result is often determined by the quality of the sample taken. Furthermore, if the object of the analysis is a graphic document, there are two important steps in the sampling process in order to keep

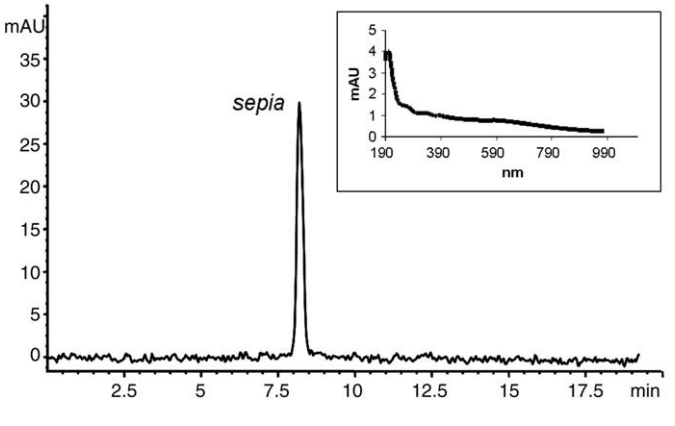


Fig. 4. Electropherogram obtained from sepia ink solutions from *Sepia officinalis* under the optimised conditions.

Table 1
Electrophoretic migration time and maximum absorption values for sepia ink.

Dye	Migration time (min)	Peak N°	Absorption (nm)	Natural source
Sepia ink	8.342	1	190, 220	*Sepia officinalis*

the physical integrity of the document: (a) sample taking technique should be non-destructive and (b) the amount of sample taken should be minimum. Using a brush imbibed with the proper solvent allows taking minimal amounts of sample keeping the physical integrity of the graphic document almost intact. Sample preparation is then easier: the ink extracted with the brush is adequately dissolved and the solution is then centrifuged and injected into the CE apparatus.

In this study, we intended to identify sepia ink in historical maps by using a new CE-DAD method. The method proposed in this paper has been applied to the historical maps belonging to The Royal Chancellery Archives of Granada (Spain).

The Royal Chancellery Archives of Granada holds the collections of the institution known as the *Real Audiencia y Chancillería de Granada* (1494–1835). The Royal Chancellery was established by the Catholic monarchs as the High Court of Justice that, as a court of appeal was in charge of cases which had been presented previously before the local courts of justice. As a consequence, The Royal Chancellery collections are of paramount importance as holders of history and laws, and also because they gather a vast source of data and important historical information on economics, social and religious ideas and local ways of thinking [18]. The maps and drawings of the collection were part of the legal proceedings, they were exhibits or evidence and obtaining them was entrusted to the recipient [19]. Their authors or painting experts were people chosen for their skills and knowledge of a given subject: architecture or building masters, alamines, stonemasons, land surveyors, painting masters, along with an extensive network of professional experts [20]. These maps and drawings were used by the judges to reach their decisions. These documents show an odd system of numbers and letters for codifying possessions, properties, geographic areas, roads and the elevation or ground plan of a building. They were used during a trial by virtue of a Royal Recipient Provision at the request of one of the parties for the preparation of the maps. They were elements of reference and inestimable value for attorneys, prosecutors and judges to pass sentence [21].

Due to the interest of these documents and the extensive use of sepia ink on said documents, their study and analysis is considered essential.

The maps analysed from the collection of The Royal Chancellery Archives of Granada come from different places of Andalusia (Spain) and they dated from the 16th to the 19th centuries.

2. Experimental

2.1. Instrumentation and software

Electrophoresis was performed with a HP^{3D} CE instrument (Agilent Technologies, Waldbronn, Germany) equipped with a DAD, a thermostated column cartridge, a high voltage built-in power supply and an autosampler. The HP ChemStation version A.0901 (Agilent) software package was used for retrieval and processing of electropherograms. Separations were carried out in fused silica capillaries (64.5 cm × 50 μm internal diameter) with a capillary inlet-detector distance of 56 cm.

An Agilent 8453E (Waldbronn, Germany) UV–vis spectrophotometer was used for recording sepia ink absorbance spectra.

All pH measurements were made with a Crison (Crison Instruments SA, Barcelona, Spain) combined glass-saturated calomel electrode using a previously calibrated Crison 2000 digital pH-meter.

An ultrasonic bath (Selecta, Barcelona, Spain) and 0.20 μm pore size nylon filters (Supelco, Bellefonte, PA, USA) were also used.

2.2. Chemicals and reagents

All reagents were analytical grade, unless stated otherwise. Water was purified by means of a Milli-Q plus system (Millipore, Bedford, MA, USA).

Sepia ink, used as reference substance, was obtained from the ink pouch of the *Sepia officinalis* cuttlefish. The fresh *Sepia officinalis* cuttlefishes were obtained from the marketplace daily.

Sodium tetraborate decahydrate and ammonium acetate were supplied by Sigma-Aldrich (St. Louis, MO, USA), sodium dihydrogen

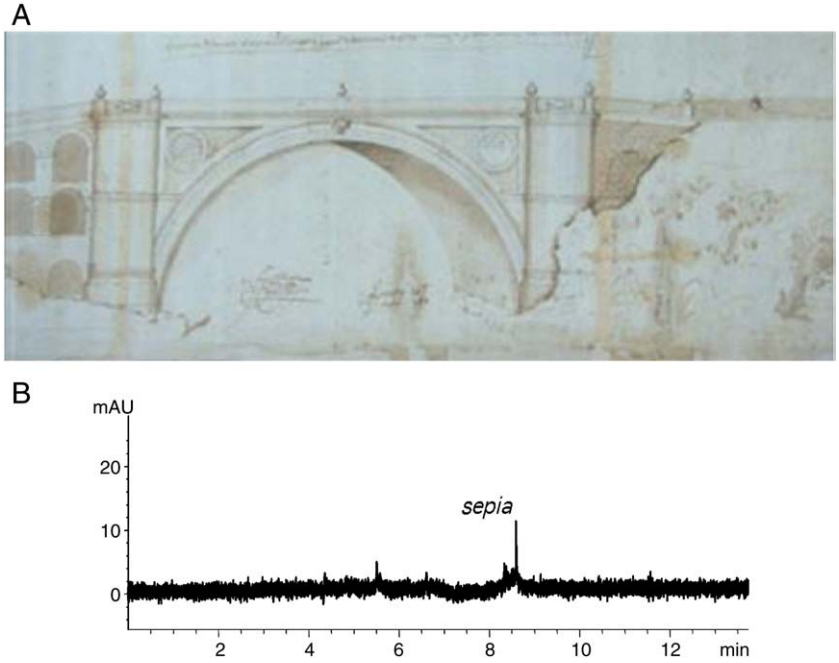


Fig. 5. (A) Map 5: "Traza nueva de un Puente sobre el Guadalquivir, Baeza". Francisco y Andrés de Valdelvira, 1570. Collection of drawings and maps from the Royal Chancellery Archives of Granada (Spain). (B) Electropherogram of map 5.

Table 2
Results obtained in the study of the collection of drawings and maps from the Royal Chancellery Archives of Granada (Spain).

Map number	Dye	Date
5	Sepia	1570
34	Sepia	1817
46	Sepia	17?
50	Sepia	1787
51	Sepia	1612
52	Sepia	1634
55	Sepia	1767
74	Sepia	17?
93	Sepia	1768

phosphate monohydrate, ammonium chloride by Fluka (Buchs, Switzerland) and hydrochloric acid and sodium hydroxide by Panreac (Barcelona, Spain).

The reagent used to prepare the reference solutions and to carry out sample taking was sodium dodecyl sulfate (SDS) from Fluka.

2.3. Extraction procedure

2.3.1. Reference substance

The sepia ink used as reference substance was obtained by extraction from the ink pouch of the *Sepia officinalis* cuttlefish. Work solution was prepared by exact weighing of the extract (3.75 mg) and dissolution into 5 mL of 0.1 M SDS solution. The process of extraction from the pouch was carried out quickly because sepia ink is unstable when in contact with air.

2.3.2. Taking and treatment of samples from maps

The taking of sepia ink from samples was carried out using the method proposed by Blanc et al. [22], using a brush imbibed with 0.1 M SDS solution and applying it directly onto the map. The extract transferred on the brush from the paper contained particles and SDS soluble compounds coming from the colouring layer. The extract was transferred to a 0.1 M SDS solution and sonicated for 5 min. The solution was centrifuged at 2000 rpm for 5 min before being injected into the capillary.

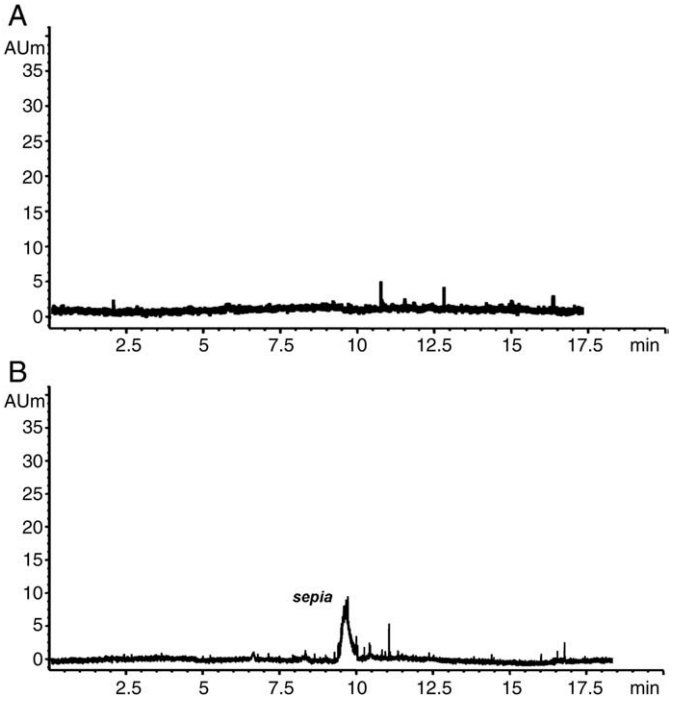


Fig. 6. Electropherograms of map samples. (A) Sample without sepia ink (map 9). (B) Sample with sepia ink (map 51).

2.4. Electrophoretic procedure

CE separation was carried out on a fused-silica capillary (50 μm internal diameter, total length 64.5 cm, a detection window was created at 56 cm from the capillary inlet). Every time a new capillary was used it was preconditioned by rinsing with 1 M NaOH for 20 min at 60 °C, followed by a 5 min rinse with deionised water and 20 min rinse with buffer solution. For the following analyses the capillary was rinsed with 0.1 M NaOH for 5 min at 25 °C, followed by a 3 min flush with deionised water to assure good repeatability. The capillary was conditioned with the running buffer (20 mM sodium tetraborate adjusted to pH 9.2) for 15 min before each sample injection.

Samples were injected hydrodynamically in the anodic end of the capillary with a pressure mode of 50 mbar for 4 s. Electrophoretic separation was performed at 25 kV for 15 min, resulting in a current of around 24 μA. The temperature of the capillary was kept at 25 °C. After each analysis, the capillary was rinsed for 3 min with deionised water.

All solutions, buffers and samples were filtered through a 0.20 μm nylon membrane filter. The running buffer was changed every 3 runs. UV detection was carried out monitoring at 220 nm. DAD was used at a range of 190–600 nm for the retrieval of to the spectral data.

2.5. Study of the stability of sepia ink

Stability of the solution of sepia ink in 0.1 M SDS was examined over a 48 h period. In the present study, the amount of melanin found in sepia ink from various cuttlefish was also examined. For this study the solutions were prepared as described previously.

3. Results and discussion

3.1. Optimization of CE method

In order to determine the optimum conditions for CE method, experimental variables and instrumental parameters were investigated.

3.1.1. Effect of pH value

To determine the optimum conditions for CE, several electrophoretic media were studied at different pH. The alkaline media was found to be the only effective media for sepia ink identification. The effect of alkaline pH was tested by adjusting the buffer (sodium tetraborate 20 mM) pH between 8 and 10 (in steps of 0.4) by adding a proper amount of 1.0 M HCl or 1.0 M NaOH. We observed (Fig. 2) that at pH 9.2 peaks resolution was good, and the analysis time was shorter. Therefore, we selected pH value 9.2 as optimum.

3.1.2. Selection of buffer. Effect of buffer concentration

Three different buffers were tested: sodium tetraborate, ammonium chloride and ammonium acetate. All of them were prepared at pH 9.2. With ammonium chloride and ammonium acetate the current was extremely high, so sodium tetraborate decahydrate was selected instead as the buffer running because it gave the best resolution in a satisfactory time.

The buffer concentration was tested at a range of 20–80 mM (in steps of 20). When the buffer concentration was increased, the analysis times became longer. We selected 20 mM sodium tetraborate as the optimum buffer concentration value because it offered the best compromise between electropherogram resolution and reasonable analysis time.

3.1.3. Effect of instrumental parameters in the CE method

The temperature was tested at a range of 20–30 °C. When the temperature was increased the analysis time was shorter. The experimental work was carried out at room temperature (25 °C).

The applied voltage was studied in a 20–30 kV range. The voltage used for obtaining the shorter analysis time and maintaining a good resolution was 25 kV.

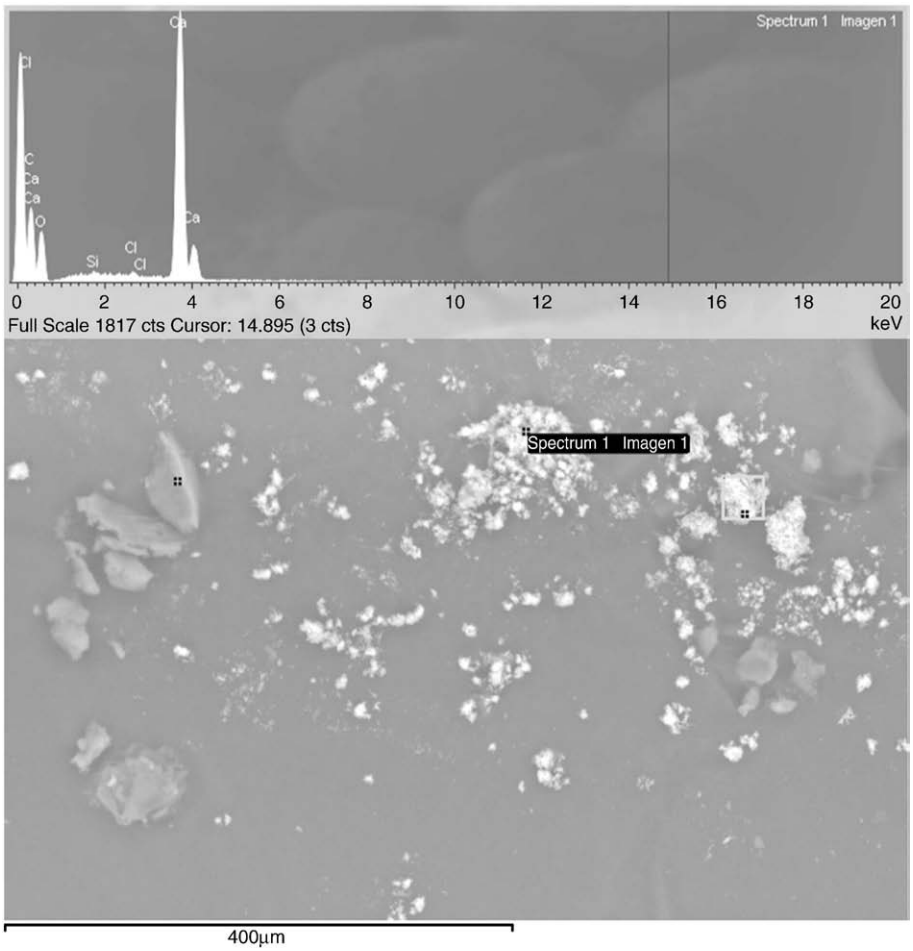


Fig. 7. SEM image of map sample.

The sample solution was prepared in 0.1 M SDS before injection on the CE system. In order to improve the detection, the injection time was varied between 4 and 12 s applying 50 mbar hydrodynamic injection. When the injection time was increased the peak height increased, but the peak shape was not successful. Therefore, 4 s injection time is a compromise between peak height and peak shape.

3.1.4. Optimized results

As the results mentioned above, the optimized conditions were obtained with the background electrolyte containing 20 mM sodium tetraborate buffer at pH 9.2, 25 kV applied voltage, 64.5 cm length and 50 µm i.d. capillary, 220 nm wavelength, 50 mbar 4 s hydrodynamic injection, and 25 °C temperature.

3.2. Sepia ink stability

Sepia ink stability in 0.1 M SDS was determined for the 48 h period, as mentioned above. A loss of peak resolution was found after 24 h. The solution of sepia ink in 0.1 M SDS was stable for, at least, one day.

The amount of melanin found in sepia ink from three different cuttlefish (A, B and C) was different. As we show in Fig. 3, the variation of migration times is minimal, but peak area changes for different cuttlefish.

3.3. Application of the method

The reported investigations were carried out in two stages. Firstly, electrophoretic measurements were carried out for sepia ink collected from various *Sepia officinalis* cuttlefish and the electrophoretic procedure was applied. Then CE data were recorded from ink extracts from the historical maps. Ink identification was based on migration times and their comparison with reference substances as well as on UV–vis spectra recorded from sample extracts and reference substances.

3.3.1. CE of Sepia ink from Sepia officinalis

Sepia ink CE was carried out by using the substance obtained from *Sepia officinalis* cuttlefishes. The electropherogram obtained under optimized conditions for sepia ink solution in 0.1 M SDS is shown in Fig. 4 together with the UV–vis spectra of identified chemical specie.

The UV–vis spectra were obtained at electropherogram peak and are similar to those spectra obtained with the reference substance in the spectrophotometric study. The migration time obtained under the electrophoretic conditions established and spectrophotometric data are shown in Table 1. The analysis time was approximately 8 min.

3.3.2. EC of extracts from maps

Samples taken from the collection of drawings and maps from The Royal Chancellery Archives of Granada (Spain), dated from 16th to 19th century, were examined using the proposed analytical method. The sepia ink peak was identified by comparing the migration time

Table 3
Precision of the electrophoretic method.

Sample	R.S.D. (%)
Map 5	2.36
Map 51	2.89
Map 93	2.44

and UV–vis absorption spectrum obtained from the reference substance. An example of sepia ink identification is shown in Fig. 5. The results found are summarised in Table 2.

3.4. Validation of the method

In order to validate the feasibility and validity of our developed method in the analysis, routine criteria such as specificity, precision and use of the other analytical technique were assessed as described below.

3.4.1. Specificity of method

The matrix composition of the samples from the maps is very complex due to the simultaneous presence of dyes, pigments, minerals, polysaccharides and/or proteins. It was found that the peak of sepia ink was not interfered under the optimized conditions and it was separated from other components as shown in Fig. 6. Fig. 6A is the electropherogram of the sample without sepia ink and Fig. 6B displays the peak of sepia ink. It showed good specificity for the identification of the sepia ink.

3.4.2. Precision

Precision was evaluated by measuring relative standard deviations (R.S.D.) of peak area samples. The precision was performed by analyzing the samples in 1 day for five times. The results (see Table 3) implied that the operating conditions selected above could provide a stable background with good repeatability.

3.4.3. The use of other analytical technique

The drawings and maps from The Royal Chancellery Archives in Granada (Spain) were also analysed using scanning electron microscopy (SEM). By SEM examination of the samples we were able to confirm that the writing ink was an organic ink with inorganic salts. SEM was not able to verify the presence of sepia ink in the samples: SEM images showed that the samples had a great amount of organic components and in the spectra obtained did not appear inorganic components compared to other writing inks (Fig. 7).

4. Conclusions

Sepia ink characterisation from the *Sepia officinalis* (cuttlefish) was successful, which indicates that CE-DAD is an optimal method of analysis for sepia ink identification. The CE method proposed permits the use of very small samples (microsamples), an essential characteristic in order to analyse the ink from graphic documents to keep the physical integrity of this material.

In the collection of maps under study here, sepia ink was detected in the writing, decorative elements and drawings, mainly applied with watercolour technique. Sepia ink was found on 9 maps dated 1570 to 1817.

Sepia ink identification will help to determine the best restoration treatments for the maps and drawings where this material is present.

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