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Sampling and identification of natural dyes in historical maps and drawings by liquid chromatography with diode-array detection

Rosario Blanc [a,*], Teresa Espejo [b], Ana López-Montes [b], David Torres [c], Guillermo Crovetto [a], Alberto Navalón [a], José Luis Vílchez [a]

[a] *Research Group of Analytical Chemistry and Life Sciences, Department of Analytical Chemistry, Faculty of Sciences, University of Granada, Avda. Fuentenueva s/n, E-18071 Granada, Spain*
[b] *Department of Painting, Faculty of Fine Art, University of Granada, Avda. Andalucia s/n 18071, Granada, Spain*
[c] *Royal Chancellery Archives in Granada, C/San Agapito, s/n 18013, Granada, Spain*

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Abstract

A simple and rapid liquid chromatographic with diode-array UV–vis spectrophotometric detection (HPLC–DAD) method for identification of natural dyes has been developed. Chromatographic retention of carminic acid, indigotin, crocetin, gambogic acid, alizarin and purpurin has been studied. The mobile phase consisted of 40 mM SDS–10 mM phosphate buffer solution (pH 2.3)–0.1% TFA (eluent A) and acetonitrile (eluent B) using a programmed gradient (5% B to 95% B). Analyses were carried out on a Phenomenex, Luna 5u NH_2 100[a] column (250 mm × 4.60 mm i.d., 5 μm particle) and the operating conditions were: 0.6 ml min^{-1} flow rate, 20 μl volume injection and 35 °C column temperature. Extracts of samples of natural dyes taken from historical maps belonging to The Royal Chancellery Archives in Granada were successfully analyzed using the proposed method including a new technique for sampling.
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Keywords: Liquid chromatography; Natural dyes; Historical maps and drawings analysis

1. Introduction

Nowadays, the use of chemical analysis in the study of art and archived documents is a general procedure for their care, conservation and restoration. We can date the beginning of the application of chemical analysis to art in the first years of the XIX century, when Chaptal published in 1805 his work entitled "La chimie, peut-elle servir aux arts?". Ostwald in 1905, and Raehlmann in 1910 determined the bases of the historical identification of supports, dyes and gums throughout the micro chemical analysis leading to the creation of multidisciplinary teams focused in the study, conservation and restoration of cultural goods. However, in the field of document restoration these advances have been limited, because of the limited amount of samples that can be used in the analysis and the need to use not aggressive methodologies. Similar dyes could be used along several centuries and therefore we should use very precise techniques of analysis. In the present work we introduce a new methodology for the chemical analysis of historical documents, text and graphic, based on the liquid chromatography (LC) with diode-array detection. It is useful for librarians and archivists because knowledge of the nature or type of dyes within the artefacts is essential to classify and to use the adequate procedure to restore and preserve them [1]. For example, the use of an organic solvent could give problems when restoring an artefact because it could dissolve some dye present.

The amount of analytical work done in artefacts analysis has increased recently and many techniques have been developed. Guineau et al. examined the pigments on one fifteen-century French manuscript using UV–vis in reflection [2]. Wallert describes the use of UV–vis in solution, X-ray diffraction (XRD) and infra-red spectrometry (IR) for identifying organic red pigments on three fifteenth-century Italian manuscripts [3]. Burandt discussed the use of Fourier-transform IR spectrometry (FTIR) for identifying drawing inks [4]. Clark and Gibbs also examined pigments on one-thirteenth century "Bizantine/Syriac"

* Corresponding author. Tel.: +34 958 243326; fax: +34 958 243328.
E-mail address: mrblanc@ugr.es (R. Blanc).

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manuscript using Raman spectrometry [5]. Fluorescence spectrometry and three-dimensional fluorescence spectrometry has been used for analysis of a yellow and a purple organic pigment by Quandt and Wallert [6]. Thin layer chromatography (TLC) has often been employed to separate the chemical components of natural dyes, but the detection, identification, and quantitative spot evaluation procedures are limited. They are significantly alleviated applying high-performance liquid chromatography (HPLC) with UV–vis detection. Vest and Wouters used this technique to identify lac, indigoid, madder and tannin in 54 bindings of manuscripts and printed books dating from medieval times to the end of the 18th century [7]. In this case, due to strong absorption of dyes in the UV–vis range, identification of individual chemical components of natural dyes can be based not only on retention times but also on the UV–vis spectra. Orska-Gawrys et al. identify natural dyes using HPLC with UV–vis detection, fluorescence detection and liquid chromatography–mass spectrometry (LC–MS) in historical Coptic textiles [8–10]. In the case of HPLC with fluorescence detection, more times additives are used to enhance fluorescence of the compounds and to increase the sensitivity. Capillary electrophoresis with UV–vis diode-array detection (DAD) and electrospray mass spectrometric (ESI-MS) detection has been used for the identification of anthraquinone color components of cochineal, lac-dye and madder [11]. Pyrolisis-gas chromatography has been used for characterization of organic azo-pigments in paint samples [12]. Domenech-Carbó et al. have identified different natural dyes by Pyrolisis-gas chromatography/mass spectrometry and abrasive voltammetry at paraffin-impregnated graphite electrodes in solid works of art samples [13,14].

In general, the use of these techniques entrails two problems: the size of the samples to be taken with as small damage as possible and the physical integrity of the artefact as a whole. Many artefacts are complex, in the simplest case containing two components, medium and pigment(s) and/or dye(s). By "pigment" we mean an inorganic material and by "dye" an organic material. Pigments identification has been carried out at the past by many efficient techniques: energy dispersive X-ray analysis (EDX) [7], X-ray fluorescence (XRF) [15], particle induced X-ray emission (PIXE) [16], etc. But we think there is still room for improvement in the case of dyes. Therefore, one aim of our investigation has been the development of analytical methodologies in the case of dyes used in manuscripts. Of course, the selection of sensitive and selective analytical techniques and the use of adequate procedures on the taking of samples should be most welcome.

Table 1
Parameters for gradient elution

Time (min)	%AcN	%SDS	Flow rate (mL min^{-1})
0	5	95	0.6
1	5	95	0.6
25	30	70	0.6
30	60	40	0.6
33	60	40	0.6
38	95	5	0.6
40	95	5	0.6
40.5	95	5	1
44	95	5	1
47	5	95	0.8
55	5	95	0.8
55.5	5	95	0.6
58.5	5	95	0.6

Dyes can be found directly in extracts from natural species or become coloured after various chemical reactions such as complexation with metals, hydrolysis or oxidation. Knowledge derived from the chemical identification of natural substances used in dyes found at archive materials could help in dating and locating their origins as well as provide invaluable insights into the treatments to be applied in the preserving and restoration processes. Chemical composition of extracts from archive materials depends on different factors such as the source of natural dyes, the dyeing procedure, storage conditions through the centuries, ageing processes and on extraction conditions.

Usually, only qualitative analysis have been performed because of problems related with the extraction of dye, which depends on the kind and quality of dye, and the kind of mordant used in the case of fibre samples. Additional problems arise when samples contain several organic and inorganic impurities difficult to remove completely and when such dyes decompose and deteriorate with time.

Sampling process is really a crucial step here as the reliability of an analytical result is often conditioned by the quality of the sample taken. Further, if the object of the analysis is an artefact, there are two important steps in the sampling process in order to

Table 2
Solubility of dyes in different solvents

	Carminic acid	Indigotin	Gambogic acid	Crocetín	Alizarin and purpurín
Water Milli-Q	++	−	+	++	++
Ethanol	+	−	++	+	++
Ethanol/water Milli-Q 1:1 (v/v)	+	−	++	+	++
Metanol	+	−	++	+	++
Methanol/water Milli-Q 1:1 (v/v)	+	−	++	−	−
1-Propanol	+	−	++	++	++
Acetonitrile	+	−	+	+	++
Acetonitrile/water Milli-Q 1:1 (v/v)	+	−	++	++	+
Acetic acid	+	++	++	++	+
SDS	++	−	++	++	++
Piridine		++			

(−) Non-soluble; (+) low solubility, coloured solution with precipitate; (++) soluble.

respect its physical integrity: (a) the technique for taking samples should be non-destructive and (b) the amount of sample taken should be minimum.

We wished to identify the natural components of dyes present in historical maps and drawings improving as well the taking of samples steps using a new HPLC-DAD method.

The method, here proposed, has been applied to the historical maps belonging to The Royal Chancellery Archives in Granada and the selected natural dyes are: carminic acid, indigotin, crocetin, gambogic acid, alizarin and purpurin.

The Royal Chancellery Archives are located at the Institution known as "Real Audiencia y Chancillería de Granada". This was some sort of High Court of Justice (1494–1835), a valuable source of data for research on historical, economic, social and religious life within the period. Maps and drawings were used for litigation supervised by qualified judges. Such maps, previously prepared, were incorporated into the lawsuits by virtue of a Royal Recipient Provision at the request of one of the litigant parties.

Most of them come from different places of Andalucia (Spain), were drawn and hand painted on paper at the 18th and

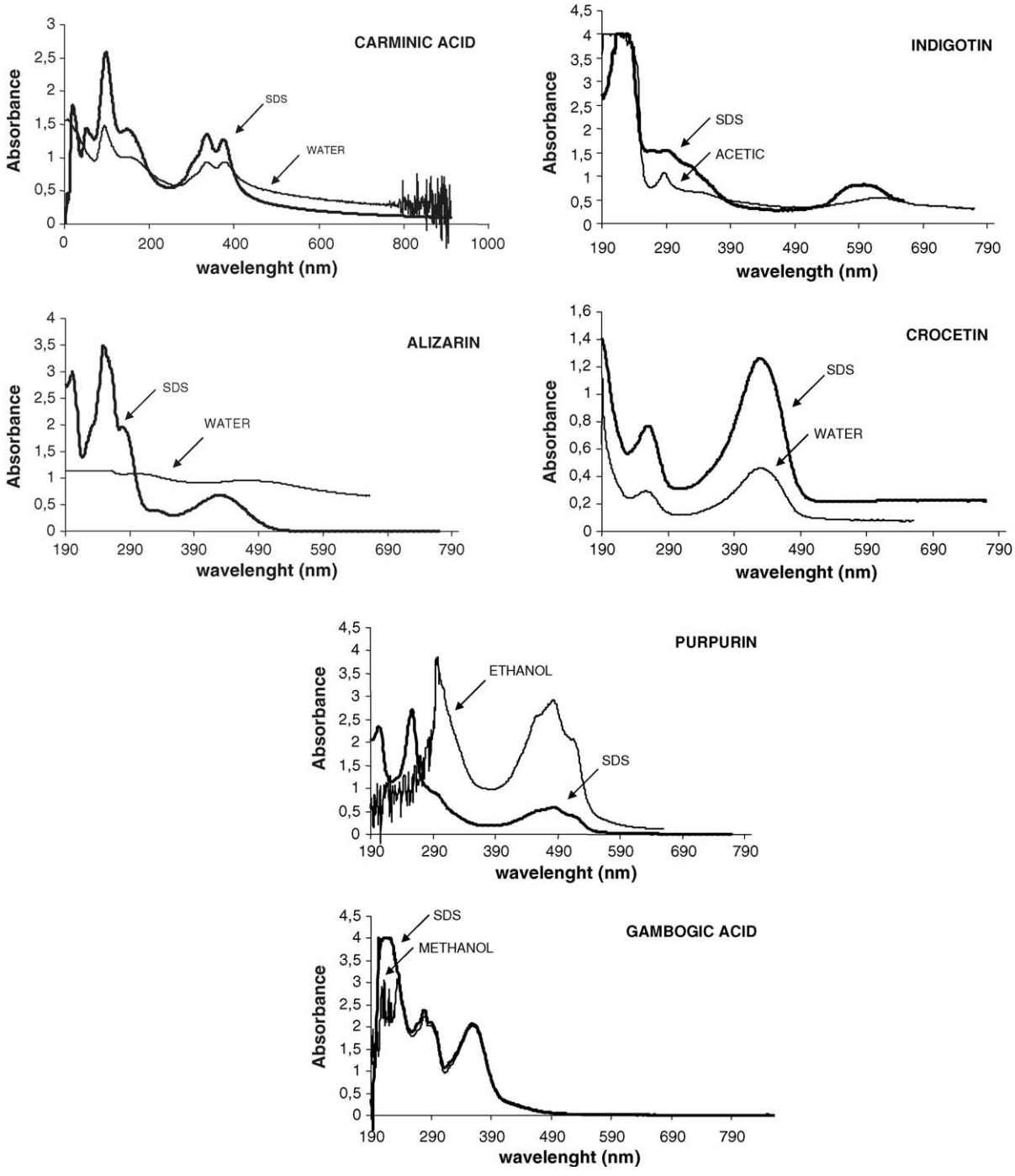

Fig. 1. Spectrum of dyes in different solvents.

19th century and can be dated accurately. Map 2 was however painted on paper manufactured from rags. Aquarelle techniques were used for applying the colour in all cases.

2. Experimental

2.1. Instrumentation and software

The chromatographic system consisted of an Agilent 1100 series HPLC (Agilent Technologies, Palo Alto, CA, USA) equipped with a quaternary pump, an on-line degasser, an autosampler, an automatic injector, a thermostated column compartment and a diode-array detector connected on-line. The chromatographic system was controlled by ChemStation for LC 3D (Agilent) software package.

Chromatographic separations of studied compounds were achieved on a Luna 5 μm NH_2 100[a] column (250 mm × 4.6 mm i.d., 5 μm particle) from Phenomenex (Torrance, CA, USA). The column was protected with a NH_2 amine-aminopropyl (Phenomenex) pre-column (4 mm × 3mm i.d.).

An Agilent 8453E (Waldbronn, Germany) UV–vis spectrophotometer was used to record absorbance spectra of natural dyes.

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

2.2. Reagents

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

The natural dyes used as reference substances were obtained from different natural sources: carminic acid from *Coccus cacti* insect, indigotin from *Isatis tinctoria* pressed leaf, crocetin from *Crocus sativus* L. stigmas, gambogic acid from *Garcinia hanburü* resin and alizarin and purpurin from *Rubia tinctorum* root.

Coccus cacti insects, *Isatis tinctoria* pressed leaf, *Crocus sativus* L. stigmas, *Garcinia hanburü* resin and *Rubia tinctorum* root were supplied by Kremer-Pigmente (Krakow, Poland).

Alizarin by Merck (Darmstadt, Germany) and purpurin by Fluka (Buchs SG, Switzerland) were used as a standard to get spectra and obtaining thus identifying chromatograms of *Rubia tinctorum* root.

The solvents used were: methanol (HPLC-hipergradient grade), acetonitrile (HPLC-hipergradient grade), acetic acid (HPLC-gradient grade), 1-propanol (HPLC-preparative grade),

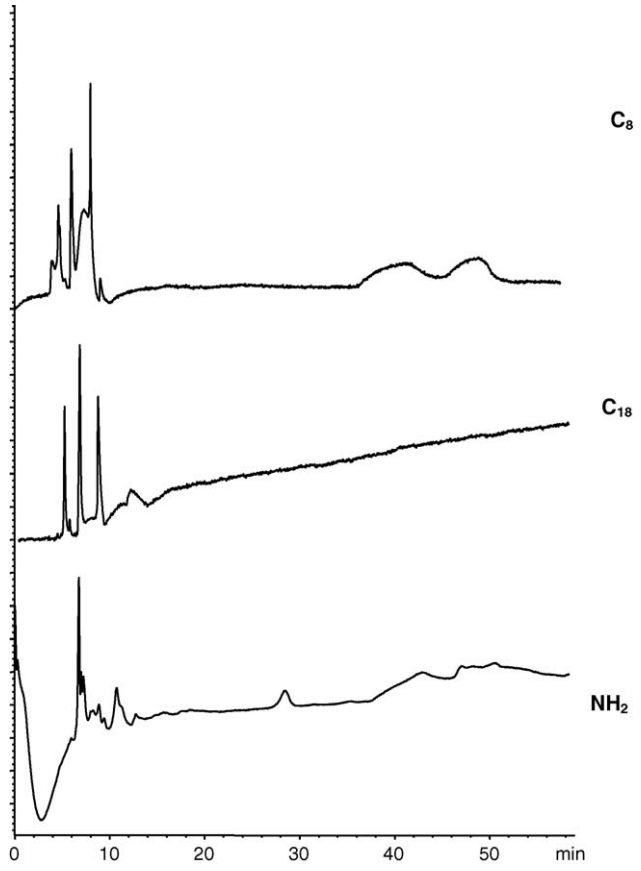

Fig. 2. Chromatograms obtained with water (A)/methanol (B) as mobile phase in C_8, C_{18} and NH_2 as stationary phase and programed gradient (5% B to 95% B).

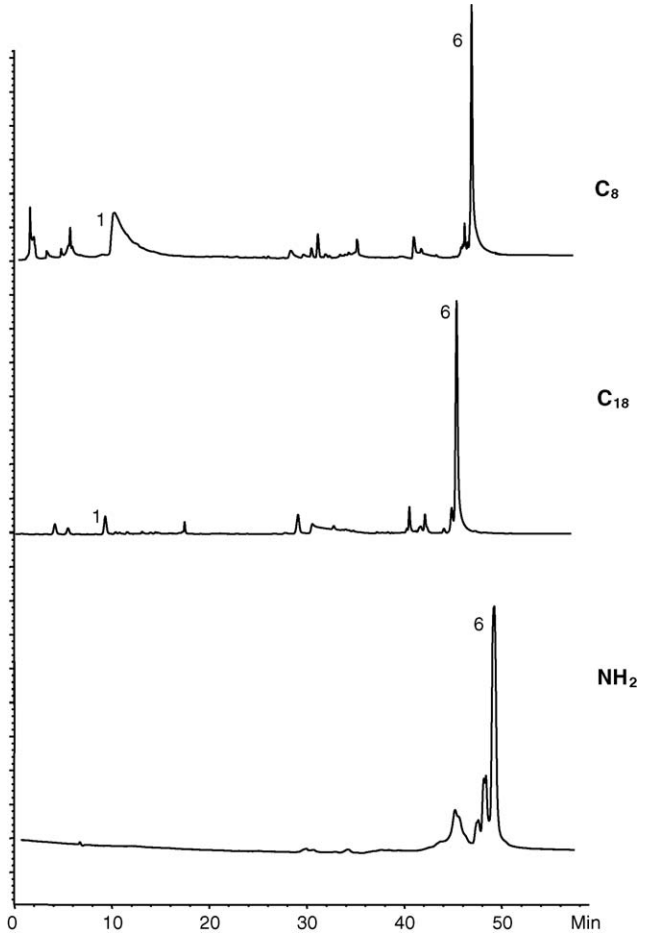

Fig. 3. Chromatograms obtained with water (A)/acetonitrile (B) in C_8, C_{18} and NH_2 as stationary phase and programed gradient (5% B to 95% B) (peaks: (1) carminic acid; (4) crocetin and (6) gambogic acid).

hydrochloric acid 37% (ANALPUR grade) and sodium hydroxide (analytical grade), ethanol absolute (HPLC-gradient grade) from Panreac; and trifluoroacetic acid (99%) from MERCK.

The reagent used to prepare mobile phase and stock solutions was sodium dodecyl sulfate (SDS) from FLUKA.

Buffer solutions of the required pH were made from 10 mM sodium phosphate (Panreac) solution and 10 mM phosphoric acid (Panreac) solution.

2.3. Extraction procedure

2.3.1. Reference substances

The reference substances were obtained by extraction from different sources described above using the adequate solvent. Carminic acid, crocetin, alizarin and purpurin were extracted with water Milli-Q. Gambogic acid was extracted with metanol in an ultrasounds bath for 20 min. The extracts were evaporated to dryness and dissolved in 0.1 M SDS.

Indigotin was extracted using 17.5 M acetic acid in an ultrasounds bath for 45 min, and a solution was prepared in 17.5 M acetic acid–0.1 M SDS (50:50).

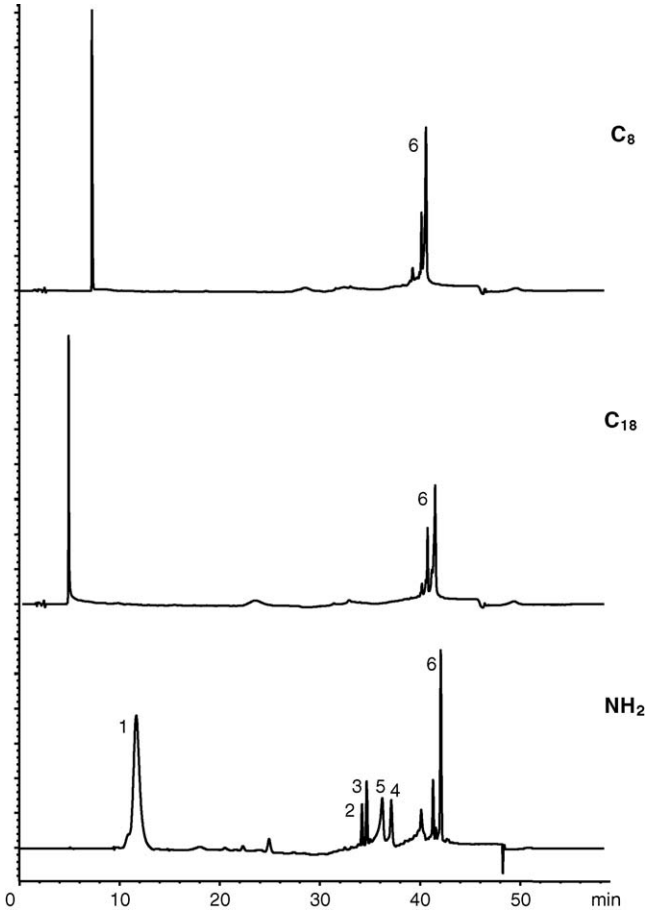

Fig. 4. Chromatograms obtained with SDS/acetonitrile in C_8, C_{18} and NH_2 as stationary phase and programed gradient (5% B to 95% B) (peak 1: carminic acid; peak 2: alizarin; peak 3: indigotin; peak 4: crocetin; peak 5: purpurin and peak 6: gambogic acid).

2.3.2. Take of sample from maps

The extractions of dyes from maps were carried out using a brush imbibed with 0.1 M SDS and applying directly onto the map. The extract transferred on the brush from the paper contained particles and SDS soluble compounds coming from the colouring film. The extracts were transferred to 0.1 M SDS and sonicated for 45 min. The solutions were centrifuged at 2000 rpm for 5 min before being injected into the column.

Indigotin is not soluble in SDS but is transferred onto the brush from the paper imbibed in the gum components of the picture film soluble in SDS. Acetic acid is added to dissolve the indigotin.

2.4. Experimental procedure

The mobile phase consisted of 40 mM SDS–10 mM phosphate buffer solution (pH 2.3)–0.1% TFA (eluent A) and acetonitrile (eluent B). Chromatographic separation was carried out using the programmed gradient given in Table 1. This gradient was employed for reference substances and sample analysis. The column temperature was set at 35 °C and the injection volume was 20 μl. The DAD installed in the instrument provided spectral information collected at 2 nm steps from 190 to 950 nm during the entire chromatographic analysis.

3. Results and discussion

3.1. Method development

The most serious problem for the development of the method was the selection of the adequate solvent, because not all these compounds are soluble under the same conditions. Further, the solubility or not solubility of the dyes in different sol-

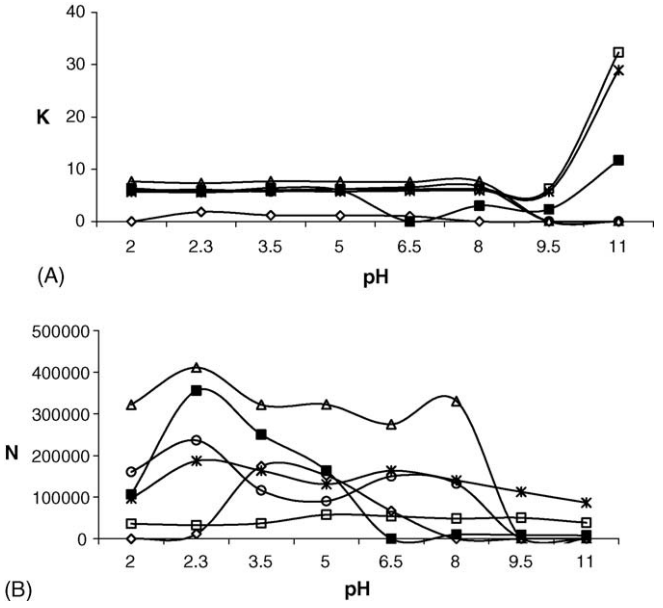

Fig. 5. Influence of pH on the retention factor (A) and plate number (B) of natural dyes: (◊) carminic acid, (■) indigotin, (Δ) gambogic acid, (□) crocetin, (✱) alizarin and (◯) purpurin.

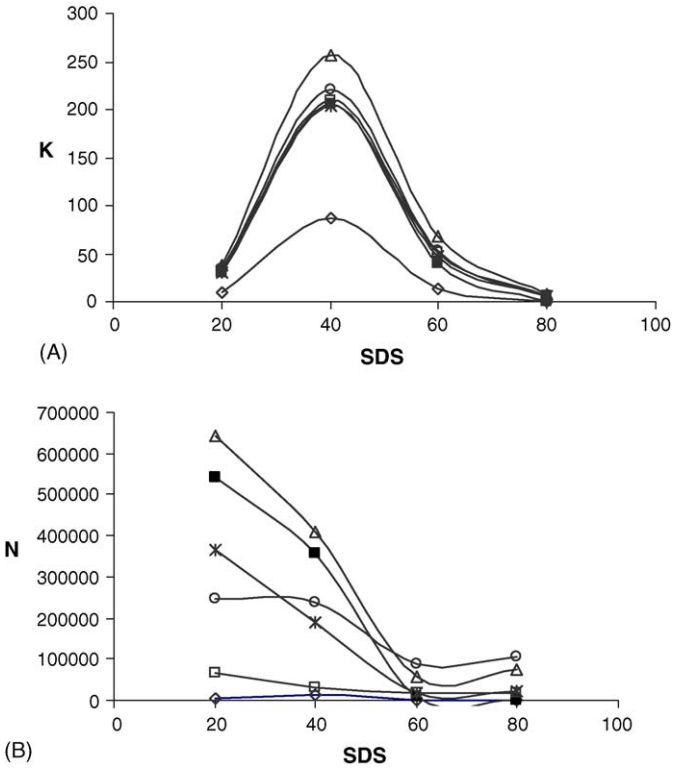

Fig. 6. Influence of SDS concentration on the retention factor (A) and plate number (B) of natural dyes: (◊) carminic acid, (■) indigotin, (Δ) gambogic acid, (□) crocetin, (✱) alizarin and (◯) purpurin.

vents involves not only the taking of samples but the choice of the solvent used as mobile phase and the choice of the stationary phase. The study of the solubility was carried out for the selected dyes: carminic acid, indigotin, crocetin, alizarin, purpurin and gambogic acid collected from different sources as previously stated. The solvents tested were: water Milli-Q, ethanol, water–ethanol (1:1, v/v), methanol, water–methanol (1:1, v/v), 1-propanol, acetonitrile, water–acetonitrile (1:1, v/v), acetic acid (17.5 M), 100 mM SDS (pH 4) and pyridine. It was found (Table 2) that all the dyes, except indigotin, were soluble in 100 mM SDS (pH 4). Indigotin was only soluble in acetic acid and pyridine. For this reason, the extracts of carminic acid, alizarin, purpurin, crocetin, gambogic acid and indigotin were dissolved in 100 mM SDS (pH 4). It is found that in 100 mM SDS (pH 4) solution the spectrum obtained for identification of dyes show better analytical morphology than in other tested solvents (Fig. 1). Therefore, the solvents tested as mobile phase were water/methanol, water/acetonitrile and 100 mM SDS (pH 4)/acetonitrile.

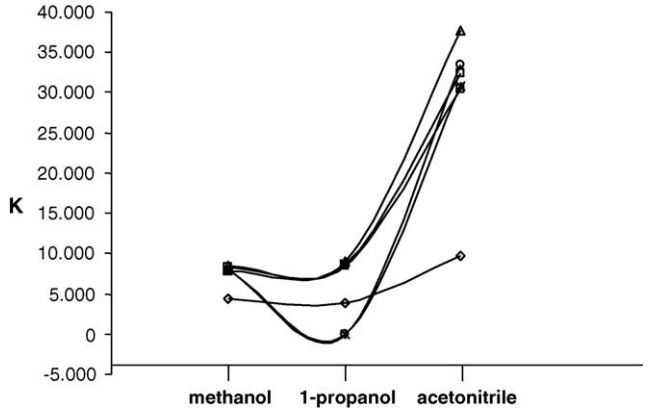

Fig. 7. Influence of different organic solvents on the retention factor of natural dyes using SDS as mobil phase ((◊) carminic acid, (■) indigotin, (Δ) gambogic acid, (□) crocetin, (✱) alizarin and (◯) purpurin).

C_8, C_{18} and NH_2 bonded stationary phases using gradient and isocratic programs were checked to select the adequate stationary and mobile phases. When the mobile phase was water (A) and methanol (B) using C_8, C_{18} or NH_2 the chromatographic peaks of dyes appear overlapped at the first 12 min (Fig. 2). Using water (A) and acetonitrile (B) as mobile phase some dyes do not elute in all stationary phases studied (Fig. 3). If the mobile phase was SDS–0.1% TFA (A) and acetonitrile (B), in C_8 and C_{18} column the chromatographic peaks of dyes appear overlapped during the first 3 min excepting gambogic acid (t_R 42 min). However, with NH_2 column, the resolution of the chromatographic peaks was good and all the dyes were identified (individually and mixtures) (Fig. 4). Therefore, the solvent choice as mobile phase was 100 mM SDS (pH 4) and the stationary phase choice was NH_2.

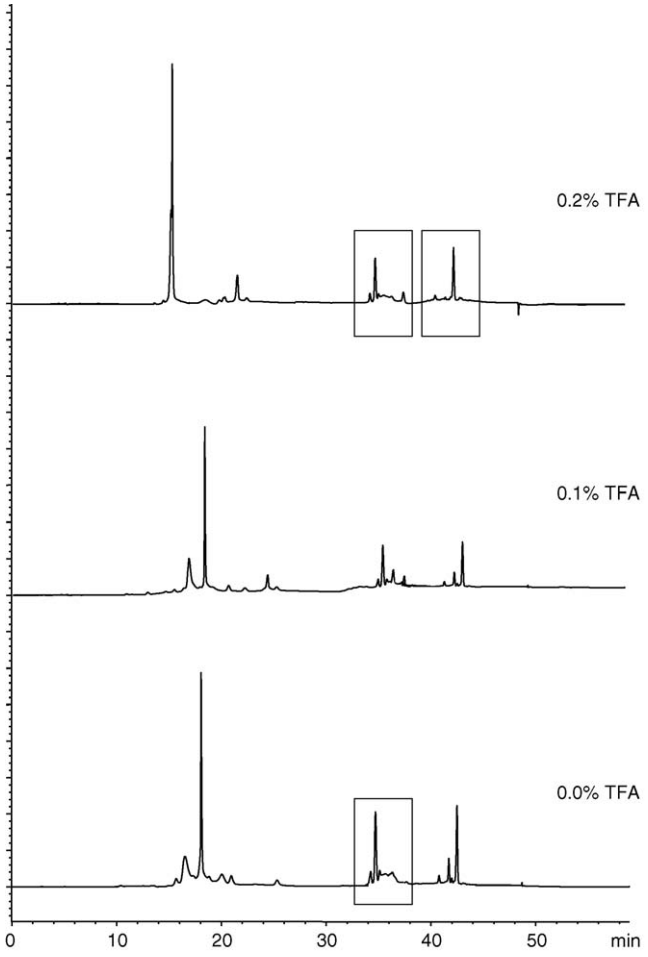

Fig. 8. Chromatograms obtained for different concentrations of TFA.

The pH of the mobile phase was tested in the usual working pH range of the column (1.5–11.0). Column efficiency is found related to plate number but although pH influence on peak resolution is no significant it is found that the best peaks are obtained at pH 2.3 (Fig. 5). The selected buffer for keeping the optimum pH was phosphate buffer.

SDS concentration varied in the range 20–80 mM. At SDS concentrations greater than 80 mM a precipitate appeared due to the mixture with the organic modifier. SDS concentration selected was 40 mM because at this concentration the retention factor for different reference substances was found to be the best and the number of theoretic plates was favourable also (Fig. 6).

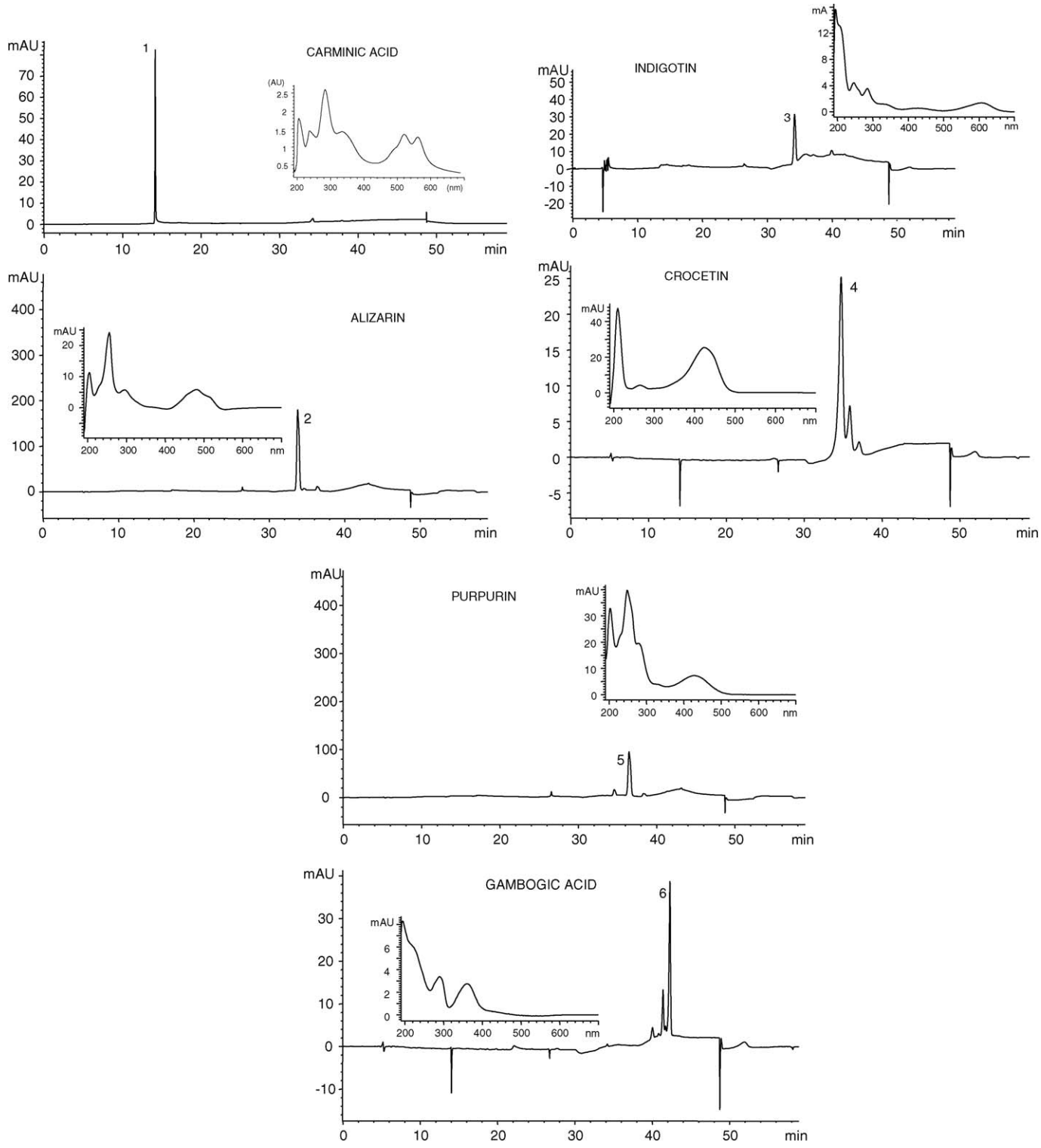

Fig. 9. Chromatograms obtained for solutions of natural dyes extracted from natural sources.

Table 3
Chromatographic retention time and absorption maxima for studied dyes

Dye	Retention time (min)	Standard deviation	Peak no.	Absorption (nm)	Natural source
Carminic acid	14.448	0.003	1	206,234,284 334,521,563	*Coccus cacti*
Alizarin	33.501	0.001	2	201,252,280,430	*Rubia tinctorum*
Indigotin	33.777	0.002	3	227,294,608	*Isatis tinctoria*
Crocetin	34.650	0.001	4	259,431	*Crocus sativus* L.
Purpurin	36.286	0.004	5	205,257,489,521	*Rubia tinctorum*
Gambogic acid	42.378	0.001	6	205,236,282 290,364	*Garcinia hanburii*

Different organic solvents (1-propanol, methanol and acetonitrile) were tested to modify the eluent strength. Acetonitrile was selected as the more adequate [17] (Fig. 7).

The chromatographic peaks displayed an asymmetry. The addition of trifluoroacetic acid provides the best well-shaped peaks because acidic and basic solvent additives sharpen elution bands by minimizing interaction with basic and acid silanol sites, respectively, on silica columns [18]. TFA was chosen because it is a volatile acid and experience has shown that volatile additives avoid possible salt precipitation within the system reducing pump maintenance by as much as 50%. The selected concentration of trifluoroacetic acid was 0.1% because higher and lower concentrations provide overlap between the chromatographic peaks (Fig. 8).

Other parameter studied was the solvent flow and the best compromise in terms of resolution, retention time and pressure of the HPLC system finding it to be 0.6 ml min^{-1}.

3.2. Taking of samples study

As explained in the introduction, an important goal was to improve the technique used to take the sample. Use of an extremely small sample ensures the physical integrity of an artefact.

At the best of our knowledge no examples can be found about identification of dyes by HPLC on maps and drawings, albeit there are examples on the use of HPLC on textile samples.

Extraction of dyes from textile fibres samples is usually done taking between 50 μg and 3.0 mg of sample [8,9]. Therefore, the processed samples are subject to a lengthy preparation before analysis.

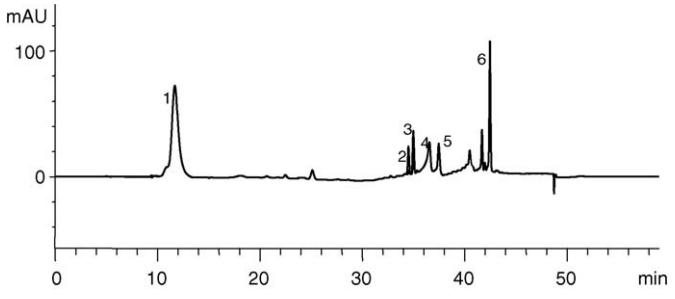

Fig. 10. Chromatogram of a mixture of the different natural dyes studied obtained under the optimised conditions (peaks: (1) carminic acid; (2) alizarin; (3) indigotin; (4) crocetin; (5) purpurin and (6) gambogic acid).

Moreover, the physical integrity of artefacts is damaged or even worse destroyed during the sampling. Extraction by hydrolysis, centrifugation, filtering, drying and re-dissolution, larger times of analysis and other sources of errors are implied.

Here, a brush imbibed with the proper solvent leads to amounts of sample taken being a minimum. Sample preparation is then easier, the dye extracted with the brush being adequately dissolved, the solution being centrifuged and injected into the HPLC.

Sampling techniques such as the use of the scalpel, of hyssop of cotton, the addition of a drop of solvent on the coloured film and the use of blotting paper have been tried too. The scalpel damages, the hyssop of cotton, the adding of a drop of solvent causing stains or the use of blotting paper are not recommended.

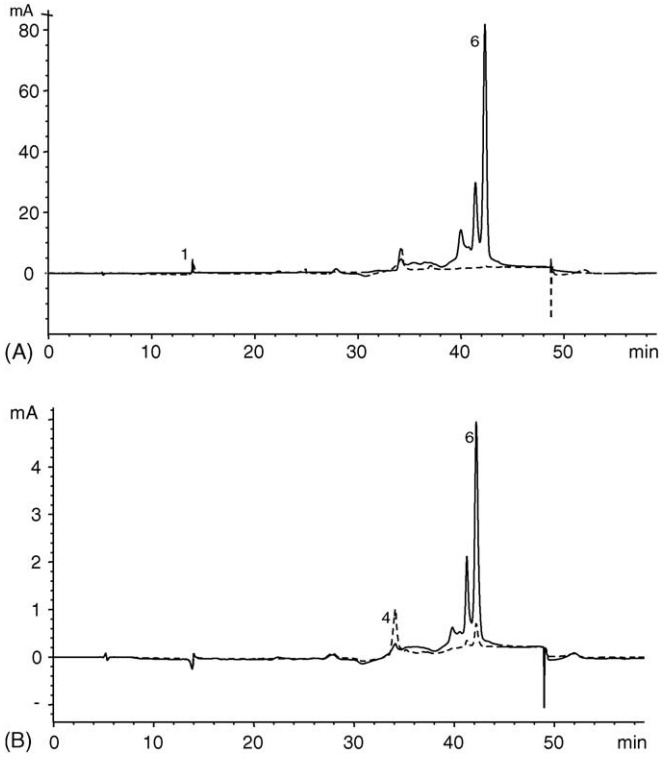

Fig. 11. Chromatogram obtained for an extract from two maps: (A) map 94 and (B) map 11.

Table 4
Identification of dyes in maps

Map	Color	Identified dye
2	Yellow	Gambogic acid
2	Red	Carminic acid
11	Brown	Crocetin
		Gambogic acid
11	Green	Crocetin
		Gambogic acid
37	Red	Carminic acid
41	Orange	Carminic acid
		Gambogic acid
41	Yellow	Gambogic acid
83	Blue	Indigotin
94	Brown	Carminic acid
		Gambogic acid

3.3. Application of the method

The reported investigations were carried out in two stages. Firstly, chromatographic measurements were carried out for natural dyes collected from various sources and the experimental procedure was applied. Then HPLC data were recorded for extracts of dyes from historical maps. Identification of dyes was based on retention times and their comparison with reference substances as well as on UV–vis spectra recorded for sample extracts and reference substances. Identity of UV–vis spectra was confirmed when agreement between their maxima was obtained within ±1 nm.

3.3.1. HPLC of natural dyes

Chromatographic identification of natural dyes was carried out with the use of these substances purchased from different natural sources previously indicated. Chromatograms obtained for solutions of natural dyes are shown in Fig. 9 together with the UV–vis spectra corresponding to identify chemical species. The UV–vis spectra were obtained at chromatographic peak and are similar to those spectra obtained with reference substances. The complete list of examined natural dyes is shown in Table 3, together with their retention times in the chromatographic conditions used and spectrophotometric data.

Fig. 10 shows a representative chromatogram of a mixture of the different natural dyes studied obtained under the optimised conditions. It shows that the chromatographic procedure selected is adequate for the separation of the analytes involved. The time for one analysis was around 45 min.

3.3.2. HPLC of extracts from maps

Samples taken from different historical maps from different places belonging to The Royal Chancellery Archives in Granada, and dated from the eighteen and nineteen century, have been examined using the proposed analytical procedure. Fig. 11 shows a chromatogram obtained for an extract from some analysed maps, the results being summarised in Table 4.

4. Conclusions

Liquid chromatography with diode-array UV–vis spectrophotometric detection has been proved to be a very powerful technique for separation and identification of dyes in historical maps due to its high sensitivity and resolution. The amount of sample needed for analysis is minimum, the artefact is not damaged practically and furthermore the technique used for taking of sample with a brush imbibed with an appropriate solvent, keeps the physical integrity of an artefact almost in their total ness.

The proposed method has been successfully applied to historical maps from The Royal Chancellery Archives in Granada. The method allows the identification of the natural dyes involved but not of the natural sources used by the authors.

Acknowledgements

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