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Application of LC–MS to the analysis of dyes in objects of historical interest

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ABSTRACT

High-performance liquid chromatography (HPLC) with photodiode array and mass spectrometric detection permits dyes extracted from objects of historical interest or from natural plant or animal dyestuffs to be characterized on the basis of three orthogonal properties: HPLC retention time, UV–visible spectrum and molecular mass. In the present study, we have focused primarily on yellow dyes, the bulk of which are flavonoid glycosides that would be almost impossible to characterize without mass spectrometric detection. Also critical for this analysis is a method for mild extraction of the dyes from objects (e.g., textiles) without hydrolyzing the glycosidic linkages. This was accomplished using 5% formic acid in methanol, rather than the more traditional 6 M HCl. Mass spectroscopy, besides providing the molecular mass of the dye molecule, sometimes yields additional structural data based on fragmentation patterns. In addition, coeluting compounds can often be detected using extracted ion chromatography. The utility of mass spectrometry is illustrated by the analysis of historical specimens of silk that had been dyed yellow with flavonoid glycosides from *Sophora japonica* (pagoda tree) and curcumins from *Curcuma longa* (turmeric). In addition, we have used these techniques to identify the dye type, and sometimes the specific dyestuff, in a variety of objects, including a yellow varnish from a 19th century Tibetan altar and a 3000-year-old wool mortuary textiles, from Xinjiang, China. We are using HPLC with diode array and mass spectrometric detection to create a library of analyzed dyestuffs (>200 so far; mostly plants) to serve as references for identification of dyes in objects of historical interest.

1. Introduction

The substances used to impart color to various objects can be divided into two general groups: dyes and pigments. Dyes are organic compounds that are soluble in a solvent (usually water) and are able to penetrate into the object being colored. By contrast, pigments are generally insoluble in most media and are applied to the surface of an object. The vast majority of substances used to color textiles are dyes, and until about 1860 all dyes were natural products extracted from plant and some animal materials. Since most dyes are organic compounds with strong chromophores, they are particularly amenable to being separated by high-performance liquid chromatography (HPLC), especially reversed-phase HPLC, and of being detected by virtue of their absorbance in the ultraviolet and/or visible regions of the electronic spectrum.

The use of HPLC for the analysis of dyes in textiles was introduced in the 1980s primarily through the pioneering work of Wouters and collaborators [1,2]. Although most dyes absorb in the ultraviolet region of the spectrum and can be detected at a single wavelength (e.g., 254 nm), the introduction and utilization of the diode array detector (DAD) for dye analysis, c.f. [2], meant that detection could be done at any wavelength in the UV or visible spectrum, and that a complete spectrum of any substance eluting from the HPLC column could be obtained. As a result, dye molecules could be characterized in terms of retention time from the HPLC column and their electronic spectral characteristics. Although NMR (nuclear magnetic resonance) is the most widely used spectrometric technique for characterizing organic compounds, it has never been applied to textile dye analysis because it is not sensitive to the minute amounts of material available for analysis. The second most valuable analytical tool, mass spectrometry (MS), only became useful really for textile dye analysis with the introduction of electrospray ionization techniques that allowed it to be interfaced with HPLC systems.

Another factor impeding the use of mass spectrometry (aside from a lack of access to this relatively expensive instrumentation) was that it was not initially realized how much structural information the technique could provide. Until relatively recently, the standard procedure for extracting natural dyes from textiles involved heating in 6 *M* methanolic hydrochloric acid [1–4]. This

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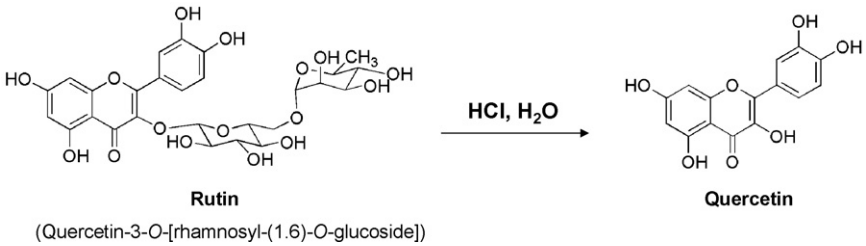

Fig. 1. Strong acid (HCl) catalyzed hydrolysis of rutin (quercetin-3-*O*-[rhamnosyl-(1.6)-*O*-glucoside]) [$m/z = 610$] to quercetin [$m/z = 302$].

process was suitable for dyes, particularly blue, reds and some yellows, that are unchanged by strong acid. On the other hand, the majority of yellow dyes are flavonoid glycosides, and heating in strong HCl hydrolyzes glycosidic linkages. As a result, only the yellow aglycone chromophore is detected, and most of the information regarding the original dye molecules and their plant sources is lost. Literally thousands of flavonoids are known [5] and probably hundreds of flavonoid producing plants have been used as dyestuffs. To prevent these losses, we developed milder procedures for extracting dyes from textiles without destroying the glycosides [6].

Identifying the components in the often complex mixtures of dyes requires a more discriminating tool than UV–vis spectroscopy because the flavonoid aglycones and their glycosides often have identical electronic spectra. However, their molecular masses are often different, so mass spectrometry in conjunction with separation by HPLC is invaluable in characterizing these molecules. In the work described below, we use HPLC with on-line diode array and mass spectrometric detection, namely HPLC–DAD–MS, or LC–MS, for short. With this system, we can characterize eluted molecules in terms of their retention times from the HPLC column, their UV–vis absorption characteristics, and their molecular masses.

We have had two goals in our work. The first is to create a library of dyestuff profiles, in which component dye molecules are characterized in terms of retention time, UV–vis spectra and molecular mass. The second is to use this information to identify and gain an improved understanding of the plant or animal materials used to dye textiles and other objects of historical and archaeological interest.

2. Experimental methods

2.1. Extraction of dyes from textile threads

Dyes were extracted from woolen or silk threads (estimated to weigh 0.2–0.8 mg in most cases) using formic acid/methanol (5:95, v/v) or, for comparison, HCl/methanol/water (2:1:1, v/v) as described by Zhang and Laursen [6]. The extracts (including textile fibers) were dried under vacuum over NaOH pellets. The residues were then suspended in 50 μL of methanol/water (1:1, v/v) and centrifuged to separate the particulate matter. The upper 30 μL of solution was removed with a pipetor for HPLC–DAD–MS analysis (20 μL was injected), as described in the next section.

2.2. Analysis of extracts

Analysis of extracts was performed with an Agilent 1100 liquid chromatography system (HPLC) consisting of an automatic injector, a gradient pump, an HP series 1100 diode array detector (DAD) and an Agilent series 1100 on-line atmospheric pressure electrospray ionization mass spectrometer (MS). Dye components were separated on a 2.1-mm diameter Vydac C4 reversed-phase column as previously described [6]. Mass spectra were usually obtained

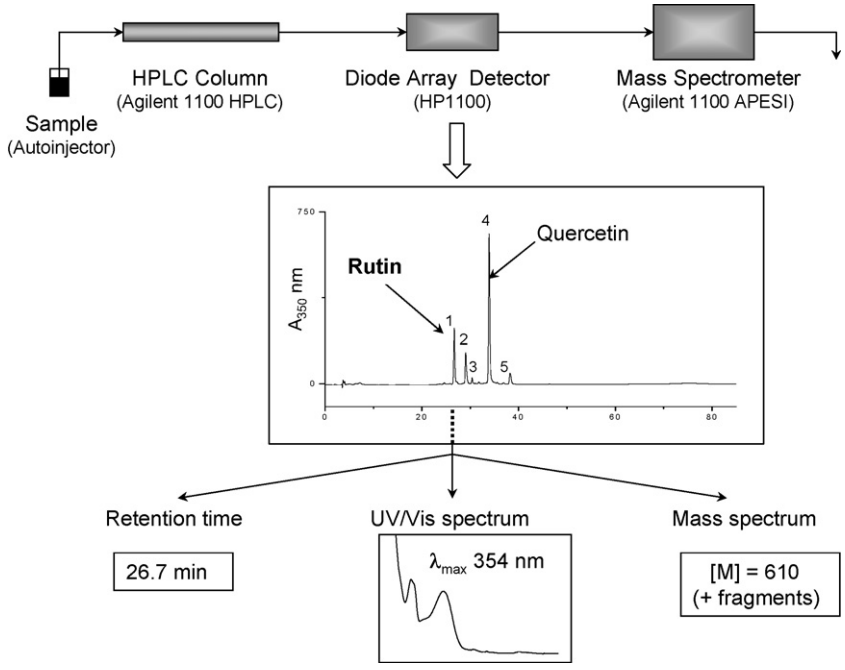

Fig. 2. Analysis of a dye extract by HPLC–DAD–MS. In this case, the dye components are characterized in terms of their retention times, UV–vis spectra and mass spectra.

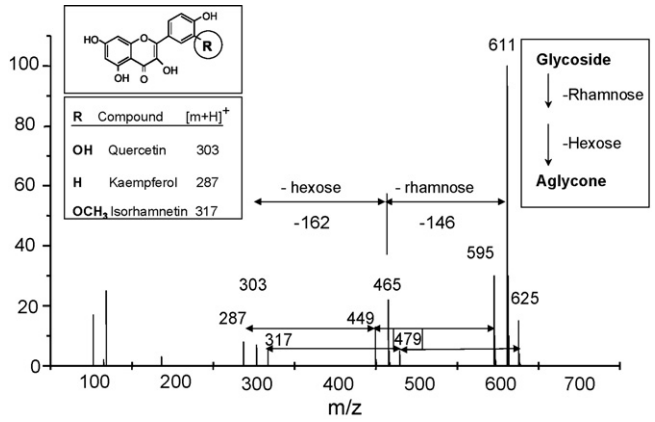

Fig. 3. Fragmentation pattern of positive ions from peak 2 (see Fig. 2) of an extract of pagoda tree bud dyed silk. Three parent ions are seen at m/z = 625, 611 and 595 Da. Each of these peaks fragments by loss of a 146-Da unit, followed by a 162-Da unit.

in the negative ion mode, which gives the greatest sensitivity for phenols and carboxylic acids, and records $[M-1]^-$ ions. In some cases, positive ion spectra were obtained. Positive molecular ions, $[M+1]^+$, tend to produce fragments resulting from sequential loss of sugar units, which aid in structure elucidation.

3. Results

3.1. Extraction of dyes

As described in more detail elsewhere [6,7], we have developed two mild methods for extracting dyes from textile fibers. The first uses ethylenediaminetetraacetate (EDTA) to disrupt the dye–metal (mordant) chelate complex, whereas the second uses 5% formic acid. In both cases, flavonoid (and other) glycosides are extracted intact. As it turns out, the formic acid extraction method – a micro-modification of one described by Shibayama et al. in 1991 [8] – is more convenient to use, so we employ it almost exclusively. Since our original publication [6], other investigators have reported using dicarboxylic acids such as oxalic acid, with equal or superior results [9].

Although heating with 6 *M* HCl hydrolyzes glycosidic linkages (see Fig. 1), this procedure can actually be quite useful at times, e.g., for identification of the aglycone part of the molecule. Because plant dyestuffs do not generally contain chelating metal ions, dye molecules can be extracted using solvents such as methanol–water mixtures. Fig. 1 illustrates the result of treating the glycoside, rutin, with a strong acid. In this case rutin (m/z = 610) is deglycosylated to quercetin (m/z = 302). However, rutin is stable to extraction with 5% formic acid.

3.2. Analysis of extracts

Fig. 2 is an outline of the overall procedure used for the analysis of textile extracts. In this example, a sample of silk cloth dyed in our lab with pagoda tree (*Sophora japonica*) buds was extracted using 5% formic acid as described above. The components of the extract were separated by HPLC on a C_4 reversed-phase column, and the column effluent was monitored on-line, first by a diode array detector and then a mass spectrometer. In this way each peak can be characterized by its retention time, UV–vis spectrum and mass spectra. In this case, rutin elutes at 26.7 min and has a maximal absorbance at 354 nm, which turns out to be characteristic of a 3-*O*-substituted flavonol (see Fig. 1). If data are collected in the negative ion mode, an $[M-1]^-$ = 609 Da is detected. In the positive ion mode, $[M+1]^+$ = 611 Da is seen, along with fragments caused by sequential loss of the sugar units (see below).

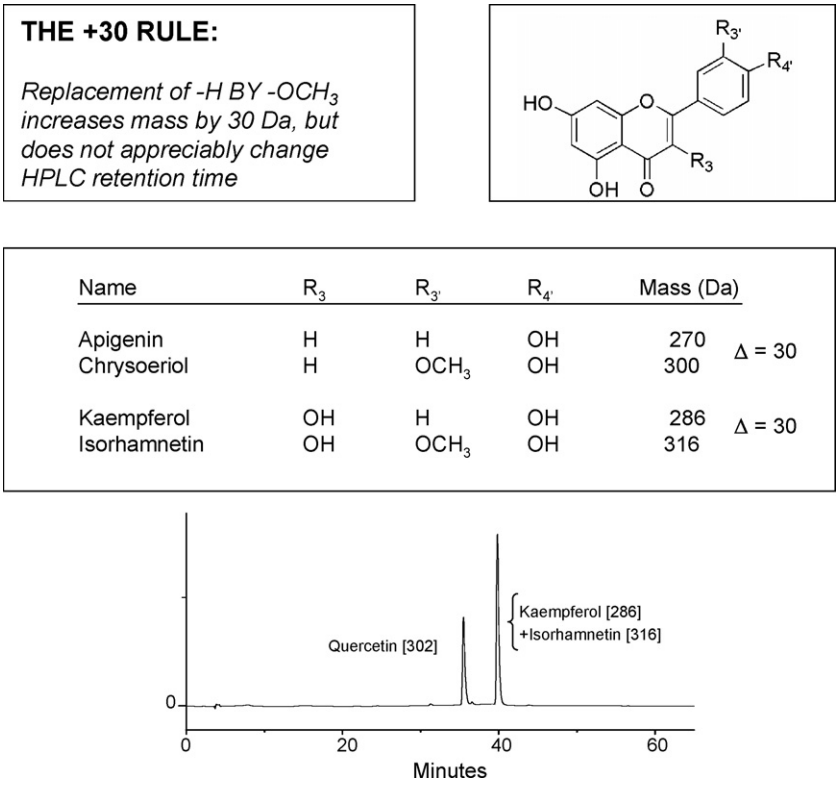

Fig. 4. Illustration of the "+30" rule. The middle panel shows examples of pairs of flavonoids that elute together (from a C_4 reversed-phase column), even though their masses differ by 30 Da. The lower panel, illustrates this phenomenon for kaempferol and isorhamnetin.

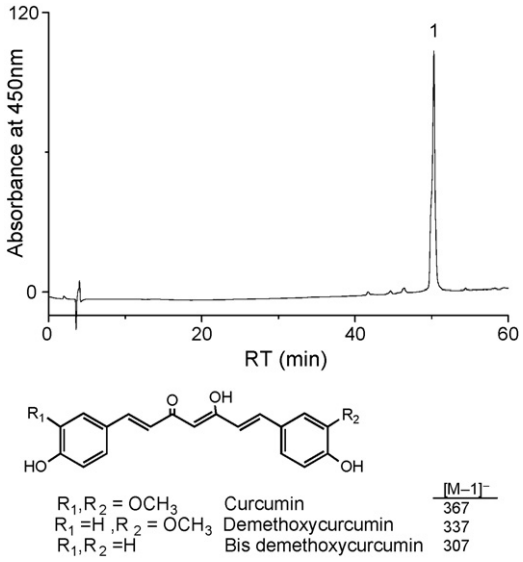

Fig. 5. Separation of curcumins by HPLC. Upper panel: HPLC profile of a Chinese silk extract. Lower panel: the structures of the three curcumins present in the single HPLC peak.

Judging from Fig. 2, with detection at a single wavelength (350 nm), one might conclude that there are only five significant components in the extract. However, mass spectrometric analysis reveals that peak 2 contains at least three components (Fig. 3). In the negative ion mode, one sees three ions, namely at $[M-1]^-$ = 623, 609 and 593 Da. In the positive ion mode one also sees three ions, at $[M+1]^+$ = 625, 611 and 595 Da, and, *in addition,* fragments of each parent ion corresponding to sequential loss of rhamnose (146 Da) and a hexose (162 Da). These correspond to the rutinosides of isorhamnetin, quercetin and kaempferol—or isomers of them. Since rutin (peak 1) is itself quercetin rutinoside, the quercetin derivative in peak 2 must be an isomer of this.

3.3. The "+30" rule

We have noted many instances where apparently single peaks in HPLC profiles contain two components whose masses differ by 30 Da (Fig. 4). The presence of these components is easily seen by mass spectrometry, using data acquisition in either the negative or positive ion mode. This phenomenon is observed when a hydrogen atom is replaced by a methoxy group at a particular position, as in the pairs apigenin/chrysoeriol and kaempferol/isorhamnetin (Fig. 4). Apparently the increased polarity of the methoxy oxygen is almost exactly counterbalanced by the increased hydrophobicity of the methyl moiety. It is possible to resolve these pairs by HPLC using a C_{18} column, which is more efficient than the C_4 column used in most of work reported here, but the retention times are still very close.

An even more dramatic demonstration of the "+30" rule is seen for the extract of a specimen of 19th century Chinese yellow dyed silk [10]. In this instance only a single peak is seen when the column is monitored at 450 nm (Fig. 5). However, mass spectrometry shows that three components are present, differing in mass by 30 and 60 Da, or by one and two methoxy groups, respectively [10]. These correspond to the three known dye components of turmeric: curcumin ($[M-1]^-$ = 367), demethoxycurcumin ($[M-1]^-$ = 337) and *bis*demethoxycurcumin ($[M-1]^-$ = 307) (Fig. 5) [11]. The three

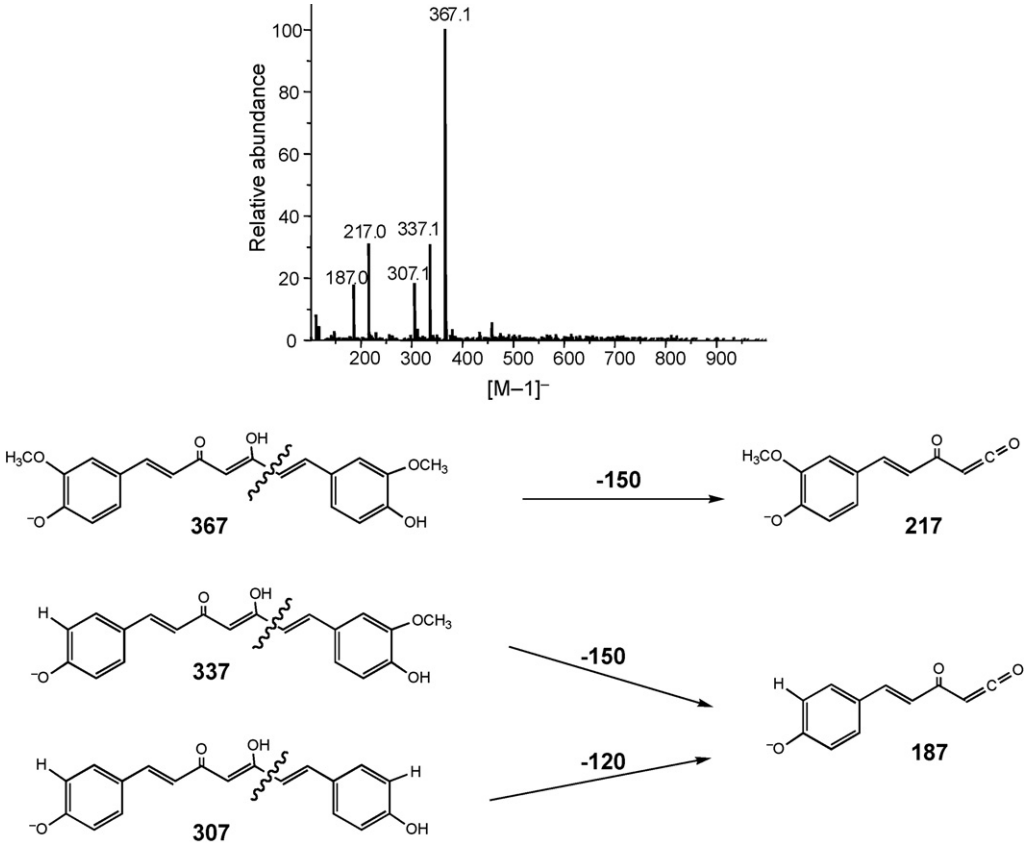

Fig. 6. Fragmentation of curcumins in the mass spectrometer. Upper panel: fragmentation pattern of negative ions observed for the peak in Fig. 5. Lower panel: chemical interpretation of the fragmentation pattern. Because of the various keto-enol tautomerization possibilities, cleavage could also occur on the left hand side of the molecules.

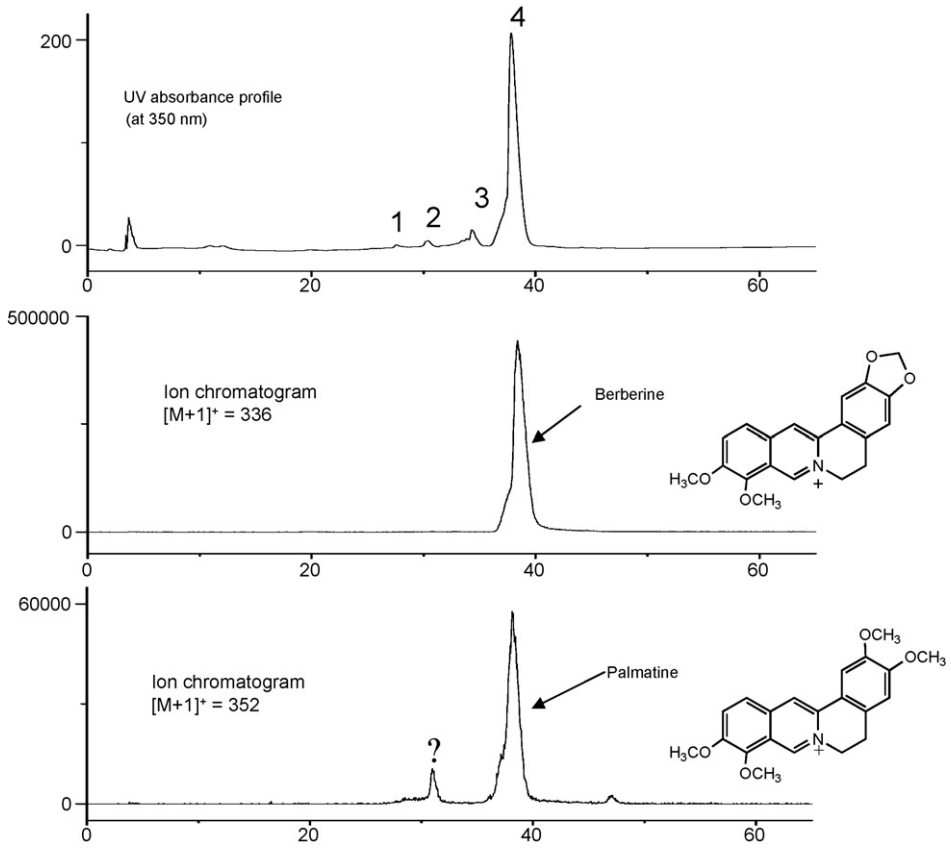

Fig. 7. HPLC profiles of the extract from a yellow varnish taken from a Tibetan altar. Top panel; elution profile seen by monitoring the absorbance at 350 nm. Lower two panels: profiles seen when the eluate is monitored for ions at $m/z = 336$ and 352 Da.

components, though not differentiated in the HPLC profile shown, are clearly detected by mass spectrometry. [They are also easily separated by thin layer chromatography [12].] First of all, three masses ($[M-1]^-$ = 367, 337 and 307) are detected in the single peak; second, ion extraction (data not shown; cf. Section 3.4) shows all three ions; and finally, the parent ions show fragmentation patterns consistent with the proposed structures (Fig. 6). The lower panel in Fig. 6 shows an interpretation of the fragmentation seen in the upper panel. Other fragmentation mechanisms can be proposed, but all lead to the same observed ions.

3.4. Analysis of protoberberines—ion extraction

Analysis of a yellow varnish applied over metallic foil to simulate gold on a late 19th/early 20th century Tibetan altar in the collection of the Philadelphia Museum of Art [13] revealed the presence of protoberberine alkaloids (Fig. 7; Table 1). The bulk of the colorant was in peak 4 of Fig. 7 (top panel). All of the four peaks gave UV–vis spectra characteristic of the protoberberines, but mass spectrometry provided much more information about their identity. In particular, mass spectrometry revealed that peak 4 contained two compounds: berberine ($[M+1]^+$ = 336) and palmatine ($[M+1]^+$ = 352), which we knew from previous work to coelute at about 37 min (Table 1). Extracted ion chromatograms, in which the elution profile is scanned for ions of a specific mass, confirmed the presence of two compounds eluting with masses of 336 and 352 Da, which are consistent with berberine and palmatine, respectively (Fig. 7, lower two panels). Based on the relative intensities of the two ions, the ratio of berberine to palmatine is about eight to one. Although we cannot be certain of the source of this yellow dye, the elution profile is typical of a number of species of barberry (*Berberis* spp.) that grow in the Himalayas (unpublished observations), consistent with the origin of the altar.

Table 1
Identification of protoberberine compounds Tibetan altar dye (cf. Fig. 7)

Peak	Retention time (Min)	Mass[a] $[M+1]^+$ (Da)	Possible compound
1	29.8	324.0	Not identified
2	33.4	338.1 (322.1)	Isomer of jatrorrhizine + (Berberrubin or isomer)
3	33.9	338.1	Jatrorrhizine
4	37.4	336.1 (352.1)	Berberine + (palmatine)

[a] Mass analysis showed that some peaks contained more than one compound. Masses for the major components are shown. Smaller mass peaks are shown in parentheses.

3.5. Yellow dyes from ancient Central Asian textiles

Recently we had the opportunity to analyze dyes in some 3000-year-old textile fragments from the Taklamakan Desert region of Xinjiang Province in western China [14]. Among the colorants detected were two yellow dyes that seemed to be derived from different plant sources. Although the major component in both dyes was luteolin 7-glucoside (and some free luteolin), which is characteristic of weld (*Reseda luteola*), a dyestuff widely used in Europe, careful analysis of minor components suggests that these two dyes (labeled FN6-2 and FN6-6 in Fig. 8) were derived from different sources, and that neither of these was *R. luteola*. Characterization of these dyes would have been impossible without the aid of mass spectroscopy because the UV–vis spectra of all the dye components

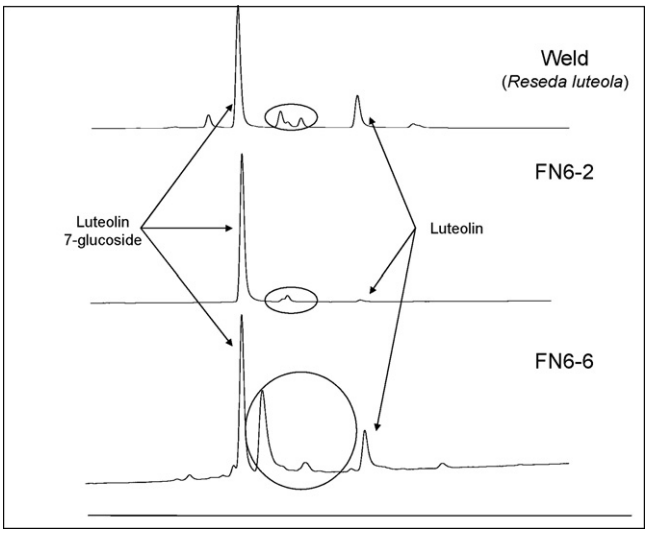

Fig. 8. HPLC profiles of extracts of (top panel) weld (*Reseda luteola*), and (middle panel and lower panels) extracts of FN6-2 and FN6-6, respectively, dyed fibers from ancient textiles from Xinjiang Province.

are similar (Table 2). Fig. 9 shows enlarged views of the minor components circled in Fig. 8, and Table 2 lists their masses, along with the UV–vis maxima. Although the ratios of components from a particular plant dyestuff can be quite variable, the presence or absence of a particular component is often an indication that different plants were used. For example, peak 3 in the HPLC profile of weld (*R. luteola*) appears to be an isomer of luteolin 7-glucoside because both compounds have the same mass (m/z = 448 Da), yet peak 3 seems to be completely absent in FN6-2 (Fig. 9 and Table 2). On the other hand, peak 4 in FN6-6 is tentatively identified as luteolin glucuronide based on its mass (m/z = 462 Da) and higher polarity (earlier retention time) than chrysoeriol glucoside (peak 2), which has the same molecular mass. Peak 4 is completely absent from both FN6-2 and from the many samples of weld we have analyzed. We have concluded, given the remoteness of the area where the textiles were found, that these dyes were probably not derived from weld, which may not have been known in Xinjiang, but from so-far-unidentified local plants [14].

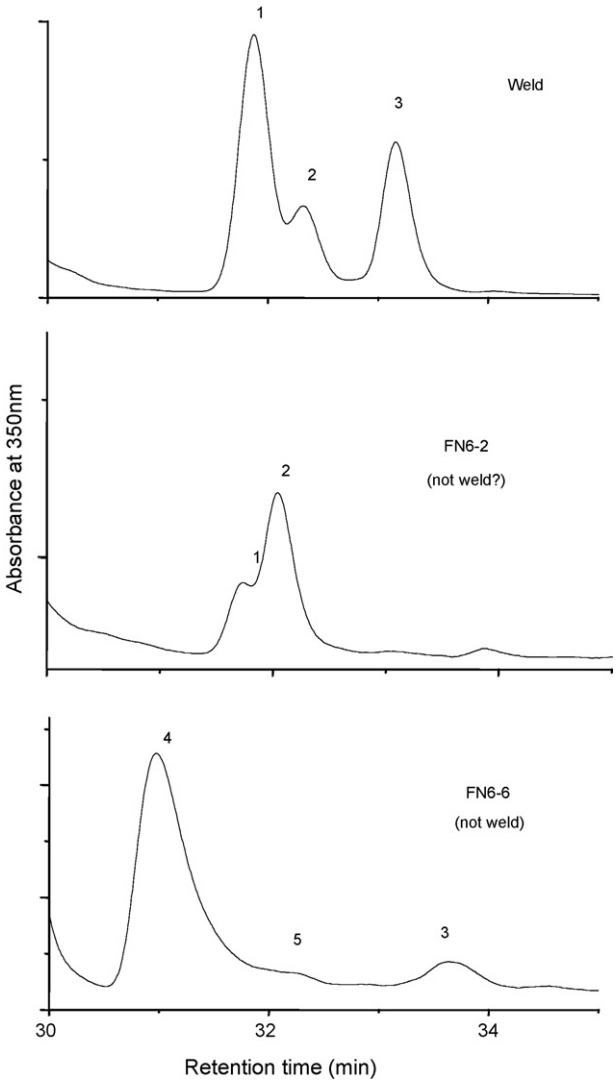

Fig. 9. Detailed views of the circled areas in Fig. 8. Numbered peaks are discussed in the text.

4. Discussion

The introduction [1,2] of HPLC with diode array detection (DAD) to the analysis of dyes extracted from textile fibers and other dyed objects represented a "quantum jump" forward in comparison with older thin layer chromatographic methods [cf. 12,15]. Not only did HPLC provide much higher resolution, but also the diode array detector enabled one to obtain a complete UV–visible spectrum of each component. In many cases, the spectral data along with retention times, if reference compounds were available, allowed for identification of specific dye molecules and, sometimes, identification of the dyestuff, too. For example, the red dyes from lac, kermes and madder all have unique dye components, or patterns of components, that allow the source of the dye to be identified.

Table 2
Yellow dye components in ancient textiles from Xinjiang (cf. Fig. 9)

Peak	Retention time (min)	Absorption maximum (nm)	Mass (Da)	Possible compound
1	31.7	332	432	Apigin glucoside
2	32.3	348	462	Chrysoeriol glucoside
3	33.6	350	448	Isomer of luteolin glucoside
4	30.9	348	462	Luteolin glucuronide
5	32.3	348	434	Not identified

However, HPLC–DAD alone is not adequate for yellow dyes. First of all, there are many more, perhaps hundreds of yellow dyes and yellow dye sources. The majority of these are flavonoids, and there are over 8000 known flavonoids [5], although not all have been used for dyeing. Furthermore, most of these flavonoids are glycosides, consisting of a sugar attached to a flavonoid aglycone. Since the UV–visible spectra of flavonoid glycosides, within a given class, are indistinguishable, electronic spectra alone cannot identify a dye molecule. HPLC retention times can help, but in the majority of cases well-characterized reference compounds are either not available or are very expensive. Mass spectrometry, introduced a number of years ago [8,16–18] either as an off-line detection method, or in parallel with HPLC–DAD, added a new dimension – namely mass measurement – to the analysis of dyes of all types. However, the need to collect individual HPLC peaks, evaporate the solvent and then reinject often vanishingly small samples into the mass spectrometer, limits the use of the off-line mode.

On-line mass spectrometric detection overcomes many of the problems mentioned above. Not only does it provide the mass of

each component at any point in the elution profile, greatly reducing the number of structural possibilities, but sometimes it gives fragmentation patterns that yield even more structural information. Ion extraction allows one to detect compounds that coelute, if they have different masses, as seen in Fig. 7. However, versatile as this technique is, mass spectrometric detection is best combined with DAD detection. One can obtain total ion current (TIC) profiles of compounds eluting from a HPLC column, but this profile does not reveal the color of the eluted peaks: frequently one detects extraneous, non-dye components, especially in extracts of plant material. UV–vis spectrometric detection allows one to select just those peaks that have a particular color. Therefore, it is preferable to have both DAD and MS detectors.

In our work, we use a simple Agilent series 1100 VL on-line atmospheric pressure electrospray ionization mass spectrometer in tandem with an HP series 1100 diode array detector. With a more sophisticated (and much more expensive) system, we could to MS/MS analysis and presumably obtain more structural information. With our current system, if we find a mass of 448 Da, we cannot say for sure whether this is luteolin 7-glucoside, a very common flavonoid dye, or one of dozens of possible isomers—either flavonoids containing different hexoses, or hexoses attached to any of the several hydroxyl groups attached to the flavone ring. However, by hydrolysis of the glycoside, one can usually identify the aglycone, in this case, luteolin, based on its retention time.

In the end, one is limited by the type of instrumentation available and the goals of the research. With a simpler LC–DAD–MS system, such as we have used, one can screen hundreds of extracts and get partial identification (mass and UV–vis spectra) of most of the components. With a more sophisticated mass detector, one can generate fragmentation patterns and get more structural information—but not have time to screen large numbers of extracts.

With regard to hydrolysis of glycosidic bonds, it was for a long time assumed that the actual dyes (in the case of flavonoids) were aglycones. Not only were methods not available for characterizing glycosides, but also the standard method for extracting dyes from textile fibers involved heating with concentrated hydrochloric acid—a process that cleaved glycosidic linkages. Therefore, as described elsewhere [6], we had to devise dye extraction methods that preserve the glycosidic bonds.

5. Conclusions

On-line mass spectrometric detection of dye molecules eluted from HPLC columns, in conjunction with diode array detection, allows one to obtain a great deal of information about the structure of a dye molecule. MS is particularly important for the analysis of yellow dyes. Not only are yellow dyes much more numerous that other colors, but also most yellow dyes are flavonoids, and most flavonoids are glycosides. Characterization of these molecules would be almost impossible with out mass spectrometry. Because most plants have unique patterns of flavonoid components, it is often possible to identify the plant used to produce the dye. However, as we have shown above, if one does not have the appropriate plant reference material, one cannot reliably identify the plant source. This is a problem because thousands of plants contain flavonoids (and some other classes of yellow colorants). So far, although we have analyzed and obtained dye profiles for over 200 plants (most of which contain yellow compounds), we frequently encounter profiles from textile extracts that do not match any of the profiles in our library. Some of these colorants are relatively modern synthetic dyes (which tend to be easily distinguished from natural dyes), but many clearly are of natural origin. Identification of these unknown dyestuffs will require the collaboration of chemists, botanists and experts in traditional dyeing processes.

Acknowledgements

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