

Abstract

The feasibility of determining metallic mordants or dyes with inorganic constituents was tested using inductively coupled plasma–mass spectrometry, an elemental analytical technique of analysis with very low limits of detection, in the range of parts per billion or below, for comparison with other well-established analytical methods. Modern, historic and archaeological samples were investigated. Mordants containing copper, iron, tin, aluminium or uranium were successfully tested as well as an organic dye with a bromine substituent.

Keywords

textile, mordant, dye, inductively coupled plasma–mass spectrometry, elemental analysis

Accuracy, precision and investigation: mordant analysis on antique textiles by various methods

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Introduction

Textile conservators and textile historians always seek to know more about the objects that they study and work on. The colour palette of a textile is dependent not only on the dyestuff but also its method of application: mordant or metal ligand that complexes the dye and holds it to the fibre or substrate. Different cultures and different periods used different mordant systems and procedures to produce certain hues.

The most common mordants are alum ($K_2SO_4 \cdot Al_2(SO_4)_3 \cdot 24H_2O$) and iron sulfate ($FeSO_4 \cdot 7H_2O$) but other mordants exist: copper sulfate ($CuSO_4 \cdot 5H_2O$), tin chloride ($SnCl_2 \cdot 2H_2O$) and potassium dichromate ($K_2Cr_2O_7$).

A wide range of well-known analytical methods is used to investigate dyes and mordants. Chemical tests involve reagents known to react specifically to some particular components. Thin layer chromatography (TLC) compares chromatograms of known dyes to those of the unknown. High-performance liquid chromatography alone or in combination with gas chromatography–mass spectrometry, is done for complete structural identification of the organic structure. Mordanted samples of different types of textile were successfully analysed for aluminium, iron, copper, tin and chromium using scanning electron microscopy (SEM) coupled to energy dispersive X-ray spectrometry (EDS) (Koestler et al. 1985). As interest is growing in inductively coupled plasma–mass spectrometry (ICP–MS) analysis (Montaser 1998, Lee et al. 2003, Dussubieux and Ballard, 2005) in the museum environment to study ancient artifacts, we explored the possibilities offered by this technique to identify metallic mordants or inorganic components of dyed textiles.

Instrumentation

The instrumentation is a Perkin Elmer Elan 6000 ICP–MS connected to a Scott-type Rytan[®], double-pass spray-chamber fitted with a standard cross flow nebulizer as sample-introduction device.

The parameters of the ICP–MS are optimized to ensure a stable signal with a maximum intensity over the full range of masses of the elements and to minimize oxides and double ionized species formation (XO^+/X^+ and X^{++}/X^+ less than 3 per cent). For that purpose, nebulizer gas flow, lens voltage, detector analogue stage voltage and detector-pulse stage voltage are adjusted.

The limits of detection (lod) are calculated for some elements of interest as the concentrations equivalent to three times the standard deviation of signal intensities obtained with 10 analyses of a 1.5 per cent HNO_3 blank solution (Table 1). They are 1 part per billion (ppb) for iron or below.

Table 1. Limits of detection (lod)

Isotope	²⁷ Al	⁵² Cr	⁵⁴ Fe	⁶³ Cu	⁷⁹ Br	¹²⁰ Sn
lod (ppb)	0.05	0.02	1	0.3	0.07	0.01

Method

Textiles have an organic matrix that has to be eliminated because the presence of too much carbon in the sample solutions can cause interference. For that reason, textile samples were ashed at 600 °C for 18 h in a porcelain crucible to oxidize carbon. The oxidization was completed by acid digestion. One millilitre of ultra-pure nitric acid was added to the ashed samples. Some solid residues were visible at the bottom of the vials. The solution was then filtered, using paper filter and diluted to 50 ml with ultra pure water. The first step of the procedure (ashing) was skipped when elements with low melting points were predicted. For example, bromine can be part of some dye chemical formulas. This element has a very low boiling point (59 °C), and would disappear if heated at 600 °C. The solutions were run using ICP–MS with no internal or external standardization. Results are qualitative.

Samples

The choice of the samples was made according to their nature and the mordant. We wanted to test a large range of textiles and a large range of mordants. Wool, silk, flax and cotton samples were selected. Some of them were not mordanted and served as controls. The other ones were mordanted with Cu, Fe, Sn, Al or U-based mordants. Some samples were mordanted with two types of mordant (Table 2).

Table 2. List of the samples investigated

Ref no	Fibre	Mass (mg)	Date	Mordant or dye expected	Miscellaneous information
4°	Wool	9.2	Modern	No	
5°	Wool	16.1	Modern	Cu	
6°	Wool	13.5	Modern	Al	
7°	Wool	13	Modern	U	
8°	Wool	10	Modern	Sn	
9	Wool	12.8	Modern	Fe	
10	Wool	14.4	Modern	Al	
11	Wool	15.6	Modern	Fe and Al	
12	Wool	13.2	Modern	Al	
13	Wool	13.9	Modern	Sn	
14	Wool	16.7	Modern	Al	
15*	Wool	6.7	19th century	Cu	Aubusson tapestry, brown tone
16*	Flax	4.3	About 1700	Fe	Brocade fabric, Italy, black lining
17*	Cotton	3.7	About 1900	Al	Sari, India
18*	Silk	2.4	About 1900	Al	China
19*	Silk	3.5	First half of the 18th century	Al	Tapestry
20**	Silk	1.8	About 1800	Al or Sn	Red silk stole
21**	Wool	2	About 6–8th century	Al	Red brown Coptic wool fabric
22**	Wool	5	17–18th centuries	Al	Furniture fabric, red
23**	Wool	8.7	17–18th centuries	Al	Furniture fabric, yellow
24	?	12.1	8th century BC	Br	2003-Tx-6
25	No	9.2	—	—	Brownish material

*Schweppe (1988); *Schweppe (no date b), volume 1. **Schweppe (no date b), volume 2.

We started by testing modern samples and as we were able to determine successfully their mordant, we undertook the same kind of analysis on ancient textiles.

Our study was completed by the analysis of an archaeological textile excavated at Gordion, Turkey. The sample is from Tumulus MM, a tomb dating to the 8th century BC and thought to belong to the Phrygian King Midas or his father.

Results

Modern textiles

Eleven modern wool samples were analysed using the ICP–MS procedure described earlier.

First, we present the results for samples 4–9 (Table 2). The range of mordants investigated included Fe, Al, Sn, Cu and U. A plain wool sample was run and used as control. The masses of the dissolved samples range from 9.2 to 16.1 mg.

We tested six different elements: Cr, Cu, Sn, Fe, Al and U. The signal intensities are calculated by subtracting a blank signal (obtained by acquiring a signal with HNO₃ acid solution) from signal intensities measured for each element while running the sample solutions. The 'plain' sample produces signal intensities higher than that of the blank solution whatever the element. This is likely due to the presence of remaining carbon in the solution that forms polyatomic species. They induce the presence of interfering peaks that increase the intensity levels of the background noise. The 'plain' sample would be more suitable as 'blank' solution rather than just an acid solution. Such 'plain' samples exist for modern wool but in the case of ancient or archaeological samples would be more difficult to obtain. The signal intensities presented in Table 3 are corrected from the weight of the samples. Table 3 shows that, for every sample, the signal corresponding to the element supposed to be involved in the mordanted process is several times stronger (from 6.5 for iron to 72,724 times for uranium) in the mordanted samples compared with the plain sample. Aluminium is an exception. The same quantity of aluminium was detected in every sample including the plain wool sample except one: the tin mordanted sample. The omnipresence of aluminium is unexpected.

Table 3. Plain wool signal intensity on mordanted wool signal intensity ratio

Mordant expected	Copper/ plain	Aluminium/ plain	Uranium/ plain	Tin/ plain	Iron/ plain
Fe	0.5	0.5	0.6	0.8	6.5
Cr	0.02	0.1	0.7	—	0.5
Cu	33.8	0.4	2.6	0.2	0.6
Sn	0.5	1.0	0.7	15.7	0.3
Al	0.7	0.8	0.9	0.1	0.9
U	6.8	8.1	72,724	0.2	0.6

SEM–EDS on samples 4–9 shows similar features: significant amounts of Cu, Sn, U and Fe were detected only in samples expected to be mordanted by one of these elements. Similar quantities of Al were detected in every sample but the one containing tin. Thus, results with ICP–MS and SEM–EDS concur well.

Our investigation expanded to a second series of modern wool samples mordanted with aluminium, iron and tin (Table 2, reference numbers 10–14). This time, no control was analysed: the signal intensities, corrected of the weight of the sample, for a given element were compared (Table 4). Iron was expected in sample 11. The signal intensity for 11 is from 13 to 42 times stronger in this sample compared with the other samples. Tin is expected in sample 14. The signal intensity of tin for 14 is from 30 to 40 times stronger in this sample. Aluminium is expected in every sample except 14. The aluminium signal intensities of the samples 10, 11, 12, 13, 15 are from 8 to 21 times stronger than that of 14. For every sample and every element, the results matched our expectations.

Table 4. Signal intensities, corrected for the weight of the samples. Bold type indicates intensities corresponding to the presence of element expected as mordant

Reference number	10	11	12	13	14
Fe	532	7000	378	543	168
Cr	355	169	134	99	177
Cu	1096	1781	930	1249	11,211
Sn	158	179	187	6423	220
Al	60,919	28,633	78,383	3683	62,151

These analyses showed that the use of an acid solution as a blank solution rather than a matrix solution did not jeopardize the accurate identification by ICP–MS of the elements involved in the mordanting process. The analysis of a control (a plain textile sample) can be helpful for comparison, but to compare

samples treated with different mordants is generally sufficient to determine an abnormally high quantity of an element related to a specific mordanting process.

Ancient textiles

Eight historic textiles were investigated. The textiles date as early as the 6–8th centuries AD. Wool and silk, cotton and flax samples with various mordants were analysed. The mordant and/or dye used on these ancient textiles were identified previously using chemical analysis and/or TLC. The mass of the samples ranged from 1.8 mg (silk) to 8.7 mg (wool). No control sample was used in this series. For ancient textile analysis we would have needed, for each ancient mordanted sample, a similar unmordanted sample that would have had the same history so as to take into account exposure to contaminants and degradation of the sample over the time.

The signal intensity of the elements of interest was corrected for the weight of the sample (Figure 1).

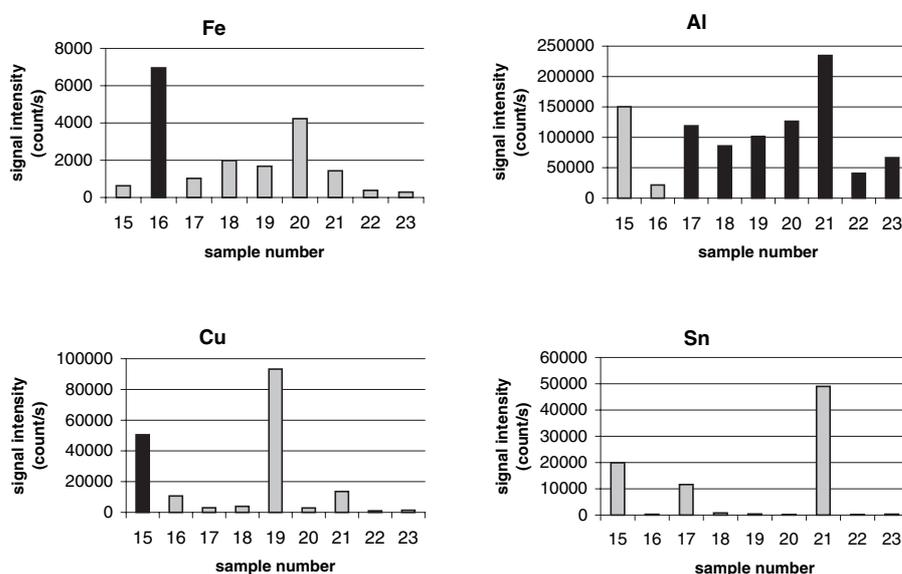


Figure 1. Signal intensity for iron, aluminum, copper and tin for the samples 15 to 23. In black are the samples supposed to be mordanted with the element reported in the graph

Copper was detected in significant quantities in two samples: 15 and 19. If copper was expected in the first sample (15) it was not in the second. Sample 16 contains significant quantities of iron as expected. Iron was detected in sample 20 too.

Aluminium was found in every sample. The smallest quantity was measured in 16 and is consistent with the fact that this element is not supposed to be involved in the mordanting process in this case. The quantity of aluminium varied over one order of magnitude.

Tin was detected in significant quantities in three samples (15, 17 and 21), even when this element was not expected in these cases.

Among the nine ancient textile samples tested, the results obtained using ICP–MS matched our expectations for four samples previously analysed by ashing and/or chemical tests (16, 18, 22 and 23). As far as the other samples are concerned, other elements were detected in addition to that element identified as associated with the mordanting process (Table 5). Thus, ICP–MS correctly detected all the mordants: all mordants previously analysed by chemical detection were recognized by ICP–MS. The difficulty is to determine which element is associated with the major mordant and which elements are present due to the use of a combination of mordants or to contamination occurring during the mordanting process or afterwards.

Table 5. Comparison of the mordant determined by chemical analysis and/or TLC and by ICP-MS

Reference number	15	16	17	18	19	20	21	22	23
Expected mordant	Cu	Fe	Al	Al	Al or Sn	Al	Al	Al	Al
Mordant identified using ICP-MS with only weight correction	Cu Al Sn	Fe	Al Sn	Al	Cu Al	Fe Al	Al Sn	Al	Al

Archaeological samples

We analysed an archaeological textile excavated at Gordion, Turkey. The sample is from Tumulus MM, a tomb dating to the 8th century BC and thought to belong to the Phrygian King Midas or his father.

The sample was badly preserved, but purple in colour. It was embedded in a brownish material of unidentified nature. Risk of contamination of the textile by this brown material was high. A purple coloured textile can be achieved by dyeing with a mixture of organic dyes (madder and indigo), with a single dye like logwood with alum, or with the vat dye, 6,6'-dibromo-indigo also known as Tyrian purple. To learn about the source of colour on the purple textile from Gordion, we measured the quantity of bromine. Al, Sn, Fe, Cr and Cu were also tested as there could be part of metallic salts used as mordant if a non-vat dye was present. We compared the amount of each element in the brown material and in the textile and it appeared that there were not significant differences (Table 6).

Table 6. Comparison between the signal intensities in the textile and in the brownish material (BM)

Isotope	Signal intensity		Ratio textile/BM
	Textile	BM	
²⁷ Al	881	923	1.0
⁵² Cr	917	1102	0.8
⁵⁴ Fe	5548	6574	0.8
⁶³ Cu	2786	2326	1.2
¹²⁰ Sn	31	31	1.0
⁷⁹ Br	49	65	0.8

No specific element, characteristic of a mordant, was detected with a greater intensity in the textile rather than in the brown material. Actually, the brown material and the purple sample have very close compositions. The 'textile' on 'brown material' ratio (corrected for the weight of each sample) is close from 1. SEM-EDS shows that the difference in composition between the 'textile' and 'brown material' lies in their silica, sulfur and calcium concentrations, all elements that are not related to the colouring or mordanting process but more on the nature of the material itself. Our Midas mystery persists though our reference bromine in a modern piece of wool dyed with 6,6'-dibromo-indigo was successfully detected.

Comments

Generally, we observed a good match between confirmed or earlier results and those we obtained using ICP-MS. In every case, ICP-MS was able to determine the element(s) expected to be involved in the mordanted process. In many cases, however, other elements, in addition of the expected ones, were detected. Contamination of the samples can explain such a result. Copper, iron and even tin are widespread elements, and copper-, iron- or tin-containing objects may have been in contact with the samples. These elements can be oxidized easily and produce corrosion that will turn into dust and diffuse easily in the environment. Museum soils routinely contain aluminium, silica and iron. This contamination can also occur during dyeing from tools or containers or later, while the textile is used or stored. We wonder about the presence of unexpected elements as indications of sloppy habits—by ourselves as researchers or by the original dyers: contamination can also be explained by insufficient care with a unique set of

containers and tools and successive handling of samples. When the testing only provides the presence of major constituents, such problems may pass unnoticed. With ICP–MS, your own mistakes and those of the dyer are more easily noticed!

The feasibility of determining metallic mordants or dyes with non-organic elements was successfully demonstrated. From an analytical point of view, the analysis of a control can help with the interpretation of the results; but in the case of ancient textiles for which such control does not exist, it is still possible to determine which mordant was used by comparing the signal intensities in the different samples.

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