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# Liquid chromatography as analytical tool for the study of natural and early synthetic dyes in traditional Saxon textiles

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## Abstract

Confirmed since the twelfth century, the Saxon community in Transylvania developed over the years in a rigorous powerful society, with its own lifestyle, social, economic, cultural and artistic standards. Together with research in historic documents, this society is now revealed by material studies of eighteenth– twentieth century objects in the Emil Sigerius collection, preserved in the ASTRA Museum, Sibiu, Romania. Embroideries made in Saxon households as well as representative Saxon coats manufactured in workshops, and dated between 1892 and 1908 (years embroidered on objects), were studied in terms of dye analysis, in order to understand if adoption of new materials goes together with the stylistic improvements. Dye analysis were performed by liquid chromatography with UV–vis and mass spectrometric detection (LC-DAD-MS), nowadays the most appropriate technique for the characterization and identification of colour components in heritage textiles. MS detection, with a triple quadrupole mass analyser, was used to achieve clear identification of each dye in a complex matrix. Construction of suitable spectral libraries through studies on standard dyes and dyed textiles definitely improved the ability to detect natural and early synthetic with greater certainty. Identification of fuchsine (1856), methyl violet (1861), orange II (1876) brilliant green (1879), quinoline yellow (1881) and rhodamine B (1887) in textiles dated about 20 years after the dyes first synthesis prove that transition from natural to synthetic dyes in the Saxon community was very fast, especially for textiles made in specialized workshops. The analytical configurations used prove their competence in textile studies, based on natural and early synthetic dyes research, and promotes the use of advanced analytical techniques in heritage science applications.

**Keywords** Natural dyes, Early synthetic dyes, Saxon textiles, Liquid chromatography, Mass spectrometry, Identification

## Introduction

Traditional textiles are among the most representative material witnesses to document the nineteenth century and twentieth century rural life in the three historical provinces of modern Romania: Wallachia, Moldavia and Transylvania. Located in Transylvania, in the very centre of Romania, the Astra Museum in Sibiu preserves an exhaustive and eclectic textile collection characterized by diversity and multiculturalism. Representative for Romanians, Hungarians, Saxons, Roma and so on, the collection preserves a large variety of items, from raw materials to the most beautiful garments and decorative objects

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which adorn the traditional houses and churches. These skilfully manufactured objects illustrate the peasants creativity' and artistic taste' in the period before industrialization and until mid-twentieth century [1].

The Saxon textile collection preserved in the Astra Museum emerged from the care of the Saxon ethnologist Emil Sigerius, who gathered the first objects at the end of the nineteenth century, and has been enlarged by the museum specialists since then. The collection contains objects dated between the seventeenth and the twentieth century, most of them from the rural areas of Transylvania [2]. The Saxon community in Transylvania arrived from Germany in successive waves, starting from the twelfth century, when they were brought by King Geza II of Hungary. They settled in different areas and developed over the years in a rigorous powerful society, with its own lifestyle, social, economic, cultural and artistic standards, strongly connected with Western Europe [3]. If one examined what the rural Saxon society appreciated in terms of materials, patterns, colour and fashion, the collection of objects in the ASTRA museum would be considered as a synthesis of the ethnic group that provided it. Most of the items (e.g. components of the traditional costume or home textiles) are handmade products, made in households by the community members, while others (such as the sheepskin coats) are supplied by workshops, or bought from specific shops as products worked in the nearby towns with local or imported traded goods (velvet, ribbons, hats/ head covers, fine fabrics or brocades) [4, 5]. Integrated in an approach aiming to better understand the ASTRA museum collection and document the social evolution of each ethnic group, objects belonging to the Saxon community were carefully studied, which also included material investigation and dye analysis.

Liquid chromatography with UV-vis (diode array) detection became the standard method for the identification of natural dyes in historical textiles since its first use in 1985 [6]. It combines high separation efficiency with the possibility of unambiguous attributions, especially when dedicated references libraries are used [7–9]. In order to achieve even more certain identifications by bringing new criteria for dyes recognition, mass spectrometers are added in the configuration [10, 11]. Due to the possibilities for tuning the selectivity as well as to increase sensitivity, through appropriately exploiting the functioning modes, ion trap or triple quadrupole mass spectrometers are preferred. They are usually equipped with electrospray ionization sources [12–16]. Further to the individual dyes recognition which is supported by experiments performed on standards, the interest is to evaluate the biological sources most likely used. This is facilitated by building dedicated databases to contain information accumulated on fibres dyed in the laboratory

with well documented biological sources, mentioned in literature as being used for textile dyeing [17, 18]. In-depth studies have been developed to characterize certain biological sources [19–22] or to discriminate between related ones, in order to recognize them down to the specie level [23–26]. The biological sources for natural dyes were used only locally before the moment they became subject of trade. Nowadays, the commercial routes and related historical periods are recorded. Consequently, historical objects could be dated with respect to the composition of the biological sources and the documented moment when such a biological source became subject of trade [17]. Following their first discovery in 1856, a large number of synthetic dyes were produced and became commercially available [27–29]. They were adopted with enthusiasm, due to the bright hues and the variety of colours they could provide. The advantage of giving easily reproducible colours, which eliminated the dependence of natural sources, also contributed to their success.

Studies performed on traditional textiles in Romanian collections evidenced the use of various colour sources, natural or imported, as well as of 'early synthetic dyes' [30, 31], which is the name adopted for a selection of about 67 synthetic dyes, the most frequently used between 1856 and 1900 [32]. An in-depth survey on materials in traditional Romanian shirts decoration in a Transylvanian rural area less than 50 km long, not far from Sibiu, revealed some phases in the transition from natural to the early synthetic dyes: first, the three main colours red, yellow and blue were achieved by using natural dye sources such as madder, carminic-acid-based dyes, dyer's broom, sawwort, tannins and indigo dyes, on wool; the colour palette was then enriched with orange or black hues by using mineral pigments lead chromate and Prussian blue; further on, natural dyes were applied on silk; finally, bright pink, violet, orange, blue or green colours were produced exclusively with synthetic dyes on silk [33].

The present study aims to document the Saxon community in Transylvania as it results from the materials used and the interest to adopt new alternatives, such as artificial fibres and early synthetic dyes. Research hopes to bring scientific arguments for understanding the development of this particular ethnic group in relation and compared to the rest of the society, as well as to trace any possible differences between rural and urban areas, ethnic interferences, European links and connectivity. The approach is based on a survey which includes handmade textiles dated from the seventeenth to the twentieth century as well as a collection of sheepskin coats documented as manufactured in workshops, and having

embroidered on them the year of fabrication, which is between 1876 and 1908.

## Experimental

### Sample description and preparation

Sixty samples from 18 objects belonging to ASTRA Museum were taken during the conservation procedures in the Textile Conservation Department. Two of them come from weavings while the rest are embroidery yarns used in decorations of sheepskin coats, head covers or home textiles. The museum archive mention the sheepskin coats as worked in dedicated workshops, between 1892 and 1908. The other objects are dated between the seventeenth century and the nineteenth century; some of them are handmade while the others are not documented (Table 1). Samples were first observed under the microscope at 10–80× magnification and then non-destructively investigated by attenuated total reflectance infrared spectroscopy (FTIR-ATR), for fibres identification. If larger samples were available, only yarns about 3 mg (~0,5 cm long) were cut and 200 µL mixture 37% HCl/CH<sub>3</sub>OH/H<sub>2</sub>O 2:1:1 (v/v/v) were added for dyes extraction. Although the advantages of the mild extraction techniques in the case of (natural) flavonoid dyes were known, the use of acid hydrolysis was an assumed decision. The compromise was based on the existence of an in-house built database, with information collected on acid

hydrolysed extracted natural and early synthetic dyes standard dyed fibres. The coloured yarns were kept in the solutions for 10 min, at 100 °C, and then extracts were evaporated to dryness in a vacuum desiccator. Each sample was re-dissolved in 100 µL solution CH<sub>3</sub>OH/H<sub>2</sub>O 1:1 (v/v) and centrifuged at 12,000 rpm for 10 min. The supernatants were transferred into chromatographic vials and injected into the chromatographic system. For the visual blue, green, violet and black samples, where the presence of indigo based dyes was suspected, a second extraction in 100 µL dimethyl sulfoxide (DMSO) was made, with the samples kept at 80 °C for 10 min. The two solutions were merged and analysed.

Integrated with the results obtained on the 18 objects mentioned above, data previously reported on another Saxon embroidery, dated 1841, will be discussed (Table 1) [34].

### Fibre identification

Fibres documentation and image collection were made with a Nikon SMZ 1000 stereomicroscope coupled with a Nikon DSLR camera, model D3100 Kit AF-s 18–55 mm VR DX. Investigation was made by infrared spectroscopy (FTIR-ATR), where a Bruker Optics Alpha spectrometer equipped with a Platinum ATR single reflection diamond ATR module was used.

**Table 1** Details on the objects discussed: date, analysis, number of samples

No	Object	Inv. number	Date	Analysis		No. of samples
1	Towel, embroidery	inv. 2490	Seventeenth century	LC-DAD-MS	Handmade	1
2	Pillow cover, embroidery	inv. 3386	Seventeenth century	LC-DAD-MS	Handmade	1
3	Handkerchief, embroidery	inv. 3383	1779	LC-DAD-MS	Handmade	1
4	Stove towel, embroidery	inv. 1958 T	1802	LC-DAD	Handmade	3
5	Towel, embroidery	inv. 1936	1832	LC-DAD-MS	Handmade	3
6	Bed cover, embroidery [33]	inv. 2075	1841	LC-DAD-MS	Handmade	4
7	Pillow cover, embroidery	inv. 2491	Nineteenth century	LC-DAD-MS	Handmade	1
8	Pillow cover, embroidery	inv. 2954	Nineteenth century	LC-DAD-MS	Handmade	3
9	Handkerchief, embroidery	inv. 2186 T	Not dated	LC-DAD	Handmade	1
10	Towel, embroidery	inv. 1861	Not dated	LC-DAD-MS	Handmade	1
11	Towel, embroidery	inv. 2940 T	Not dated	LC-DAD	Handmade	2
12	Head cover, embroidery	inv. 6050	1876	LC-DAD-MS	Not documented	4
13	Head cover, embroidery	inv. 6081	1869	LC-DAD-MS	Not documented	5
14	Head cover, embroidery	inv. 7515	Not dated	LC-DAD-MS	Not documented	2
15	Sheepskin coat, embroidery	inv. 5931P	1897	LC-DAD	Workshop	6
16	Sheepskin coat, embroidery	inv. 6787P	1908	LC-DAD	Workshop	5
17	Sheepskin coat, embroidery	inv. 6984P	1892	LC-DAD	Workshop	7
18	Sheepskin coat, embroidery	inv. 7230P	1903	LC-DAD	Workshop	8
19	Sheepskin coat, embroidery	inv. 9008P	1900	LC-DAD	Workshop	6

Spectra were acquired in the 4000–400  $\text{cm}^{-1}$  domain, with a resolution of 4  $\text{cm}^{-1}$ . Data collection and processing were made with a dedicated software, Opus 7.0.

### Dye analysis

Samples were analysed in two different campaigns, part of them by liquid chromatography with UV–vis (diode-array) detection—LC-DAD on System 1, and the other by liquid chromatography with UV–vis and mass spectrometric detection, LC-DAD-MS on System 2 (Table 1).

System 1 (LC-DAD) is an Agilent 1260 Infinity II series liquid chromatograph (Agilent Technology, Santa Clara, CA, USA) consisting of a quaternary pump (G7129A), a standard autosampler (G7111B), a column thermostat (G7116A) and multi-channel diode-array detector (G7115A). OpenLAB CDS software was used for the chromatographic system control, data acquisition and processing. A Zorbax C18 column, 150 mm length, 4.6 mm i.d. and 5  $\mu\text{m}$  particle size, was used, thermostated at 40 °C. The mobile phase consists of a mixture of aqueous 0.2% (v/v) formic acid (solvent A) and methanol/acetonitrile (1:1, v/v) plus 0.2% formic acid (as solvent B). Gradient elution was applied by using the following profile: at 0 min, 15% solvent B; from min 0 to 5, linear increase to 25% solvent B; from min 5 to 10, constant at 55% solvent B; from min 10 to 16, linear increase to 100% solvent B; from min 16 to 18, constant at 100% solvent B; and step jump at 15% solvent B, with 5 min re-equilibration period between runs (post-time). The flow rate was set at 0.8 mL/min and the injected volume of the samples was 10  $\mu\text{L}$ . The UV–vis spectra were acquired from 200 to 900 nm, with a simultaneous monitoring at five wavelengths (255, 275, 295, 420 and 490 nm), with a frequency of 0.03 min and a 2 nm resolution.

System 2 (LC-DAD-MS) was an Agilent 1260 LC, composed of the following modules: quaternary pump (Model G1311C), automatic injector (G1367E) and column thermostat (G1316C). The diode array detector (G4212A) and the triple quadrupole mass spectrometer (G6410B) were serially connected. UV–Vis spectra were acquired with a DAD detector which was placed between the column and the MS ion source. Spectra were collected over the 190–640 nm range, with a resolution of 2 nm. The MS used an ESI ionization source (ESI, Model G1948B), operated under negative and positive ion monitoring modes. Chromatographic separation was the same as for System 1, except for Solvent B which was methanol/acetonitrile 1:1 (v/v) with no formic acid content. As for System 1, injection volume was 10  $\mu\text{L}$ . For the MS detector, the following ESI operation parameters were used: drying gas temperature 350 °C; drying gas flow 8 L/min; pressure of the nebulising gas 40 psi; Vcap 2500 (–) in negative ion mode and 2500 (+) in positive ion mode.

The triple quadrupole used MS2 type scan when used as a single MS instrument; the data storage was set on profile and the peak width at 0.07; fragmentor 135 V;  $\Delta\text{EMV}$  400 V. The scanning interval for the mass to charge ratio ( $m/z$ ) was between 100 and 600 a.m.u., and acceleration voltage on the collision cell: 7 V; Dwell Time 500 ms. Agilent MassHunter Quantitative Analysis B.06.00 software was used to control the chromatographic system, as well as for data acquisition and processing. The analytical procedure was described in detail in an earlier publication, where an ion trap mass spectrometer was used instead of the triple quadrupole [35]. Samples were analysed with single MS detection in the Full Scan mode and the resulting data was processed by extracting chromatograms, according to the molecular ions of the dyes in the database.

### Dyes attribution, database

Dyes identification was based on their retention times, UV–Vis and MS data (where available), according to information collected on standards, dyes and dyed yarns. For natural dyes, attribution of the biological sources was based on data collected on yarns dyed in the laboratory, by following traditional dyeing recipes and was correlated with information available in literature. For the early synthetic dyes, information was acquired based on the analysis of yarns dyed in the laboratory with contemporary products available on the market (from various providers), as well as with analysis on the Schweppe collection of early synthetic dyed yarns. The collection, which contains a selection of 65 synthetic dyes, the most commonly used between 1850 and 1900 [32, 36], was offered by chemist Helmut Schweppe to European and worldwide museums in the 1960–1970, during a series of dyeing workshops with these well-documented products. In the present study, the collection prepared by Ronnee Barnett, textile restorer at the Metropolitan Museum of New York (MET) was used, offered as donation by Florica Zaharia, Muzeul Textilelor Băița, Romania (see Acknowledgements). Literature data on early synthetic dyes [28, 36–40] supplemented the analytical information from the in-house built database. Information regarding retention times, UV–Vis and MS data for the natural and early synthetic dyes discussed, is given in Table 2.

## Results

### Red, violet and orange

Seventeen samples were described as red, nine as violet and five as orange. In six samples, all characterized as red, alizarin was the main dye component detected. Its presence was evidenced by retention time correlated with UV–Vis data and was reinforced by the molecular ion

**Table 2** Natural and early synthetic dyes discussed and their analytical data (retention, UV–vis and MS data)

Dye	Biological source* Common and Latin name(s)	Abbreviation	Retention (min.)		UV–Vis max (nm)	MS data**
			System 1 (LC-DAD)	System 2 (LC-DAD-MS)		
Alkali Blue (1862) Acid Blue 110 CI 42750	–	–	–	14.7	574	–
Alizarin	Madder ( <i>Rubia tinctorum</i> L.)	al	15.2	15.2	248; 278; 430	[M-H] <sup>-</sup> 239
Alizarin (synthetic) (1871)	–	anth***	–	13.6	274; 338; 428	[M-H] <sup>-</sup> 255
Mordant Red II CI 58000	–	flavo***	–	13.8	272; 406	[M-H] <sup>-</sup> 255
Apigenin	Weld ( <i>Reseda luteola</i> L.) Dyer's broom ( <i>Genista tinctoria</i> L.)	ap	13.9	13.7	248; 278; 430	[M-H] <sup>-</sup> 239
Auramine (1883), Basic Yellow 2 CI 41000	–	–	12.1	–	352	–
		–	14.2	–	360	–
		–	15.7	–	366; 486	–
		–	16.9	–	368	–
Azo Flavine 3R (1880) Acid Orange 1 CI 13090	–	–	14.2	–	386	–
		–	16.2	–	410	–
Brilliant green (1879) =Diamond Green G Basic Green 1 CI 42040	–	–	15.4	–	428; 626	–
Carminic acid	Carminic acid based Mexican cochineal ( <i>Dactylopius coccus</i> C.) (see text)	ca	8.8	8.7	276; 310; 494	[M-H] <sup>-</sup> 491
Chrysoin (Tropaeolin) (1875) Acid Orange 6 CI 14270	–	–	9.8	–	384	–
Chrysoeriol	Weld ( <i>Reseda luteola</i> L.) Dyer's broom ( <i>Genista tinctoria</i> L.)	chry	–	13.7	–	[M-H] <sup>-</sup> 299
Croceine orange G (1878) Acid Orange 12 CI 15970	–	–	14.2	–	316; 485	[M-Na] <sup>-</sup> 327
Eosin A (1871) Acid Red 87 CI 45380	–	–	16.2	–	472; 498	–
		–	16.5	–	472; 500	–
		–	17.8	–	530	–
Flavokermesic acid	Carminic acid based Mexican cochineal ( <i>Dactylopius coccus</i> C.) (see text)	fk	–	13.5	285; 429	[M-H] <sup>-</sup> 313
Flavokermesic acid (C-glycoside)	Carminic acid based Mexican cochineal ( <i>Dactylopius coccus</i> C.) (see text)	dcll	–	8.6	–	[M-H] <sup>-</sup> 475
Fuchsine (magenta) (1856) Basic Violet 14 CI 42510	–	–	10.6	10.4	544	–
		–	11.2	11.1	546	–
		–	11.9	11.8	548	–
		–	12.5	–	550	–
Genistein	Dyer's broom ( <i>Genista tinctoria</i> L.)	ge	–	13.4	208; 260	[M-H] <sup>-</sup> 269
Kermesic acid	Carminic acid based Mexican cochineal ( <i>Dactylopius coccus</i> C.) (see text)	ka	–	13.5	275; 305; 490	[M-H] <sup>-</sup> 329
Luteolin	Weld ( <i>Reseda luteola</i> L.) Dyer's broom ( <i>Genista tinctoria</i> L.)	lu	13.0	12.7	254; 266; 348	[M-H] <sup>-</sup> 285
Indigotin	Woad ( <i>Isatis tinctoria</i> ) or Indigo ( <i>Indigofera</i> sp.)	ind	16.2	15.9	285; 330; 610	[M-H] <sup>-</sup> 261

**Table 2** (continued)

Dye	Biological source* Common and Latin name(s)	Abbreviation	Retention (min.)		UV-Vis max (nm)	MS data**
			System 1 (LC-DAD)	System 2 (LC-DAD-MS)		
Malachite green (1877) =Diamond Green B		–	13.4	–	312; 412; 594	–
Basic Green 4 CI 42000		–	13.6	–	314; 418; 606	–
Methyl Violet (1861)	–	–	14.0	–	320; 426; 620	–
Basic Violet 1 CI 42535		–	13.9	–	568	–
Cristal Violet (1883)		–	14.2	–	574	–
Basic Violet 3 CI 42555		–	14.6	–	582	–
Munjistin	Madder ( <i>Rubia tinctorum</i> L.)	Mu	–	14.1	–	[M-H] <sup>-</sup> 283
Orange II (1876) Acid Orange 7 CI 15510		–	15.4	–	482	–
Purpurin	Madder ( <i>Rubia tinctorum</i> L.)	pu	16.4	16.2	256; 294; 480	[M-H] <sup>-</sup> 255
Quinoline yellow (1882)	–	–	12.5	–	416; 438	–
Acid Yellow 36 CI 47005		–	12.8	–	416; 434	–
		–	13.2	–	426; 446	–
		–	15.0	–	420; 444	–
Rhodamine B (1887)	–	–	14.9	–	556	–
Basic Violet 10 CI 45170		–	15.1	–	558	–
Victoria Blue B (1883)		–	15.4	–	306; 346; 604	–
Basic Blue 26 CI 44045		–	15.7	–	308; 350; 616	–

\* Although some dyes are present in more than one biological source, only those discussed in the present study are given in the table;

\*\* MS data is given only for the dyes detected by MS in the present study

\*\*\* *anth* anthrapurpurin, *flavo* flavopurpurin

(for alizarin [M-H]<sup>-</sup>, m/z 239), in cases where the mass spectrometric data was available (Table 3).

Detection of alizarin together with other natural anthraquinones suggest the use of madder (*Rubia tinctorum* L.), while the use of synthetic alizarin, a dye which became available in 1871, would be evidenced by alizarin and two marker compounds, anthrapurpurin and flavopurpurin [41]. According to the analysis performed, the presence of purpurin and/or munjistin (for purpurin [M-H]<sup>-</sup>, m/z=255 and for munjistin [M-H]<sup>-</sup>, m/z=283 respectively) in 5/6 samples (1958\_P5, 2075\_P5, 2491\_P1, 1861\_P1, 2940\_P3) confirm the use of madder while in one case (2186\_P2), where only UV-Vis data was available, no other dyes were detected to reveal a natural or synthetic source of alizarin. Madder was used on wool in a bed cover dated 1841, on silk in a nineteenth century towel and on cotton embroidery yarns in textiles dated 1802 or not dated. However, detection of madder and putting results in correlation with earlier data on traditional Romanian textiles [33] would be an argument to date the respective object (inv. 1861) in the nineteenth century or earlier.

Carminic acid was identified in six samples (3383\_P1, 1936\_P1, 2075\_P6, 2954\_P2, 6081\_P3, 7515\_P1). As was the case for alizarin, the presence of carminic acid was based on retention time and UV-Vis data and also supported by the presence of its molecular ion (for [M-H]<sup>-</sup>, m/z=491), when mass spectrometric data was available. Carminic acid is the main dye component in a large number of insects, three of which played an important role in textile dyeing: Mexican cochineal (*Dactylopius coccus* C.), Armenian and Polish carmine scale insects (*Porphyrophora hameli* and *Porphyrophora polonica*). Identification down to the specie level is nowadays possible based on the calculation of relative ratios between minor compounds: flavokermesic acid C-glycoside (also called dcII, whose structure was recently elucidated [42]), kermesic and flavokermesic acids [23–26]. Unfortunately, for five of the samples mentioned above it was impossible to apply the methodologies cited before, as samples were too small for the minor compounds to be visible. For the one remaining sample (2075\_P6), it was estimated that Mexican cochineal was used for dyeing. This supposition is based on studies performed in the same research team

**Table 3** Results obtained for the studied samples

Sample	Colour	Fiber	Results			Source
			Dyes			
			DAD	MS		
Towel (weaving), inv. 2490, seventeenth century Biertan						
2490_P1	Blue	Cotton	ind		ind	Indigo-based-dye
Embroidery, inv. 3386, seventeenth century Transylvania						
3386_P1	Blue	Silk	ind		ind	Indigo-based-dye
Embroided handkerchief, inv. 3383, 1779 Transylvania						
3383_P1	Red	Silk	ca		ca	Carminic acid-based-dye
Embroidery, stove towel, inv. 1958 T, 1802, Hamba, Şura Mare, Sibiu						
1958_P1	Blue	Wool	ind		–	Indigo-based-dye
1958_P2	Yellow	Wool	lu		–	Luteolin-based-dye
1958_P5	Red	Cotton	al, pu		–	Madder
Embroidery, towel, inv. 1936, 1832 Cisnădioara						
1936_P1	Red	Wool	ca		ca	Carminic acid-based-dye
1936_P4	Yellow-Green	Silk	lu		lu	Luteolin-based-dye
1936_P7	Blue	Wool	ind		ind	Indigo based dye
Embroidery, bed cover, inv. 2075, 1841 [34] Apold, Sighișoara						
2075_P2	Blue	Wool	ind		–	Indigo-based-dye
2075_P3	Dark blue	Wool	ind		–	Indigo-based-dye
2075_P5	Red	Wool	al, pu		al, pu, mu	Madder
2075_P6	Red	Wool	ca		dcll, ca, fk, ka	Mexican cochineal (DC)
Mattress cover (weaving), inv. 2491, nineteenth century Transylvania						
2491_P1	Red	Cotton	al		al, mu	Madder
Embroidery, pillowcover, inv. 2954, nineteenth century Transylvania						
2954_P1	Blue	Silk	ind		ind	Indigo-based-dye
2954_P2	Pink-Violet	Silk	–		ca	Carminic acid-based-dye
2954_P3	Yellow	Silk	–		lu	Luteolin-based-dye
Embroidery, handkerchief, inv. 2186 T, not dated Gârbova Sebeş						
2186_P2	red	Silk	al		–	Madder or synthetic alizarin
Embroidery, towel, inv. 1861, not dated Sibiu						
1861_P1	red	Cotton	al		al, mu	Madder
Embroidery, towel, inv. 2940 T Transylvania						
2940_P1	Blue	Silk	ind		ind	Indigo-based-dye
2940_P3	Red	Silk	al, pu		al, pu	Madder
Embroided head cover, inv. 6050, 1876, Slimnic						
6050_P1	Green	Silk			lu, ap, chry	Weld
6050_P2	Blue	Silk	Alkali blue (1862)			
6050_P3	Yellow	Silk			lu, ap, chry	Weld
6050_P4	Red	Silk	Crocein orange G (1878) and red syntehtic dye (not identified, see text)			

**Table 3** (continued)

Sample	Colour	Fiber	Results		Source
			Dyes		
			DAD	MS	
Embroided head cover, inv. 6081, 1869 Slimnic					
6081_P1	Orange	Silk	Crocein orange G (1878)		
6081_P2	Green	Silk		lu, ge, ap, chry	Dyer's broom and weld
6081_P3	Red	Silk	ca	–	Carminic acid-based-dye
6081_P4	Blue	Silk	Blue synthetic dye ( not identified, see text)		
6081_P5	Violet	Silk	Fuchsine (1856)		
Embroided head cover, inv. 7515, not dated (early 20-th c. due to the use of rayon, or interventions) Sura Mica Sibiu					
7515_P1	Red	Rayon	ca	ca	Carminic acid-based-dye
7515_P2	Violet	Rayon	Fuchsine (1856)		
Sheepskin coat, embroidery, inv. 5931P, 1897 Sibiu					
5931_P1	Dark orange	Silk	Orange II (1876)		
5931_P4	Yellow	Silk	Auramine O (1883)		
5931_P6	Orange	Silk	Orange II (1876)		
5931_P7	Violet	Silk	Fuchsine (1856)		
5931_P8	Green	Silk	Quinoline Yellow (1882) Victoria Blue B (1883)		
5931_P9	Black	Silk	Methyl violet (1861) Victoria Blue B (1883)		
Sheepskin coat, embroidery, inv. 6787P, 1908 Transylvania					
6787_P2	Violet	Silk	Fuchsine (1856)		
6787_P3	Yellow	Silk	Auramin O (1883)		
6787_P4	Red	Silk	Chrysoin (Tropaeolin) (1875) Orange II (1876) Rhodamine B (1887)		
6787_P5	Green	Silk	Brilliant green (1879)		
6787_P6	Dark green	Silk	Methyl violet (1861) Brilliant green (1879)		
Sheepskin coat, embroidery, inv. 6984P, 1892 Sibiu					
6984_P1	Red	Silk	Fuchsine (1856) Eosin A (1871) Azo Flavine 3R (1880)		
6984_P2	Yellow	Silk	Quinoline yellow (1882)		
6984_P3	Dark green	Silk	Malachite Green (1877)		
6984_P5	Green	Silk	Malachite Green (1877) and unknown dye (see text)		
6984_P6	Violet	Silk	Methyl violet (1861)		
6984_P7	Yellow	Silk	Yellow dye ( not identified, see text)		
6984_P8	Brown-Black	Wool	Prussin Blue (FTIR/ATR) and traces unknown yellow dyes (see text)		
Sheepskin coat, embroidery, inv. 7230P, 1903 Sibiu, Noul Roman					
7230_P1	Blue	Silk	Victoria Blue B (1883)		
7230_P2	Violet	Silk	Fuchsine (1856) Methyl violet (1861) Rhodamin B (1887)		
7230_P3	Red	Silk	Rhodamin B (1887)		



**Table 3** (continued)

Sample	Colour	Fiber	Results		Source
			Dyes		
			DAD	MS	
7230_P5	yellow	Silk	Auramine O (1883)		
7230_P6	Red–Orange	Silk	Rhodamine B (1887) Orange II (1876)		
7230_P7	Yellow	Silk	Quinoline yellow (1881)		
7230_P8	Brown	Silk	Malachite green (1877) Methyl Violet (1861)/Cristal Violet (1883) Auramine O (1883)		
7230_P9	Violet-Pink	Silk	Rhodamine B (1887)		
Sheepskin coat, embroidery, inv. 9008P, 1900 Sibiu					
9008_P1	Orange	Silk	Orange II (1876)		
9008_P2	Dark red	Silk	Orange II (1876)		
9008_P3	Orange	Silk	Orange II (1876)		
9008_P4	Violet	Silk	Fuchsine (1856)		
9008_P6	Yellow	Silk	LUTEOLIN based dyes and unknown yellow dyes (see text)		
9008_P8	Brown	Silk	Methyl violet (1861) and unknown dye (see text)		

When natural dyes were detected, the biological sources are also presented. Dyes abbreviation, UV-Vis and MS data are given in Table 2

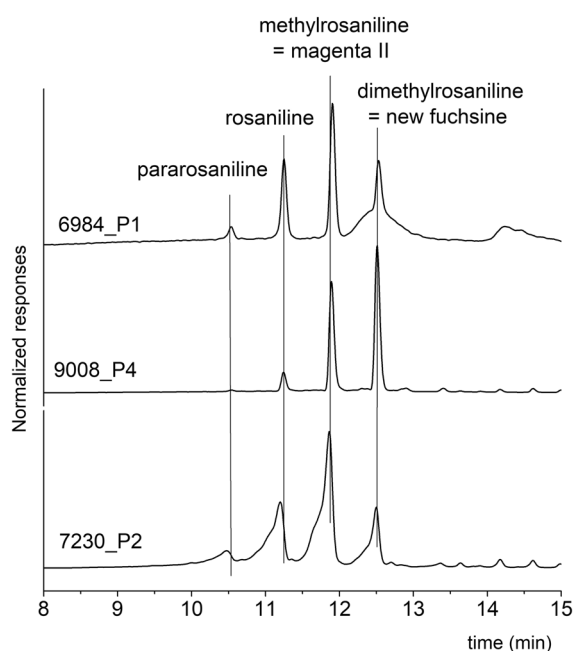
[43], where large amounts of flavokermesic acid C-glycoside relative to carminic acid were observed in the Mexican cochineal dyed samples. Carminic acid-based-dyes were used on wool in a towel dated 1832, on silk in a handkerchief dated 1779, a head cover dated 1869 and a nineteenth century pillow cover. It was also identified on rayon in a head cover not dated but could be considered as twentieth century due to the use of rayon (if the rayon yarn is not a later intervention). Mexican cochineal was used on wool in a bed cover dated 1841.

Synthetic dyes were detected in fourteen from the twenty-six samples described as red and violet. Fuchsine (1856) and methyl violet (1861), representatives of triaryl-methane, the first group of synthetic dyes which became available, were identified in 8/14 samples. Fuchsine (also called magenta) was evidenced based on the detection of one or more of the four marker compounds described in literature: pararosaniline ( $\lambda_{\max}=544$  nm), rosaniline ( $\lambda_{\max}=546$  nm), methylrosaniline ( $\lambda_{\max}=548$  nm) and dimethylrosaniline ( $\lambda_{\max}=550$  nm) [28, 36, 38, 44] in seven samples, once on rayon and the others on silk. As stated in literature [38] and also discussed in a previous publication with reference to the use of early synthetic dyes in Romanian traditional textiles [33], two production processes were reported, which would result in the so called “early fuchsine”—characterized by a mixture of the four compounds mentioned above and “late fuchsine”—to give mainly methylrosaniline (also called magenta II) and dimethylrosaniline (new fuchsine). “Early fuchsine” is

mentioned as obtained in the late nineteenth century by heating an oxidant with a coal tar distillate containing a mixture of aniline and toluidine in various ratios, with or without further inclusion of carbon tetrachloride, while “late fuchsine” would be the result of a later process that involved reaction of 4,4'-methylene-di-o-toluidine and o-toluidine [37]. Consequently, samples 6081\_P5 from a head cover dated 1869 and samples 5931\_P7, 6787\_P2, 6984\_P1, 7230\_P2 from decorations in sheepskin coats dated 1897, 1908, 1892 and 1903 respectively were dyed with “early fuchsine” and samples 9008\_P4 (dated 1900) and 7515\_P2 (on which fuchsine was used on rayon), with “late fuchsine” (Fig. 1).

All the samples where fuchsine was used as single dye were violet while for the others they received the colour of the dyes used for combination: red in sample 6984\_P1, when used with red dyes eosin A and traces of azo flavine 3R and violet in sample 7230\_P2 when methyl-violet and rhodamine B were added. In what methyl-violet (1861), the other dye in the red and violet group which represents the triarylmethane class is concerned, apart from the sample mentioned above, with reference to a sheepskin coat dated 1903, it was also identified as individual dye in a violet sample from another sheepskin coat, dated 1892 (6984\_P6).

Methyl-violet was also used in combinations with other early synthetic dyes to give dark green, brown or black hues in sheepskin coats embroidery yarns.



**Fig. 1** Image to illustrate identification of “old” fuchsine in samples 6984\_P1 and 7230\_P2 and “new” fuchsine in sample 9008\_P4, based on the two different production processes as reported in literature [38]

Rhodamine B (1887) and eosin A (1871) for the class of xanthenes, as well as chrysoin (also called tropaeolin, 1875), azo flavine 3R (1880) and orange II (1876) for the azo dye class were also detected, always on silk. Identification of rhodamine B was based on the detection of the two compounds ( $\lambda_{\max}=556$  nm and  $\lambda_{\max}=558$  nm) present in the standard dyed samples from the Schwebbe collection and also mentioned in literature [28], while similar argumentation was used to reveal eosin A, based on its marker compounds ( $\lambda_{\max}=472$ , 498 nm,  $\lambda_{\max}=472$ , 500 nm, and eosin  $\lambda_{\max}=530$  nm). According to literature, the above-mentioned compounds are revealed as eosin without one bromine substituent and eosin methylester [45]. Rhodamine B was used twice as individual dye and twice in combinations with other synthetic dyes, always in the embroideries of sheepskin coats dated 1908 and 1903. It should be mentioned that this dye was detected four times in the same object (dated 1903), twice as individual dye and in two combinations to give different violet and red hues. Eosin A was identified only once, in a dyeing combination with fuchsine and traces of azo flavine 3R to achieve a red colour in a sheepskin coat dated 1892.

Chrysoin (Acid Orange 6), azo flavine 3R (Acid Orange 1), orange II (Acid Orange 7), and crocein orange G (Acid Orange 12) are all indexed as orange dyes, and became available between 1875 and 1878. Chrysoin and azo

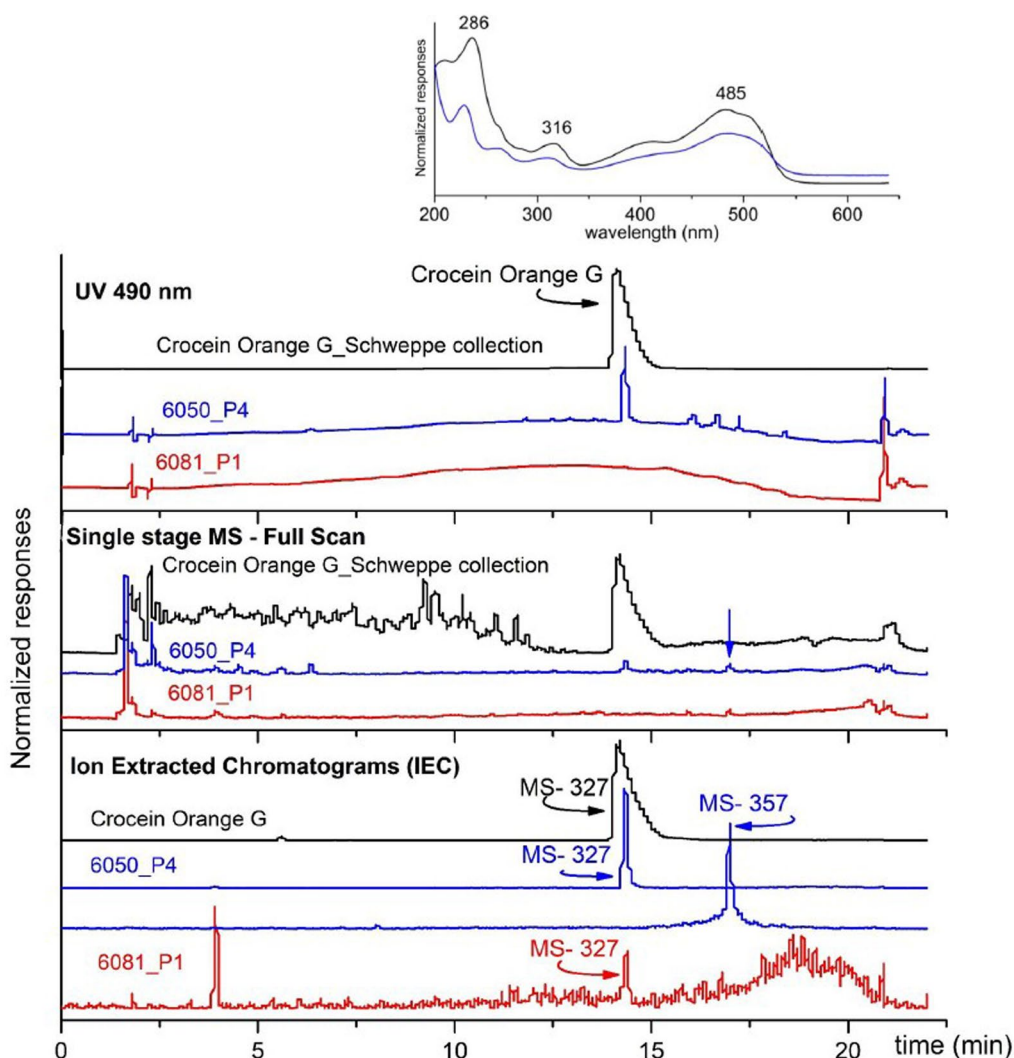
flavine 3R were identified only by UV–Vis spectrometric data and were used in dyeing combinations with other early synthetic dyes, such as orange II and rhodamine B for the first, and fuchsine and eosin A for the second. In both cases, they were used in sheepskin coats dated 1908 and 1892 respectively. The use of mixtures of three synthetic dyes in the sheepskin coats, documented as manufactured in workshops, evidence the dyers interest to provide a large variety of colours, the artistic taste of the craftsmen and their flexibility to answer the requests received from the community, in the early stages of the synthetic dyes. By opposite to the two aforementioned dyes, orange II was quite a popular dye. In perfect accordance with references from modern standards and the Schwebbe collection, as well as with literature, in the present study Orange II was evidenced based on retention and UV–Vis ( $\lambda_{\max}=482$  nm) data. It was used as individual dye or with Rhodamine B, in 5 other samples, characterized as orange or orange-red, which means in all cases where an orange hue was intended. It was also detected in other traditional textiles from Romanian collections studied in the same research group [30].

Crocein orange G was identified based on retention, UV–Vis ( $\lambda_{\max}=485$  nm) and mass spectrometric data ( $[M-Na]^-$  327), as compared with a standard dyed fibre from the Schwebbe collection labelled Crocein orange G, Acid Orange 12, CI 15970 in two red silk samples (6050\_P4 and 6081\_P1) in embroidery heads dated 1876 and 1869 respectively (Fig. 2).

Another dye component with the main ion  $m/z=357$  was also present in sample 6050\_P4, probably to give the fibre a red hue. Identification of crocein orange G in silk fibres from two different head covers would suggest that the two objects were repaired, probably in the same context. This is very probable, as they are documented as acquired from the same village (Slimnic), in 1981. As crocein orange G is an early synthetic dye which was not in use in 1981, the interventions should be dated before the two head covers became part of the ASTRA collection.

### Yellow

Eleven samples were described as yellow. Luteolin was identified in 5/11 cases, always by retention and UV–Vis data ( $\lambda_{\max}=254$ , 266, 348 nm) and certified by the presence of the molecular ion (for  $[M-H]^-$ ,  $m/z=285$ ), when mass spectrometric data was available. Luteolin is the main dye component in several plants, three of which played an important role in textile dyeing in Romania. With reference to the acid hydrolysed extracts, weld (*Reseda luteola* L.) is characterized by the presence of luteolin, apigenin and chrysoeriol while luteolin, apigenin and 3-methyl-quercetin are expected for sawwort (*Serratula tinctoria* L.) samples. Dyer’s broom (*Genista*

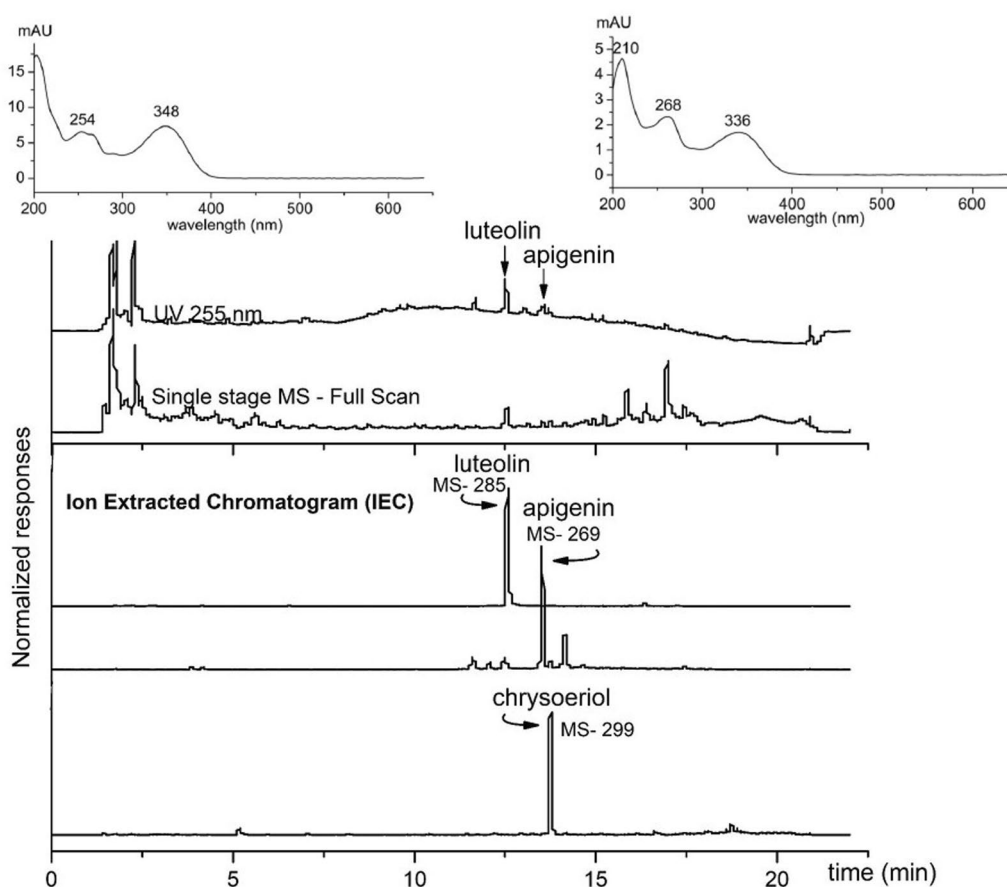


**Fig. 2** Comparative analytical data for crocein orange G dyed wool from Schweppe collection (black line), sample 6050\_P4 (blue line) and 6081\_P1 (red line) to support identification of crocein orange G in the two samples. From top to bottom: LC-DAD (490 nm); Single stage MS Full Scan; Extracted Ion Chromatograms (EIC) according to  $m/z=327$  [M-Na]. EIC according to  $m/z=357$  (major ion) suggests the presence of another synthetic dye (see text)

*tinctoria* L.) acid hydrolysed extracts are defined by luteolin, genistein and apigenin as main compounds, and chrysoeriol and diosmetin as minor components. Unfortunately, in the present study, luteolin was the only dye component detected in 3 samples, probable due to the very small sample sizes, which made any attribution impossible. Apigenin and chrysoeriol were detected in one case (6050\_P3) to confirm the use of weld (Fig. 3), while in one other sample (9008\_P6) luteolin was accompanied by dyes ( $\lambda_{max}=338$  nm;  $\lambda_{max}=350$  nm and  $\lambda_{max}=340$  nm) which match none of the existing references in the database.

Except for the last case discussed, luteolin- based-dye sources (including weld) were identified in textiles defined as handmade, dated 1802, 1832, nineteenth century and 1876. Weld and dyer’s broom were also identified in visual green samples, also from objects dated 1876 and 1869 (which will be discussed in the section dedicated to green).

The presence of two early synthetic dyes was evidenced in the visual yellow samples: auramine O (1883), with a diphenylmethane structure and quinoline yellow (1882). The first was detected based on retention and UV-Vis data ( $\lambda_{max}=352$  nm,  $\lambda_{max}=360$  nm,  $\lambda_{max}=366$ , 486 nm and  $\lambda_{max}=368$  nm), as individual dye. It was



**Fig. 3** Image to support identification of weld in sample 6050\_P3. From top to bottom: LC-DAD (255 nm) and UV-vis spectra of luteolin and apigenin; Single stage MS Full Scan; Extracted Ion Chromatograms (EIC) according to  $m/z=285$   $[M-H]^-$  (luteolin),  $m/z=269$   $[M-H]^-$  (apigenin),  $m/z=299$   $[M-H]^-$  (chrysoeriol)

also detected together with other dyes in a visual brown sample. Quinoline yellow was detected as individual dye source in two yellow silk yarns as well as together with a blue dye in one other case, to achieve a green hue. Both auramine O and quinoline yellow were used for dyeing the decoration yarns in workshop manufactured sheepskin coats dated 1897, 1892, 1908 and 1903. A dye with  $\lambda_{max}=390$  nm, which did not match the dyes in the database was detected in a yellow silk sample from a sheepskin coat dated 1892. Unfortunately, no mass spectrometric data was available for the respective sample.

### Blue

From the eleven samples described as blue, indigotin was identified in eight cases, which suggests the use of indigo based dyes. Indigotin was evidenced in DMSO extracted samples by retention, UV-Vis ( $\lambda_{max}=285, 330, 610$  nm) and mass spectrometric data (for  $[M-H]^-$ ,  $m/z=261$ ), when available. Although there are several biological sources which contain indigotin precursors, two of them

may have been used in the traditional Saxon textiles: woad (*Isatis tinctoria* L.), available in Europe since Neolithic, and indigo (*Indigofera tinctoria* L.) accessible in the area since the seventeenth century [30, 33]. From the analytical point of view, it is not possible to distinguish between the two species neither to differentiate natural from synthetic indigo, which was first produced in 1882. However, considering that indigo based dyes were identified in handmade textiles dated seventeenth–nineteenth century, on wool (four cases), silk (three samples) and cotton (one sample), it is obvious that one of the natural sources was responsible for the colour. According to previous studies on textiles in Romanian collections [30, 31, 33], indigo-based-dyes were the only source of blue in traditional textiles, until synthetic dyes became available.

Two blue early synthetic dyes were also identified in visual blue samples from the present study: Alkali blue (1862), and Victoria Blue (1883), in one case each. They were evidenced based on retention correlated with UV-Vis data, according to information accumulated on

standards and available in literature. The two dyes were all identified on silk, in objects dated 1876 and 1903. Victoria Blue seems quite a popular dye at the end on the 19-th beginning of the twentieth century, as it was also identified in Romanian traditional shirts decoration previously studied [33], in two other samples from this group, in combination with different synthetic dyes to achieve green and black hues. An un-identified blue synthetic dye ( $\lambda_{\max}=270; 310; 600$  nm) was present in head cover inv. 6081. However, this decoration should be considered as intervention at a later date, as the object is dated 1869, and the only synthetic dyes available at that time were indigo carmine and alkali blue, but they present different analytical features.

### Green

Seven samples were characterised as green. In two cases, natural yellow dyes such as weld and dyer's broom (already discussed under the yellow section) were identified, which were probably used with iron mordants to obtain green hues. The two dye sources were detected in silk decorations in two head covers, dated 1876 and 1869. Dyer's broom was a very popular source of colour at the end of the nineteenth century, as results from its frequent identification in traditional textiles in Romanian collections as well as the numerous mentions in a collection of dyeing recipes edited by the Romanian Academy in 1914 [46].

Early synthetic dyes were identified in the other 5/7 green samples. In one case quinoline yellow and Victoria blue, two dyes discussed in the respective sections, were found together in a silk sample from a sheepskin coat dated 1897. Brilliant Green, also called Diamond Green G (1879), was revealed in two cases, both from the sheepskin coat dated 1908 and Malachite Green, also called Diamond Green B (1877), in the other two, in sheepskin coat dated 1892. Each of the above-mentioned green dyes was identified as individual dye in one case, while in the other in a dyeing combination with other dyes (methyl violet or an unknown dye) to give a darker green hue. The unknown dye components present in green sample 6984\_P5 have the following profiles:  $\lambda_{\max}=408, 578$  (retention time 12.6 min) and  $\lambda_{\max}=384$  (14.2 min). The dyes Brilliant Green and Malachite Green were identified based on retention time and UV-Vis data, which were in perfect correlation with data collected on the respective standard dyed fibres in the Schweppe collection and with literature.

### Brown and black

Two visual brown and two visual black samples were available in the study, all belonging to sheepskin coats decorations. In all cases these hues were achieved by

combination of dyes. Methyl violet was detected in all but one samples, always on silk: once with malachite green and auramine O (7230\_P8), in one other case with unknown dye having as characteristics  $\lambda_{\max}=564$  nm and  $\lambda_{\max}=408$  nm (9008\_P8) and in the other with Victoria blue B. In the remaining (brown-black wool sample), Prussian blue was detected (by infrared spectroscopy) and unknown yellow dyes ( $\lambda_{\max}=358$  and  $\lambda_{\max}=364$  nm) were revealed by LC-DAD. Prussian blue was also detected, together with carminic acid-based-dyes, in a black silk yarn decoration from a Romanian shirt, from the same area, also preserved in the ASTRA Museum [30]. It could be supposed that the two colouring compounds identified were used on a darker shade of wool to give it a brown-black hue.

### Discussion

Nineteen objects were available for study, eleven were characterized as handmade, three are not documented and five were made in dedicated workshops. All the handmade objects are dated seventeenth–nineteenth century and natural dyes were exclusively identified. Embroidery is made in the three main colours: red (including pink-violet hues), yellow and blue. The two samples from weavings are both blue. Red was obtained with madder or carminic acid-based-dyes, yellow with luteolin-dye sources and blue with indigo-based-dyes. In most of the samples available, these dyes were on wool, in some cases on cotton or on silk. The early objects where silk embroidery yarns were used are revealed as precious: embroidery inv. 3386 dated seventeenth century, handkerchief inv. 3383 dated 1779 and pillow cover inv. 2954 which is dated nineteenth century. It is very probable that towels inv. 1861 and inv. 2940, where only natural dyed embroidery yarns were used, mentioned in the museum archives as handmade but not dated, are also dated in the nineteenth century or earlier. It is also credible that handkerchief inv. 2186, also handmade and not dated, was made in the nineteenth century or earlier. This supposition is based on the fact that, according to previous analysis, synthetic alizarin was rarely used on silk (mostly on cotton), so it is more reasonable for madder to be responsible for dyeing. It is not documented if head covers inv. 6050 dated 1876, inv. 6081 dated 1869 and inv. 7515, undated in the museum archives, are handmade or produced in dedicated workshops. A possible explication could be that these objects were assembled in the households by using industrial produced components or that peasants bought the head covers readymade but unfinished, and decorated themselves with rich handmade embroidery. Both natural and early synthetic dyes were detected in the embroidery yarns which decorate the head covers. Crocein orange G (1878), as well as the

un-identified red, and blue dyes, present in the dated objects, should be the result of interventions at a later date. Alkali blue (1862) for inv. 6050 and fuchsin (1856) for inv. 6081 could be seen as very early adoptions of the synthetic dyes. In the case of head cover 7515, identification of rayon in both of the samples available suggest that either the decoration yarns studied are later interventions or that the object dates from the twentieth century. According to the textile restorer, all the head covers underwent several conservation interventions which altered their original sewing and lining, and make impossible to trace the successive materials used.

Extremely valuable information could be achieved from the study of the five sheepskin coats dated between 1892 and 1908 and documented as manufactured in dedicated workshops (Fig. 4).

Except for the detection of luteolin in one yellow sample, synthetic dyes, used individual or in combinations of two or three, were responsible for the colours. By contrary with the first objects discussed, where embroidery yarns were only in the three main colours, in the sheepskin coats decoration bright colours such as orange, violet, green as well as dark hues like brown and black were used. This coloration was obtained with the recent available synthetic dyes, discovered even only 15 years before, as in the case of malachite green (1887) in sheepskin coat inv. 6984P (dated 1892). These results help us to establish that the new synthetic dyes were quickly adopted by local Transylvanian workshops in their products. Moreover, the analytical evidence of the use of early synthetic dyes helps the textile conservator to take documented decisions for the objects preservation and specific treatments [47].

## Conclusion

Natural and early synthetic dyes were successfully identified in traditional Saxon textiles and in sheepskin coats decoration. In the oldest objects studied, which are dated seventeenth–nineteenth century, natural dye sources such as madder, carminic acid, luteolin and indigo-based-dyes were revealed. Their use was limited to achieve the three main colours, red, yellow and blue, mostly on wool, in homemade textiles for domestic use. The use of silk was reserved to valuable textiles, as for example a handkerchief dated 1779 where carminic acid-based-dyes on silk were revealed. Coloured silk was also used to decorate head covers. Apart from the above-mentioned natural dyes, the first available synthetic alternatives were immediately adopted to obtain brighter hues, as proves the use of fuchsine (1856) in 1869 or alkali blue (1861) in 1876. The Saxons enthusiasm to rapid adopt the brilliant palette of the early synthetic dyes was evidenced by the large number of representatives, available for the first time between 1856 and 1887, and used in silk decorations of sheepskin coats dated from 1892 to 1908, manufactured in workshops.

Transition from the natural to the early synthetic dyes respects the same scenario observed for the Romanian traditional shirts decoration in objects from the area of Sibiu, also preserved in the ASTRA Museum collection. As the synthetic dyes identified in the two studies are almost the same, it may be supposed that they represent the offer of choice that existed at that time.

The analytical strategy elaborated succeeded to successfully identify twelve natural and fifteen synthetic dyes, with different structures: flavone, anthraquinone, indigoid, diphenylmethane, triarylmethane, xanthene, quinoline. Based on the use of liquid chromatography with UV–Vis (diode array) and mass spectrometric detection, the methodology was strongly supported by the in-house built databases, which included data collected on



**Fig. 4** Image and detail of sheepskin coat 7230P dated 1903. Eight early synthetic dyes were identified, individual or in combinations, in the 8 samples available (Table 3)

the Schuppe collection of fibres, dyed with a selection of the most frequently used early synthetic dyes.

Finally, the results provide an instrument to enrich the existing information on traditional textiles, based on the materials used, which will be helpful to characterize undocumented traditional objects. Further on, documented local textile collections would be helpful to better integrate the Romanian heritage in a European and world-wide context.

#### Abbreviations

a.m.u.	Atomic mass unit
ATR	Attenuated total reflectance
DAD	Diode array detection
FS	Full scan mode
FTIR	Fourier transform infra red spectrometry
HPLC	High performance liquid chromatography
EIC	Extracted ion chromatogram
m/z	Mass to charge ratio
MS	Mass spectrometry

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#### Author contributions

IP and IT designed the research and wrote the main manuscript; IT provided and documented the samples; SV and IP settled the LC–DAD analytical method, analysed the samples and processed the data; FA and AM set up, together with IP, the LC–DAD–MS analytical protocol and provided all the support for LC and MS data acquisition and procession. All authors reviewed and accepted the manuscript.

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#### Availability of data and materials

Not applicable.

#### Declarations

#### Competing interests

The authors declare that they have no competing interests.

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