

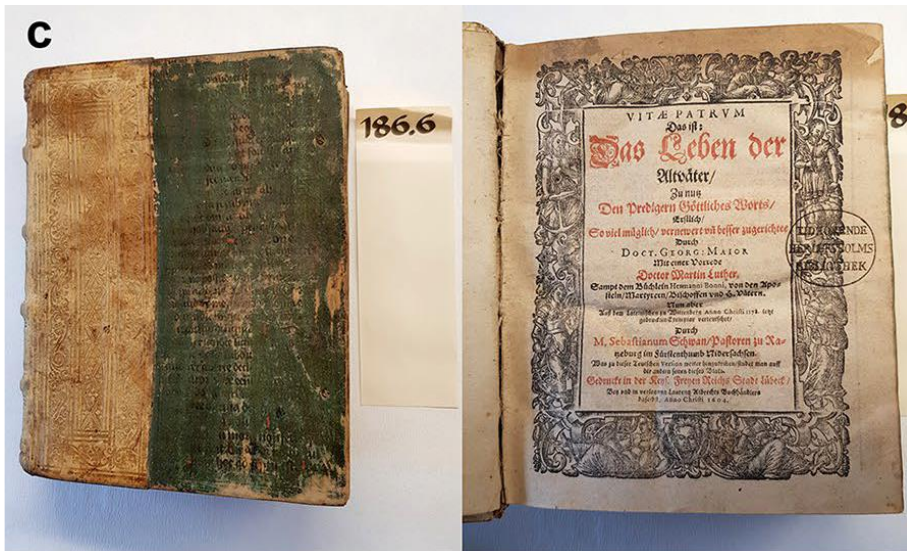
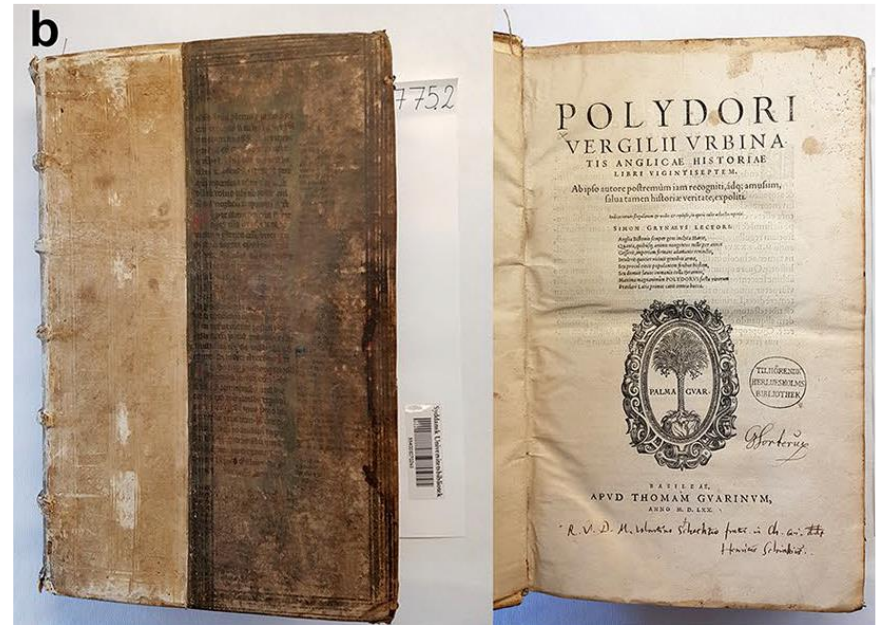
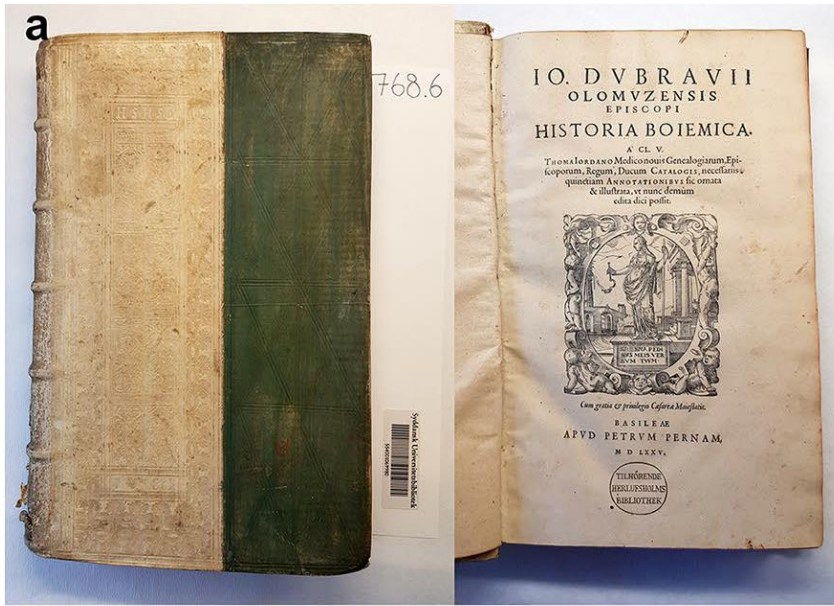
Part 1

Background

In the novel *The Name of the Rose*, by Umberto Eco, a Benedictine monk laced the pages of a book with a poison and, in this way, killed all the people who read it.

Fantasy or reality? Can you use a book to kill a person? Do poisonous books exist?

Three books were found in a library, their covers decorated with green paint (pictures in the next slide). As you can see, old manuscripts were reused to make the book covers and green paint was applied on the manuscripts. A quick analysis using X-ray fluorescence spectrometry (XRF) revealed the presence of arsenic in the covers. This information was made public, and this led to the discovery of a fourth book, in a different library, which had similar characteristics. All four books date back to the XVI and XVII centuries.



Here you have the XRF analysis results for all four books. The analysis was semiquantitative (using reference standards), except for Hg, Ag and Sb (for these three elements only signal intensity (total counts) were recorded).

Element	a		b		c		d	
	Concentration, wt%	RSD, %	Concentration, wt%	RSD, %	Concentration, wt%	RSD, %	Concentration, wt%	RSD, %
Si	5.64	0.1	6.36	0.1	6.73	0.1	5.34	0.1
Al	0.144	1.9	0.625	0.5	0.439	0.6	0.492	0.5
Ca	1.67	0.1	4.31	<0.0	3.06	<0.0	2.44	<0.0
K	1.35	0.1	0.617	0.1	0.696	0.1	1.89	0.1
Ti	0.055	0.3	0.071	0.3	0.042	0.4	0.023	0.6
Sr	0.011	0.3	0.026	1.3	0.028	1.8	0.002	1.5
As	14.7	<0.0	2.66	<0.0	8.47	<0.0	8.46	<0.0
S	6.30	0.1	2.23	0.1	3.52	0.1	3.52	0.1
Fe	0.22	0.1	0.26	0.1	0.266	0.1	0.224	0.1
Mn	0.013	0.4	0.014	0.5	0.014	0.5	0.011	0.6
Cu	0.004	1.4	0.033	0.2	0.015	0.6	0.007	1.0
Zn	0.036	0.2	0.007	0.8	0.005	1.2	0.023	0.3
Pb	0.010	1.0	0.008	1.0	0.008	1.2	0.005	0.7
Ba	–	–	0.006	1.2	0.011	0.7	0.021	0.3
Rb	0.001	0.3	0.002	0.3	0.002	0.2	0.002	0.2
Hg (counts)	1.94×10^7		1.37×10^6		1.39×10^6		–	
Ag (counts)	4.10×10^5		2.37×10^4		2.02×10^5		3.02×10^5	
Sb (counts)	2.44×10^4		0.85×10^4		2.54×10^4		3.69×10^4	

Absolute calibration of the concentrations has been performed by the DCCR-method (Direct Calibration from Count Rates) using the standard reference material NIST-2711 for most of the elements and NIST-610 for S. The relative standard deviation (RSD) is listed for each element. No standardisation was done for Hg, Ag, and Sb; instead the observed count rates are listed

What additional information would you like to get on the book covers? What for?

Part 2

Book A

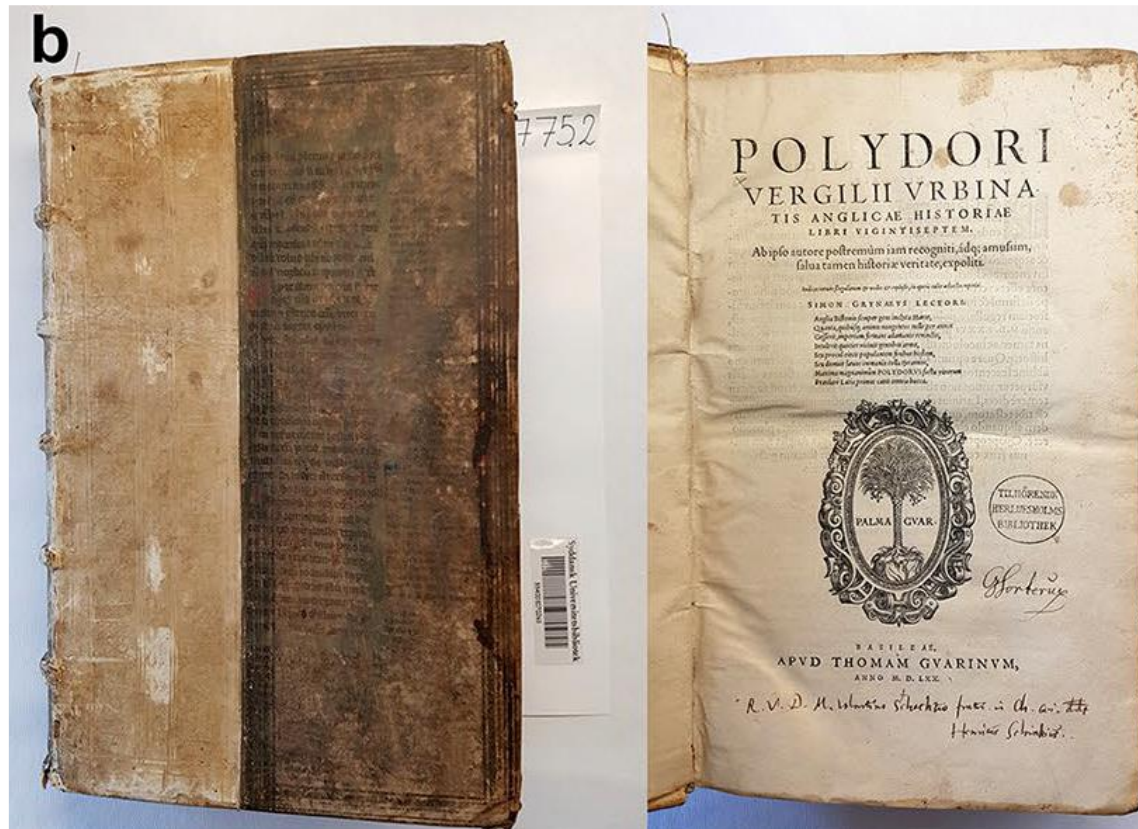


Year of publication: 1575

31.5 × 20 × 3 cm

Cover: green paint on an unidentified medieval manuscript, on parchment

Book B



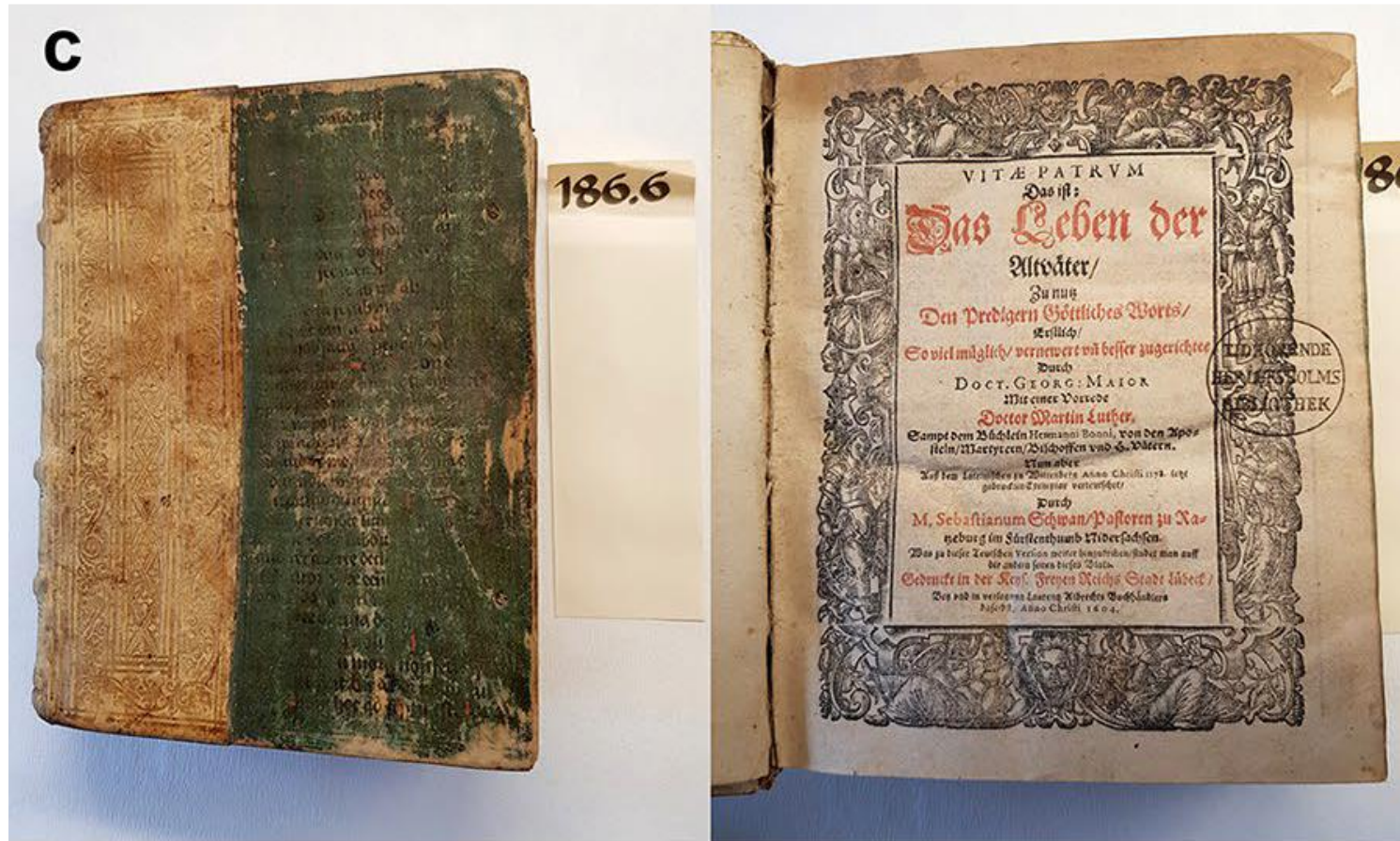
Year of publication: 1570
34 × 21 × 5 cm

Cover: green paint on a medieval manuscript

Front cover: Corpus Iuris Canonici, De rescriptis, Sexti Decret. Lib. I. Tit. III. Cap. XII-XIV.

Back cover: Corpus Iuris Civilis (Justinian), Feudorum Lib. I, Tit. IX-XIII.

Book C



Year of publication: 1604
19 × 15.5 × 5 cm

Cover: green paint on a medieval manuscript (parts of Sancti Gregorii Homiliarum in Ezechielem, Liber I, Homilia X i.a.)

Book D



Year of publication: 1602

35 × 23 × 5.6 cm

Cover: green paint on an unidentified medieval manuscript

XRF

ARTAX-800 μ -XRF, Bruker-Nano
 beam diameter: 60-64 μ m
 50 kV, 600, 30 s, under a constant flow of He

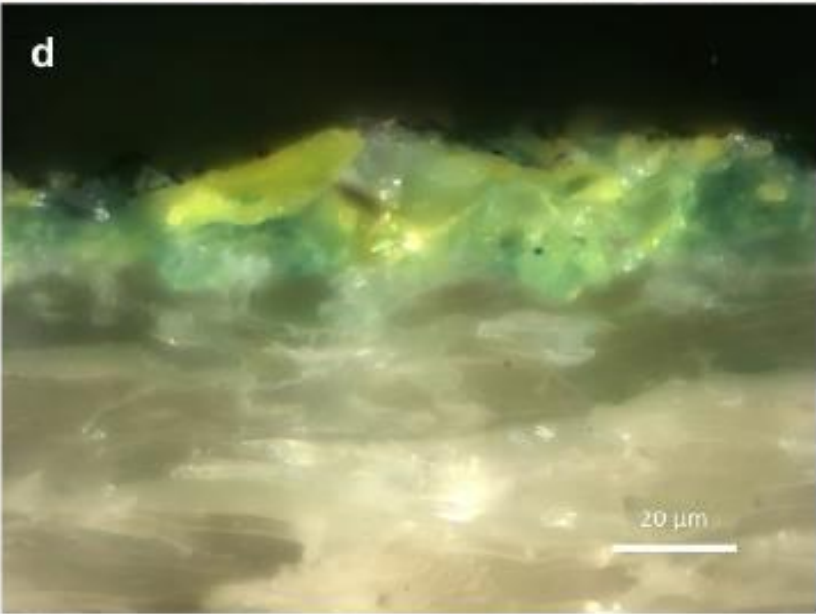
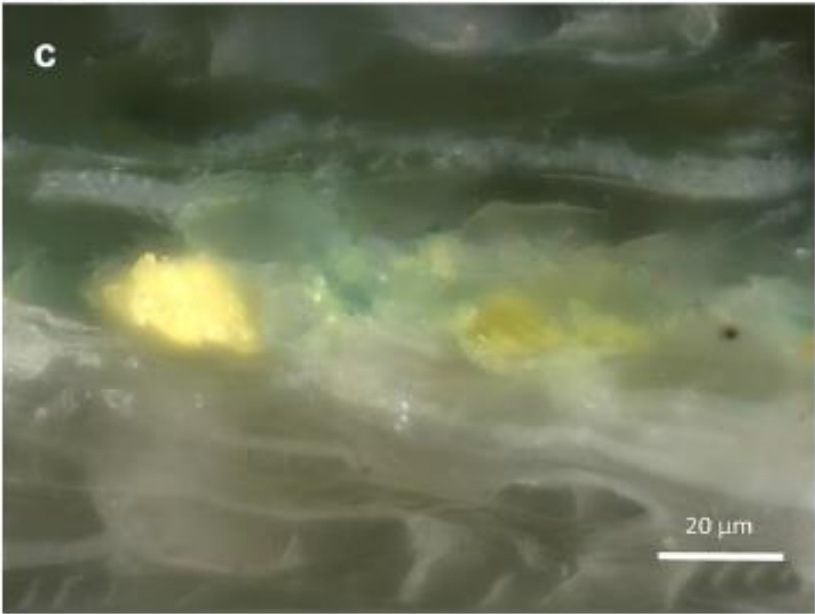
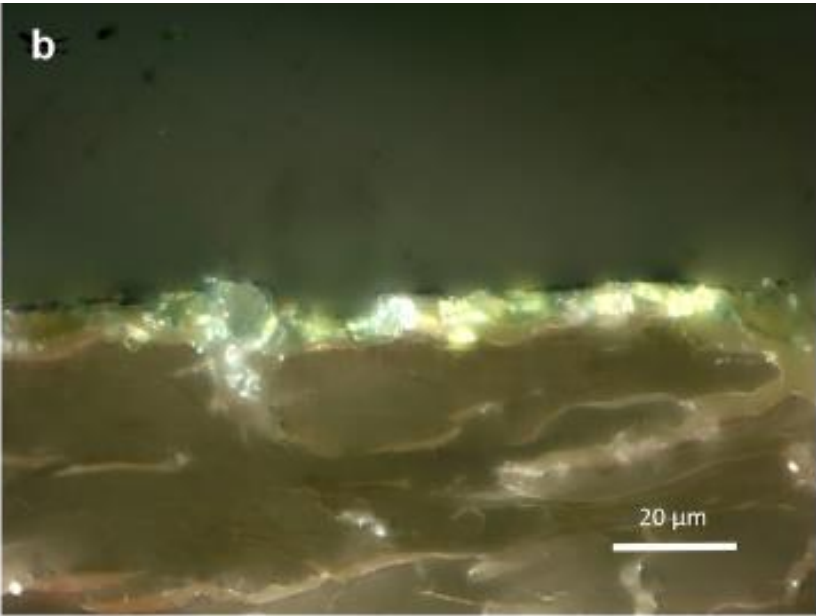
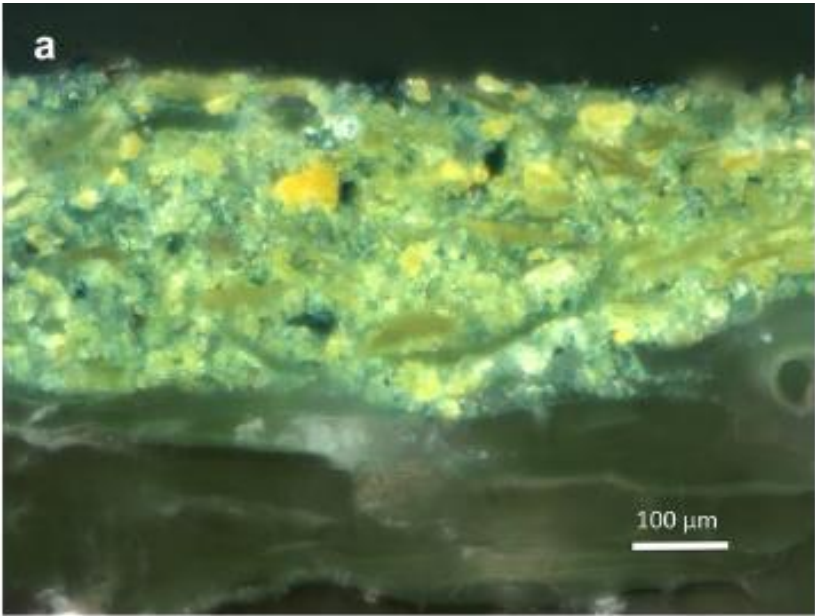
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A large sample size is needed for XRD analysis. The conservators in charge of both collections have yet to decide if they will allow sampling for the analysis you proposed.

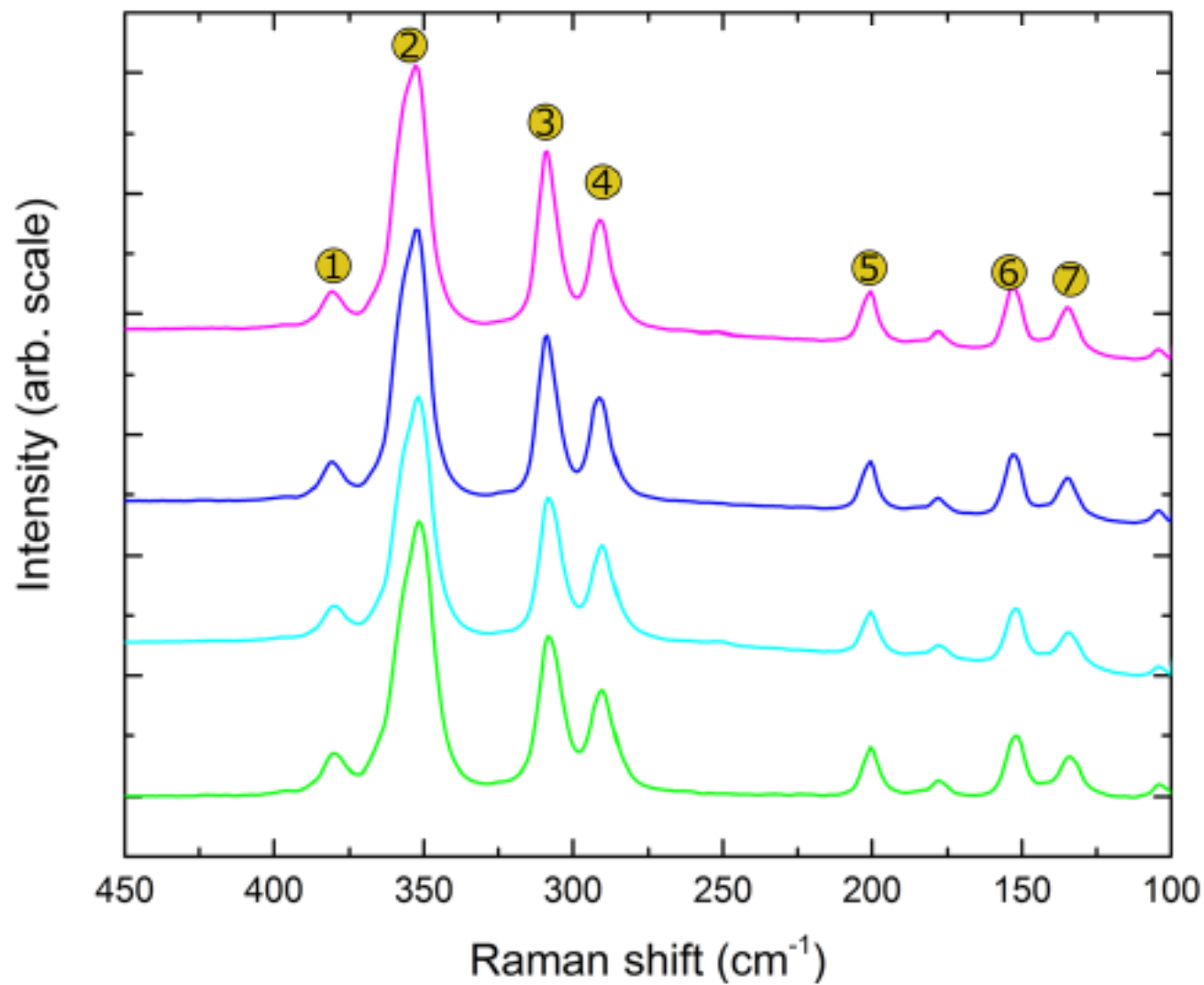
Meanwhile, work was started with tiny green paint samples already detached from the books (they were found in the ziplock bags in which the books had been stored). These samples were mounted in epoxy and analyzed with optical microscopy and Raman.

Optical microscopy



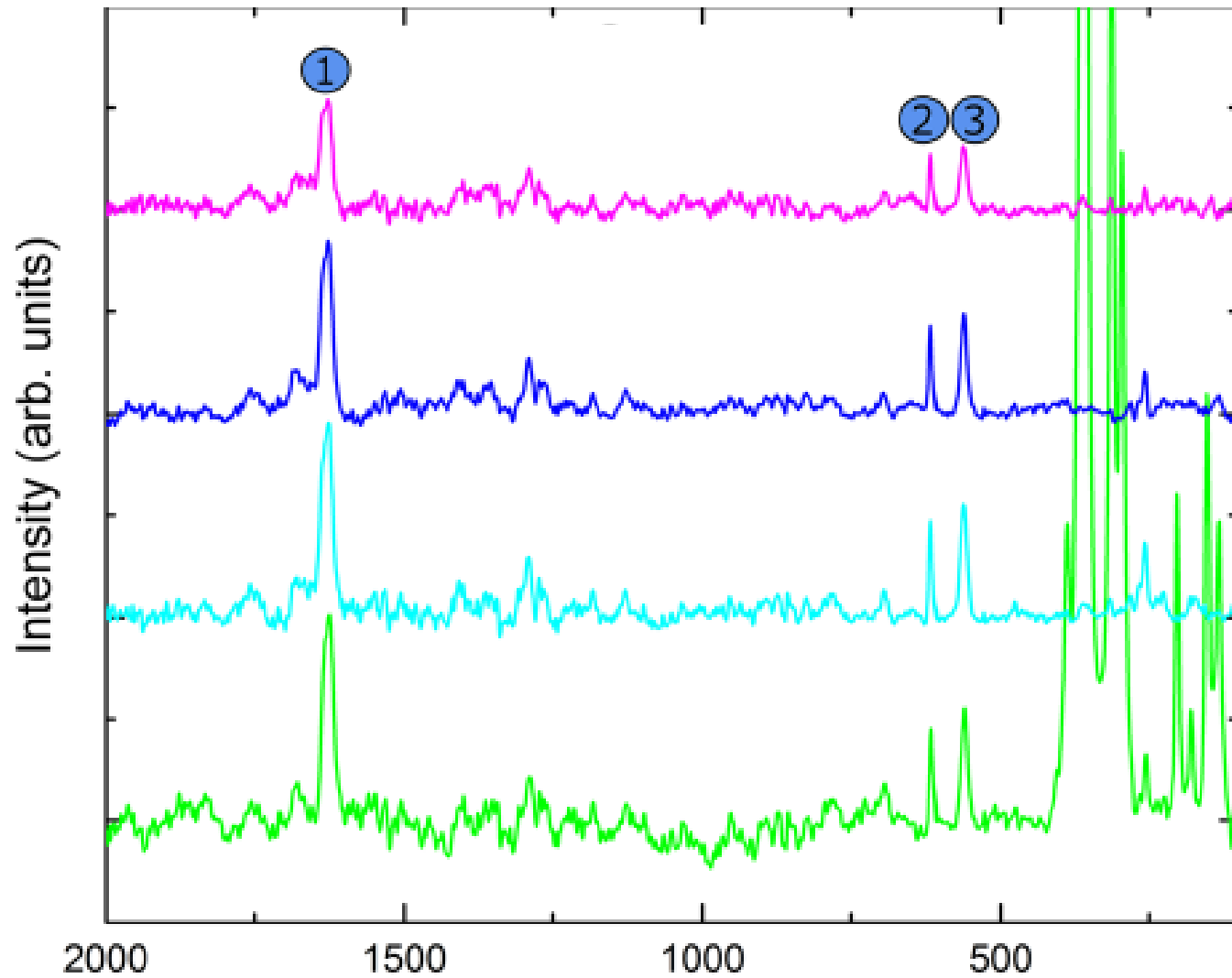
Raman

Analysis of yellow particles



Raman

Analysis of blue particles



Arsenic analysis in air

Arsenic and arsine were analyzed in air to determine exposure of a person that is actively manipulating the books.

For arsenic analysis, samples were collected in mixed filter cassettes (37 mm mixed cellulose ester filter, MCEF). The analysis was performed using OSHA method ID105 M (ICP-MS).

For arsine, samples were collected on charcoal sampling tubes. The analysis was performed by an accredited industrial hygiene laboratory following NIOSH Method 6001 M.

The results, for an 8-hour exposure was $< 0,13 \mu\text{g}/\text{m}^3$ for total arsenic and $< 0,064$ ppb for arsine.

Arsenic analysis on the books' surface

A wipe test was performed on the surface of the books following the NIOSH 9102 protocol. Samples were analyzed by an accredited industrial hygiene laboratory following NIOSH 7082 M/7300. Obtained values were in the range between 270 and 5490 $\mu\text{g}/\text{m}^2$.

Part 3

Information on the Raman instrument used in the analyses from last week:

Thermo Scientific DXR equipped with a 633 nm laser and a 10X objective. Laser power: 3 mW, spectral resolution: 5 cm^{-1} , spot size: $2.1 \text{ }\mu\text{m}$.

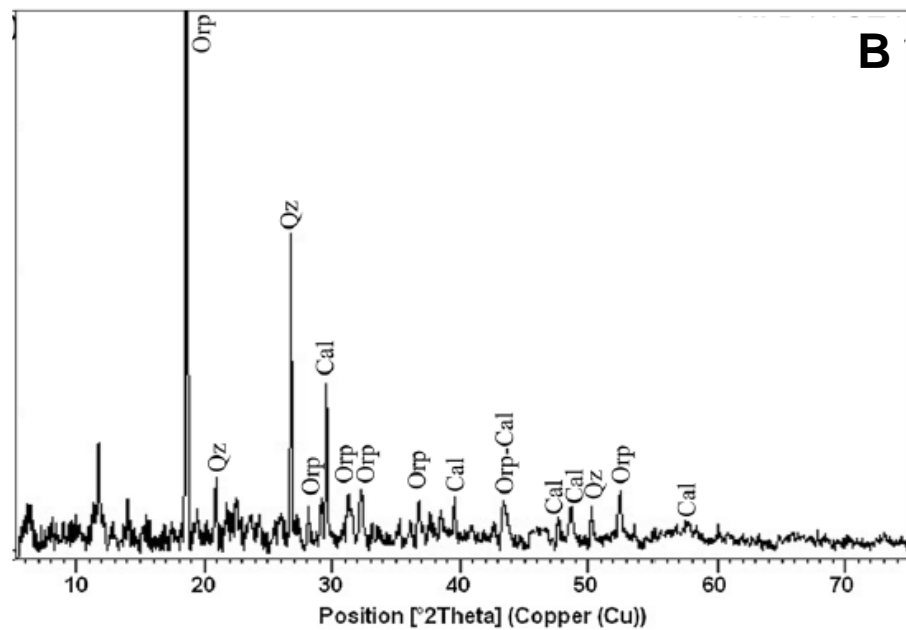
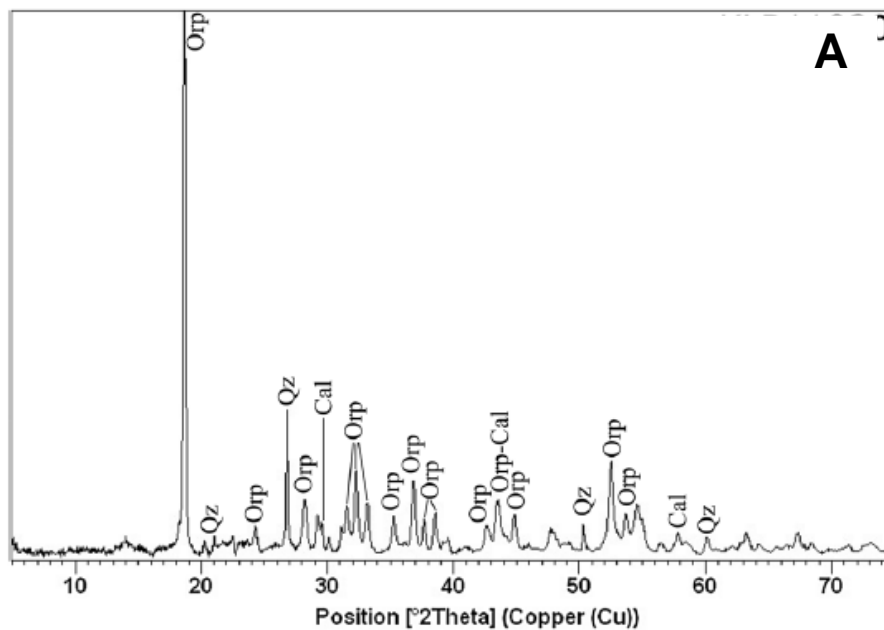
The analyses were performed on the painted surfaces of the samples taken from the book covers.

The conservator in charge of the project has decided to provide you with samples to continue the analyses. The samples are of considerable size (5 x 5 mm), since you require a large sample area to be able to perform XRD analysis. She was able to take these samples from the inside of the bookbindings, which made it possible to remove the necessary amount for you without visibly affecting the books.

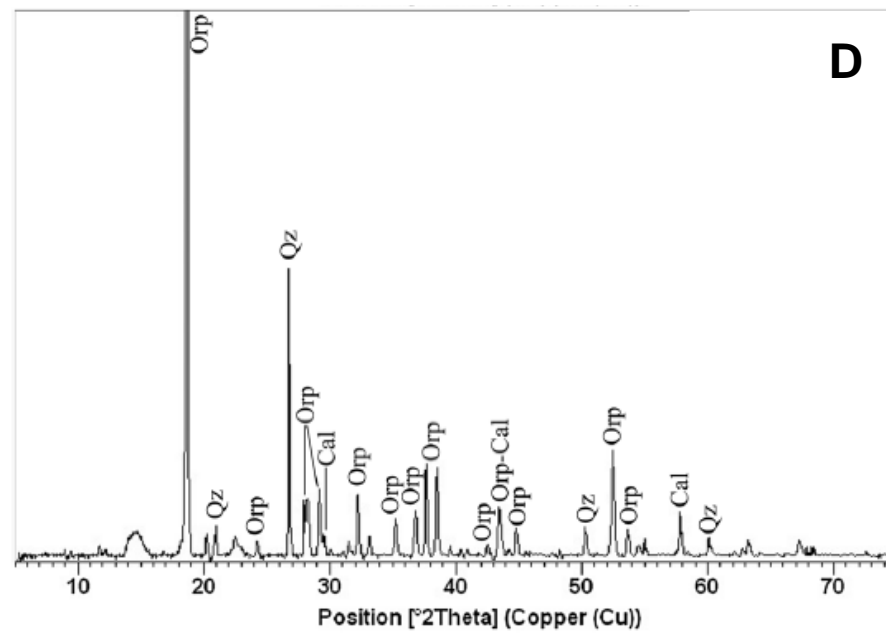
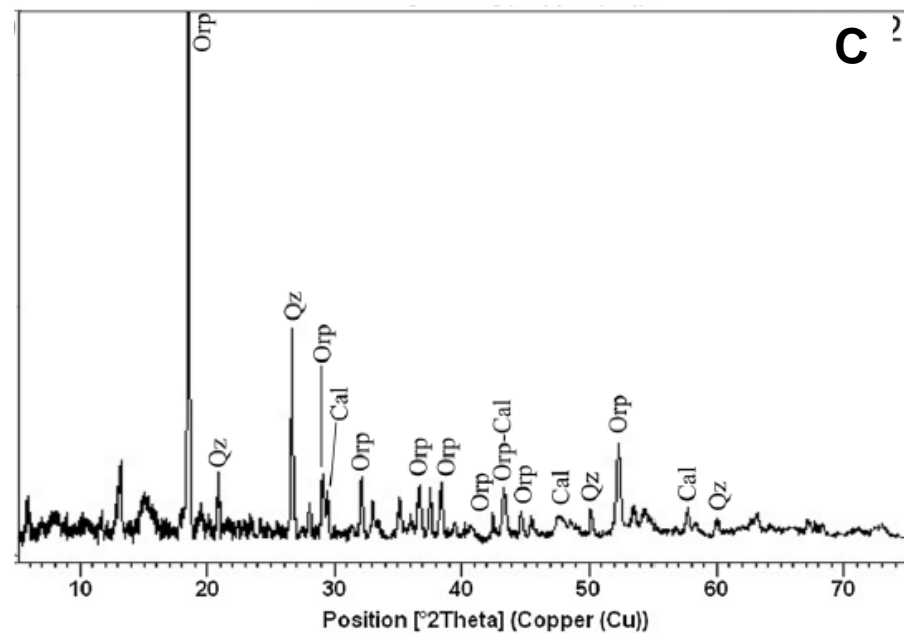
You cut the provided samples in two pieces of 2 x 5 mm. You used one of them for XRD and the other one to try to do SEM-EDS. You mounted the samples in epoxy resin, cut the resin very close to the sample and polished the cut surface to expose the sample in a way that you could see all the paint layers.

X-ray diffraction

You used a PANalytical X'Pert PRO MPD (PW3050/60) diffractometer, with the Cu K α line as source ($\lambda = 1.54 \text{ \AA}$) and a PIXcel3D detector. To mount the samples in the sample holder, you sealed them between two sheets of Kapton polyimide foil. You processed the results using Highscore Plus software and Crystal Impact Match software linked to the ICDD PDF-2 database. The results are shown on the next slide.



Qz: quartz, Cal: calcite, Orp: orpiment



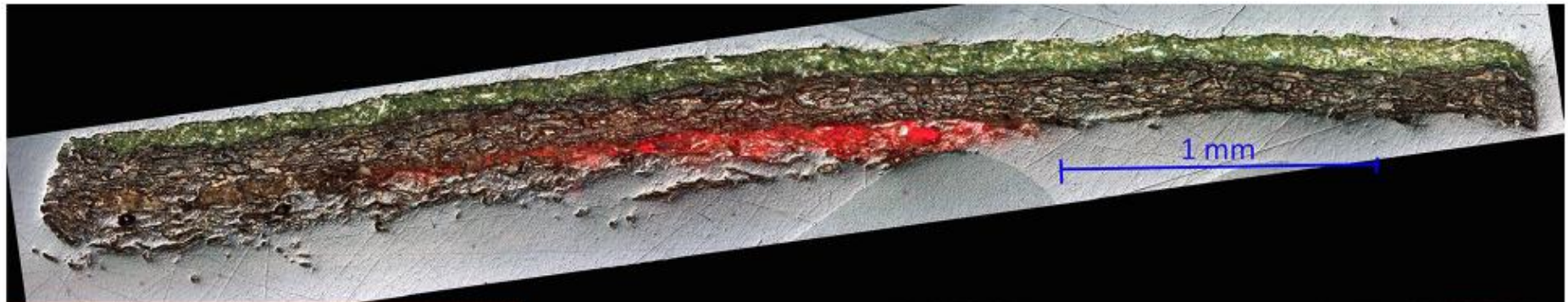
LA-ICP-MS

The SEM-EDS has been acting up all week, but you were lucky and got some analysis time with the LA-ICP-MS (laser ablation inductively coupled plasma mass spectrometry). Even though we haven't really covered that technique in class, LA-ICP-MS is very useful for elemental analysis, and it also allows you to obtain elemental distribution maps, which is the main information you wanted to get with SEM-EDS.

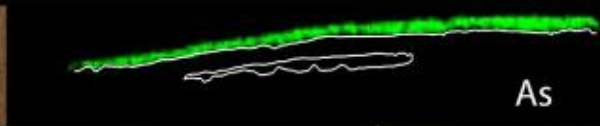
For LA you used a CETAC LXS-213 G2 equipped with a NdYAG laser. For ICP-MS you used a Bruker Aurora M90. You collected data on the following isotopes: Na²³, Mg²⁴, Al²⁷, Ca⁴⁴, Fe⁵⁷, Cu⁶⁵, As⁷⁵, Rb⁸⁵, Sr⁸⁸, Ag¹⁰⁷, Sb¹²¹, Ba¹³⁷, Au¹⁹⁷, Hg²⁰² y Pb²⁰⁸.

The results are shown on the next four slides.

Book A



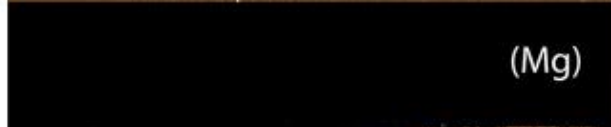
Na



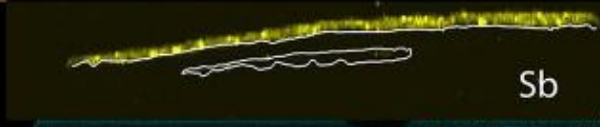
As



Ag



(Mg)



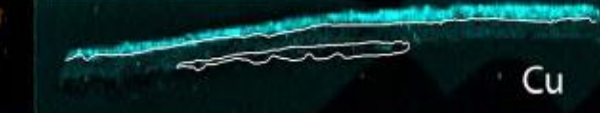
Sb



(Ba)



Al



Cu



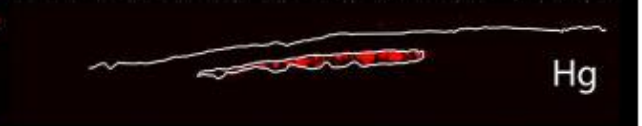
Au



Ca



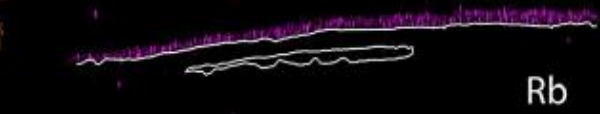
Fe



Hg



Sr

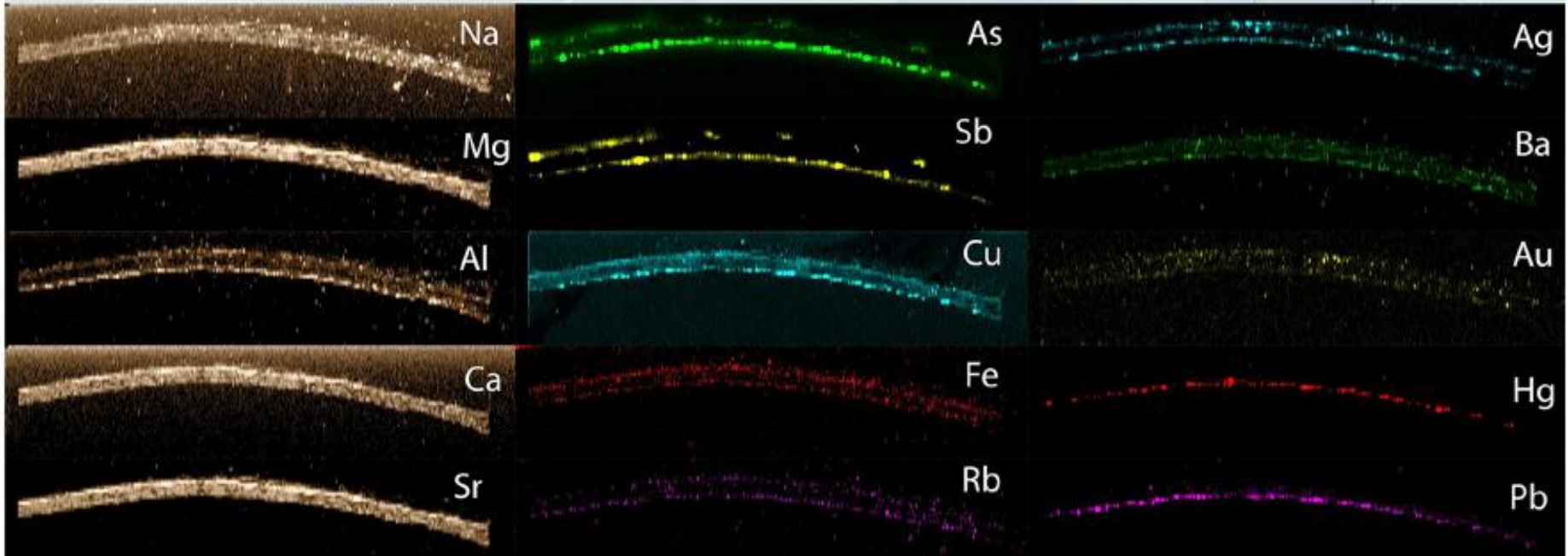
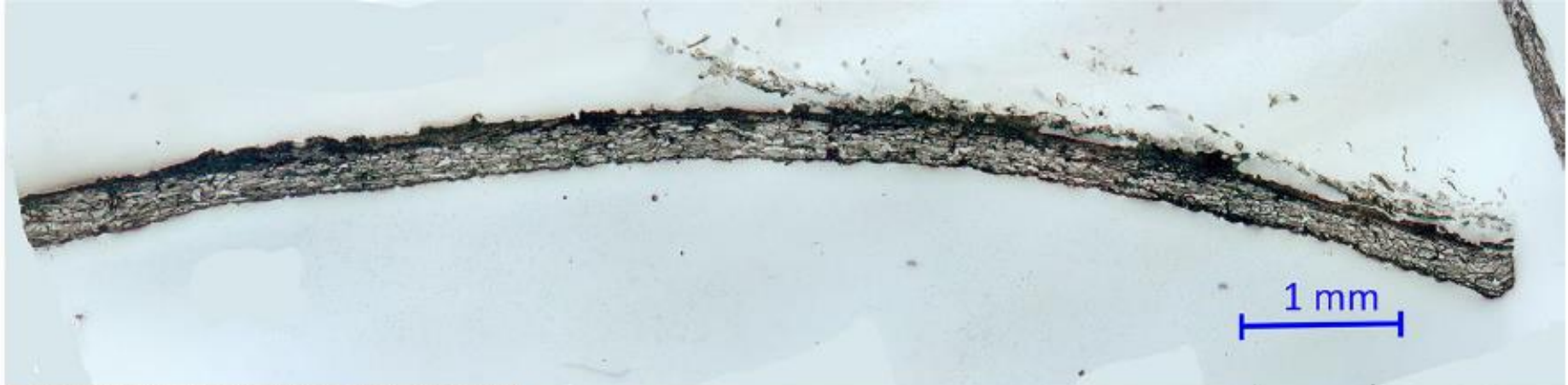


Rb

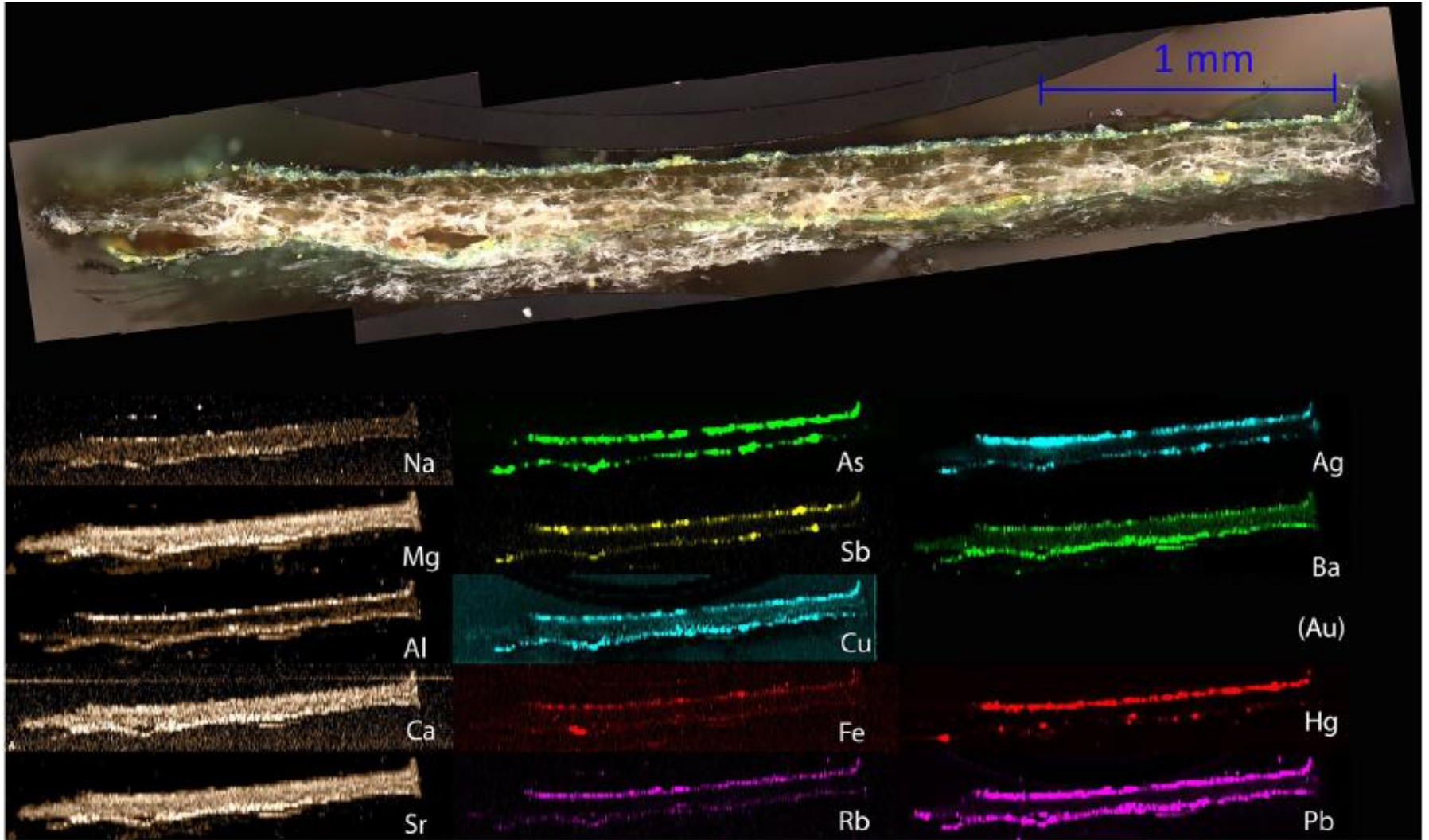


Pb

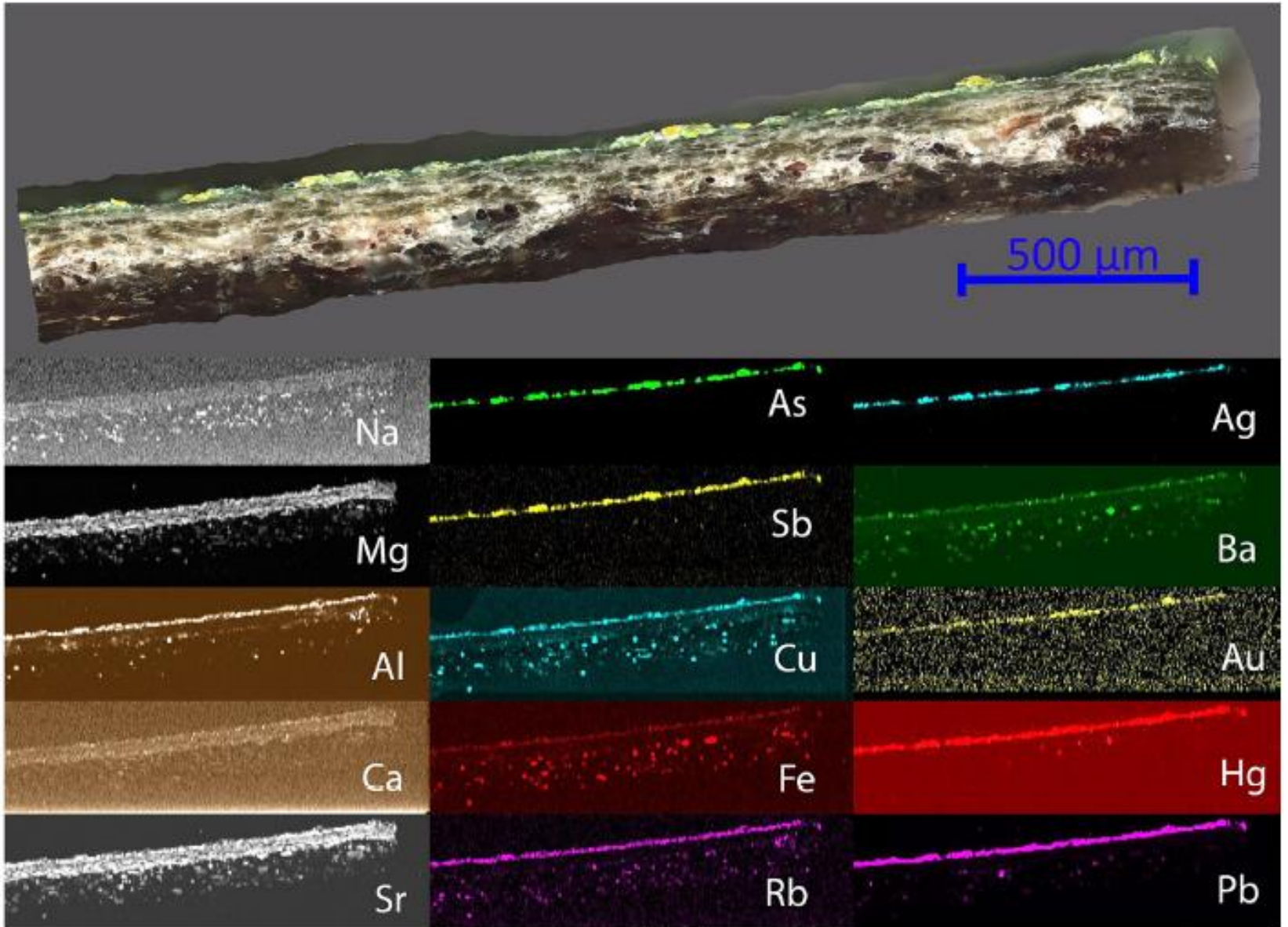
Book B



Book C

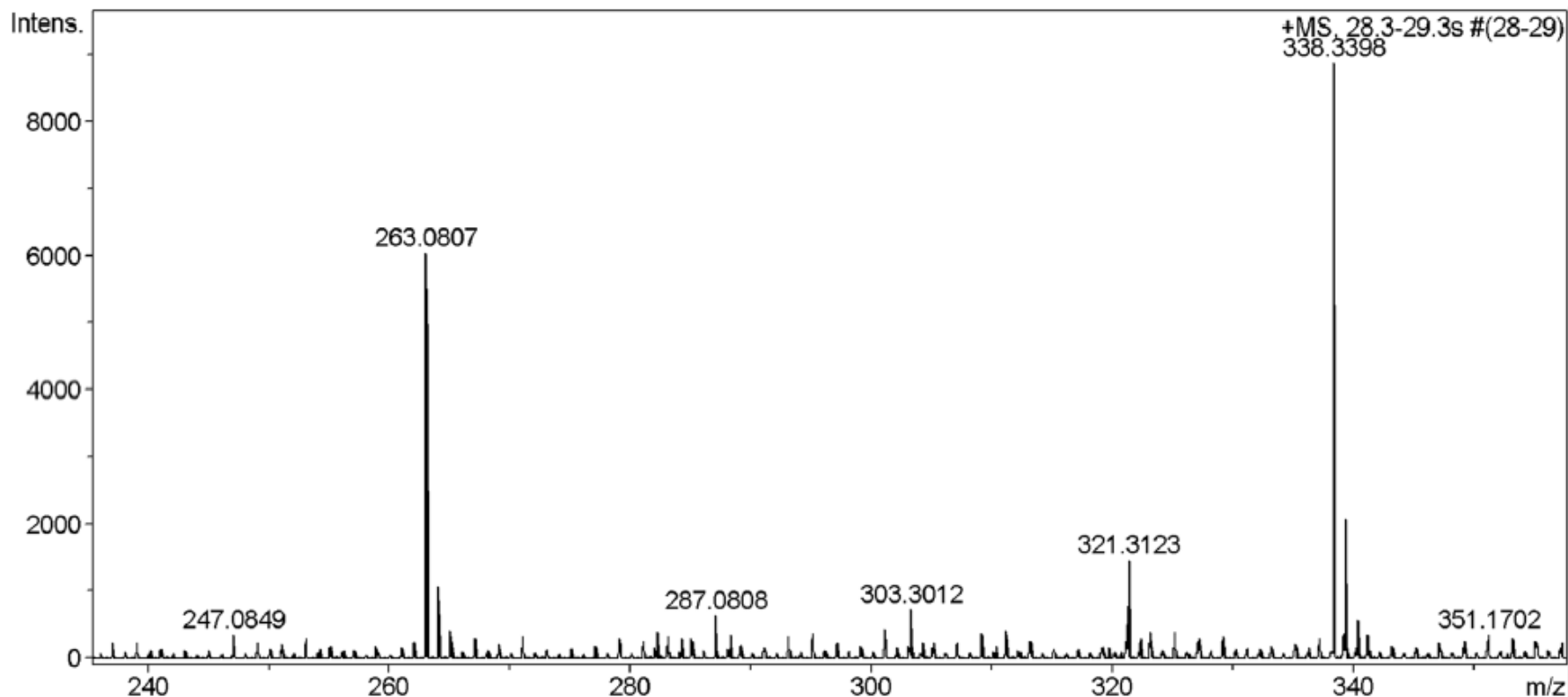


Book D



Mass spectrometry

You had a very tiny sample of green paint from Book A (less than 0.1 mg) left from your previous analysis. You dissolved the sample in acetonitrile and obtained its mass spectrum in a Bruker micro TOF QII. You worked with ESI in positive mode. The spectrum is shown below:



More poisonous books

When the conservators who work in another library heard that you were doing this study, they contacted you. They had found several books with green covers in their collection, and they're worried about the possibility of them containing arsenic. The books date to the XIX century. Unlike the first books you studied, the book covers in this case are made of cloth and they come in different shades of green.

The library sent you five of these books for analysis. You decided to do noninvasive analysis using XRF and Raman. The results are basically the same for all the books. We are giving you one XRF spectrum and one Raman spectrum, as reference:

- XRF: L1
- Raman: L2

After analyzing the data, what can you tell the conservators about these books?

Note: After processing the information and giving an answer, you can read more about these books in the Poison Book Project's website:

<https://sites.udel.edu/poisonbookproject/>