

Part 1

Background

A private Chilean stamp collection was studied in order to establish if their composition changed over a long period of time, and to build a database that help us indentify id any of this type of stamps has been forgered.

So far, we only know that a British company got an order for postage labels (stamps) by the Chilean government, in 1852. Two additional orders were received by this company in the following years.

Usually, stamps tend to be studied in 4 áreas: their color, the paper used, the ink and gum used, and the printing methods. In the following slides you could see a summary table of the diffrent stamps studied, and the preliminary X-ray fluorescence (XRF) analysis done.

First issues of Chilean stamps printed in London

#01

#02

#08

#11

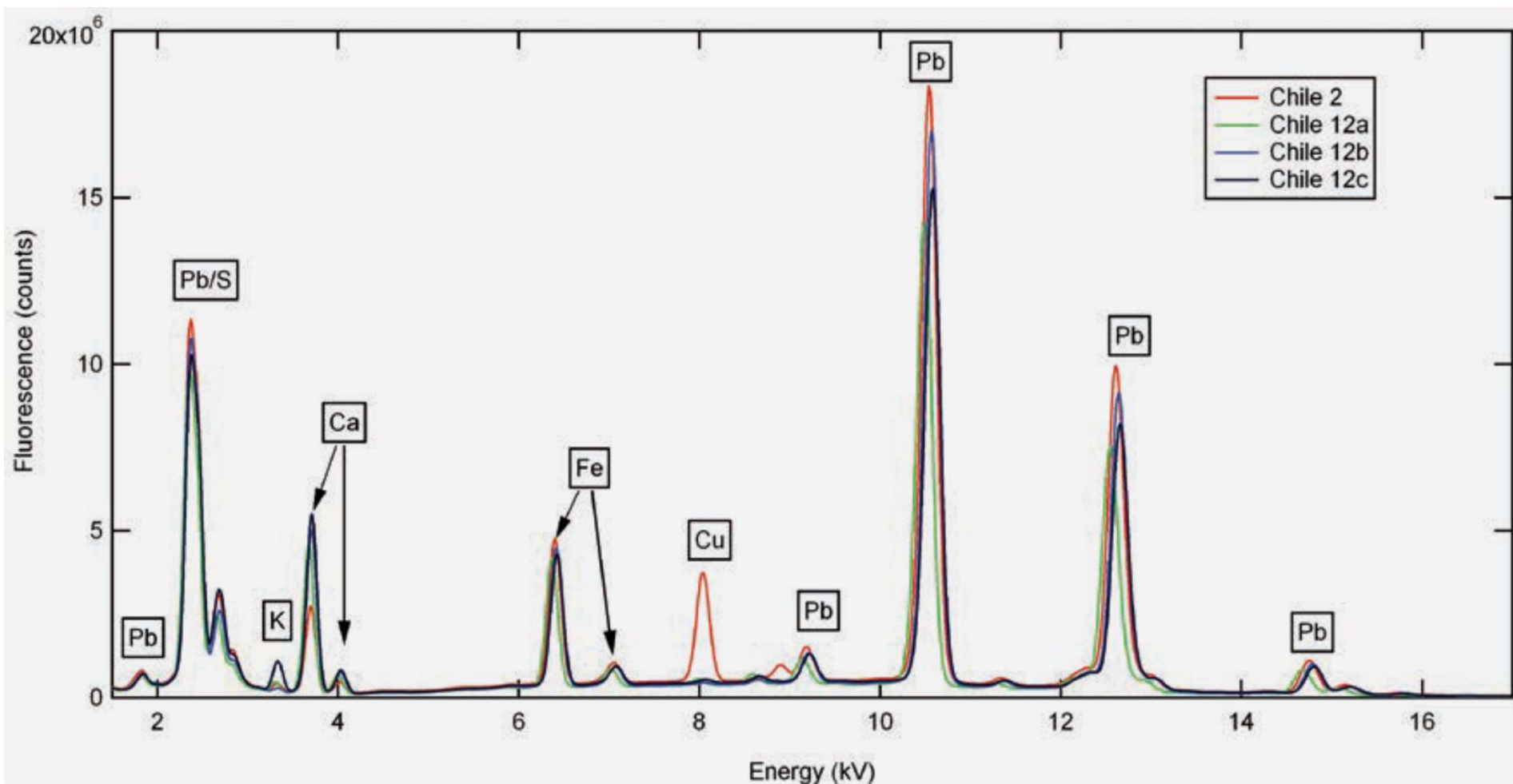
#12

#13

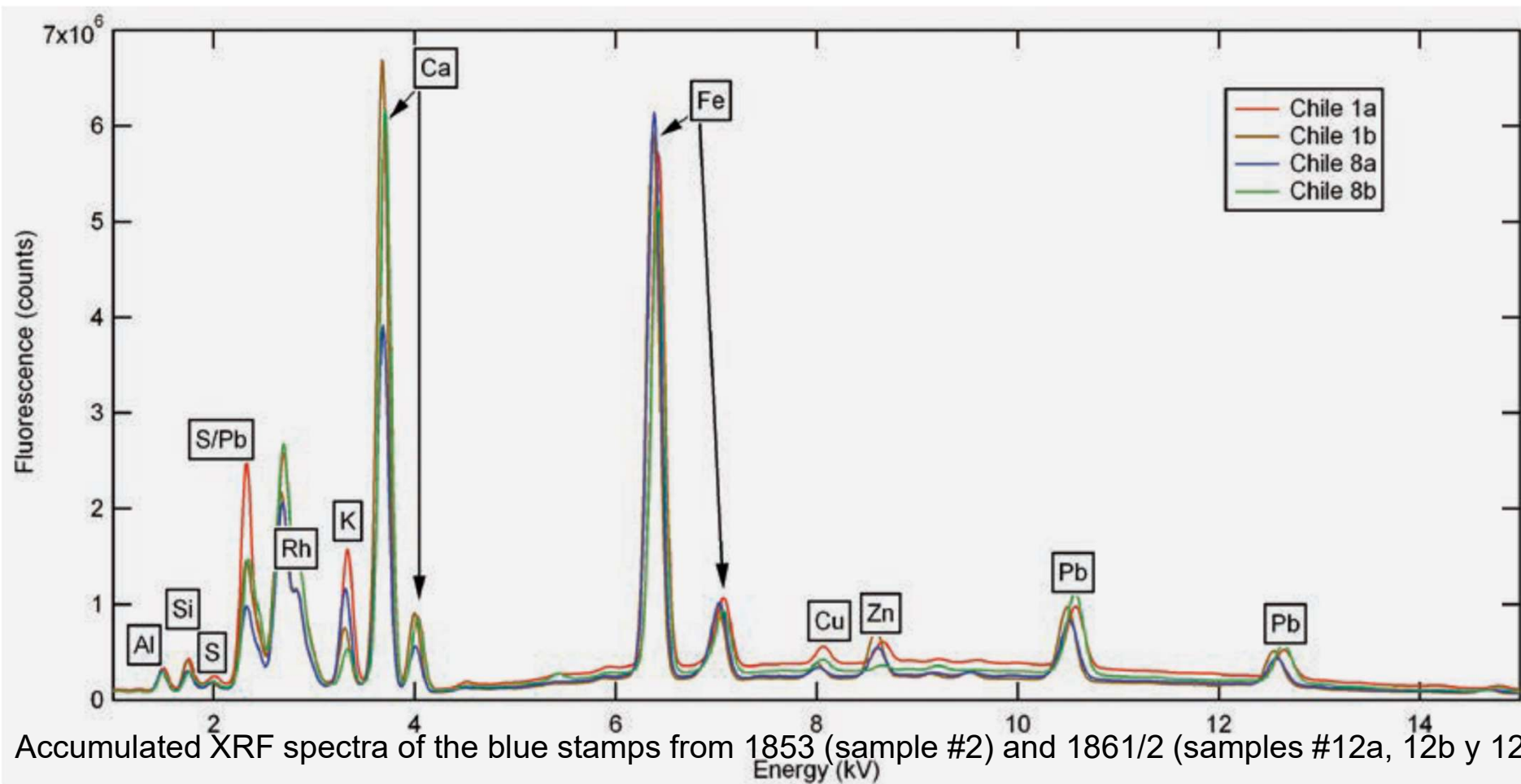


Year	1853	1853	1855	1862	1861	1862
Ink color	Brown-red	Bright blue	Brown-red	Lemon yellow	Bright blue	Green
Paper	Blue	Yellowish-white	Blue	Yellowish-white	Yellowish-white	Yellowish-white
Amount issued	300 000	200 160	2 040 000	3 000 000	3 000 000	3 000 000

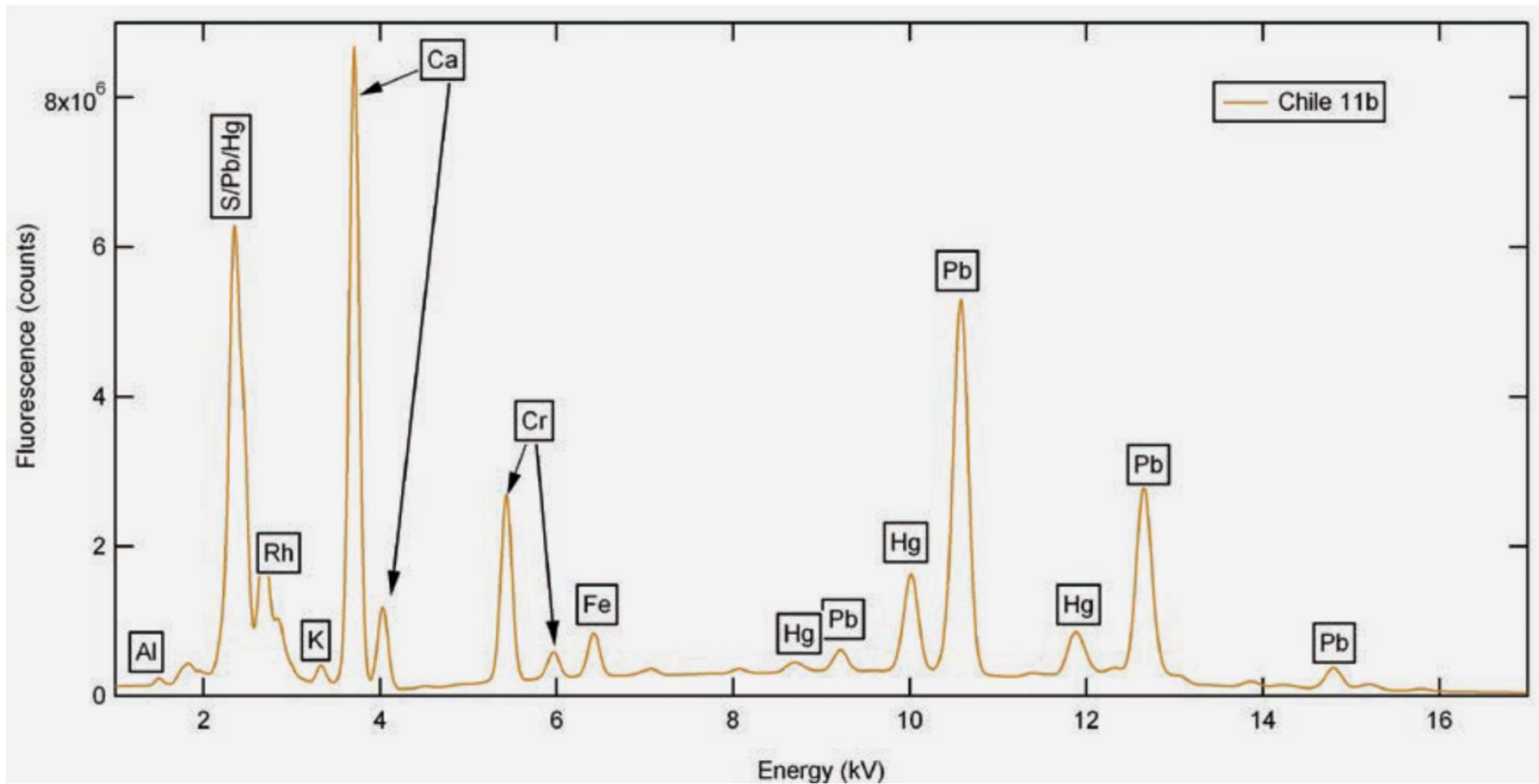
The stamps were printed in White paper handmade and all samples analyzed belong to the same private collection. In some cases, up to 20 stamps of each issue were tested.



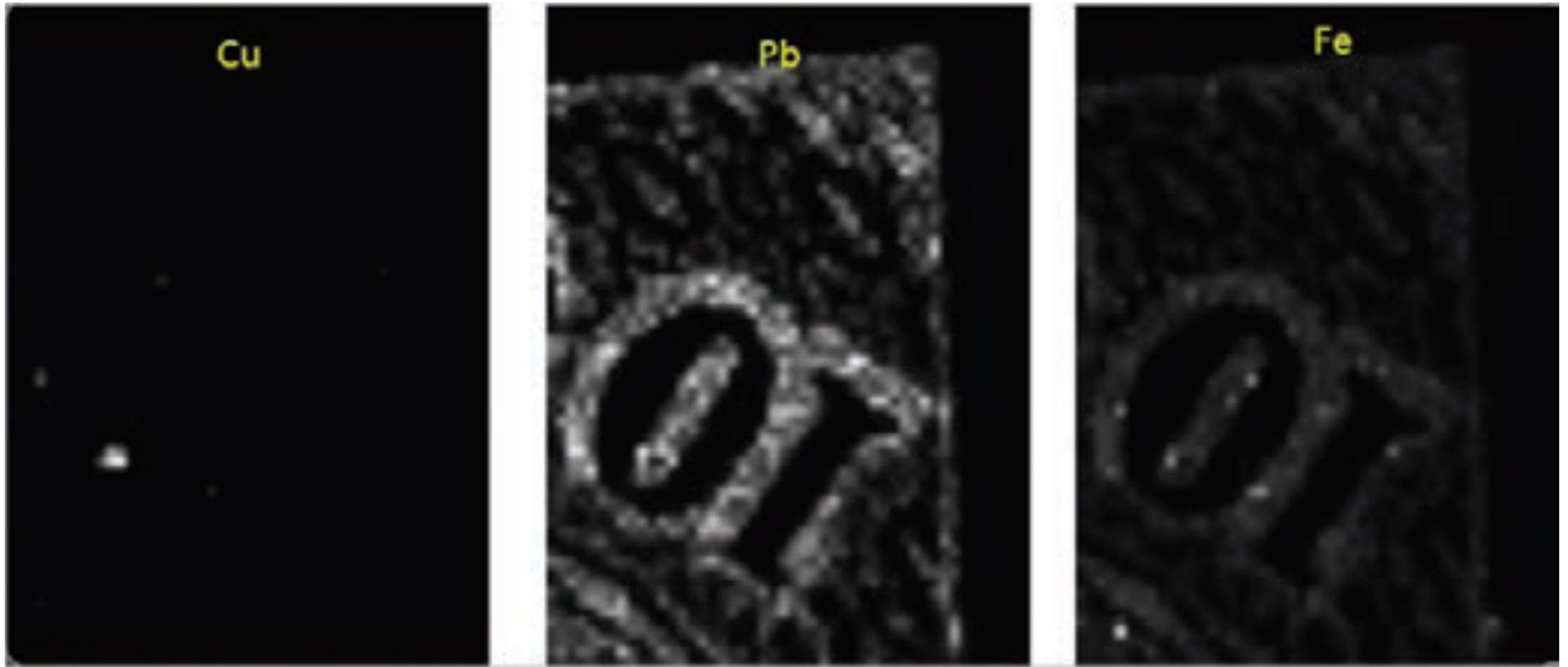
Accumulated XRF spectra of the blue stamps from 1853 (sample #2) and 1861/2 (samples #12a, 12b y 12c)



Accumulated XRF spectra of the red stamps from 1853 (samples #01a, 01b) and 1855 (samples #08a, 08b). It cannot be seen but traces of Mn were also detected in these samples.



Accumulated XRF spectrum from stamp #11



XRF map from sample #02

What kind of information could you obtain from these data?

What other kind of tests would you like to perform to analyze better this collection?

Part 2

Stamp analysis

- Some additional XRF data was found
- You have some additional information about the paper thickness
- You got optical images and the reflectance spectrum from some samples.

Element ratios of the stamps analyzed by XRF-Artax

Stamp	Number averaged	Fe/K	K/Al	S/Al	S/K	Pb/Cr
Chile 1 (red)	20	9.11	5.75	8.91	1.55	–
Chile 1 (red)	2	8.22	5.32	12.72	2.62	–
Chile 8 (red)	10	9.04	5.50	9.66	1.76	–
Chile 8 (red)	2	11.63	3.93	9.76	3.35	–
Chile 2 (blue)	10	50.63	1.48	–	–	–
Chile 2 (blue)	1	30.60	3.14	–	–	–
Chile 12 (blue)	10	68.07	1.22	–	–	–
Chile 12 (blue)	3	32.97	7.75	–	–	–
Chile 11 (Yellow)	10	10.76	1.64	–	–	2.90
Chile 11 (Yellow)	2	4.70	10.09	–	–	2.71
Chile 13 (Green)	10	95.18	0.55	–	–	5.13
Chile 13 (Green)	2	18.16	3.03	–	–	4.20



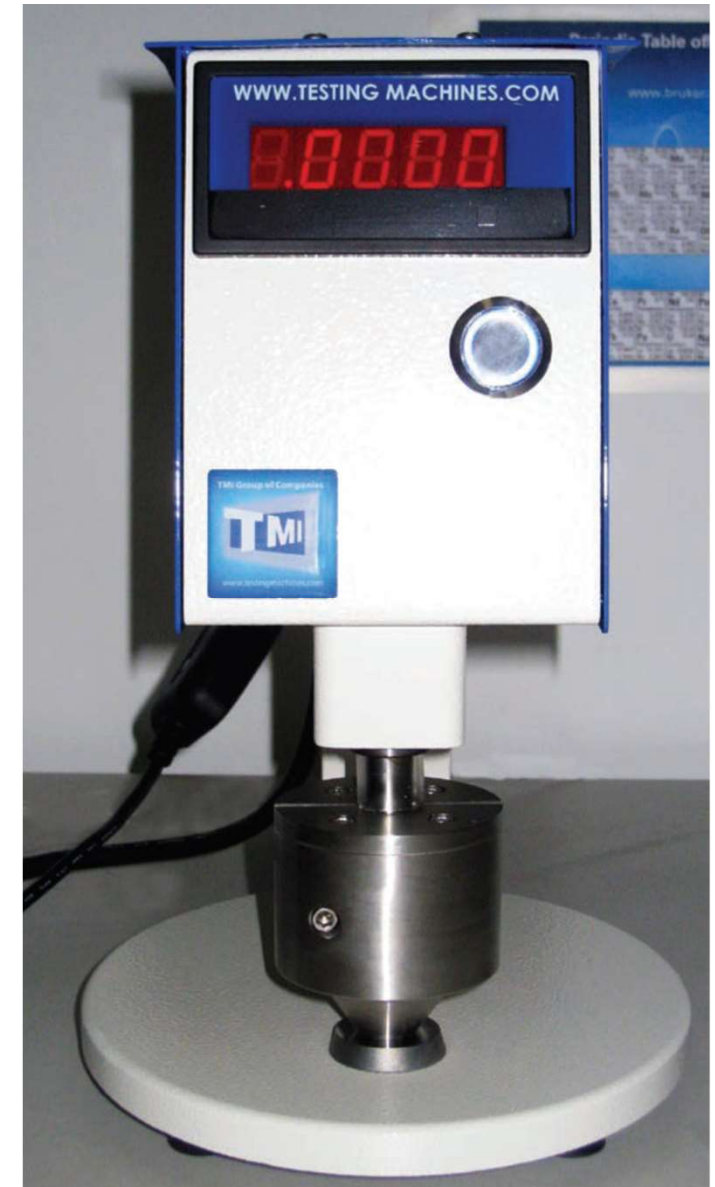
XRF results from the stamps

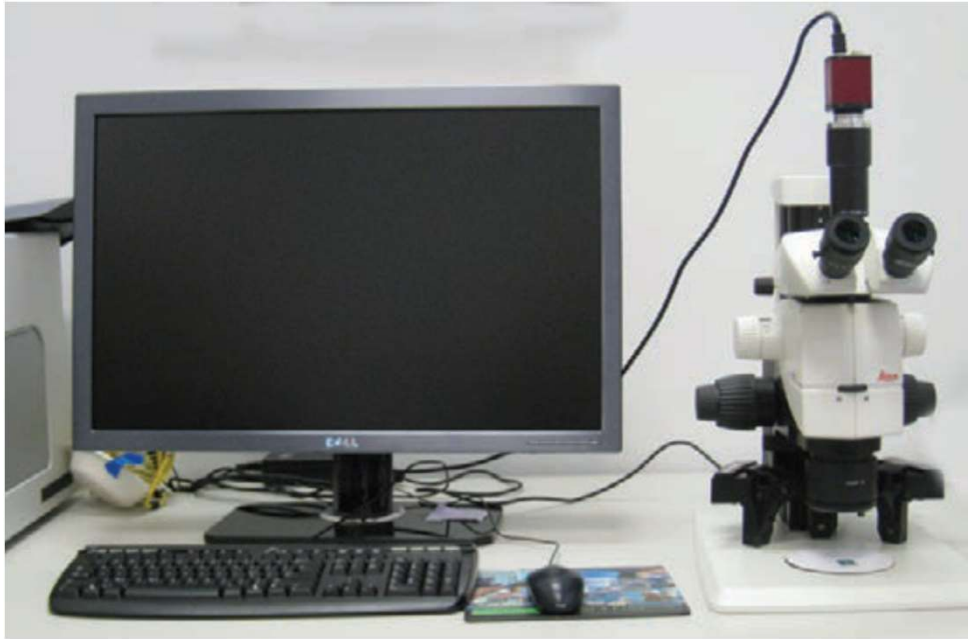
Stamps	XRF	
	Major	Minor/trace
#01	Fe, Ca	Pb, K, S, P, Al
#02	Pb, Fe	Ca, Al, K, ¿S?
#08	Fe, Ca	Pb, K, S, P, Al
#11	Ca, Pb	S, Cr, Hg, Fe, K, Al
#12	Pb, Fe	Ca, Al, K, ¿S?
#13	Pb, S	Cr, Fe, Ca, K, Al



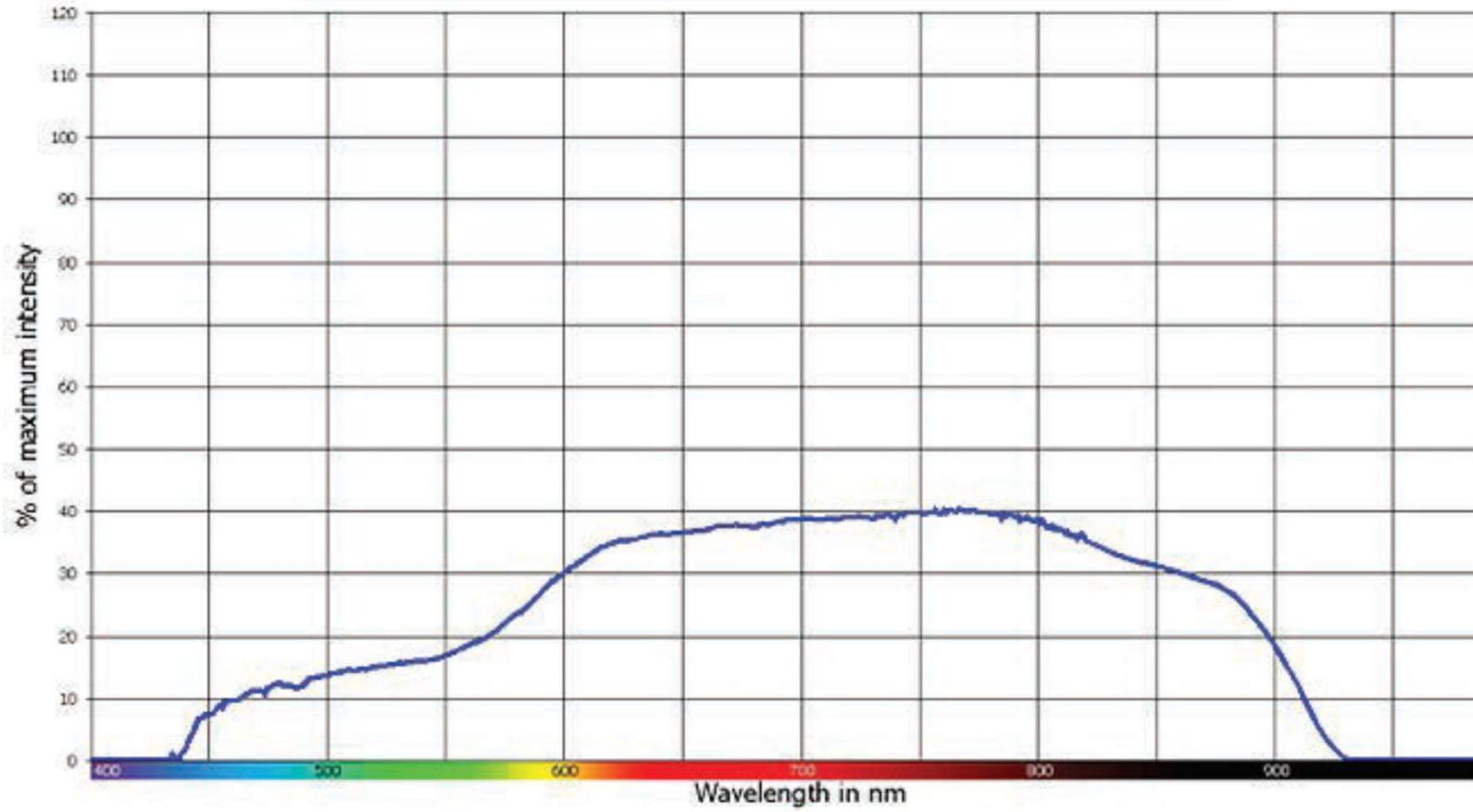
Paper thickness analysis of the stamps

Stamps	Micrometer results for 20 stamps	
	Thickness (mm)	Standard deviation (mm)
#01	0.1161	0.0028
#02	0.1227	0.0034
#08	0.1116	0.0085
#11	0.1349	0.0069
#12	0.1411	0.0022
#13	0.1098	0.0026





Stamp #01 micrograph at 100x. Image taken with a Leica microscope



Reflectance spectrum of red ink found in stamp #08

Analysis of Swedish stamps

An expert in stamp analysis told us that he has found that some of the blue stamps printed with Prusian blue in 1857 have faded. Do you think this information will be important?



Fig. 10 Swedish Skill Banco stamp of 1857 with light blue PB colour

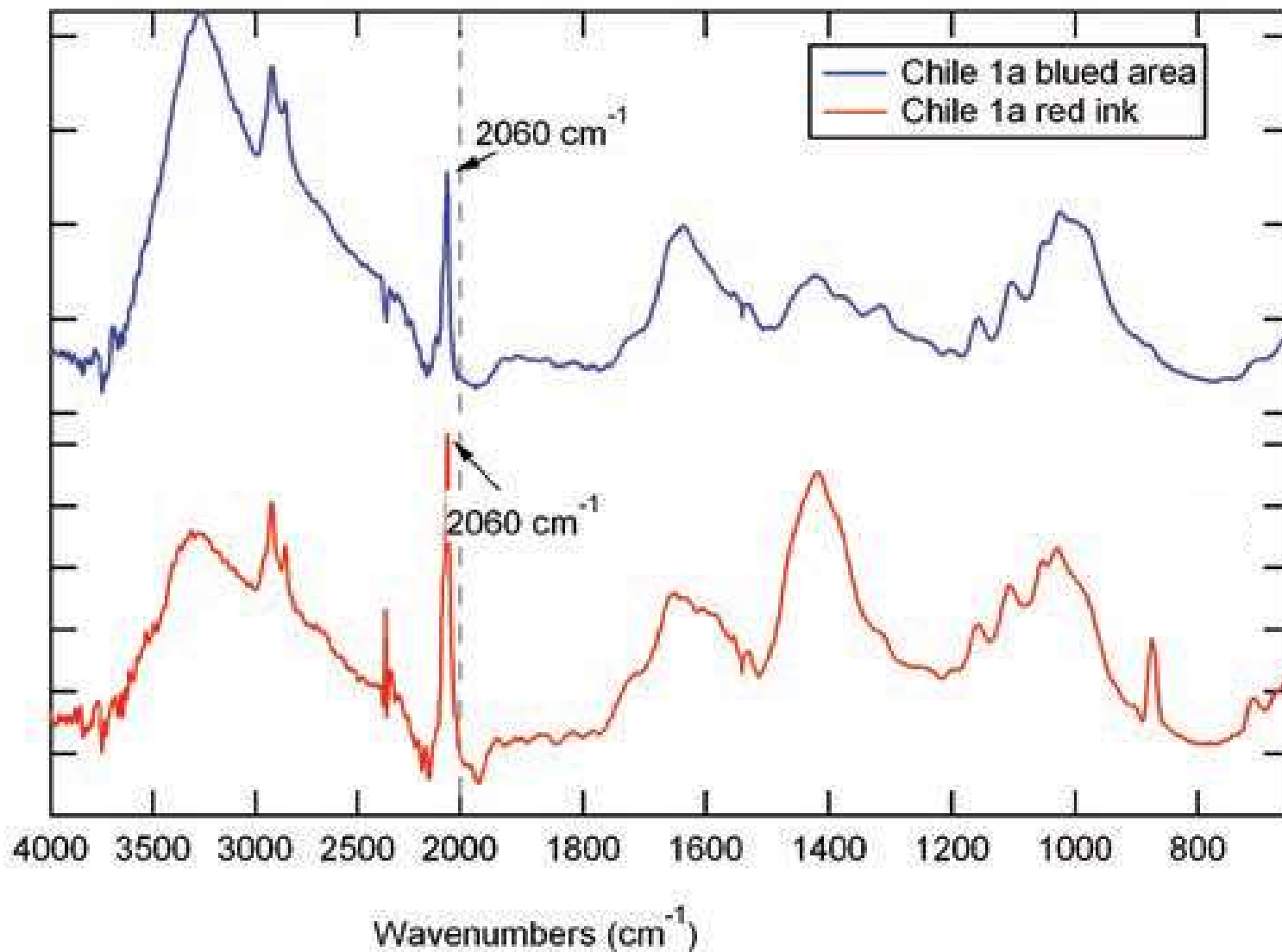
Part 3

Especially specialized chemist helped us to perform some additional instrumental analysis at a local university. The data was collected using the following equipment under certain conditions:

- **Fourier transform infrared spectroscopy (FTIR):** Spectra was collected by FTIR with attenuated total reflectance (ATR) that has a diamond crystal. Spectra were acquired with a 4 cm^{-1} resolution and 24 scans. There was an approximate penetration depth of $2\text{ }\mu\text{m}$. In certain cases, some spectra was collected with a different FTIR-ATR with a 4 cm^{-1} resolution and 64 scans.
- **X-ray diffraction (DRX):** Stamps were mounted on the sample holder using wax, and the sample spot could be focused on samples as small as $100\text{ }\mu\text{m}$ in diameter. Care was taken to avoid scanning the stage nor the wax. Data were collected for 5 minutes using a 0.8 mm collimator while the goniometer was fixed at 0° (Φ) and 20° (Ω).
- **Raman spectroscopy:** Spectra were collected with a microscope coupled to a Raman spectrometer with 2 excitation sources (632.8 nm and 514 nm).
- **Optical microscopy** from one of the stamps evaluated



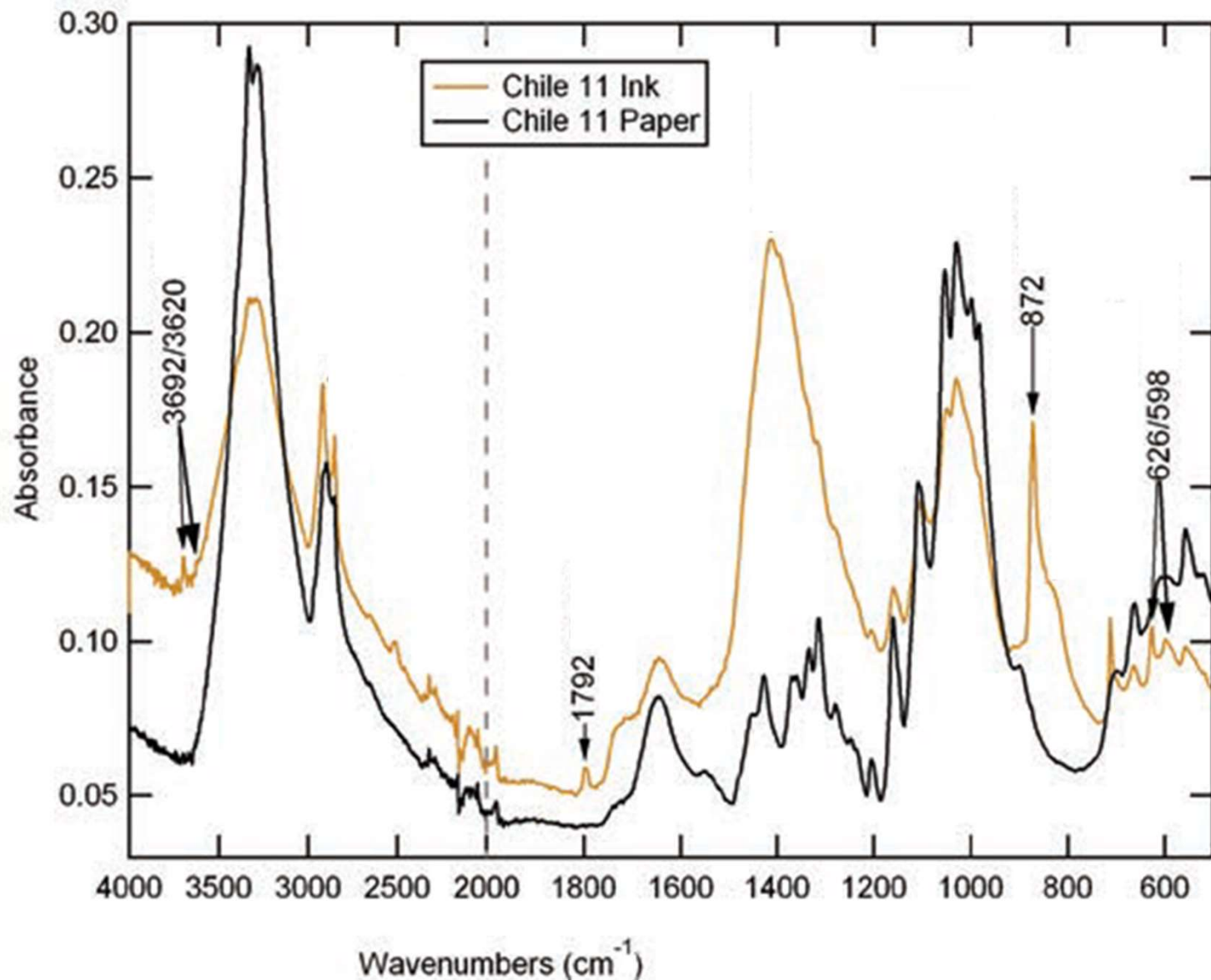
Absorbance



Micro-FTIR-ATR
spectra from blue
área and red área
in stamp #01



FTIR-ATR spectra
from front and
reverse of stamp #11



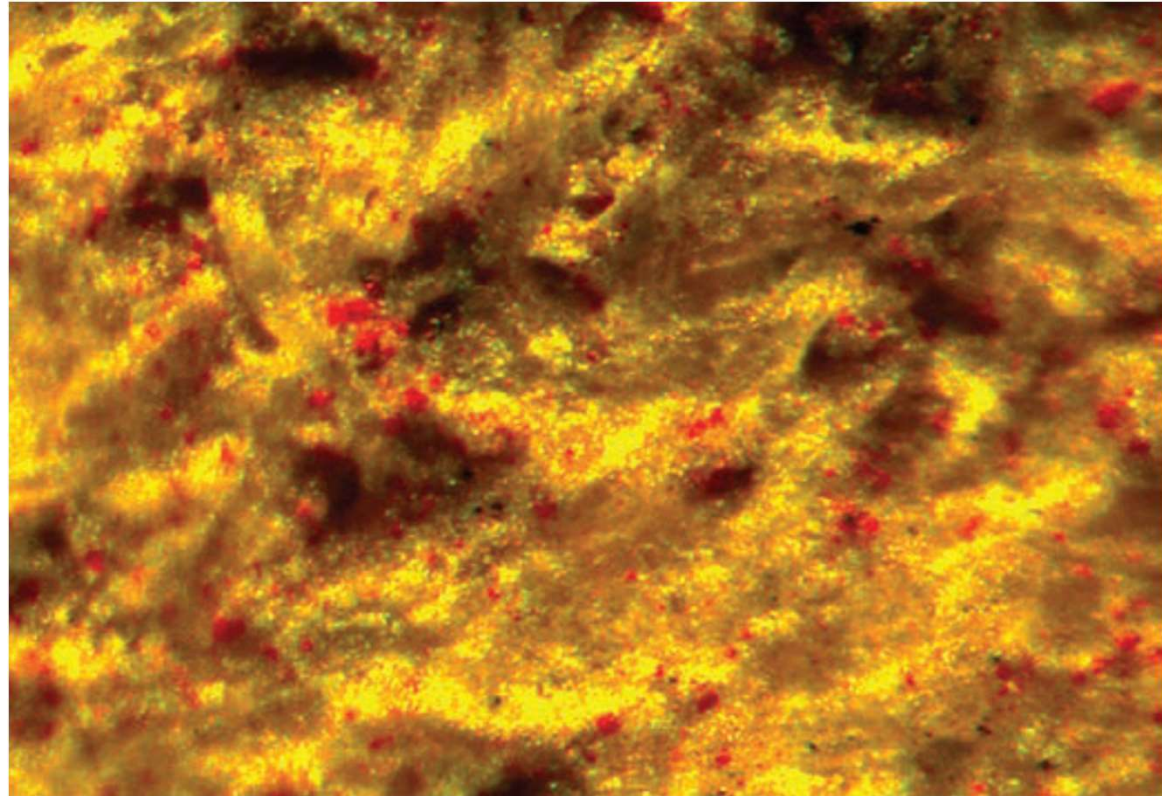
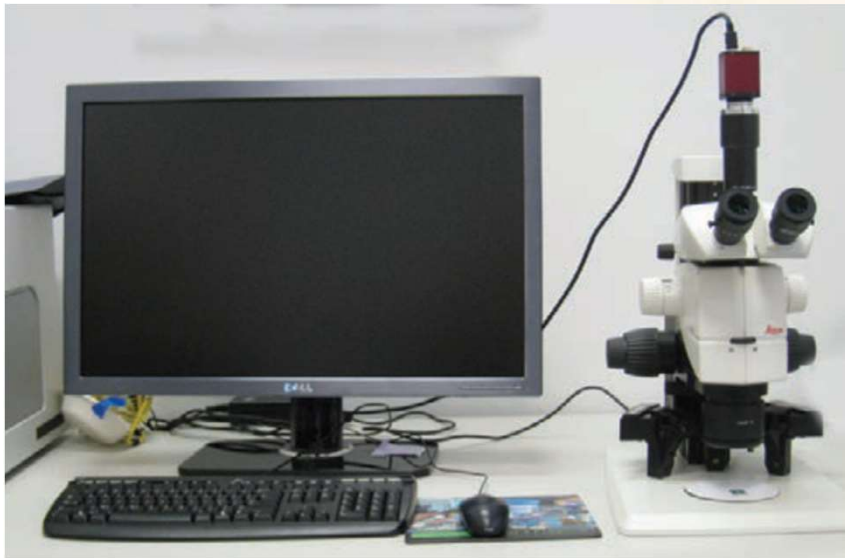
FTIR analysis from all types of stamps

Stamps	FTIR
#01	872; 1400; 2060; 2080; 3600; 3695
#02	678; 872; 1400 (br); 1510; 1540
#08	872; 1400; 2060; 2080; 3600; 3695
#11	596; 627; 872; 1400
#12	678; 872; 1400 (br); 1510; 1540; 2088
#13	596; 627; 850; 872; 2086

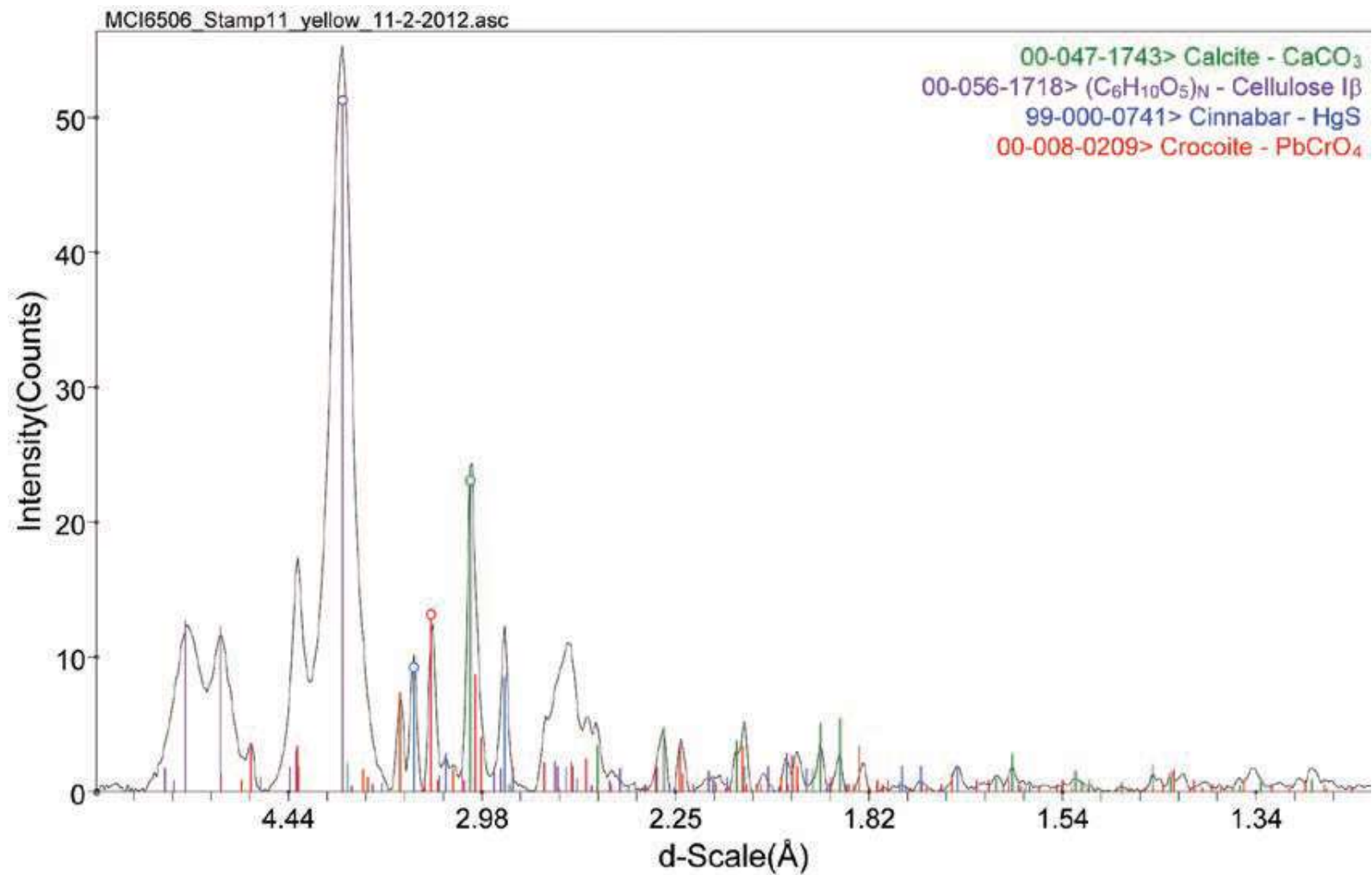
*br: broad band



#11



Micrograph from stamp #11 with a 1600x amplification

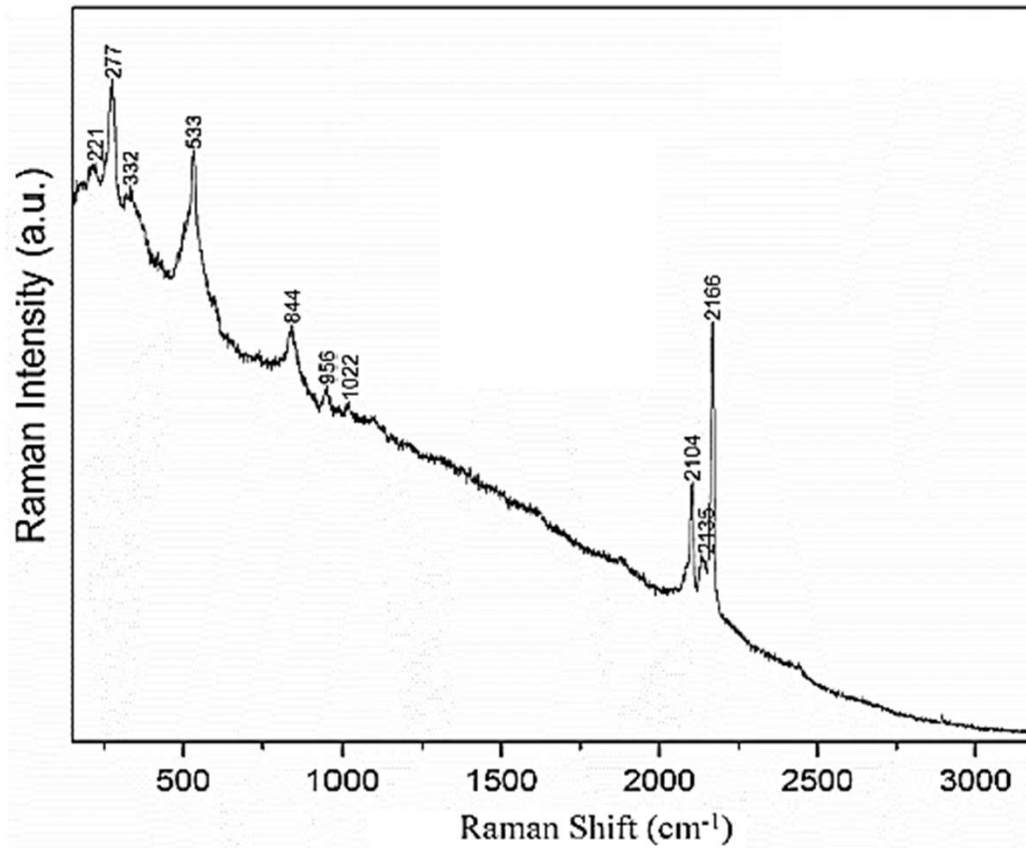


XRD spectra from yellow ink area in stamp #11

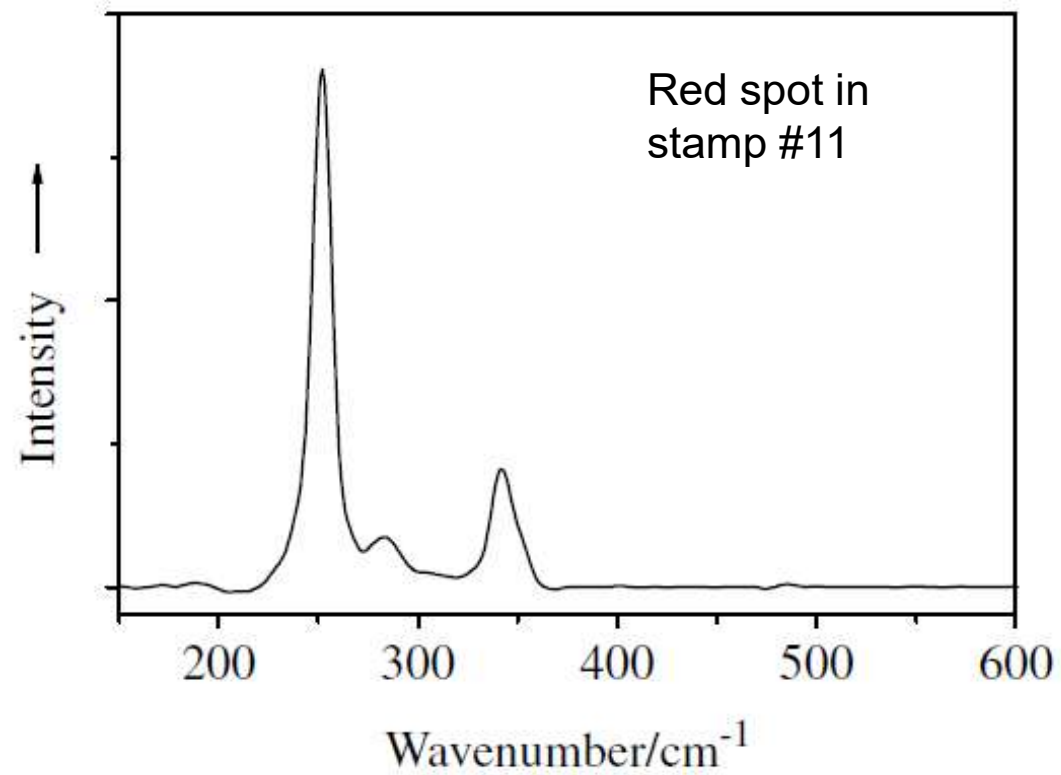
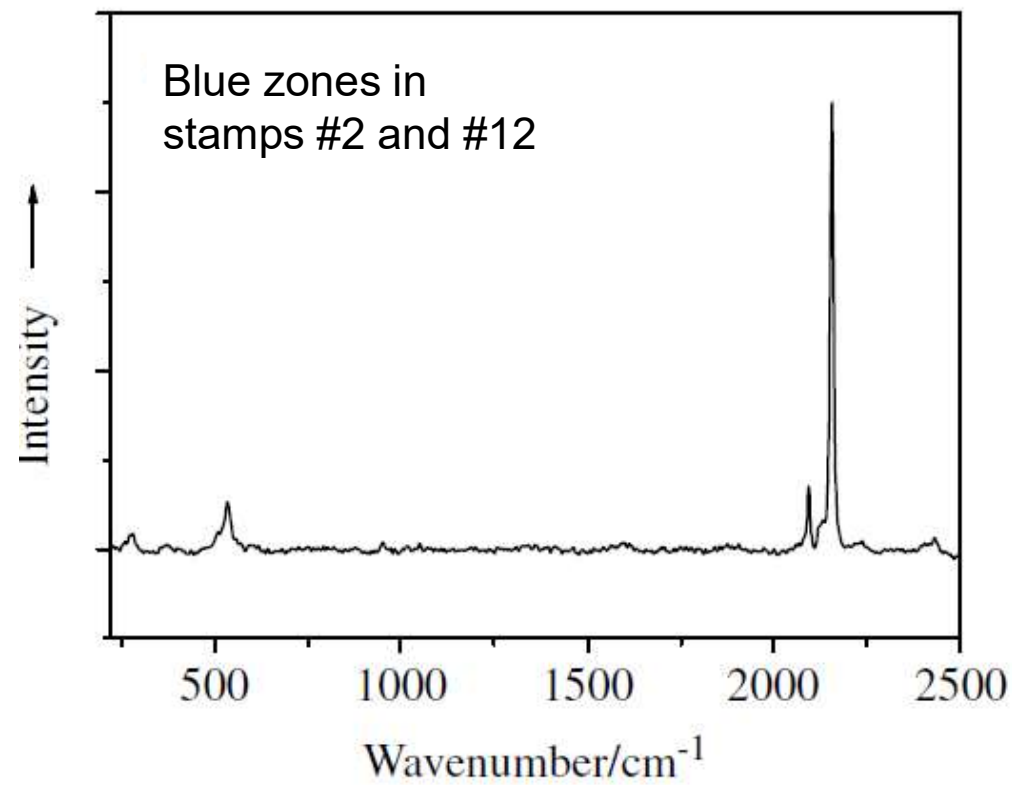
XRD analysis from different types of stamps

Stamp	XRD
#01	Calcite, fatty acids soaps
#02	Hydrocerussite, cerussite, calcite
#08	Calcite
#11	Lead chromate, vermilion, calcite
#12	Hydrocerussite, cerussite, calcite
#13	Lead Chrome, calcite?, minium or red lead?





Collected Raman spectrum of stamp #13 with a 785 nm excitation source. Under the microscope, one could see that stamp #13 has yellowish-orange and blue particles.



Raman spectra collected with a 632.8 nm excitation source