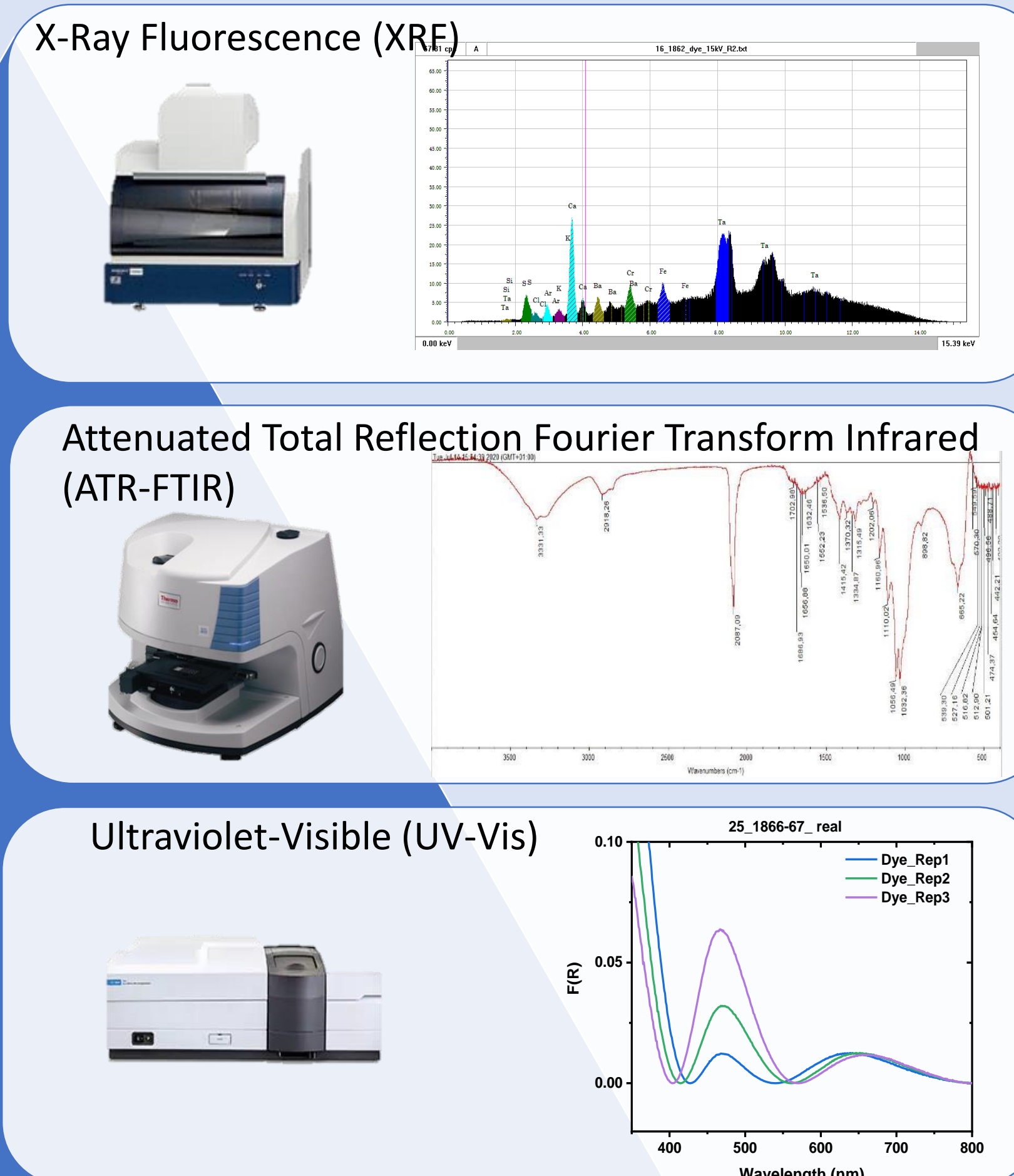


Introduction

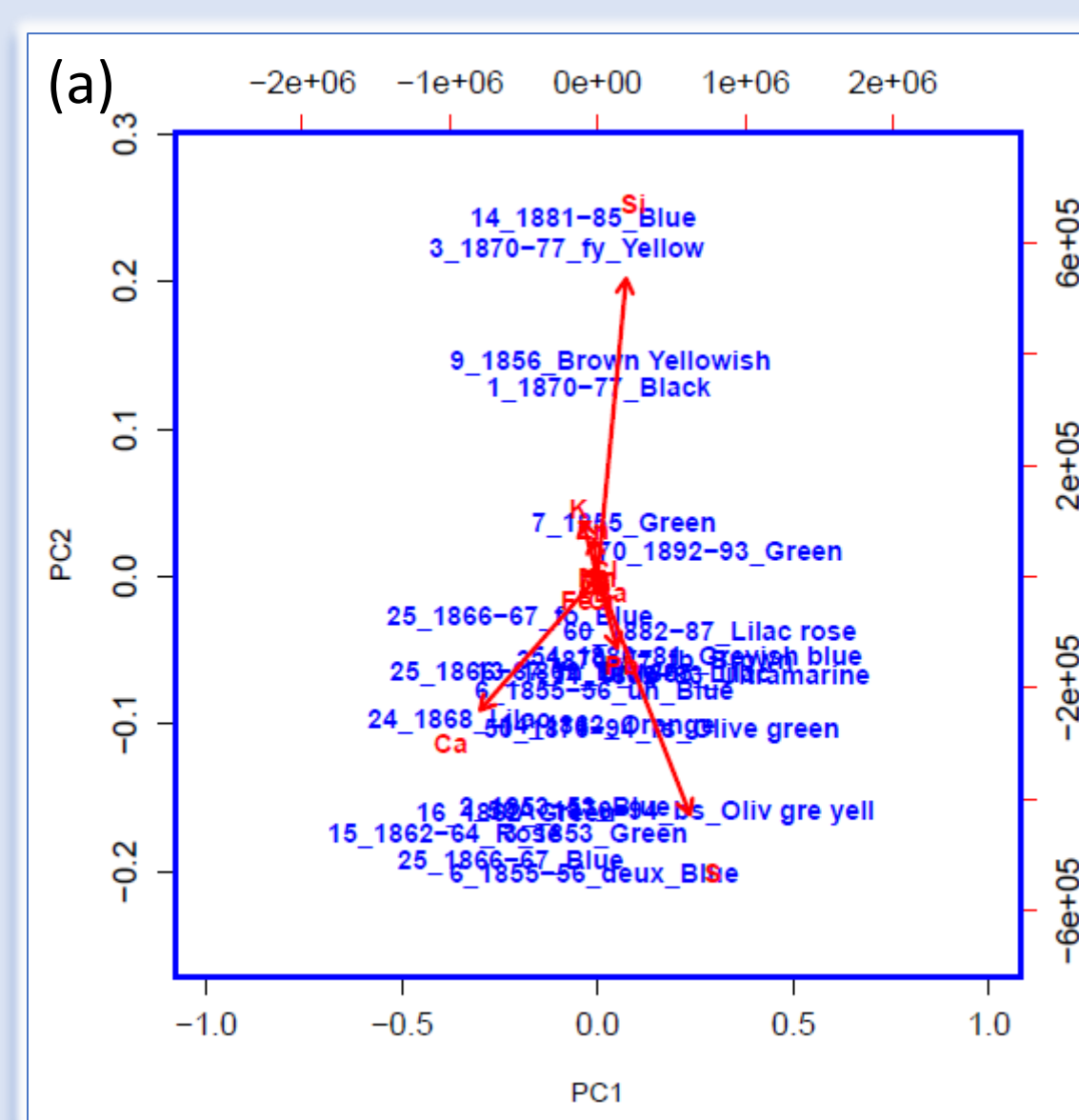
The chemical characterization of postage stamps has been a topic of increasing interest in the last decade with a focus on specimens of different countries from the XIXth century. [1-3] This interest is raised in both historical and forensic areas.

In this work, a sample of postage stamps of the XIXth century (from 1853 to 1894) is analysed. It consists of 23 Portuguese specimens together with 5 from some of the respective colonies: one from Cape Verde, 4 (1 real and corresponding forgery, and 2 additional forgeries) from São Tomé & Príncipe.

Analytical Techniques



Results



It is observed, from Figure 1, that the main components in the paper matrix, clearly obscure the pattern found in the dye pigment printed region. These main components are identified as silicon, sulphur and calcium. These elements have not been considered in the dye/pigment study.

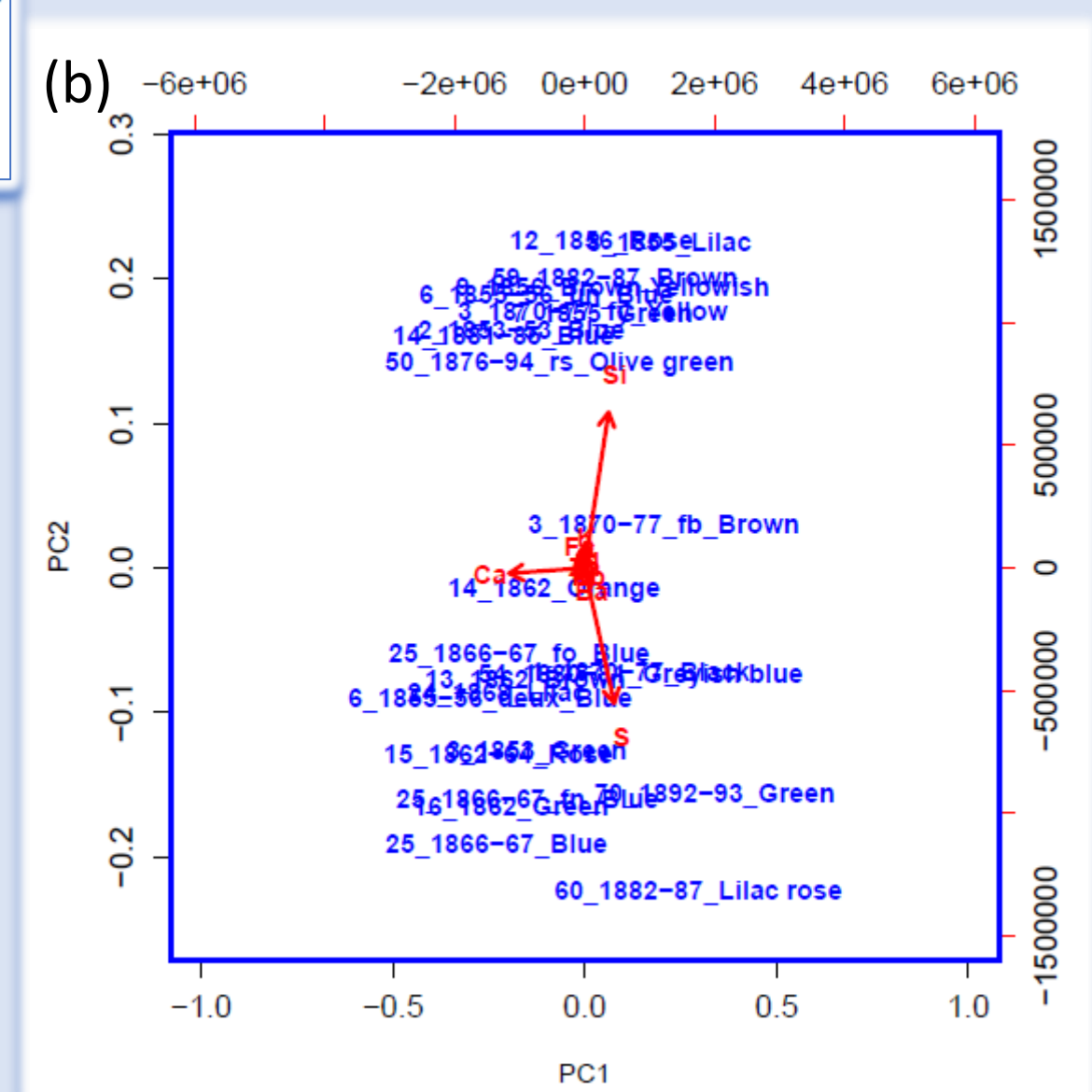


Figure 1: Biplot using covariance matrix for (a) dye/paper and (b) paper XRF results. The loadings corresponding to silicon, sulphur and calcium dominate all the others.

XRF mapping, see Figure 3, allows to identify unequivocally in which matrix of the stamp is present each element. If it delineates the printed region it is contained in the dye/pigment.

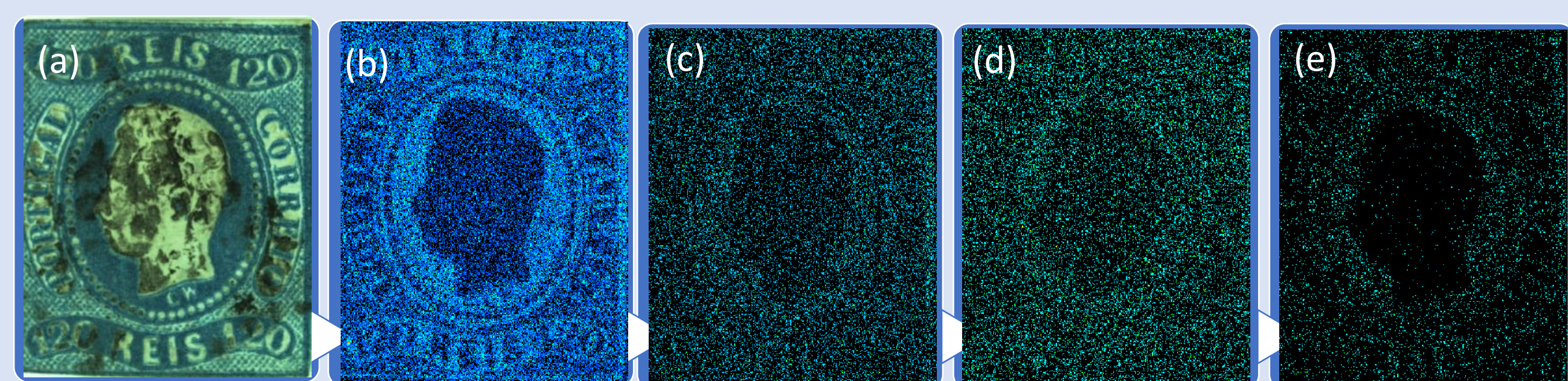


Figure 3: Stamp image and XRF mapping images for 25_1866_67_blue. Key: (a) stamp image, (b) Fe scanning at 15 kV, (c) Ba, 15 kV, (d) S, 15kV and (e) Pb, 50 kV.

ATR-FTIR contributed to clearly identify one of the pigments present in this sample and helped establishing some the additives used in the stamps.

Conclusions

The use of various analytical techniques allowed finding some important features of the first Portuguese postage stamps. In turn, chemometrics provided the means for an understanding of the underlying patterns.

References

- [1] C. Pinto, J. Sérgio Seixas de Melo, *Pure Appl. Chem.*, **2018**, 90, 435-445.
- [2] S. Araki, E. Kondo, T. Shibata, T. Yokota, M. Suzuki, T. Hirashita, K. Yamaguchi, H. Matsumoto, Y. Murase, *Bull. Chem. Soc. Jpn.*, **2016**, 89, 595-602.
- [3] M. Conceição Oliveira, A. Dias, P. Douglas and J. S. Seixas de Melo, *Chem. Eur. J.*, **2014**, 20, 1808-1812.

The Hierarchical Cluster Analysis of the XRF results of the dye/pigment matrix reveals the existence of 5 clusters, see dendrogram in Figure 2. The respective bar plots present the average composition responsible for this cluster structure.

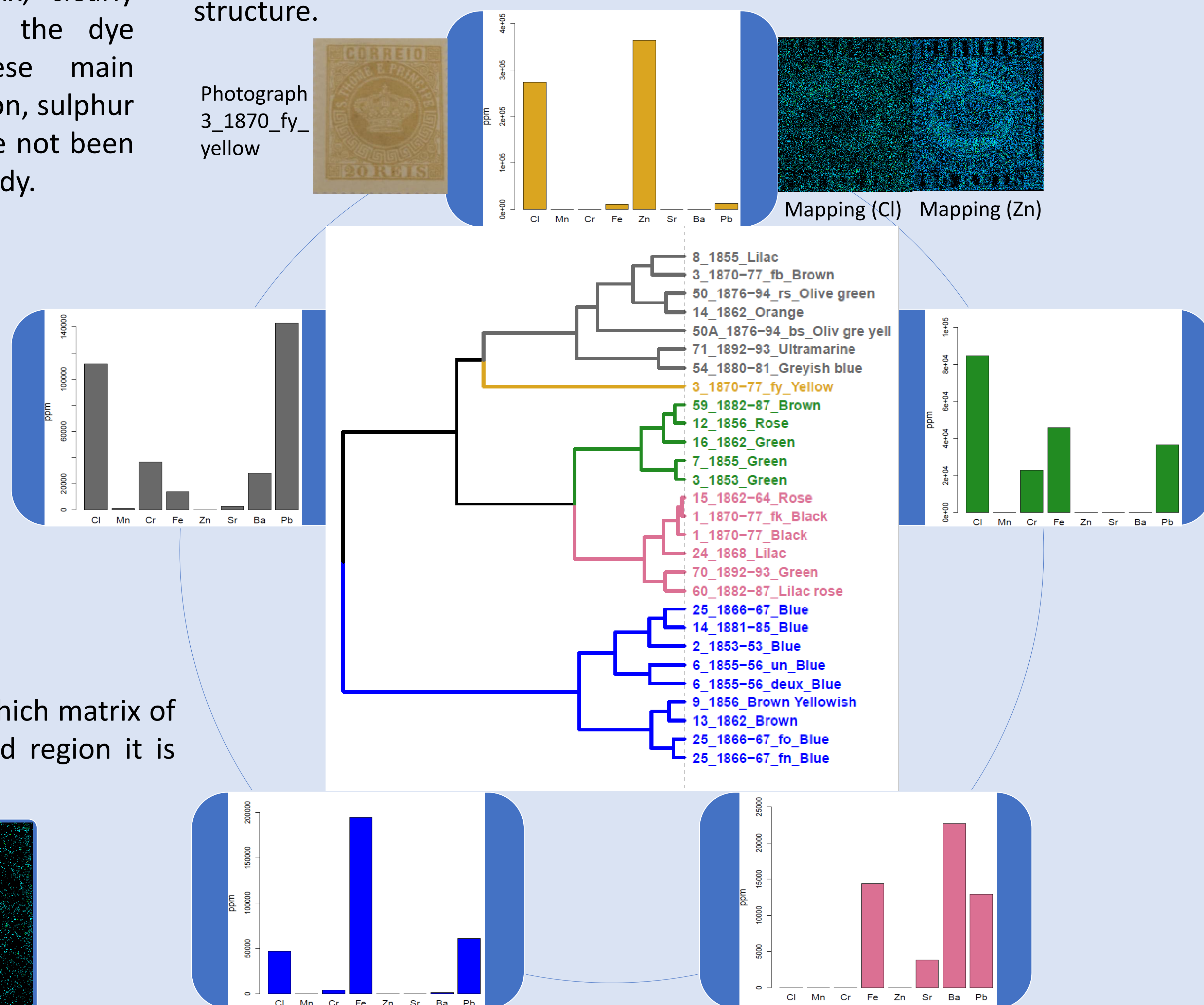


Figure 2: Dendrogram obtained with Ward's linkage for dye/pigment XRF results. The bar plots present the average composition of each cluster.

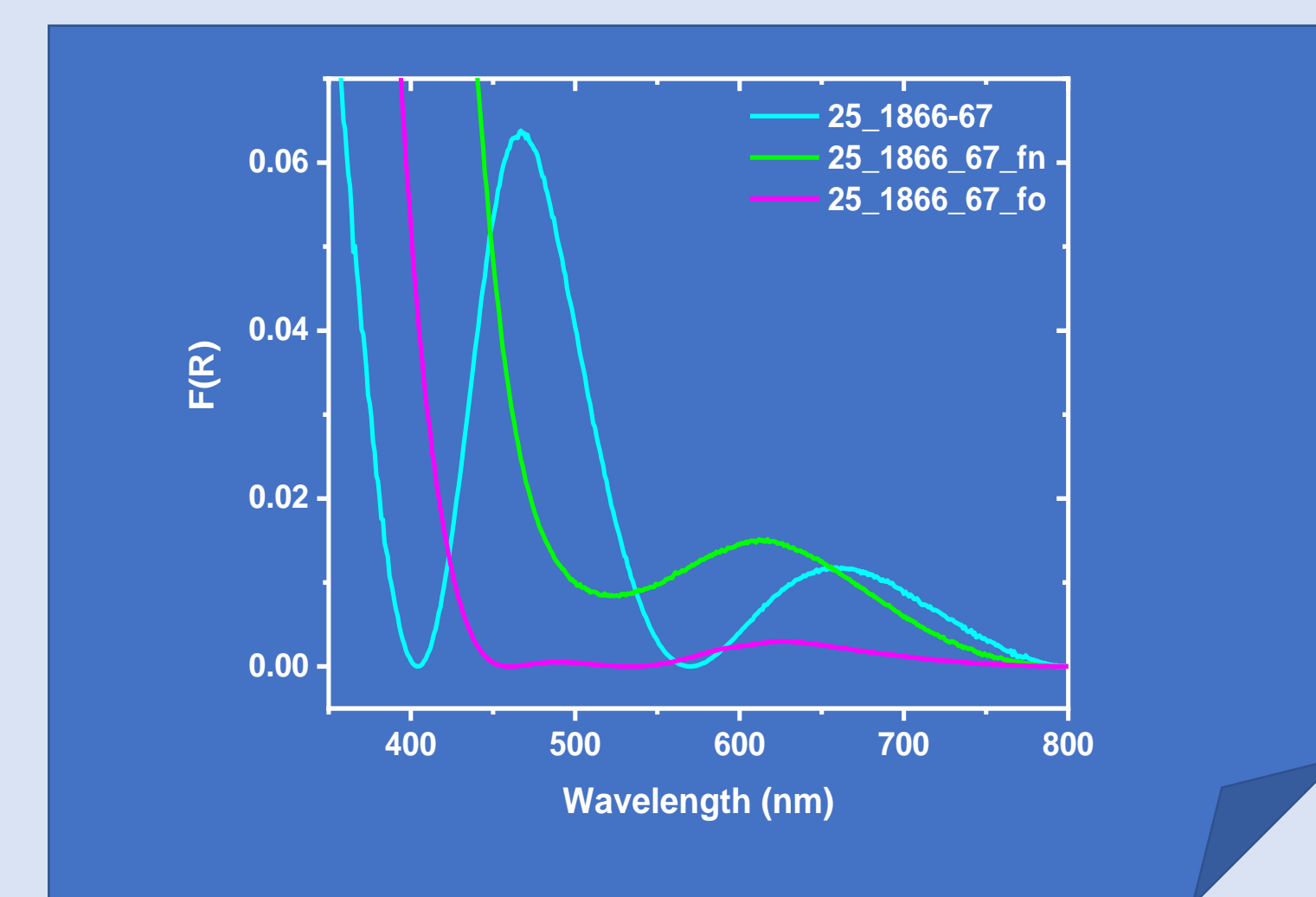


Figure 4: UV-Vis spectra of sample 25_1866-67 and respective fakes.