

Chemistry of the first Portuguese postage stamps

S.C.R. Ferreira, A.A.C. Pais and J.S. Seixas de Melo

CQC, Department of Chemistry, University of Coimbra, Rua Larga, Coimbra 3004-535, Portugal simonecrferreira@gmail.com

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.

Analytical Techniques



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 & Principe.



Results



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.

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.

-2e+06 0e+00 2e+06 4e+06 6e+06

12_18**8**6<u>1</u>895eLilao

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





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.



(b)

-6e+06

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.

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

25_1866-67_fo

(fake old).





Conclusions

The use of various analytical techniques allowed finding some important ^{25_1866-67.} 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.

Acknowledgements: The authors would like to thank the financial support from the Centro de Química de Coimbra, FCT (Ref. UIDB/00313/2020 and UIDP/00313/2020). SF also thanks FCT and CQC for a PhD grant (UI/BD/150815/2021).



FCTUC FACULDADE DE CIÊNCIAS E TECNOLOGIA UNIVERSIDADE DE COIMBRA





25_1866-67_fn

(fake new).

 $\tilde{\mathbf{g}}_{\mathbf{h}}^{(n)} = \begin{pmatrix} 0.02 \\ 0.02 \\ 0.00 \\ 0.0$

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

DEPARTAMENTO DE QUÍMICA

11C