1428
doi:10.1017/S1431927613009136

Microsc. Microanal. 19 (Suppl 2), 2013


# Quantitative SEM-EDX Analysis of Smalt Pigment Under Variable Pressure Conditions

Veronika Kugler[1], Marika Spring[2] and Julia Hudson[1]

[1.] Carl Zeiss Microscopy Ltd, 509 Coldhams Lane, CB1 3JS Cambridge, UK
[2.] National Gallery, Trafalgar Square, WC2N 5DN London, UK

Between the sixteenth and eighteenth centuries a blue pigment, called smalt, was commonly used in paintings. Smalt is a potash glass that derives its colour from cobalt; however, it is not stable and it can lose its colour so that oil paint containing this pigment can become grey or brown over time [1, 2]. Quantitative SEM-EDX analysis provides valuable data on the degree of degradation, through measurement of the potassium content, while the quantity of cobalt present gives an indication of the original intensity of the colour [3, 4].

It is desirable to analyse samples from old master paintings in the form of cross-sections without a carbon coating to allow subsequent study by other techniques. This requires the use of a charge compensating gas within the SEM chamber to minimise charging effects. However, accurate quantitative analysis under variable pressure conditions is challenging owing to interaction of the electron beam with the chamber gas, which influences the results in various ways. One factor is the beam skirt effect where material tens of microns from the point intended for analysis can contribute to the x-ray spectrum [4–8]. Since smalt particles are on average only 10–40 µm in size, and since in old master paintings they are often mixed with other pigments such as lead white, this effect is important for this type of sample. The analytical parameters can strongly influence the accuracy of the SEM-EDX results, and the aim of the experiments reported here was to select those that would minimise the beam skirt effect.

The effect of varying Beam Gas Path Lengths (BPGL), chamber pressure and charge compensating gas was studied in a Carl Zeiss EVO MA15 SEM, using an Oxford Instruments X-MAX 80mm EDX detector and INCA EDX system to collect the X-ray spectra. A reference sample of modern smalt mixed with lead white and linseed oil, prepared as a polished section in a polyester resin block was examined (Figure 1). EDX analysis was carried out using air and water as the charge compensating gas, with pressures ranging from 10 Pa and 100 Pa at both 1 mm BPGL and 16 mm BPGL. An electron beam energy of 20 keV and a probe current of 200 pA were used for all measurements.

The smalt pigment in the reference sample does not contain lead, but when carrying out EDX analysis under variable pressure conditions, the beam skirt effect causes a small fraction of the primary beam to be scattered, giving rise to a Pb x-ray signal from the lead white surrounding a smalt particle. The variation in Pb concentration measured at differing experimental conditions for the reference sample, shown in figure 2, is therefore an indication of the degree of beam-skirting. The nominal Pb concentration in the reference sample is minimised when water vapour and a BGPL of 1 mm are used. These parameters therefore provide the optimum conditions for reliable EDX analysis of smalt pigment in paint samples.

References:
[1] M. Spring, C. Higgitt and D. Saunders, ‘Investigation of Pigment-Medium Interaction Processes in Oil Paint containing Degraded Smalt’, National Gallery Technical Bulletin, 26 (2005), pp. 56–70
[2] A.R Burnstock, C.G. Jones and A.D. Ball, ’Morphology of the blue artist's pigment smalt using scanning electron microscopy’ In: Non-Destructive testing and Microanalysis for the Diagnostics and Conservation of the Cultural and Environmental Heritage, R. van Grieken, K. Janssens, L. Van't dack and G. Meersman Eds, University of Antwerp (Publ), 2002, Published in full on CD-ROM.
[3] L. Robinet, M. Spring, S. Pages-Camagna, D. Vantelon, and N. Trcera, ‘Investigation of the discoloration of smalt pigment in historic paintings by Co K-edge micro x-ray absorption spectroscopy’, Analytical Chemistry, 83(13), 2011, 5145–5152.
[4] D. E. Newbury, J Res Natl Inst Stand Technol 107 (2002) 567–603.
[5] N. W. Bower, Fresenius J Anal Chem 348 (1994) 402.
[6] E. Doehne, Scanning 19 (1997) 75–78.
[7] G. D. Danilatos, Ad Electronics Electron Phys 71 (1988) 10.
[8] M. Spring, V. Kugler and S. Bean, ‘Qantitative energy dispersive X-ray analysis of the blue pigment smalt’ In: Historical Technology, Materials and Conservation. SEM and Microanalysis, N. Meeks, C. Cartwright, A. Meek and A. Mongiatti eds., Archetype publications, 2012, 114–122.

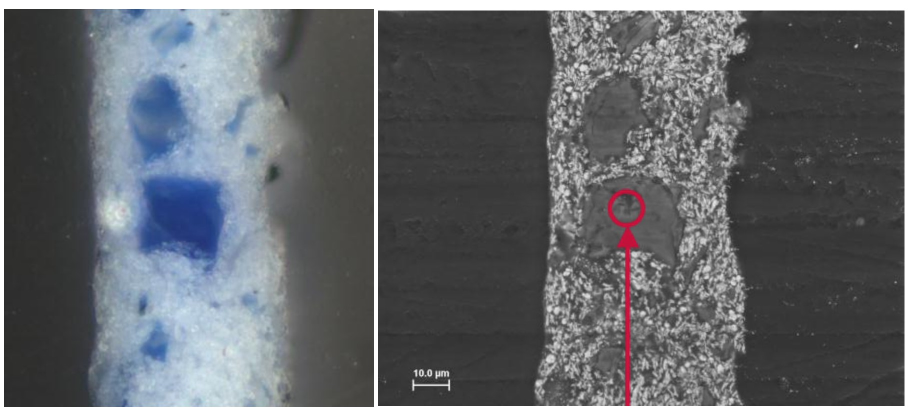


**Figure 1.** a) visible light microscope image of a test sample of smalt and lead white in oil; b) backscattered image of the same specimen. The red arrow points to the area of the smalt particle that was analysed.

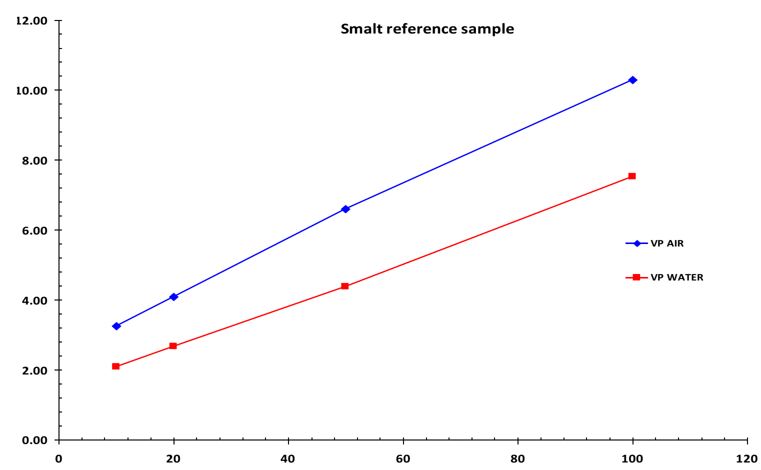


**Figure 2.** The effect of chamber pressure and charge compensating gas (air and water) on the EDX analysis results (Pb compound %).

https://doi.org/10.1017/S1431927613009136 Published online by Cambridge University Press