

Applications of RIGAKU Dmax Rapid II micro-X-ray diffractometer in the analysis of archaeological metal objects

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During material analysis of archaeological metal objects, especially their inlays or corrosion products, not only microstructure and chemical composition, but mineralogical composition is necessary to be determined. X-ray powder diffraction (XRD) is a widely-used method to specify the mineralogical composition. However, when sampling is not or limitedly allowed due to e.g. the high value of the object, the conventional XRD analysis can hardly be used. Laboratory micro-XRD instruments provide good alternatives, like the RIGAKU Dmax Rapid II micro-X-ray diffractometer, which is a unique combination of a MicroMax-003 third generation microfocus, sealed tube X-ray generator and a curved 'image plate' detector. With this instrument it is possible to measure as small as 10 μm area in diameter on the object. Here we present case studies for the application of the micro-XRD technique in the study of archaeological metal objects.

In the first case niello inlay of a Late Roman silver augur staff was analysed. Due to the high value of the object, since it is the only piece known from the Roman Empire, only non-destructive analyses were allowed. To reconstruct the preparation of the niello, SEM-EDX analysis was performed on the niello inlays to characterise their chemical composition and microstructure. Two types of niello are present: a homogeneous, silver sulphide niello (acanthite) and an inhomogeneous silver-copper sulphide niello (exsolution of acanthite and jalpaite or jalpaite and stromeyerite). The micro-X-ray diffractometer was used to verify the mineralogical composition of the niello, supposed on the base of SEM results.

In the second case corrosion products of a Late Roman copper cauldron with uncertain provenance were examined, since they may hold clues about the burial conditions (pH, Eh, etc.) of the object. A layer by layer analysis was performed in cross sections of small metal samples by using electron microprobe and micro-X-ray diffractometer. The results show two corrosion zones: 1) the original (internal) surface zone of the metallic copper object was replaced by copper(I) oxide (cuprite), while 2) basic copper(II) carbonate (malachite) was deposited (externally) on the original surface. In our view these two minerals were formed during long-time burial, and protected the cauldron from further corrosion. Rarely copper(I) chloride (nantokite), basic copper(II) trihydroxychloride (atacamite/paratacamite) and basic copper(II) sulphate (brochantite) were also identified in the two corrosion zones. Their uneven distribution on the cauldron and their known formation conditions indicate, that these latter mineral phases may be the results of active corrosion, started possibly after excavation.