GRAPHIC DOCUMENTS WORKING GROUP of ICOM-CC
Interim Meeting 2010 - Copenhagen / Royal Library - 22-23 of April 2010

CHOICES IN CONSERVATION - PRACTICE VERSUS RESEARCH

Extended abstract for oral presentation

Title: Analysing intaglio printing ink

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1. Introduction (105 words)

Usually more components are found during analyses of intaglio prints than could be accounted for. One reason for this could be the presence of material that was abraded from the intaglio plate during the printing process. Discussed are recent analyses of reconstructions carried out with modern materials under controlled circumstances, to be sure what components came from where. The first results seem to show that it is possible to identify elements coming from the printing plate only. These concern minor amounts of elements that in earlier analyses results could not be explained for or were ignored. The present results give possibilities for future print analysis.

2. Main body of text (1505 words)

Research of historical printing ink at molecular level is still in its infancy, although it has been carried out in the field of incunabula in the past decades. [2, 3, 4, 5, 7] The present authors concentrated on questions in the field of printing inks used for historic engravings and etchings. Results of laboratory analyses on reconstrucctions made with modern materials are compared with research into art technological sources in order to elucidate questions in the field of historic intaglio printmaking, more in particular the printing of engravings and etchings.

Before 1900 only pigments made from charred animal or vegetable matter are used for intaglio ink. Frankfurt black, produced by charring lees of wine, is by far the most common black pigment for intaglio printing ink. A count of available ink recipes showed 160 references from the earlier 17^{th}- to the beginning of the 20^{th} century to Frankfurt black, compared to a few dozen references to other black pigments. [6] Boneblack is found in some historical recipes and this pigment is nearly always used for black intaglio inks after 1900. Only in recent years synthesised metal oxides, such as black oxide of iron (FeO-Fe_2O_3) and Spinell black ($Cu(Cr, Fe)_2O_4$) became available in qualities fine enough for use in intaglio printing inks. Their use in commercial inks is limited, though.

Blue toners give black inks a cooler cast, while brown and red toners give them a warmer cast. The metal contents of Prussian blue, found as toner in sources from the 18^{th} century onwards, or of the chrome pigments used as toners in the 19^{th} century, show in analysis due to the presence of Fe and Cr respectively. Another documented toner is indigo which, being a dyestuff, is more difficult to trace as a constituent in printing ink. Fillers and conditioners, such as chalk or kaolin, and the modern aluminium hydrate or magnesium carbonate, could be expected, although they are rarely documented. Tracing these materials is more or less difficult depending on the detection limits of the equipment used.

Lead-containing driers reveal themselves clearly in X-ray photographs of some 17^{th}-century etchings. Charred blacks do not show on X-ray pictures because they do not contain heavy elements and the addition of lead driers is not found in historic recipes for black intaglio inks. A drier such as litharge (PbO), is commonly added in the preparation of oil-varnish for letterpress ink, however, a practice that continued until way into the 20^{th} century. The presence of a lead drier in intaglio ink would therefore point to the use of varnish for letterpress ink applied in the preparation of intaglio ink.

Analysis of oil-varnish used as a binding medium in printing ink can mainly be done destructively. The results may show that particular fatty acids have been used and that the oil has been heated at temperatures below or above 200 ºC, little more can be found. However, historical oil-varnishes are always made by heating vegetable oil at temperatures around 300 ºC. [1]

Analyses of historic pigments are supportive in ink research, but suffer under a rarity of pre-1900 pigment reference collections to calibrate the equipment and train the researcher. Nearly all research on pigments relies on modern reference materials, if not on freshly bought colorant. But even if any deposits of pre-1800 colorants would be available, the appearance of pigment grains changes during the preparation of the printing ink. Oil-varnish and pigment are mixed together and then thoroughly ground on a stone with a stone muller to prepare ink. The grinding crushes the agglomerates of pigment particles and the larger grains are crushed further, which changes their appearance.

A returning question is what metal the printing plate is made of, while on the other hand any analysis of still available historic printing plates is nearly absent. Generally copper was used for engraving and etching before 1800, while brass, bronze, iron and tin are mentioned for particular purposes. The use of zinc and steel intaglio printing plates is only found after 1800. Several thousands of historical printing plates have survived and they will be representative for the plates produced since the 15th century. They do not give information on the working methods of a particular engraver, though, let alone give information on a plate used for a particular print. Those few ink analyses that are carried out showed the presence of elements that could not be explained from the printing ink or the paper. It means that either these elements are related to historical printmaking practices or are perhaps introduced at a later stage during the keeping or restoring of the object. The tests made by the present authors showed possibilities for detecting plate materials in intaglio printing inks, which opens further perspectives in this field.

Reconstructions are prepared for analysis by mixing dry pigments with linseed oil-varnish. The oil-varnish is taken from the container using stainless steel paint knives. The inks are mixed (not ground) with plastic cards on a glass plate to limit the introduction of foreign metals (fig. 1). Graphic Chemical & Ink burnt plate oil #00 is mixed with three different pigments: bone black (Scheveningen-Oud Holland), carbon black (Peter van Ginkel) and wine lees black charred from lees of local wines at the Kanazawa College of Art (Japan). Copper, iron and zinc etching plates are used. All plates are printed with all inks giving nine different combinations in total. The printing paper is Johannot by Arches.

A portable EDXRF (energy dispersive X-ray fluorescence) tool is selected, because it provides immediate multi-element results and allows non-invasive analysis. EDXRF is a valuable technique for *in situ* analyses, because museums, archives and archaeological sites will not allow artifacts to be moved and often prohibit sampling objects by destructive techniques. No other method surveys all but the lightest elements on the periodic table without having to remove a sample. It is possible to analyse about twenty elements with a single measurement starting from phosphorus to lead. Both the possibilities and limitations of the technique must be understood to avoid misinterpretations and unrealistic expectations.

To detect elements in the printmaking materials, paper and prints the EDXRF analyses are processed with a portable InnovX® spectrometer: an EDXRF, Innov-X Alpha Series®, which employs a miniature, low power X-ray tube as source of sample excitation. The end-window transmission Ag-anode tube operates at up to 40 kV with a maximum of 50 μA of current. A high performance Si PiN thermo electronically cooled diode detector with an energy resolution of ≤230 eV is used to detect and register the characteristic X-rays from the constituent elements of the print samples. An Innov-X Alpha Serie® is driven by an HP IPAQ pocket PC using Soil Mode software including light element analyses (LEAP). For the metal printing plates the Metal/Alloy analytical mode is used. Detection and analytical data of elements are considered as semi-quantitative results. Glindsman

The tool is positioned vertically and the test print placed on top of the measuring window to avoid any possible background contamination (fig. 2). Measurements are read from a mini PC unit (fig. 3). The metals of the three printing plates, samples of paper, dry pigments and oil-varnish are measured separately. The prints are measured at three positions: at the ink lines, at the plate tone in between ink lines and on the blank paper next to the impression of the plate. Comparison between the analytical results of the prints, of the metal printing plates and of the raw materials accounted for the elements and impurities found. For example, the wine lees black contained a high amount of Fe and traces of Cu, Cr, Mn and Pb. The paper contained a high amount of Ca, with a little Fe and traces of Ba. Traces of Fe are measured in the oil-varnish. This means that iron is found in all cases, its total amounts depending on the combination of materials (fig. 4).

The use of EDXRF instrumentation has practical limitations, such as the instrument cannot take account of the variations in a heterogenic matrix. X-rays pass through the paper support, but the paper itself contains inorganic Ca and Ba fillers and other additives. Further, composite heterogenic materials sometimes have spectra with overlapping peaks that will affect the determination of some elements. That is why the suitability of the equipment also depends on the experience of the operator.

Paper and printing materials are heterogeneous, which makes it difficult to get accurate results. The absolute amounts of particular elements will differ from spot to spot, depending on the material available and depending on the proportions of elements at the measuring spot. Handmade ink in particular will be less homogeneous than inks prepared by machines. Note that zinc is absent in paper, oil-varnish and pigments, but Zn is significantly present in all measurements of prints taken from zinc printing plates. This means that part of the surface of the zinc printing plate is abraded during printing and Zn is contained in the ink on the sample print. Similar results are visible with copper plates.

3. Conclusions (136 words)

Based on the authors’ former experiences using immovable equipment such as SEM-EDX, XRF, XRD and EDXRF machines, it can be acknowledged that modern portable EDXRF tools are safe and sensitive enough for analysing prints. This multi-element technique can be used to analyse inks in prints. The sensitivity of the equipment shows by the measurements of metals in the ink that are abraded from the plates during printing. Portable equipment allows working in the institutions where the prints are kept instead of bringing objects to the laboratory. Furthermore, our results give ideas to standardise working methods. Studying more reference samples that have known chemical composition will improve results, while interpretation of results will be easier as more experience is gained. This project proves that research of historical art technology in combination with scientific analyses gives optimal results.

4. Bibliography (224 words)

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Aknowledgements (84 words)

The authors gratefully acknowledge the cooperation of Peter Hallebeek and Ineke Joosten at the Netherlands Institute for Cultural Heritage, Amsterdam (the Netherlands) in earlier analyses of printing inks; paper conservator students who graduated in spring 2008 and interior conservation students, group HIK06 from the Metropolia University of Applied Sciences, Helsinki (Finland) for their technical assistance with EDXRF measurements; Yoshio Kamitami, Tsuneo Ueda and Ayumi Yasui from the Kanazawa College of Art, Kanazawa (Japan) for sharing information and materials concerning their research into Frankfurt black.

5. CV (85 words)

Ph.D. Ulla Knuutinen is working as a lecturer of conservation chemistry and materials science at the Helsinki Metropolia University of Applied Sciences. She is a member of the COST D 42 management committee and working group 2, doing research for developing non-destructive and non-invasive analytical methods for studying heritage materials.

Ad Stijnman is a professional printmaker and a specialist in historical printmaking techniques. He cooperates in the Virtuelles Kupferstichkabinett project (Germany) and is compiling his dissertation on the history of engraving and etching techniques, 1400-2000.

Figure captions

Fig. 1 - The three kinds of test inks are mixed on a glass plate with plastic cards.

Fig. 2 - Test prints are placed on top of the measuring window for analysis.

Fig. 3 - A mini PC unit is used for reading the measuring results.

Fig. 4 - Diagram with values of the elements Fe, Cu and Zn in the sample prints. The standard deviations are marked +/-.