

SIMS (Secondary Ion Mass Spectrometry) STUDIES ON ARCHAEOLOGICAL MATERIALS

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ABSTRACT

The present study includes examples of recent applications of Secondary Ion Mass Spectrometry (SIMS) in different archaeometric projects. Fingerprint mass spectra of different pottery types were studied in order to characterize the wares and to establish a probable kinship to other wares. Mass spectra of the glaze of crucibles were used to establish a relation to alloys possibly melted in the crucibles. Elemental analyses of an Iron Age fibula of both the bronze shaft and the iron needle were performed. The fingerprint mass spectra of the blue paint of a van Dyck painting were compared with both indigo-blue and Berlin-blue samples in order to investigate its authenticity. Diffusion profiles of numerous elements in the enamel of teeth have been shown to reveal a strong potential for archaeological dating (DET).

Introduction

Heavy duty SIMS instruments are quite rare around the world. There are only three such instruments in Scandinavia. The high costs involved, both in purchase and analysis, and the need for highly qualified personnel are certainly deciding factors. The instrument at the SIMS laboratory, Department of Physics at the Chalmers University of Technology in Gothenburg, which was used in the present study, is the only interdisciplinary SIMS in Scandinavia. This instrument, a Cameca 4F ion probe, is therefore especially suitable for the use in archaeometry. Archaeometric investigations have been performed at the laboratory since 1984.

The present study is separated into two parts: the first part deals with principles and features of SIMS in general and of the actual instrument used in the current studies. The second part shows the potentials of SIMS in archaeometrical investigations, exemplified by resumé of studies of archaeological objects and a painting.

Principles and features of SIMS

Mode of operation

Secondary ion mass spectrometry is based on the

following functions (fig 1; cf Lodding 1988):

- Bombardment of the sample surface by focused primary ions, with sputtering of the outermost atomic layers.
- Mass spectrometric separation of the ionized species (sputtered atoms, molecules and clusters) according to their mass-to-charge ratios.

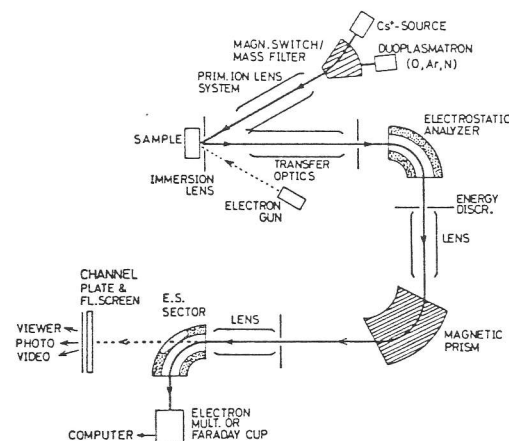


Fig 1. Schematic drawing of a Cameca 4F ion probe.

- Collection of the separated secondary ions as quantifiable mass spectra, as in-depth or along-surface (step.scan) profiles of elemental concentra-

tions, or as element distribution images of the sputtered surface.

The primary ions (usually O_2^+ , O^- or Cs^+) are accelerated and focused at a selected impact area on the specimen. The focused beam can be narrow (micro-probe; 0.02-1.0 microns) or relatively wide (10-300 microns), enabling different modes of analysis and imaging. The collision cascade following the incidence of a primary ion results in the reshuffling of some 50-500 matrix atoms, and emission of secondary particles either neutral or ionized. Secondary ions from the specimen are extracted into the mass spectrometer, the operation of which is based either on electric/magnetic deflection fields (eg the Cameca 4F) or on the quadrupole/time-of-flight principle. Secondary ions with a given mass-to-charge ratio, and within a certain range (window) of kinetic energy, are collected for pulse or current measurements, ion-optic imaging, and data processing.

The high sensitivity of SIMS to chemical and isotopic detection (ppb-ppm), and the good morphological resolution (submicrons both in depth and laterally) make it superior to many other analytical techniques (see tab 1) used in industry and in interdisciplinary sciences. The SIMS equipment in Gothenburg performs multidisciplinary research and has been especially adapted for quantitative uses. In archaeometry, the current SIMS equipment has recently been applied to bronze, iron and lead objects, to ceramics, to pigments, and to biomaterials such as teeth and bones. In industry, the instrument has been applied eg to superconductors, semiconductors, composite alloys, glass and ceramics for the disposal of nuclear waste, and in bone.

Table 1. Typical features of major surface analytical techniques.

Method ^b	Element Range (Atomic No.)	Lateral Resolution (μm)	Information Depth (Å)	Detection Limit (atom ppm)
EMP, AEM	≈ 5	2	10 ⁴	10 ³
AES, SAM	≈ 3	10 ⁻¹	10	10 ²
ESCA, XPS	> 2	10 ³	20	10 ⁴
LEIS	> 2	10 ²	5	10 ³
HEIS, RBS	≈ 5	2	10 ²	10 ²
PIXE	≈ 10	5	10 ³	1
AINR	≤ 10	5	10 ³	10
FIM-AP	All	10 ⁻²	10	10 ³
SIMS, IMMA	All	1-10 ⁻¹	5	10 ⁻⁴ -10

^a Order-of-magnitude figures, applying to routine analysis of elements with average ease of detection.

^b EMP, electron microprobe; AEM, analytic electron microscopy; AES, Auger electron spectroscopy; SAM, scanning Auger microprobe; ESCA, electron spectroscopy for chemical analysis; XPS, X-ray photoelectron spectrometry; LEIS, HEIS, low- and high-energy ion scattering spectrometry; RBS, Rutherford backscattering; PIXE, proton-induced X-ray emission; AINR, accelerator-induced nuclear reactions; FIM-AP, field ion microscopy-atom probe; SIMS, secondary ion mass spectrometry; IMMA, ion microprobe mass analysis.

An advantage of SIMS which is especially important to archaeometry is that the method can be considered to be nearly non-destructive apart from the fact

that the sample size should not exceed 25 mm by 12 mm. Analyzed samples can be returned.

Sample preparation

The surface or the section of samples can be analyzed, either in a step-scan or in-depth mode. Sections of samples are polished with silicon carbide grinding paper, grit 600, and held in the SIMS sample holder (D. 25 mm, max. height 12 mm) by means of an embedding resin. The embedding procedure is the same as regards other surface analyses. Insulating samples (eg pottery, pigments and biomaterials) are further thinly gold-coated under vacuum, in order to make the exterior conducting - a precondition of all SIMS analyses.

Archaeometric applications

Characterization of pottery

In an earlier study Canaanite pottery from Swedish excavations in Cyprus was investigated by SIMS (Fischer 1990). Grouping according to diverging clay matrix elements was performed, and a possible provenance was suggested considering comparative neutron activation data from Cyprus and the Levant (Artzy et al 1973, 1976).

In the present study the Red Lustrous Wheel Made ware (hence abbreviated R.L.), dated to Late Cypriot II (c 1375 - 1360 BC ; P. Åström, personal communication) was compared with four different wares excavated on Cyprus: White Painted Cross Line, Red Painted IV-V, Monochrome, and different Canaanite wares (see above). These wares are dated earlier, contemporaneously or later than R.L. The aim of this pilot study was to demonstrate the instrument's potential and to show similarities and differences between R.L. and the other wares.

The analyzing instrument was used in the slow-spectrum mode. The polished sections of the specimens were bombarded by a beam of O- primary ions, c 25 microns in diameter, accelerated through 12.7 kV at a primary current of c 200 nA. The beam raster was 250x250 microns. The secondary positive ions were extracted and transmitted for mass separation from an analyzed area of 110x110 microns. The kinetic energy window admitted only ions in the 75 eV to 125 eV range. The build-up of surface charge was countered by automatically adjusting the high voltage sample potential. All existing masses from 1 to 250 were exhibited in a single table for each sample analysis. For statistical reasons each sample

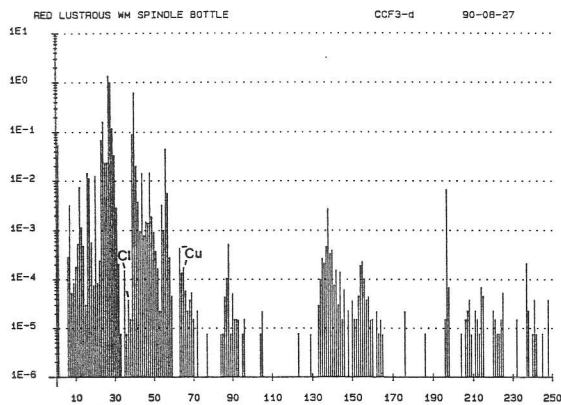


Fig 2. Red Lustrous Wheel Made ware spectrum. Mass numbers on x-and intensity on y-axes.

was analyzed at three different points. Average sputtering time for each analysis was c 750 seconds. Since the area under analysis was as "large" as 110 square microns it was important to avoid areas unrepresentative of the clay matrix, eg large inclusions. Consequently, each clay matrix spot to be analyzed was marked in a stereo microscope prior to the SIMS analysis. This afforded an excellent topographical definition.

It was shown that R.L. incorporates two elements with much higher intensity than found in the others: chlorine (isotopes 35 and 37) and copper (isotopes 63 and 65); see figure 2. Another common but less prominent trait was that of the low lithium intensity. Simply expressed the high chlorine and copper intensities, and to some extent the low lithium intensity, characterize R.L. and make it distinguishable from the other wares, even if some kinship tendencies to the other wares could be observed.

Most chemical methods of analysis are used to ascertain the elemental composition of a ceramic sample as a whole, including inclusions. Petrographic analyses often measure the percentage of the inclusions, and study their nature. SIMS offers the possibility to measure the elemental composition of the clay matrix separated from inclusions, or if required the actual inclusions.

Fingerprint element analyses of the glaze of crucibles and alloys

Some crucibles were found during the excavation of an Iron Age site in West Sweden. The aim of this investigation was to show if it is possible to find out which alloys were produced in three of these crucibles by studying fingerprint elements in the glaze of the crucibles. The results of the glaze analyses were compared with analyses of different metal objects

found at the same site.

The SIMS instrument was used both in the slow spectrum mode (see above) and in the in-depth profiling mode, where 24 of the most interesting elements were precisely analyzed according to their percentage distribution. Both the glaze of crucibles and different metal objects were analyzed in the above modes.

The most common elements both in the crucibles and the alloys were: Fe, Cu, Zn, Sn and Pb. By comparing the percentage distribution of these elements it was shown with quite a high amount of probability, that two of the crucibles had been used to produce two of the metal objects. One of these objects was a brass alloy and the other a tin alloy (see fig 3).

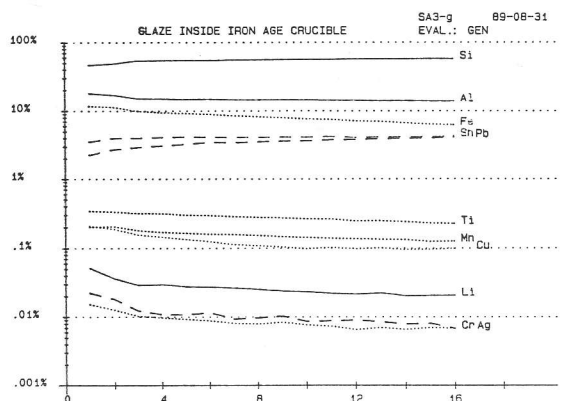


Fig 3. In-depth analysis of glaze of a crucible (observe high Sn and Pb values); "c" on x-axis means number of cycles (=repeated measurements at increasing depth).

This investigation is only a pilot study. Many archaeological and chemo-physical factors must be studied thoroughly before definite conclusions can be drawn. Items such as: has a certain crucible been used for a certain alloy? ; do certain elements adhere better than others to the glaze of crucibles? ; and, has the type of clay used in a certain crucible had any affect on the type and amount of the remaining elements? A series of analyses of modern crucibles and different modern alloys is planned, which will, hopefully, answer the above questions.

Elemental analyses of a bronze/iron fibula

During the Swedish Jordan Expedition (Swed Jord Ex 1989) a fibula with a decorated bronze shaft and an iron needle including a spiral fibula was found in the Jordan valley (Fischer in press). It was dated to 600 BC. The aim of the SIMS investigation was to characterize the bronze, and to show impurities in

both the bronze and iron parts.

The sample size of both metals was c 1 mm² each. The SIMS instrument was used both in the slow spectrum, and in the in-depth profiling mode (see above), where 24 interesting elements were further studied.

As expected, Cu was found in abundance in the bronze part (fig 4a). Ca, Zn, Pb and Sn were found in decreasing order of magnitude. The presence of a considerable amount of Zn could indicate a brass alloy. The relatively high amount of Pb, clearly identified by its isotopes 204, 206, 207 and 208, is somewhat surprising together with the low values for Sn (112, 114 -120). The presence of Ca (40, 44) can possibly be explained by diffusion from the surrounding environment during corrosion. The development of quantitative procedures for "bronze" and "brass" are part of a current research project at the SIMS laboratory in collaboration with the metallurgical institute at the Chalmers University in Gothenburg.

The iron needle is a Fe-Ni alloy (fig 4b). The following impurity elements were found: Li, B, Na, Mg, Al, Si, Cl, K, Ca, Ti, Cr, Mn, Co, Cu, Zn and Sr. Quantitative methods are under development (see the above paragraph).

Van Dyck blue

Anthony van Dyck's painting "Amaryllis and Mirtillo", the scene of Guarinis 'Pastor Fido' (c 1632), which is usually on display at the Gothenburg Museum of Art, is now under restoration at the Studio of the Western Sweden Conservator's trust (ref. T. Peteus and M. Ekroth-Edebo). In connection with the restoration work a SIMS analysis of a c 0.3 x 1.5 mm flake of "vanDyck-blue" was performed in order to find out the type of blue pigment used. The sample was taken from the lower part of the central female's dress, close to her left foot. The section of the flake, embedded in resin, was analyzed in the step-scan mode. This mode involved the analysis of a certain number of points, a constant distance apart (12 microns), along a straight line on the surface of the samples' section. The 12 micron step-scan mode with an analyzed area of 6 square microns turned out to provide maximal information about the distribution of the 19 chosen elements.

A "pure" indigo blue pigment (vegetable glycoside) does not usually contain any considerable amounts of iron or potassium. The analysis of the current

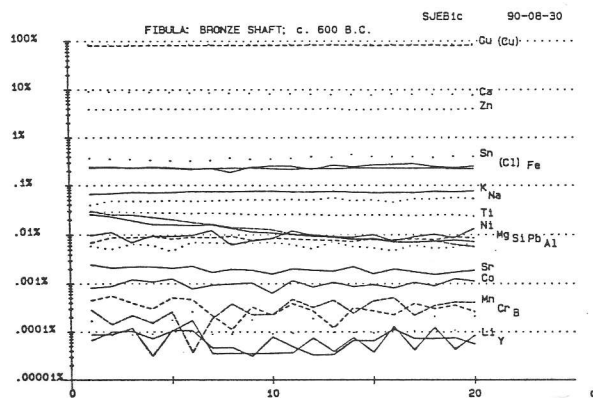


Fig 4 a. Bronze/iron fibula. In-depth analysis of bronze shaft.

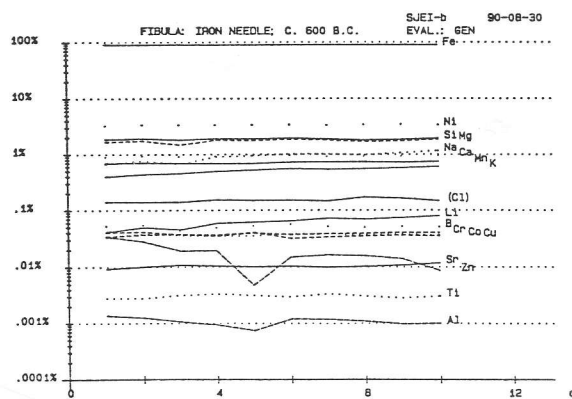


Fig 4 b. Bronze/iron fibula. In-depth analysis of iron needle.

sample (see spectra in fig 5) revealed *ia* about 5 % Fe and 16 % K. These relatively high values are interesting, and could possibly indicate the colour called Berlin-blue, pottassium ferric ferrocyanide (other synonyms are Prussian-, Paris-, Antwerp- and Chinese blue). This colour was first made by Diesbach in Berlin c 1704 as a result of the action of potash on iron vitriol (Gettens et al 1966). There are obvious discrepancies in time, since van Dyck died in 1641. On the other hand one can not exclude the possibility that van Dyck used an individual indigo blue mixture for this painting, resulting in the above

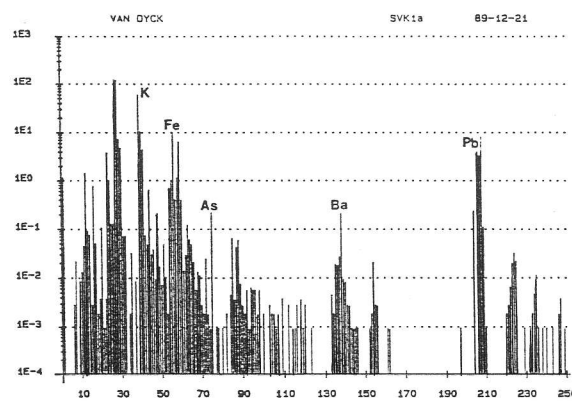


Fig 5. Mass spectrum of van Dyck's blue paint.

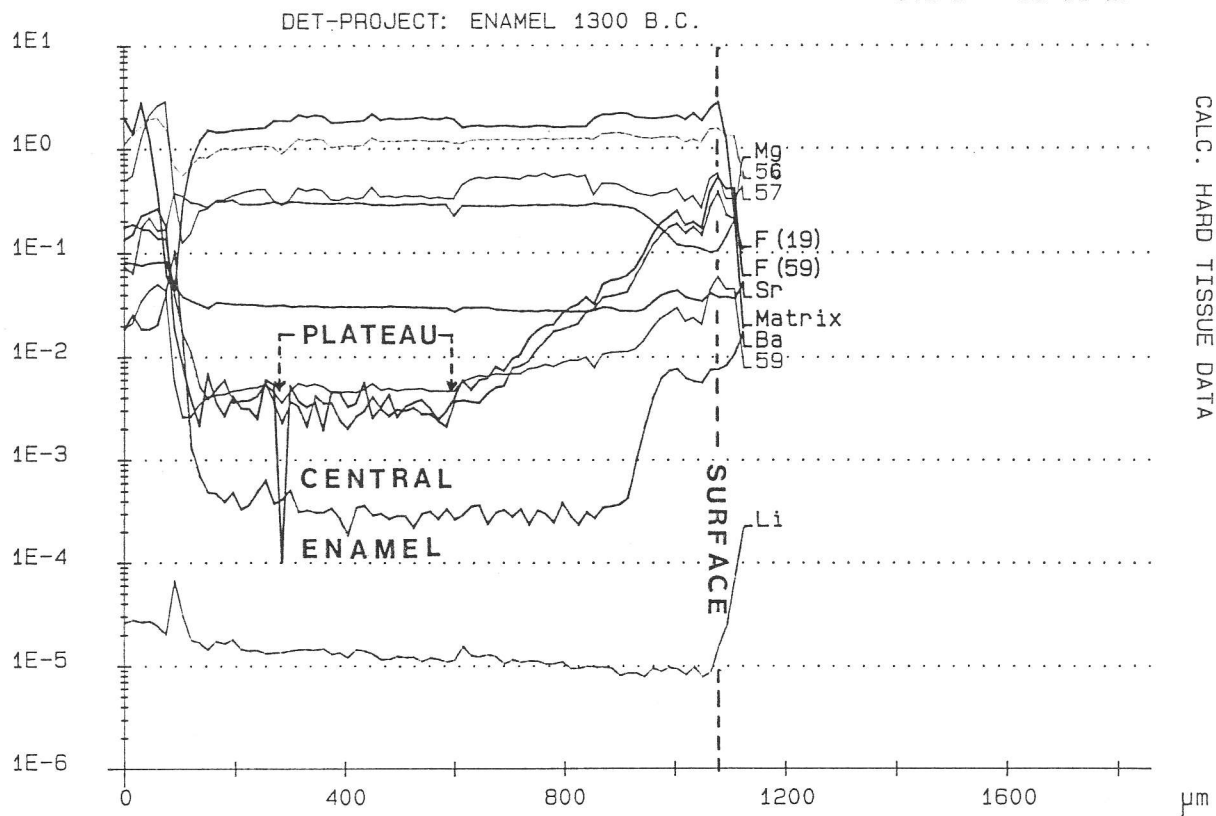


Fig 6. DET-project: typical diffusion profiles of elements in enamel.

composition. Analyses of other van Dyck paintings are planned in order to get more information about the type of the blue paint he used.

The results from the SIMS analyses of the above van Dyck sample were compared with indigo blue and Berlin-blue samples. One can certainly not expect the composition of the "modern" pigments to correspond exactly to the old ones, however there are tendencies that the blue of the actual van Dyck painting resembles, to a large extent, the "modern" Berlin-blue rather than the indigo blue pigments.

DET-dating: dating by diffused elements in teeth

Diffusive interaction between teeth and the surrounding environment take place *intra vitam* and *post mortem*. The SIMS laboratory in Gothenburg has, since 1984, carried out research on the possibility of dating samples by studying the diffusion pattern of certain elements, especially fluorine, in the enamel of teeth (see eg Fischer et al, 1985, 1986, 1989a and b). Until recently only human teeth were studied. Bovine teeth from the Jordan Valley belonging to three periods (3200, 1400 and 600 BC) were recently investigated by SIMS. Their diffusion

pattern was found to be comparable to human teeth.

Each tooth analyzed was cut by a microtome perpendicularly to the labial/buccal surface, thus giving a cross section from surface to pulp. The instrument was used in a quantitative step-scan mode, *ie* the primary beam was moved in steps of 5-15 microns along a straight line, perpendicularly to the enamel surface, from the dentine throughout the enamel. The average number of points measured was 100-150, thus giving an average measured distance of 1-2 mm. The specimens were bombarded by a 25 micron beam of O- primary ions as described in the preceding studies. The analyzed area of each spot was 6 microns.

The DET model is based on the following observations (fig 6):

a. Uniform maximal fluorine concentration in the outermost enamel: it is normally restricted to c 3000 ppm, regardless the absolute age of a tooth ("saturation level").

b. Sponge effect: the above maximal concentration is achieved within a short period regardless of the con-

centration of the fluorine carrying agent (*intra vitam* eg saliva, food and water; *post mortem* eg soil and water): ie the calcium apatite of the enamel functions as a sponge, absorbing fluorine from an outer fluorine source, and reaching almost immediately a higher fluorine concentration than the outer source.

c. *Fluorine diffusion from the "depot"*: the fluorine-rich outermost enamel is supplemented in time by fluorine from external sources. It provides a depot for an almost linear diffusion to the central part of the enamel (approximately 0.5 mm from surface).

d. *"Plateau" effect*: in the central part of the enamel the fluorine concentration at birth is near zero, but it increases with age. The fluorine concentration is found to form a "plateau" over a distance of about 0.2 mm in the central part of the enamel.

e. *Dating*: the level (concentration) of the c 0.2 mm wide plateau gives the absolute age of an "unknown" tooth. The absolute age can be computed by using the following formula, utilizing the rate of fluorine diffusion into the central part of the enamel: $DF = 5 \times 10^{-14} \text{ cm}^2/\text{sec}$. A site calibration is necessary depending on variations in the speed of the diffusion process as a result of different environmental conditions.

Among the over 30 diffused elements which were investigated by SIMS, realistic chances of archaeological dating seem to exist also with other diffused elements such as Ba, Sr, Al, Si, Mg, B, Li and C (significance for chronological studies in decreasing order). These elements may be expected to diffuse on a different time scale compared with fluorine.

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