

#### **Definition**

The use of an instrument to determine the presence of particular elements in a material/sample. The range of elements which can be detected as well as the accuracy, precision and sensitivity (limit of detection) vary widely between different instruments (see below).

#### **Purpose**

Chemical analysis of archaeological and historical metals and metalworking debris is undertaken for a number of different reasons. In some cases, chemical analysis is undertaken to confirm an idea gained from a simple visual examination of a material. For example, a metal artefact may have a green surface but chemical analysis can be used to confirm that it contains copper. In some cases, however, it may be necessary to determine a range of elements, in particular to identify the type of alloy. In many cases, especially where a substantial body of comparative data is available, it may be useful to quantify the presence of a wide range of elements. Such quantitative analysis of metals and metalworking debris may tell us how a metal was made, where the raw materials came from and how it was traded. Scientific analysis requires time (and sometimes money) and many techniques will lead to at least some damage to the material. It is essential that analysis is only undertaken once it has been determined that the potential research outcomes outweigh the cost, time and potential damage.

#### **Corrosion and sample preparation**

Corrosion is a significant factor in the chemical analysis of any archaeological or historical material. Exposure to the environment (especially a burial environment) for hundreds or thousands of years will lead to changes in the chemical composition of the surface of metals and metalworking debris. If chemical analysis is applied to this surface then it may provide information of limited use; for example, copper alloys which contain zinc (HMS Datasheet 202) may have corroded surfaces which have suffered from zinc loss to such an extent that virtually none of this element is detected. To obtain a chemical analysis which is representative of the material as originally manufactured, it is necessary for the analysis to be of the uncorroded core: in most cases, this will require taking a sample. These are often prepared in the same way as metallographic samples (HMS Datasheet 105): they are embedded in resin and ground and polished to reveal a cross-section. The samples once prepared can be archived for future analysis (HMS Datasheet 108). Some techniques make use of material which is removed using a drill (or even a laser, see below) but these samples are usually consumed during analysis.

#### **Homogeneity and sample size**

Some materials are homogeneous and a small sample from virtually any part of the artefact will be suitable for analysis. In most cases, however, metals and metalworking debris are not homogeneous and care must be exercised in selecting a sample. Some techniques (see below) allow the analysis of milligrams of material taken from an area tens

of microns across (1000 microns = 1mm). While this is attractive to those keen to ensure the long-term curation of metal artefacts and metalworking debris, it may not be useful for heterogeneous materials. Most metals contain non-metallic inclusions which can be tens of microns across and most metalworking debris contains at least two different phases, each of which may be hundreds of microns across. The only certain way to determine the appropriate sample size for chemical analysis is to examine the microstructure (HMS datasheet 105). Some instruments (see below) allow the simultaneous examination of microstructure and determination of chemical composition. This is particularly important where the same elements are present in both the metal and the non-metallic inclusions.

#### **Precision, accuracy and sensitivity**

The interpretation of quantitative chemical analyses requires a careful consideration of precision, accuracy and sensitivity. The most straight-forward issue is sensitivity which is also often known as limit of detection (LoD). Most instruments will indicate the concentration of a particular element, but only down to a certain concentration, the limit of detection. The element in question may be present at lower concentrations but cannot be detected. Data should never be reported as containing 0% of a particular element; instead nd (for not detected) or <0.1% (less than 0.1wt%, if this is the limit of detection) should be used. Note that the limit of detection depends on the element, the type of sample, the instrument used, and even the presence of other elements.

Most instrumental techniques will provide data with a high degree of precision but with poorer accuracy. The distinction between accuracy and precision is an important one which can be illustrated by analogy with a wrist watch. This will usually indicate the time to within one second; it tells the time with a precision of one second. Nevertheless, the watch might be a full minute slow or fast; it is not an accurate indication of the time. Accuracy of chemical analysis can be improved through the analysis of reference materials of known composition. Ideally a number of reference materials of similar composition to the unknown material would be analysed at the same time. The reference materials can be used to correct the initial data obtained from the unknown samples. Unfortunately there is limited availability of reference materials relevant to early metallurgy. In some cases the analyst is faced with a sample for which there are no suitable reference materials.

#### **EDXRF**

The most versatile technique employed for the chemical analysis of archaeological and historical metals and metalworking debris is without doubt energy dispersive X-ray fluorescence (EDXRF) spectrometry. X-rays are fired at a sample or object which then gives off (fluoresces) new X-rays: the characteristics of these fluorescent X-rays reflect the range of elements present and their respective concentrations. The X-rays are detected using a silicon chip which allows the simultaneous detection of almost all elements in the sample (light elements such as boron,

oxygen and nitrogen are rarely detectable). An EDXRF spectrometer will produce a spectrum which contains many different peaks (depending on the range of elements present). The simultaneous detection of all elements makes EDXRF a fast technique. EDXRF sensitivity varies depending on the instrument used and the element sought: it can be as high as 1wt% or as low as 1ppm (part per million). Depending on the instrument, the X-ray beam may be directed on an area as large as several millimetres across or as small as a few tens of microns across.

EDXRF can be used semi-quantitatively in a completely non-destructive manner or it can be used quantitatively on carefully prepared samples. The ability to analyse artefacts without damaging them makes this technique appealing to museums and others concerned with the long-term curation of metal artefacts and metalworking debris. The availability of portable versions of EDXRF spectrometers allows the chemical analysis of artefacts which are too large for transport to a laboratory. EDXRF is, however, a surface technique and if it is applied to a corroded surface it will usually provide information about that corroded surface rather than the uncorroded core.

#### WDXRF

A wavelength dispersive X-ray fluorescence (WDXRF) spectrometer operates in a similar way to an EDXRF spectrometer; however, the X-rays are detected with the aid of a crystal which allows the examination of just a part of the spectrum in detail. This provides the WDXRF with its superior sensitivity compared to EDXRF, however, it means that the analysis usually takes longer to complete.

#### SEM-EDS

Fluorescent X-rays are also generated when a material is examined using a scanning electron microscope (SEM). The strength of a SEM fitted with an energy dispersive X-ray spectrometer (usually abbreviated to SEM-EDS or SEM-EDX) lies in the simultaneous examination of microstructure and chemical composition. Inclusions within a material as small as a few microns across can be imaged and analysed. SEM-EDS can be used to map the distribution of elements across part of a sample (X-ray mapping). Such instruments usually provide better chemical analysis for light elements (sometimes including light elements such as boron) compared with EDXRF; however, the sensitivity for many heavy elements (strontium for example) is generally worse.

#### SEM-WDS (microprobe)

An SEM may also be fitted with a wavelength dispersive X-ray spectrometer which will improve the sensitivity (limit of detection) of the chemical analysis compared to SEM-EDS but will require more time to complete the analysis. Some instruments of this general type have been designed specifically with chemical analysis in mind rather than imaging. Such electron microprobes or electron probe micro-analysers (EPMA) provide high-quality chemical analyses.

#### ICP

Inductively coupled plasma (ICP) spectrometers offer improved sensitivity compared to the techniques described above; however, the samples analysed (which can be as small as a small as a few milligrams) are destroyed in the process of analysis (the sample is heated to temperatures in excess of 7000°C). Most ICP spectrometers use samples which have been dissolved in strong acids, although some instruments use a laser to remove material from the surface of an object (leaving a hole tens of microns across, that is invisible to the naked eye). There are two different types of ICP that have been commonly used: atomic emission spectroscopy (ICP-AES) and mass spectroscopy (ICP-MS). ICP-AES generates a light spectrum which reflects the range and concentration of the elements present in a material. ICP-MS divides the plasma (using a magnetic field) into constituent elements/isotopes.

#### XRD

X-ray diffractometers (XRD) do not provide direct information on chemical composition but can be used to identify crystalline materials. This is especially useful where a sample may contain allotropes (same chemical composition, different crystal form). In addition, many compounds have only subtly different chemical formulae (e.g. copper-iron-sulphides) and so may be difficult to identify on the basis of chemical analysis alone. XRD samples are usually prepared by crushing to a fine powder.

#### EBS

An electron back-scattered diffraction (EBSD) detector fitted to an SEM can provide information about the nature of crystalline materials within a polished specimen. It can also indicate grain orientation.

*David Dungworth  
October 2012*