AN INTRODUTION TO THE CONSERVATION SCIENCE OF ARCHAEOLOGICAL INORGANIC OBJECTS

KOEZUKA Takayasu
FURIHATA Junko

NATIONAL RESEARCH INSTITUTE FOR CULTURAL PROPERTIES, NARA

1. Introduction

The conservation science is involved with cultural and social sciences, such as archaeology, art history, the history of handicrafts, architectural history, and ethnology. From the viewpoint of material science, conservation science makes it possible to provide important information both to cultural and social science. In addition, conservation science is intrinsically associated with almost all fields of natural science, and is growing as a field of disciplinary research.

When we consider cultural properties according to the types of materials, we can classify them generally into three categories. The first is organic objects that have their origin in the animal and/or plant. The second is inorganic objects made of metals, siliceous and related materials. The last is the objects that form a heterogeneous, such as metal with wood. Most cultural properties are made out of a number of materials, rather than single material.

Archaeological objects are often unearthed in good conditions, although they are buried in the ground for long periods of time. This proceeds probably from the slightly stable conditions of subterranean. However objects are found in good condition, some deterioration come in rapid. By excavation their environment change and it is trigger for the deterioration of excavated objects. This sometimes result in their retainment nothing of the original that was formed when they were excavated. In particular, this occurs excavated wooden and iron artifacts.

All materials including the archaeological materials have a life span and are faced with a process of deterioration. Cultural properties reveal a lot of information about the past, and often have great artistic value. It is important to extend the life of cultural properties and preserve them as long as possible, without impairing the information and the value they contain.

Here is shown the outline the nature of excavated materials and the application of the science that is intended to preserve them for future generations.

2. Research Methods for inorganic objects

In conservation science, the research is preferable to examine the materials without collecting samples so as to save from damage or destruction.

2-1: Research methods for materials

Non-destructive methods for research materials are generally performed by using some equipment such as X-ray fluorescence analysis, PIXE analysis and radio-active analysis. The X-ray fluorescence analysis is the most widely used for investigative(Fig.1). The elements in the specimen are identified from their place in the X-ray spectrum or their energy and a quantitative analysis is made, by measuring the intensity of the X-rays. The equipment used for this research is usually modifications of standard system to adapt various size and shape. However, radio-activation analysis and X-ray microanalysis are also often used. These are possible to carry out qualitative and quantitative analyses on a quite small sample.

Fig.1 X-ray fluorescent spectrometer

In the case of collecting sample is permitted, atomic absorption spectroscopic analysis and plasma luminescent spectroscopic analysis are widely used to research for cultural properties. The X-ray diffraction method is also used to identify the crystal structures that sort of mineral composition, deposit on stone statues, corrosion and pigments (Fig.2). It is difficult to carry out non-destructive measurement using any of the above methods, but they need small amounts of sample.

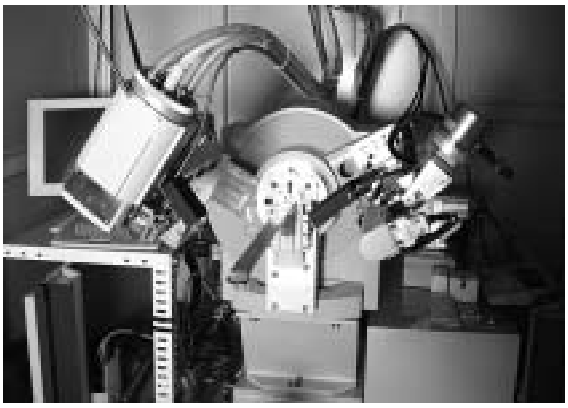


Fig.2. Non-destructive X-ray diffraction system

2-2: Investigate into the inner structure

In order to study and preserve archaeological objects, it is necessary to know exactly what is inside them, as well as to examine the exteriors of the objects. This process is indispensable for clarify the techniques how to make the objects, but it helps also to obtain the information needed to clean and restore the objects. In the field of conservation science, X-ray radiography has become a popular method for investigating the inside of objects. Recently, computer image processing has also begun to be used. X-ray computerized tomography (CT) which allows you to obtain a three-dimensional view of the inside an object. So it has become possible to get much more detailed information. Neutron radiography has also been put to practical use to develop a method to obtain different information from that of X-ray radiography.

2-3:Influence of environment

It is necessary for keep them safe that the environment where excavated objects were buried is cleared. For example, by examining the environment you will be able to learn the causes of deterioration and weathering. The results of this examination will provide important information during the investigation of the materials. In addition, it will also be used to determine optimal conditions (temperature, humidity, and lighting) for exhibiting the cultural property and for designing the storage.

In these modern times, metallic and stone cultural properties that are displayed outdoors are often damaged by acid rain or automobile exhaust fumes. Furthermore, research in prevent damage by mold and insects is also important to creating a good environment for storage and display.

2-4: Restoration

Traditional techniques for preserving and restoring cultural properties have always been recognized to be important, as well as the selection of the correct materials and the best technology. We emphasized that traditional materials and techniques are important for preserving or restoring works of art, handicrafts, and buildings. For example, when one repairs *Urushi* handicraft object, one should use the same typed of *Urushi* as was used on original. Historical Japanese buildings are usually repaired and preserved by *miyadaiku* (carpenters who specialize in building shrines and temples), who have learned the traditional techniques for generations.

However most of the cultural properties are not clear how they were manufactured, and so there are no known traditional restoration techniques. Since the objects have already been changed because of the physical and chemical processes of aging, it is necessary to use available restoration techniques that take advantage of science.

3. Conservation science of Inorganic Objects (Metals)

The inorganic object embraces earthenware, pottery, roof tiles, stone artifacts, glass, metallic artifacts or the like. Ancient metallic artifacts are made of many materials. Some are made of a single metal, such as iron, gold, copper, silver, tin or lead. Some are made of bronze (copper alloy). There are also composite objects made of several metals, like plated copper onto iron base. Metallic artifacts occur a great problem due to their corrosion, especially if they have been buried in the ground, and they are also difficult to protect against oxidation while in storage.

Fig.3. The Iron cannon ball excavated from sea and natural dried. Iron rust has increased rapidly.

Corrosion is caused by the interaction of oxygen, water and various ions. Chloride ions play a major role in the advance of corrosion (Fig.3,4). Excavated metallic objects are usually scientifically examined to know their inner structure and materials, and applied preservation treatment before display or store. In the study of cultural properties, the shapes and surface of the objects are very important, and therefore you must not alter their shapes for the sake of research.

Fig.4. The bronze disease is formed with the chemical reaction of copper and the chloride ion.

In general object research is performed by using some methods such as non-destructive analysis and/or microanalysis. The study of metallic objects usually attempts to know the techniques used for producing them and the extent they have corroded. X-ray radiography has long been used for these purposes. The first use of this method in Japan was in 1935, to research a pillow made of glass beads which was excavated from the *Inariyama*-tumulus in *Osaka* prefecture. In 1978, a sword was excavated from the *Inariyama*-tumulus in *Saitama* prefecture and X-ray radiography was used with great success. It was able to decipher a 115-character inscription written in gold inlay on that sward. Since that time, the use of X-ray radiography has spread rapidly in the research for excavated objects and nowadays X-ray CT is also applied to investigate objects. This has made it possible to observe in more detail by obtaining sectional images of an arbitrary part or by constructing 3-D images.

In addition, with the development of new analytical equipments and advances in computer technology, examining methods for inorganic objects have also progressed rapidly. At present, the most popular method is X-ray fluorescence analysis, which allows non-destructive analysis. In this method, primary radiation from the X-ray tube strikes the object, which emits characteristic X-ray spectra of the elements contained in the specimen. According to these characteristic X-ray spectra measured, the elements in the specimen are identified and the intensity of X-ray beam will permit a quantitative analysis. The use of the PIXE method for examining objects has also been attempted.

However, most metallic objects corrode while they were in the ground and their surfaces change greatly so it is difficult to measure their original composition. This makes it difficult to interpret the results of non-destructive analyses correctly. Recently new X-ray fluorescence analysis equipment has been developed that can be used to examine micro-areas (10μmφ). After an extremely small area is polished, the freshly exposed surface can be analyzed to show the original composition and this leads to the study of material history and the site where the material was produced.

Generally, an excavated metallic object is covered with various types of oxides. In some cases, the oxides will insulate the object from further corrosion, while in other cases some kinds of oxide make the original material more corrode. To inhibit the growth of corrosion after excavation, it needs identifying the causes of the corrosion and removing them. Commonly there are two causes of metal corrosion, one is both oxygen and water in the environment, the other is soluble salts contained in secondary products (such as oxidized materials) adhering to the objects. Analyzing these secondary substances could lead to better understandings to the object.

A：Iron Objects

Iron objects are usually covered with oxi-iron hydroxide and they have three types: α-, β-, and γ-FeOOH. The γ-FeOOH is produced in the presence of chloride ions and causes a particular problem for preservation. This corrosion product was first discovered by Matsuo Nambu, inside an iron meteorite, about 30 years ago. After that, it was reported that γ-FeOOH is present in excavated iron objects (Fig.5) and it get into by chloride ions (Makoto Shima and Hideo Yabuki, 1979). At present, before preservation, we examined by X-ray diffraction analysis to know the extent of oxidation on iron objects. To determine the treatment method, the presence of chloride ions and anions such as sulfide ions, fluorine ions, and nitrate ions are analyzed quantitatively. Chloride ions are a major cause of the corrosion action on objects (especially in Japan, where the relative humidity is so high), and so they should be removed (i.e., the object should be desalinated) to the best extent possible. There are two methods for desalinating iron objects: the dry methods and the solution (or washing) methods. The alkaline solution method is widely used in Japan as follows; Iron objects soaked in deoxidized water are put in an autoclave that is a modified medical sterilizer. Regulate the temperature inside the autoclave at 120 degrees centigrade with high pressure as mean of extracting chloride ions

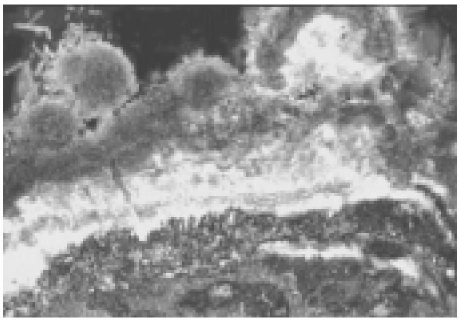


Fig.5. β-FeOOH, “AKAGANEIT” This corrosion products was found from the inside of sword.

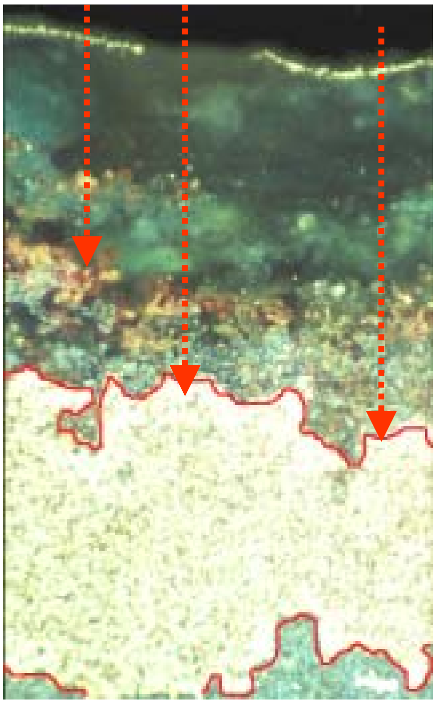
Fig.6.The High temperature and high pressure device. (chloride removal for iron objects.)

and sulfide ions. Iron objects are then impregnated with acrylic resin in order to consolidate and to insulate the objects from the air.

B : Copper objects

Copper and bronze objects, as well as irons, corrode and degrade in the presence of chloride ions. For example, bronze mirrors that seemed stable when excavated often corrode within some years, and finish its life with degradation of the entire object. This phenomenon is called “bronze disease”. Copper chloride is detected in the corrosion that develops on bronze objects. The non-destructive X-ray diffraction analysis with parallel beams can be used to obtain diffraction data about corrosion without damaging cultural property and contribute to the early detection of bronze disease. Bronze disease is interfere by removing the causative substance, the chloride ions. However, the removal of chloride ions from bronze objects is difficult in most cases, because there is often a risk of change the color of the object or damages it in other ways. Therefore, bronze objects are usually protected from chloride ion attack by giving them a protective film over the fresh metal to prevent the corrosive action. This is called the benzotriazole method (Fig.7), a type of chemical protection. It is generally used for treating excavated copper and bronze objects.

B T A



$CuO + BTA \rightarrow Cu\ BTA$

$Cu_2O + BTA \rightarrow Cu\ BTA \rightarrow Cu\ BTA + Cu\ BTA$

Fig.7. BTA treatment:BTA makes a stable thin protective film around the inside of the copper-metal as the chemical reacts with copper-metal and copper-oxide. This film protects the metal from chloride. This method has been used all over the world since 1968.