Abstract: Following modern trends in art objects connoisseurship, through examination of the structure of art objects supports traditional studies conducted by art historians based on composition, iconographic and stylistic comparisons. It must be emphasized that complete technological examinations are carried out by means of comprehensive physical and chemical studies. Among various methods used for the examination of art objects, methods which apply neutrons such as instrumental neutron activation analysis (INAA), prompt gamma activation analysis (PGAA) and neutron-induced autoradiography are crucial due to their high sensitivity, reproducibility and capability of simultaneous determination of several tens of elements.

Systematic studies on art objects using instrumental neutron activation analysis and neutron autoradiography have been carried out in the Institute of Nuclear Chemistry and Technology. It was possible to accumulate a number of essential data on the concentration of trace elements particularly in chalk grounds and pigments (such as lead white, lead-tin yellow, smalt), Chinese porcelain, Thai ceramics, silver denarius, jewelry made of copper alloys, as well as in the clay fillings of Egyptian mummies. The above mentioned examination of art objects prior to their conservation helps to determine precisely the materials used in the process of creating art objects, as well to identify the approximate place of origin of particular materials.

1. INTRODUCTION

Neutrons are associated in many people’s minds with nuclear reactors, nuclear power station, atom bombs, and devastating effects. The thermal neutrons that generally are used to study works of art and archaeological objects are low energy, relatively mild particles. They are electrically neutral and infinitesimally small, and for these reasons will penetrate most materials with minimal disturbance. Its potential as an art and an archaeological tool was recognised not long after the dawn of the nuclear age [1, 2]. For this purpose are in common use various types of neutron activation analysis such as: instrumental neutron activation analysis (INAA), prompt gamma activation analysis (PGAA), and special variety of neutron activation analysis – neutron – induced autoradiography. At present, though there are other methods with comparable sensitivity, neutron activation analysis still offers new capabilities thanks to the development of electronics and availability of increasingly technological advanced instruments. This results in enhanced precision, accuracy and detectability.

Since 1989, systematic studies of works of art and archaeological objects have been conducted in the Institute of Nuclear Chemistry and Technology in Warsaw, in collaboration with the Academy of Fine Arts in Cracow, Academy of Fine Arts in Warsaw, the Institute of Conservation at the Nicolaus Copernicus University in Torun, National Archaeological Museum in Warsaw as well as the National Museums in Warsaw and Wroclaw. They are mainly concerned with the determination of trace elements in pigments, ceramic materials, ores and copper alloys. Recently our research capabilities have been extended by constructing a station for neutron-induced autoradiography of paintings at the MARIAC nuclear reactor at
Swierk near Warsaw. The results of these studies throw new light on the authenticity and individual history of the objects examined.

2. ACTIVITIES

The work carried out in the Institute of Nuclear Chemistry and Technology in the last decade was mainly concerned with panel paintings and archaeological objects.

Analysis of results obtained should answer the following questions: 1) are the distributions of trace elements in the materials analysed characteristic of a given material? 2) is it possible to establish groups of objects that exhibit the highest similarity? For this purpose we employ multivariate analysis of clusters using the STATISTICA program (StatSoft) [5].

2.1. Painting

The objects examined so far included:

- Polish panel painting from the Krakowsko-Sadecka School and Malopolska School from the period 15th-16th century, owned mainly by the Diocesan Museum at Tarnow (25 objects) [3,5,6,7].
- 15 and 16th century painting from the Silesian School owned by the National Museums in Warsaw and Wroclaw (18 objects) [5,6,7].
- 16th century Dutch and German paintings of the so called the Lanckorofiski Collection from the collections of the Warsaw Castle (19 objects) [5,6].
- 15-18th century Venetian painting from the collections of the National Museum in Warsaw (33 objects) [6,7].

The research was carried out in collaboration with the Academy of Fine Arts in Cracow, the Institute of Conservation at the Nicolaus Copernicus University in Torun and Academy of Fine Arts in Warsaw.

The studies were concerned with the determination of trace elements in lead white, chalk and grounds. Their purpose was to answer the question whether the trace element distribution pattern was characteristic of and unique for the material examined or whether it resembles the pattern for materials used by another important European workshop, which could have influenced the author of the painting examined.

It follows from the comparison of the data sets obtained for the paintings of the Malopolska School that masters working in their circle used lead white from various sources. The Malopolska School used lead white with high zinc concentration at a constant level of several tens of ppm. This concentration is higher than in paintings of the Silesian School. Also the trace element distribution in the case of the Silesian School is more similar to the distribution characteristic for Dutch and German paintings. It can be supposed that in the case of Malopolska School lead was obtained from local deposits from the Olkusz region. In order to determine the degree of similarity between Malopolska and Silesian Schools analysis of clusters, based on their features, was carried out. The results of analysis of 41 objects described by 32 features representing the concentrations of 32 elements are presented in Fig. 1 in the form of a dendrogramme [3,5,6,7].

2.2. Sculpture

Attempts have been made to establish the origin of a precious 14th century alabaster sculpture of St. Jack's Madonna. For this purpose alabaster from Cracow and Lvov deposits was analyzed. The concentration of trace elements in the sculpture and in samples from the quarries was compared. The results of this analysis allowed for the exclusion of one of the
Fig. 1. Cluster analysis of 41 paintings of Malopolski School and Silesian School described by 32 features.
hypotheses of art historians that the sculpture was made of alabaster from Malopolska Region in Poland as well as for the reconstruction of the original polychromed layers of the sculpture [8]. The works have been carried out in co-operation with the Academy of Fine Arts in Cracow. Comparative analyses of alabaster from other Polish deposits from the region of Opolski Silesia and Lower Silesia are still being carried out.

2.3. Archaeology

The main purpose of trace elements analysis in studies of archaeological objects is to establish the process of formation of a given work of art or an object of daily use, the place of its origin and to identify the material it is made of. It is also possible to establish commercial links between various centres.

The objects examined included:

- clay fillings of sarcophagi of Egyptian mummies from the period of 21st Dynasty, as well as from the Ptolemaic and Roman periods owned by the Archaeological Museum in [5,6].
- 12th century Chinese porcelain and 14th century Thai ceramics from the Sawankhalok region, from collections of the National Museum and Museum of Asia and Pacific Ocean in Warsaw (28 objects) [5,6].
- silver and gold antiquities from collections of the Department of the Iron Age of the National Archaeological Museum in Warsaw, dated 1st century B.C. (8 objects) [6].
- antiquities from the Roman Period (1st century B.C.?): fragments of jewelry made of copper alloys as well as and foundry moulds (century?) for tin products (17 objects).
- a selected set of 115 Roman silver denarii, minted during the period 138 A.D. to 161 A.D. have been examined in order to determine their silver and copper contents; all these denarii have been found at Romanów near Krasnystaw in Poland; the Cu/Ag mass ratios were determined for the detection of debasement and ancient counterfeiting of coins.

Analysis of trace elements in sarcophagi clay fillings of Egyptian mummies is an important source of information about the history and origin of a given sarcophagus. The concentration of the elements determined is similar for three objects (from 19th Dynasty and Ptolemaean periods), whereas the Roman sarcophagus exhibits distinct differences in the concentration of iron, arsenic, cobalt, nickel, hafnium and gold. The results obtained provide the initial data for a data base, which will enable comparisons of materials used in the Ancient Egypt [6].

The studies on Chinese porcelain and Thai ceramics aimed at solving the question of authenticity of the given object. Both extensive collections of the National Museum and Museum of Asia and Pacific Ocean are being examined using INAA and XRF in order to determine the elemental composition of the ceramics and to answer the question if wares of similar stylistic features came from one or more workshops located in the same region [5,6].

The goal of studies on the ancient silver and gold antiquities, carried out in collaboration with the National Archaeological Museum in Warsaw is to obtain information which would enable further studies on ancient goldsmith technologies, localization and range of goldsmiths' workshops, emerging and adaptation of ornamentation styles and commercial links inside the so called Barbaricum and with the Roman Empire. In our opinion, first general conclusions could be drawn on the basis of analysis of about 300 objects. In addition to objects made of ores, the examined materials include various antiquities made of other metals (copper alloys, iron, tin).

The results of preliminary analyses indicate that ancient jewelers obtained metal from local deposits-nuggets, which throws new light on the problem of old silver and gold metallurgy in the territory of Poland [6].

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2.4. Neutron-induced autoradiography

Apart from INAA, SEM-EDX and XRF, while conducting complex examination of the Venetian painting, we have included a modified neutron activation, i.e. neutron-induced autoradiography. All the paintings under analysis were irradiated in a specially designed station at the research reactor MARIA in Swierk.

Fig. 2. J. Tintoretto, *Portrait of a Venetian Admiral*

Fig. 3. X-ray image

Fig. 4. First autoradiograph with exposure time 3 hours

Fig. 5. Third autoradiograph with exposure time 32 hours

Beta rays emerging from the painting surface irradiated by thermal neutrons recorded on a X-ray film display distribution of elements used for creating individual layers of the painting. It allows for tracing the particular phases of the painting structure invisible for the naked eye.
We have obtained interesting results while examining the *Portrait of a Venetian Admiral* (oil canvas) by Jacopo Tintoretto [4] (Fig.2-a photograph taken before conservation). The X-ray reveals a hidden portrait of a man in a different garment than the admiral and with a headgear (Fig.3). The autoradiograms shows facial features and the discontinued stage of the hidden painting (Fig.4, Fig.5) [9,10].

### 3. CONCLUSIONS

The last decade of collaboration between the Institute of Nuclear Chemistry and Technology and art historians, conservators and archeologists in the field of examining works of art has proved very successful. It must be emphasized that among various methods used for technological examinations of art objects the INAA is essential, however, it can be truly beneficial only after combining results obtained from the use of other methods.

### References

1. G. Harbotle, Activation Analysis in Archaeology. Radiochemistry, 3, (1976), 33