

Characteristic Elemental Composition of Oil Pigments using Instrumental Neutron Activation Analysis

Yong-Sam Chung¹, Sun-Ha Kim¹, Gwang-Min Sun¹, Jong-Myung Lim¹, Jong-Hwa Moon¹, Young-Jin Kim¹,
Sung-Jin Lim², Yu-Na Song², Ken Kim²

¹Korea Atomic Energy Research Institute, 1045 Daedeok-daero, Yuseong-gu, Daejeon, 305-353, Korea.

²National Museum of Contemporary Art, St. 209 Gwangmyong, Gwacheoni, Gyeonggi-do, 427-701, Korea.
yschung@kaeri.re.kr

1. Introduction

The principal aim of this study is to identify the applicability of instrumental neutron activation analysis as a non-destructive examination tool for the quantitative composition analysis associated with authentication, restoration, and conservation of art objects in the field of cultural heritage. Generally, the chemical composition of pigments are associated with the colors such as white, yellow, orange, red, green, blue and black, and it varies with raw materials of pigments. According to the colors of a different pigments, chemical compositions are as follows; for example, white pigments were used for a mixture of $Pb(CO_3)_2$, $PbSO_4$, PbO , $Pb(OH)_2$, ZnO , ZnS , TiO_2 , $BaSO_4$, $CaCO_3$, Al_2O_3 , As_2S_3 , etc.; black pigments were series of carbon black, borne ash, $MnO+Mn_2O_3$, etc.; red pigments were Fe_2O_3 , Pb_3O_4 , HgS , $PbMo_4$, $CdS+CdSe$, etc.; brown and yellow pigments were $PbCrO_4$, $ZnCrO_4$, $CdS-ZnS$, $K_3[Co(NO_2)_6]$, $Pb(SbO_3)_2$, $C_{19}H_{16}O_{11}Mg$, $SrCrO_4$, etc.; green pigments were Cr_2O_3 , $Cr_2O(OH)_4$, $Cu(C_2H_3O_2)_2 \cdot 2Cu(OH)_2$, $Cr_2O_3-Al_2O_3-CoO$, etc.; blue pigments were $Fe_4[Fe(CN)_6]_3$, $CoO-Al_2O_3$, $Na_{8-10}Al_6Si_6O_{24}S_{2-4}$, etc. [1,2].

This first step is to obtain quantitative data on the concentrations of major, minor and trace elements in oil pigments and to explain pigment sources by statistical treatment as reported in many literatures [3-5]. The determination of major, minor and micro elements in the subject materials are essential in many fields of basic science and technology as well as commercial and industrial fields. In particular, direct analysis of a sample offers a more effective investigation method in these fields. Instrumental neutron activation analysis (INAA) has an inherent advantage of being a non-destructive, simultaneously multi-elemental analysis with high accuracy and sensitivity.

In order to characterize the elemental contents of art objects, the quantitative analysis of oil pigment series was carried out using NAA facilities of the HANARO research reactor at the Korea Atomic Energy Research Institute in collaboration with the National Museum of Contemporary Art in Korea.

2. Experimental

2.1 Sampling and sample preparation

23 Rembrandt oil pigments of white, black, grey, brown and green colors were recently collected at the

Korean market. The collected samples in cleaned glass bottles were naturally dried at room temperature for a week and stored in a controlled atmosphere cabinet (20°C, 50% relative humidity). For short and long term neutron irradiation of the samples, two kinds of samples of 10 ~ 200 mg were weighed and put into a fresh polyethylene vial and heat sealed.

2.2 Neutron irradiation and gamma ray spectrometry

Pigment samples were irradiated with thermal neutrons using a Pneumatic Transfer System (PTS, $\Phi_t = 4.0 \times 10^{13} \text{ n}\cdot\text{cm}^{-2}\cdot\text{s}^{-1}$, $R_{Cd} \sim 200$) in the HANARO research reactor at the Korea Atomic Energy Research Institute (KAERI). All samples were irradiated at the same position to minimize any geometric errors. For neutron flux monitoring, activation wires (R/X activation wire, Reactor Exp. Inc.) such as Au-Al and Fe were used.

Considering the given neutron flux and distribution of the irradiation facilities, the optimum analytical conditions including irradiation time, cooling time and counting time were obtained semi-quantitatively through measured signal-to-noise ratios.

For the measurement of short-lived radionuclide (^{28}Al , ^{49}Ca , ^{38}Cl , ^{66}Cu , ^{27}Mg , ^{56}Mn , ^{24}Na , ^{37}S , ^{122m}Sb , ^{87m}Sr , ^{51}Ti , ^{52}V , ^{69m}Zn), the irradiation (T_i), decay (T_d) and counting time (T_c) were less than 2 minutes, 2~6 minutes and 400 seconds, respectively. For the medium and long-lived radionuclide (^{110m}Ag , ^{76}As , ^{82}Br , ^{47}Ca , ^{115}Cd , ^{141}Ce , ^{60}Co , ^{51}Cr , ^{134}Cs , ^{42}K , ^{59}Fe , ^{181}Hf , ^{140}La , ^{99}Mo , ^{24}Na , ^{147}Nd , ^{122}Sb , ^{124}Sb , ^{46}Sc , ^{153}Sm , ^{75}Se , ^{85}Sr , ^{187}W , ^{65}Zn), the samples were irradiated for 1 hour, and measured twice controlled of cooling and counting times, $T_d = 5$ and 14 days, and counting time, $T_c = 5000$ and 20,000 seconds, respectively. The optimum analytical conditions of INAA is presented in Table 1.

Table 1. Optimum conditions of oil pigments by INAA

Radionuclide	Irradiation time	Decay time	Count time	Nuclides Used
Short-nuclides	< 2 min.	2~6 min.	400 sec.	^{28}Al , ^{49}Ca , ^{38}Cl , ^{66}Cu , ^{27}Mg , ^{56}Mn , ^{24}Na , ^{37}S , ^{122m}Sb , ^{87m}Sr , ^{51}Ti , ^{52}V , ^{69m}Zn
Medium-nuclides	1 hr.	5~7 da.	5000 sec.	^{110m}Ag , ^{76}As , ^{82}Br , ^{47}Ca , ^{115}Cd , ^{141}Ce , ^{60}Co , ^{51}Cr , ^{134}Cs , ^{42}K , ^{59}Fe , ^{181}Hf , ^{140}La , ^{99}Mo , ^{24}Na , ^{122}Sb , ^{46}Sc , ^{153}Sm , ^{187}W , ^{65}Zn
Long-nuclides	1 hr.	10~14 da.	20000 sec.	^{141}Ce , ^{60}Co , ^{51}Cr , ^{134}Cs , ^{59}Fe , ^{181}Hf , ^{147}Nd , ^{46}Sc , ^{124}Sb , ^{75}Se , ^{85}Sr , ^{65}Zn

The measurements were carried out using a calibrated gamma-ray spectrometer combined with an HP Ge semiconductor detector (GEM 35185P), a multi-

channel analyzer (919A MCB), and Gamma Vision software from EG&G ORTEC Co. The calculation of neutron flux and element contents were carried out using the new Windows PC-code, and Labview software of KAERI with a nuclear data library, which was developed at this laboratory for rapid and simple data treatment for a gamma-ray spectrum obtained from given measurement conditions.

2.3 Analytical quality control

Analytical quality control was carried out using certified reference materials (NIST SRM 2709, San Joaquin soil) and standard metals.

In INAA, main uncertainty sources are produced from sample irradiation and gamma ray measurement. Therefore, the information on a neutron flux and distribution of an irradiation site are same the basic requirements for NAA due to the variation of reactor operation conditions. Activation wires (R/X activation wire, Reactor Exp. Inc.) such as Au-Al, Ni, and Cd box were used for a neutron flux monitoring and a measurement of the cadmium ratio. These values were used for an evaluation and geometry correction of a sample when a sample was irradiated.

3. Results and discussion

For the estimation of measured data confidence, the measurement uncertainty and the detection limit of measured elements were evaluated, and the relative error of most elements were less than 10%.

For the identification of characteristic elemental composition of oil pigments, concentrations of 31 elements in the collected samples were non-destructively analyzed by using INAA. The level of concentration of major component elements such as Al, Ca, Fe, Mg, Na, S, Ti and Zn in pigments are up to 50%, except C, P and Pb which can not analyzed by INAA.

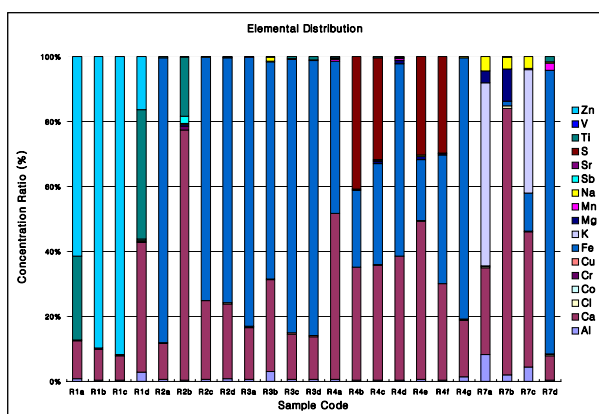


Fig. 1. Elemental distribution ratio of 23 oil pigments.

Among the analytical results obtained from INAA, the relative comparison of the concentrations of 17 characteristic elements of Al, Ca, Cl, Co, Cr, Cu, Fe, K, Mg, Mn, Na, Sb, Sr, S, Ti, V and Zn were carried out between 23 pigment samples as shown in Fig. 1. From the results, the samples can be classified into nine kind

of pigment groups and there are different chemical compositions within each group. Hierarchical cluster analysis was used to identify a raw material group [6], and the dendrogram of the results using the nearest neighbor method is shown in Fig. 2. Data below MDL accounted for about 24% in the analyzed data base. These data points were filled by the averages of the analyzed specific elemental data for statistical treatment. Seven groups can be classified from the samples, and this is quite similar to the classification for groups of pigment colors as shown in Fig. 1.

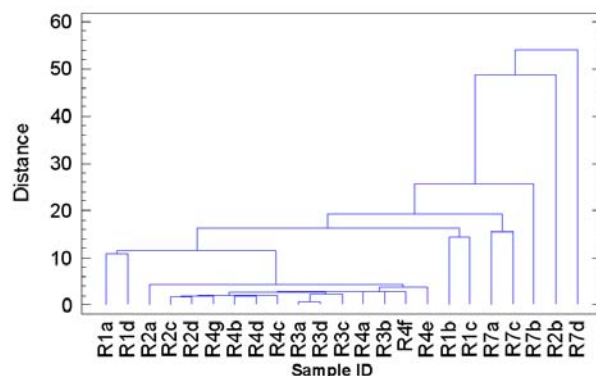


Fig. 2. Dendrogram of cluster analysis for oil pigments.

The results of INAA for the pigments were successful in classifying distinct elemental composition groups. Thus, the analytical results for major and trace elements will be useful to identify the application and the possibility of the characteristics of pigment sources, the similarity degree of constituents, the presumption and classification of place, and the period and processes of a production according to the origin of materials. Further statistical treatments such as correlation and pattern analysis, principal components analysis, multivariate and discriminant analysis will be applied to the data set measured.

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REFERENCES

- [1] R. Klockenkamper, A. von Bohlen, L. Moens, *X-Ray Spectrom.* 29, 119-129 (2000).
- [2] *Painting Materials, A short Encyclopaedia*, R. Gettens, 1966.
- [3] E. Panczyk, M. Ligeza, L. Walis, *J. Radioanal. Nucl. Chem.*, 244, 3 (2000) 543.
- [4] M. Ortega-Aviles, P. Vandenabeele, D. Tenorio, G. Murillo, M. Jimenez-Reyes, N. Gutierrez, *Anal. Chim. Acta*, 550 (2005) 164.
- [5] E. Panczyk, J. Gienza, L. Walis, *J. Radioanal. Nucl. Chem.*, 278, 2 (2008) 527.
- [6] R.A. Johnson, D.W. Wichern, *Applied Multivariate Statistical Analysis*, 3rd ed. Prentice Hall, New Jersey (1992).