

# Measurement of the natural radioactivity content of earth pigments and evaluation of radiological health risks

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**Abstract** – The natural radioactivity content in twenty samples of four different typologies of earth pigments (Raw Sienna, Burnt Sienna, Raw Umber, and Burnt Umber) was investigated through High Purity Germanium (HPGe) gamma spectrometry, with the aim of evaluating the background levels of natural radioactivity in the analyzed samples, and of assessing the radiological health risks due to the external exposure to the enquired earth pigments, by calculating the absorbed dose rate and, starting from it, the annual effective dose equivalent. Finally, the obtained results gave a promising contribution in view of the development of a database on the natural radioactivity content in earth pigments.

## I. INTRODUCTION

The scientific research strongly affects the field of archaeological and historical studies for many years now, especially those referred to the physical and chemical characterization of materials [1-3]. The knowledge of the characteristics of the materials used in the creation of works of art represents a further means towards understanding the works of art themselves, as well as their intrinsic value and the historical and social context to which they belonged [4-5]. In view of the aforementioned considerations, the compositional analysis of artifacts of many typologies, at different spatial scales and employing a variety of micro- and/or non-invasive techniques, represented the focus of much interest in archaeometry, as testified by the wide existing literature [6-9]. In particular,

as far as natural minerals and earths with colouring properties are concerned, i.e. iron and manganese oxides and hydroxides including haematite, goethite, and other minerals such as kaolinite, huntite, and others, a comprehensive view was already furnished elsewhere [10-12]. Nevertheless, a relative new aspect that has to be considered regards the characterization of earth pigments in terms of natural radioactivity content and, starting from it, the assessment of radiological health risks.

This investigation was developed here, for the first time, in twenty samples of four different typologies of earth, namely Raw Sienna, Burnt Sienna, Raw Umber, and Burnt Umber.

## II. MATERIALS AND METHODS

### A. Samples description

Investigated samples were divided into four groups (G#, # = 1, 2, 3, and 4), based on their typology, according to what reported in Table 1.

*Table 1. Investigated earth pigments, together with their identification code (Group ID), typology, and number of samples for each group.*

Group ID	Typology	Number of samples
G1	Raw Sienna	5
G2	Burnt Sienna	5
G3	Raw Umber	5
G4	Burnt Umber	5

Raw Sienna is a natural inorganic mineral pigment, obtained by crushing and grinding raw material coming mainly from Tuscany, Italy. It has high stability to light and good stability to moisture [13].

Burnt Sienna is a natural inorganic mineral pigment, obtained by calcination at 400 °C and subsequent grinding of raw material coming mainly from Tuscany. It has high stability to light and good stability to humidity. It has medium stability to moisture and high stability to temperature and light. It has fast drying and is an excellent glazing pigment. It needs a low amount of oil and forms a non-compact paste [14].

Raw Umber is an hydrated oxide of iron and manganese pigment that helps oil paints dry much more quickly. It is of medium solidity and blends well with any color which, when mixed, is transformed into a darker shade than the original color without being overwhelmed by it. Depending on the amount added, it is possible to modulate various types of shade while maintaining the same basic chromatic vibration. It is very suitable for painting, therefore combined with a binder [15].

Burnt Umber is a solid color that turns to burnt reddish and tends to alter the basic chromatic vibration of the color that is mixed with it. It is obtained from the calcination of the Raw Umber and is used to create shadows, as it adds reddish brown tones to the color to which it is mixed [16]. A photo of the investigated pigments is reported in Figure 1.

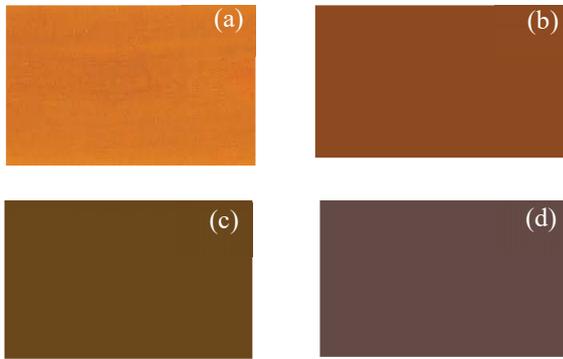


Figure 1. The investigated Raw Sienna (a), Burnt Sienna (b), Raw Umber (c) and Burnt Umber (d) pigments.

### B. Radioactivity measurements

For the gamma spectrometry investigations, samples were counted for 70000 s and spectra were analyzed to obtain the activity concentration of  $^{226}\text{Ra}$ ,  $^{232}\text{Th}$ , and  $^{40}\text{K}$ , respectively. In particular, i) the  $^{226}\text{Ra}$  specific activity was evaluated by using the 295.21 and 351.92 keV  $^{214}\text{Pb}$  and 1120.29 keV  $^{214}\text{Bi}$   $\gamma$ -ray lines, ii) the  $^{232}\text{Th}$  activity concentration was determined by using the 911.21 keV and 968.97 keV  $^{228}\text{Ac}$   $\gamma$ -ray lines; iii) for  $^{40}\text{K}$ , the evaluation was performed from its  $\gamma$ -line at 1460.8 keV. The experimental setup consists of an Ortec HPGe

detector, i.e. a positive biased detector (GEM), nitrogen liquid cooled, with FWHM of 1.85 keV, peak to Compton ratio of 64:1 and relative efficiency of 40% at 1.33 MeV ( $^{60}\text{Co}$ ), and integrated digital electronics.

A photo of the experimental setup is reported in Figure 2.



Figure 2. The experimental Ortec HPGe detector and integrated digital electronics.

A multiplex Marinelli geometry gamma source (AK-5901) of 1 L capacity, covering the energy range 59.54 keV-1836 keV, customized to reproduce the exact geometries of samples in a water-equivalent epoxy resin matrix, was employed for efficiency and energy calibrations. The ANGLE 4 code was employed for the efficiency transfer factors calculations to the 20 mL vial sample holder geometry [17].

Going on, the Gamma Vision (Ortec) software was used for data acquisition and analysis [18-19] and the specific activity ( $\text{Bq kg}^{-1}$ ) of the investigated radionuclides was calculated as follows [20]:

$$C = \frac{N_E}{\varepsilon_E t \gamma_d M} \quad (1)$$

where  $N_E$  indicates the net area of a peak at energy  $E$ ,  $\varepsilon_E$  and  $\gamma_d$  are the efficiency and yield of the photopeak at energy  $E$ , respectively,  $M$  is the mass sample (kg) and  $t$  is the live time (s) [21].

The quality of the results was certified by the Italian Accreditation Body (ACCREDIA) [22].

### C. Evaluation of radiological health risks

Several parameters, such as the absorbed gamma dose rate and the annual effective dose equivalent, were calculated in order to evaluate the potential radiological hazards and to assess the radiation risk to humans [23]. The absorbed gamma dose rate calculation is the first major step to evaluate the health risk [24]. It was calculated with the following [25]:

$$D (\text{nGy h}^{-1}) = 0.462C_{\text{Ra}} + 0.604C_{\text{Th}} + 0.0417C_{\text{K}} \quad (2)$$

where  $C_{Ra}$ ,  $C_{Th}$ , and  $C_K$  are the mean activity concentrations of  $^{226}\text{Ra}$ ,  $^{232}\text{Th}$ , and  $^{40}\text{K}$  in the earth pigments, respectively.

The estimated annual effective dose equivalent (AEDE) received by an individual was calculated using the following equations with an outdoor occupancy of 20% and 80% for indoors [26]:

$$\begin{aligned} \text{AEDE (outdoor)} (mSv y^{-1}) \\ = \text{absorbed dose} (nGy h^{-1}) \quad (3) \\ \times 8760 h \times 0.7 Sv Gy^{-1}S \\ \times 0.2 \times 10^{-6} \end{aligned}$$

$$\begin{aligned} \text{AEDE (indoor)} (mSv y^{-1}) \quad (4) \\ = \text{absorbed dose} (nGy h^{-1}) \\ \times 8760 h \times 0.7 Sv Gy^{-1}S \\ \times 0.8 \times 10^{-6} \end{aligned}$$

Worth of note, the AEDE was calculated for both “outdoor” and “indoor” exposure [27], in order to take into account all possible exposure contexts, i.e. archaeological sites, museums, churches, in which these pigments can be found [28].

### III. RESULTS AND DISCUSSION

#### A. Specific activity

The specific activity of  $^{226}\text{Ra}$ ,  $^{232}\text{Th}$ , and  $^{40}\text{K}$  in the analyzed earth pigments is reported in Table 2. For each group, the (mean value  $\pm$  standard deviation) is also reported.

Table 2. The specific activity ( $Bq kg^{-1}$ ) of  $^{226}\text{Ra}$ ,  $^{232}\text{Th}$ , and  $^{40}\text{K}$  in the analyzed samples.

Group ID	Specific activity		
	$^{226}\text{Ra}$ ( $Bq kg^{-1}$ )	$^{232}\text{Th}$ ( $Bq kg^{-1}$ )	$^{40}\text{K}$ ( $Bq kg^{-1}$ )
G1	$13.6 \pm 4.1$	$25.3 \pm 7.4$	$636 \pm 78$
	$12.1 \pm 3.8$	$20.9 \pm 5.6$	$594 \pm 71$
	$13.3 \pm 4.0$	$23.1 \pm 6.5$	$546 \pm 67$
	$10.6 \pm 3.5$	$23.9 \pm 6.9$	$498 \pm 63$
	$10.9 \pm 3.6$	$22.3 \pm 6.1$	$456 \pm 56$
Mean value	$12.1 \pm 3.8$	$23.1 \pm 6.5$	$546 \pm 67$
G2	$17.5 \pm 5.3$	$24.8 \pm 7.1$	$1113 \pm 125$
	$14.4 \pm 4.7$	$23.0 \pm 6.4$	$1022 \pm 116$
	$16.2 \pm 5.1$	$21.2 \pm 5.7$	$1156 \pm 132$
	$15.3 \pm 4.9$	$23.9 \pm 6.7$	$931 \pm 107$
	$13.1 \pm 4.5$	$22.1 \pm 6.1$	$888 \pm 100$
Mean value	$15.3 \pm 4.9$	$23.0 \pm 6.4$	$1022 \pm 116$
G3	$13.5 \pm 4.1$	$7.5 \pm 3.9$	$535 \pm 66$
	$14.6 \pm 4.3$	$6.4 \pm 3.4$	$561 \pm 69$
	$12.4 \pm 3.9$	$5.2 \pm 2.4$	$437 \pm 46$
	$11.5 \pm 3.7$	$4.1 \pm 1.9$	$411 \pm 43$

G4	$15.5 \pm 4.5$	$5.8 \pm 2.9$	$486 \pm 56$
	$13.5 \pm 4.1$	$5.8 \pm 2.9$	$486 \pm 56$
	$9.8 \pm 3.9$	$15.2 \pm 4.8$	$796 \pm 89$
	$8.2 \pm 3.1$	$17.1 \pm 6.2$	$950 \pm 107$
	$6.6 \pm 2.3$	$14.3 \pm 4.5$	$873 \pm 98$
Mean value	$9.1 \pm 3.6$	$16.1 \pm 5.1$	$719 \pm 86$
	$7.3 \pm 2.6$	$13.3 \pm 3.4$	$1027 \pm 111$
Mean value	$8.2 \pm 3.1$	$15.2 \pm 4.8$	$873 \pm 98$

It should be noted that the activity concentration of  $^{226}\text{Ra}$ ,  $^{232}\text{Th}$ , and  $^{40}\text{K}$ , measured for each sample, indicates the amount of radioactivity, and not the radiological hazards to humans. Thus, in order to evaluate them, additional factors have to be taken into account [29], as reported in the following section.

#### B. Radiological hazard indices

Table 3 reports the calculated values of the adsorbed dose rate and annual effective dose equivalent. The variability of the adsorbed and effective doses can be attributable to the different mineralogical composition of the investigated earth pigments.

Table 3. The calculated radiological hazard indices.

Group ID	D ( $nGy h^{-1}$ )	AEDE (outdoor) ( $mSv y^{-1}$ )	AEDE (indoor) ( $mSv y^{-1}$ )
G1	42.3	0.052	0.208
G2	63.6	0.078	0.312
G3	30.1	0.037	0.147
G4	49.4	0.061	0.242

In particular, the obtained values of AEDE are much lower than  $1 mSv y^{-1}$ , which is set as the maximum limit by [30], for all investigated samples, thus excluding any possible radiological health risks for human beings due to the external exposure to the enquired earth pigments.

### IV. CONCLUSIONS

In the present article, the activity concentration of natural radionuclides ( $^{226}\text{Ra}$ ,  $^{232}\text{Th}$ , and  $^{40}\text{K}$ ) in twenty samples of five different typologies of earth pigments (Raw Sienna, Burnt Sienna, Raw Umber, and Burnt Umber) was for the first time measured by using HPGe gamma spectrometry.

Obtained results were then employed in order to evaluate the radiological health risks associated with the external exposure to the investigated pigments, by assessing the absorbed dose rate and then the annual effective dose equivalent. Calculated values of AEDE turned out to be lower than the maximum limit of  $1 mSv y^{-1}$  set by ICRP, thus excluding any possible radiation hazard effects for humans.

The results reported in this article represent a preliminary but promising contribution in view of a future creation of a database on the natural radioactivity content in earth pigments.

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