Optical and fast nondestructive identification of the ages of leaded ancient pottery*

Wu Fang-Yuan (吴方媛)[a] and Yang Xiang-Bo(杨湘波)[a)b)†]

[a] *MOE Key Laboratory of Laser Life Science & Institute of Laser Life Science, College of Biophotonics, South China Normal University, Guangzhou* 510631, *China*

[b] *School of Physical Education & Sports Science, South China Normal University, Guangzhou 510631, China*

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In this paper, based on the one-dimensional (1D) optical superlattice model, we calculate the average reflectivities (ARs) of leaded ancient pottery (AP) made within the last 2000 years, and find that for incident light with a suitable wavelength, the AR of the leaded AP increases monotonously with the increase in the layer number of the silvery glaze (SG) media. Based on this property, we propose an optical nondestructive method for identifying the age of leaded AP by detecting the AR. By using the exhaust algorithm and the discriminant function of variance, we obtain the optimal wavelength range of the incident light to identify the ages of the leaded AP. It is found that in the visible light band, if we choose green light with a wavelength range of 540–540.1 nm as the incident light, leaded AP made within the last 2000 years can be identified swiftly and precisely by detecting the ARs. This will be useful for designing optical instruments for the fast nondestructive identification of the ages of leaded AP.

Keywords: optical superlattice, ancient pottery, nondestructive identification

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1. Introduction

Much ancient pottery (AP) is held in high esteem and of great interest in museums all over the world. Unfortunately, there is now lots of fake AP in the market, and it is often hard to distinguish the real AP from the fakes accurately. Consequently, people have paid much attention to finding ways to identify AP effectively, conveniently, and nondestructively.

Up until now, for the age identification of AP, there have been two main types of methods, the traditional distinguishing method and the modern scientific and technological one. The former relies on personal observation, touching, and tapping, but no uniform standard has been mapped out, and the identification results obtained by different people are sometimes quite different. The latter includes chemical composition analysis,[1−6] X-ray fluorescence testing,[7−10] thermoluminescence dating methods,[11−13] Raman spectrometry,[14−16] and the structural analysis and optical scattering testing method.[17] The chemical composition method damages AP when taking samples, and the X-ray technique can not distinguish AP from the corresponding fakes if the raw materials are composed of the same components. Distinguishing the artificial irradiation from the natural radiation is still the main problem in the thermoluminescence dating method. The Raman spectrometry method needs to construct a standard database of the fingerprints of all kinds of AP, and for the structure analysis and optical scattering testing method, the aging coefficient is related to the stress and the shape of the AP surfaces, and consequently a piece of AP may be identified to have originated from several different ages if it possesses an irregular shape. So finding a more scientific and accurate identification method for AP has recently become a noticeable research topic.

In this paper, we study the age identification of leaded AP. Since the Mid-Western Han Dynasty (about 100 BC), pottery with a leaded glaze has been made in China. The high-leaded glaze is generally referred to as green glaze (GG) because of its olive color. The production technique of GG AP reached its height in the Mid-Northern Song Dynasty (about 1040 AD), and Ding-Yao is thought of as the best representation of leaded ceramics. As an example, Figure 1 shows a precious carved-flower porcelain pillow of Ding-Yao GG made in the Song Dynasty. For the investigation of this kind of invaluable leaded AP, one of the foci is

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†Corresponding author. E-mail: xbyang@scnu.edu.cn

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age identification.



Fig. 1. (colour online) A carved-flower porcelain pillow of Ding-Yao green glaze, which was made in 1076 AD.

Now it is known that after the GG AP has been exposed to wet air, some laminal silvery glazes (SGs) will be formed on the surface because of chemical denudation and deposition, and each lamina takes about 50 years to be formed.[18,19] A scanning electron microscope image of an SG on the surface of a GG AP is shown in Fig. 2.[20] We find three zones altogether, a tectum, an SG with a multilayer structure, and a GG. In the tectum zone, the refractive index (RI) and the thickness of the tectum are about 1.5 and dozens of microns, respectively. In the SG zone, the SG is composed of many layers of SG media, which are separated from each other by thin air films. The RI of the SG medium is about 1.485–1.501, the thickness of each layer of the SG medium is about 1–3 μm, and the thickness of each layer of the thin air film is smaller than 0.3 μm. In the GG zone, the RI and the thickness of the GG are about 1.65 and 80–250 μm, respectively. Based on these experimental data,[20] the leaded AP can obviously be regarded as the one-dimensional (1D) optical superlattice that is schematically shown in Fig. 3, where A denotes an air layer, S denotes the SG medium, the leftmost layer represents the air surrounding the AP, and its thickness tends to be infinite. The thicknesses of the thin air gaps are all equal to $d_{\rm A} = 0.25$ μm. The T layer represents the tectum on the surface of the SG, whose RI is $n_{\rm T} = 1.5$ and thickness is $d_{\rm T} = 80$ μm. The RI of the SG medium is $n_{\rm S} = 1.5$, and its thickness is $d_{\rm S} = 2.0$ μm. The RI of the GG is $n_{\rm G} = 1.65$, and its thickness is regarded as infinite compared to those of the SG multilayers.

Making use of this 1D optical superlattice, in this paper we study the optical average reflectivity (AR) of the leaded AP and find that for the incident light with a suitable wavelength, the AR increases monotonously with the increase in the age of the leaded AP. Based on this feature, we propose an optical, fast nondestructive age identification method for AP with an SG on the surface. This method may be useful for the investigation of leaded AP and can be applied to the design of optical instruments for the fast nondestructive identification of the ages of the leaded AP.

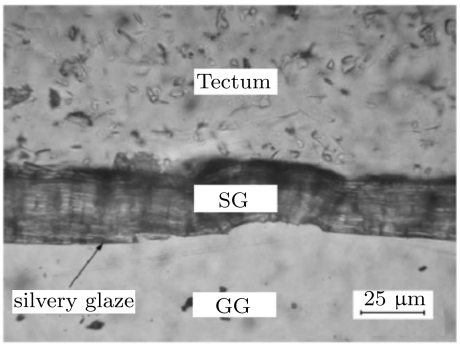


Fig. 2. Scanning electron microscope image of an SG on the surface of a GG AP.[20]

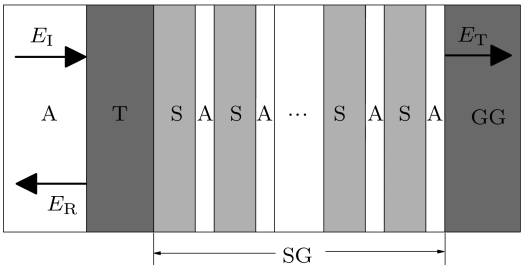


Fig. 3. Schematic diagram of the optical superlattice representing leaded AP with SG on the surface of a GG, where $E_{\rm I}$, $E_{\rm R}$, and $E_{\rm T}$ are the input, the reflective, and the output light, respectively.

This paper is organized as follows. In Section 2, we introduce the conventional trace-map theory to compute the AR through the 1D optical superlattice of leaded AP. The numerical simulation results and the discussion are presented in Section 3, and finally, a conclusion is drawn in Section 4.

2. Method and theory

Conventional trace-map technique[21] are frequently used to calculate the propagation matrices (PMs) through optical superlattices.[22–25] Here we make use of this method to compute the AR of leaded AP.

When the light propagates vertically from the air to the AP superlattice shown in Fig. 3, the PM can

be expressed as

$$\boldsymbol{M} = \boldsymbol{M}_{\mathrm{AT}}\boldsymbol{M}_{\mathrm{T}}\boldsymbol{M}_{\mathrm{TS}}\boldsymbol{M}_{\text{Total-SG}}\boldsymbol{M}_{\text{A-GG}}, \quad (1)$$

where $\boldsymbol{M}_{ij}$ $(i,j = \mathrm{A},\mathrm{T},\mathrm{S})$ stands for the PM from layer i to layer j and can be written as

$$\boldsymbol{M}_{ij} = \begin{pmatrix} 1 & 0 \\ 0 & n_j/n_i \end{pmatrix}. \quad (2)$$

The RIs n_i and n_j are chosen to be the aforementioned experimental data. $\boldsymbol{M}_{\mathrm{T}}$ represents the PM through the tectum layer and can be expressed as

$$\boldsymbol{M}_{\mathrm{T}} = \begin{pmatrix} \cos\delta_{\mathrm{T}} & -\sin\delta_{\mathrm{T}} \\ \sin\delta_{\mathrm{T}} & \cos\delta_{\mathrm{T}} \end{pmatrix}, \quad (3)$$

where δ_{T} indicates the quasi-phase of the tectum layer for the incident light with wavelength λ and can be expressed as

$$\delta_{\mathrm{T}} = \frac{2\pi}{\lambda} n_{\mathrm{T}} d_{\mathrm{T}}. \quad (4)$$

In Eq. (1), the total PM of the SG is

$$\begin{aligned} &\boldsymbol{M}_{\text{Total-SG}} \\ &= (\boldsymbol{M}_{\mathrm{S}}\boldsymbol{M}_{\mathrm{SA}}\boldsymbol{M}_{\mathrm{A}}M_{\mathrm{AS}})^{N-1}\boldsymbol{M}_{\mathrm{S}}\boldsymbol{M}_{\mathrm{SA}}\boldsymbol{M}_{\mathrm{A}}, \end{aligned} \quad (5)$$

where N denotes the layer number of the SG media (references [18] and [19] reported that producing each layer of the SG media takes about 50 years); $\boldsymbol{M}_{\mathrm{S}}$ and $\boldsymbol{M}_{\mathrm{A}}$ are the PMs through a single layer of the SG medium and that of the thin air gap in the SG, respectively, and can be defined in a similar way to $\boldsymbol{M}_{\mathrm{T}}$. The PM $\boldsymbol{M}_{\text{A-GG}}$ in Eq. (1) denotes the PM from the rightmost layer to the GG layer and can be written as

$$\boldsymbol{M}_{\text{A-GG}} = \begin{pmatrix} 1 & 0 \\ 0 & \dfrac{n_{\mathrm{G}}}{n_{\mathrm{A}}} \end{pmatrix} = \begin{pmatrix} 1 & 0 \\ 0 & 1.65 \end{pmatrix}. \quad (6)$$

By using these PMs and the traditional trace-map technique,[21] we can deduce the reflectivity of the light propagating through the leaded AP superlattice shown in Fig. 3 as

$$R(\lambda) = 1 - \frac{4}{2 + m_{11}^2 + m_{21}^2 + m_{12}^2 + m_{22}^2}, \quad (7)$$

where m_{ij} $(i,j = 1,2)$ is an element of the PM $\boldsymbol{M}$ expressed in Eq. (1). Further, we define the optical AR for the incident light in the range of λ_1 to λ_2 as

$$A_{\mathrm{R}} = \frac{1}{\lambda_2 - \lambda_1}\int_{\lambda_1}^{\lambda_2} R(\lambda)\,\mathrm{d}\lambda. \quad (8)$$

In Section 3, we will investigate the reflectivity property and the AR of leaded AP and identify the age of the leaded AP by detecting the optical AR.

3. Results and discussion

For experimental simplicity, we focus on the case using a visible light source. By using Eq. (7), we can calculate the reflectivity of leaded AP for incident light with a wavelength range of $\lambda \in$[400 nm, 800 nm]. As an example, we plot the reflective spectrum for the case of an SG possessing 20 layers of SG media in Fig. 4. From Fig. 4, we can see that the reflective spectrum is very complicated, and we cannot obtain any quantitative rule related to the layer number of the SG media. So the reflective spectrum is not used by us to identify the age of the leaded AP.

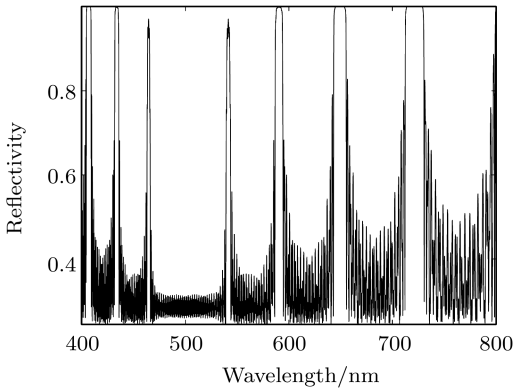


Fig. 4. The reflective spectrum of leaded AP, where the layer number of the SG media is $N = 20$.

In order to quantitatively distinguish the ages of the leaded AP, by using Eq. (8) we can compute the ARs of the leaded AP for the incident light of $\lambda \in$[400 nm, 800 nm] and plot the AR data in Fig. 5. From Fig. 5, we can see that the ARs of the leaded AP have a tendency to increase with the increase in the layer number of the SG media, but unfortunately, some tiny fluctuation exists. Using these AR data to identify the ages of leaded AP will cause some confusion. In addition, the AR distribution is very uneven, and the AR range is not very big (approximately from 0.34 to 0.44). Further, when N is larger than 8, the AR differences between the leaded AP are very small. This will prejudice the age identification of the leaded AP and requires an identification instrument based on this principle that possesses very high distinguishability. After investigating many cases, we found that for the incident light with a suitable wavelength, the AR of the leaded AP increases monotonously with the increase in the layer number of the SG media. Based on this property, we propose an optical nondestructive age identification method for leaded AP by detecting the AR through a leaded AP optical superlattice.

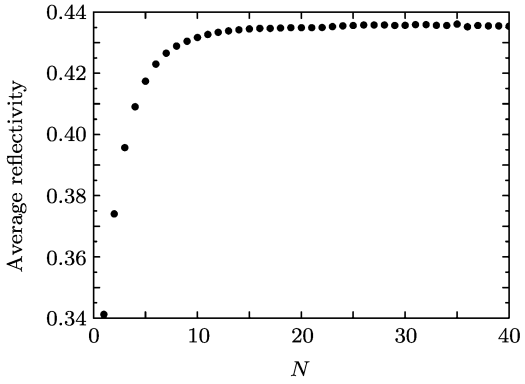


Fig. 5. The AR of leaded AP versus the layer number of the SG media, N, where the wavelength range of the incident light is $\lambda \in$ [400 nm, 800 nm].

In order to design a more practical identification instrument based on this principle, we try to choose a suitable waveband and seek the optimal wavelength span for the incident light by means of the exhaust algorithm. The steps are given as follows. First, for experimental convenience, the laser working in the visible light range is usually used, thus we choose the incident light of 400 nm$< \lambda <$ 800 nm. Then, by means of the exhaust algorithm, we choose suitable wavelength spans, in which the AR of leaded AP within 2000 years (from 100 BC to today) increases monotonously with the increase of N. Further, from these fitting wavelengths, we pick out the ones with the largest total AR differences. Finally, by using the discriminant function of variance, we select the optimal wavelength, with which the AR difference distributes evenly. The variance is defined as[26]

$$\mu_2 = \frac{1}{N}\sum_{i=1}^{N}\left(\Delta A_{\mathrm{R},i} - \frac{1}{N}\sum_{i=1}^{N}\Delta A_{\mathrm{R},i}\right)^2, \qquad (9)$$

where i is the layer number of the SG media, and $\Delta A_{\mathrm{R},i} = A_{\mathrm{R},i+1} - A_{\mathrm{R},i}$ is the AR difference between two pieces of leaded AP. By using the aforementioned method, we obtain the optimal wavelength of the incident light for identifying the ages of leaded AP. The numerical result is shown in Fig. 6, and the corresponding data are listed in detail in Table 1.

From Fig. 6 and Table 1, we can see that if we choose green light with a wavelength span of 540–540.1 nm as the incident light, the AR of leaded AP made in the last 2000 years (i.e., $N \leq 40$) increases monotonously with the increment in the layer number of the SG media, that is to say, with this detecting light, the AR of leaded AP matches the layer number of the SG media (corresponding to the age of the leaded AP). So we can identify the ages of the leaded AP made in the last 2000 years by detecting the ARs. On the other hand, the wavelength span of the detecting light is only 0.1 nm, and this can not only shorten the acquisition time to obtain the AR of leaded AP enormously, but also simplify the detecting light source immensely. So this optical nondestructive identification is fast.

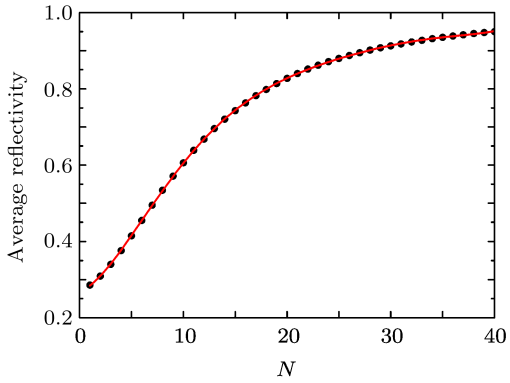


Fig. 6. (colour online) The AR of leaded AP versus the layer number of the SG media N, where the wavelength range of the incident light is $\lambda \in$ [540 nm, 540.1 nm]. The red line represents the fitting curve of the AR.

Table 1. Checklist of N, age, and AR of leaded AP made within the last 2000 years. The incident light is green light in the wavelength range 540–540.1 nm.

N	Age	AR	N	Age	AR
1	50	0.28563	21	1050	0.84001
2	100	0.30930	22	1100	0.85136
3	150	0.33999	23	1150	0.86168
4	200	0.37573	24	1200	0.87110
5	250	0.41459	25	1250	0.87968
6	300	0.45481	26	1300	0.88754
7	350	0.49499	27	1350	0.89472
8	400	0.53404	28	1400	0.90132
9	450	0.57125	29	1450	0.90737
10	500	0.60616	30	1500	0.91294
11	550	0.63855	31	1550	0.91807
12	600	0.66834	32	1600	0.92281
13	650	0.69558	33	1650	0.92719
14	700	0.72039	34	1700	0.93124
15	750	0.74291	35	1750	0.93499
16	800	0.76333	36	1800	0.93847
17	850	0.78183	37	1850	0.94171
18	900	0.79858	38	1900	0.94472
19	950	0.81376	39	1950	0.94752
20	1000	0.82752	40	2000	0.95013

Figure 6 and Table 1 also show that the ARs of leaded AP distribute almost evenly from 28.563% to

95.013% in the range $N \in [1, 40]$. The total AR difference is 66.450%, and the medial AR difference between the leaded AP of two neighboring 50 year periods is about 1.661%. This means that by making use of this incident light and detecting the ARs of leaded AP, we can distinguish the ages of leaded AP made within the last 2000 years with a high resolution. Thus, the identification instrument based on this principle can possess very high distinguishability.

However, practical leaded AP may be not produced in the year shown in Fig. 6 or listed in Table 1, which means that the experimental AR sometimes does not fit the data in Fig. 6 and/or Table 1 exactly, but instead is between two of the data values. In order to detect the ages of leaded AP more accurately, we fit the 40 dots in Fig. 6 by using a polynomial curve and obtain the following experiential formula:

$$A_{\mathrm{R}} = \sum_{i=0}^{6} a_i N^i, \tag{10}$$

where

$$\begin{aligned} a_0 &= 0.26743, \\ a_1 &= 0.01155, \\ a_2 &= 0.00571, \\ a_3 &= -5.07132 \times 10^{-4}, \\ a_4 &= 1.89825 \times 10^{-5}, \\ a_5 &= -3.39691 \times 10^{-7}, \\ a_6 &= 2.37602 \times 10^{-9}. \end{aligned} \tag{11}$$

Comparing an experimental AR with the fitting curve in Fig. 6 and/or experiential formula (10), we can more precisely obtain the age data of leaded AP made within the last 2000 years.

For example, we obtained the AR of the green pan-kou pottery vase shown in Fig. 7, which is 94.0%. Then from Fig. 6 and Table 1, we can see that the AR is between that of $N = 36$ and $N = 37$. By means of the fitting curve in Fig. 6 and/or experiential formula (10), we can obtain N to be approximately 36.65 and then deduce the age of the vase to be 1832.5 years old. Therefore, we can deduce that this GG AP was made in about 178 AD, the first year of Guanghe era of Emperor Han Lingdi at the end of the Eastern Han Dynasty.

For another example, we obtain the AR of the carved-flower porcelain pillow shown in Fig. 1, which is 81.0%. Then from the fitting curve in Fig. 6 and/or experiential formula (10), we deduce that the layer number of the SG media is about 18.70, thus the porcelain pillow is about 935 years old. Therefore, we can deduce that this GG AP was made in about 1076 AD, the ninth year of the Xining era of Emperor Song Shenzong in the Mid-Northern Song Dynasty.



Fig. 7. (colour online) The pan-kou pottery vase, which was made in the first year of Guanghe era of Emperor Han Lingdi at the end of the Eastern Han Dynasty (about 178 AD).

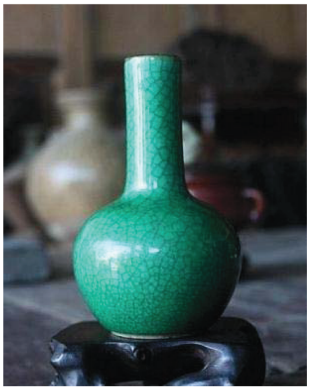


Fig. 8. (colour online) The globular porcelain vase, which was made in the 39th year of the Qianlong era of Emperor Qing Gaozong in the Mid-Qing Dynasty (about 1774 AD).

As a late example, the AR of the green-glaze globular porcelain vase shown in Fig. 8 is obtained to be 40.5%. Then the layer number of the SG media can be deduced to be about 4.73, and thus the globular porcelain vase is about 236.5 years old. Therefore, we can deduce that this GG AP was made in about 1774 AD, the 39th year of the Qianlong era of Emperor Qing Gaozong in the Mid-Qing Dynasty.

4. Conclusion

By using the optical superlattice model, we calculate the ARs of leaded AP made within the last

2000 years, and find that for incident light with a suitable wavelength, the AR of the leaded AP increases monotonously with the increase in the layer number of the SG media. Based on this property, we propose an optical nondestructive method for identifying the age of a leaded AP by detecting the AR.

By using the exhaust algorithm and the discriminant function of variance, we obtain the optimal wavelength range of the incident light for identifying the ages of the leaded AP. It is found that in the visible light band, if we choose green light with a wavelength range of 540–540.1 nm as the incident light, the ARs distribute evenly from 28.563% to 95.013%, and the leaded AP made within the last 2000 years can be identified swiftly and precisely by detecting the ARs. This will be useful for the design of practical, fast nondestructive optical instruments for identifying the ages of leaded AP.

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