

Reports

Dating Works of Art through Their Natural Radioactivity: Improvements and Applications

Abstract. *The method for approximately dating white lead, which is based upon the decay of lead-210 present in recently refined lead, has been modified to circumvent potential interferences. The modified method has been applied to additional samples of known age and finds increased utility through special treatment of the obtained data. The method was also successfully applied to a number of interesting problems of authentication.*

A method (1) for determining whether lead-bearing materials in works of art have been manufactured during the last century is based upon the natural radioactivity in such materials. This method depends upon the disruption, during the extraction of lead from its ore, of the radioactive equilibrium between lead-210 which has a half-life of 22 years and radium-226 which has one of 1600 years. The equilibrium is then restored at a rate characteristic of the 22-year half-life of Pb^{210} and thus forms the basis for an approximate indication of age. For the application of the method, measurements of the radioactive species Ra^{226} and Pb^{210} are required. In practice, the more sensitive measurement of Po^{210} is substituted for that of Pb^{210} since, after a very few years, activity concentrations of the two are virtually equivalent.

In the previous work, two possible interferences were suggested which can lead to ambiguous radiochemical analyses of white lead-bearing paint. These are the presence in the paint of (i) a soluble sulfate, such as gypsum, which can cause inadvertent and premature precipitation of radium during analysis; and (ii) an earth pigment, such as iron ochre, which may be sufficiently naturally radioactive to mask the radioactivity from a lesser amount of white lead.

Certain refinements in the analytical procedure can avoid these difficulties. To eliminate the effects of any inadvertent loss of radium during analysis, I add a small quantity ($\sim 0.005 \mu c$) of Ba^{133} as soon as a solution of the pigment is obtained. Because of the chemical similarity of barium and radium, the Ba^{133} ,

which emits only gamma rays and low-energy electrons, acts as a tracer for the radium. By measuring the barium radioactivity in the sample finally prepared for radium counting, a correction can be made for the chemical yield of the radium. By analyzing typical samples of paint to which relatively large, known quantities of radium have been added, I confirmed the validity of this method (2). Briefly, the analytical procedure consists of (i) removing lead as the sulfide (later weighed to determine lead concentration in the sample), (ii) carrying barium and radium on a precipitate of strontium carbonate, and, following dissolution of the latter, (iii) carrying barium and radium on a small quantity (0.1 to 0.2 mg) of lead chromate (3). The lead chromate is then prepared for counting by transferring the slurry obtained directly to a membrane filter cemented to a plastic holder (4).

To avoid possible interference from natural radioactive impurities in a paint sample, I selectively dissolve the white lead in the sample. Expected impurities of this type consist of earth pigments such as ochers, umbers, and siennas. These are silica-clay mixtures colored by metal oxides, chiefly of iron. Hot 5N acetic acid dissolves the white lead (and the Ra^{226} and Po^{210} present in it) from a finely ground paint sample without dissolving these impurities. I tested the method by preparing synthetic oil paints of low white lead and high yellow ochre content and analyzing the mixture using schemes based upon both selective and drastic (with nitric acid) dissolution. The individual components of the mixture were also ana-

lyzed. While the radium and polonium measurements obtained through drastic dissolution included the radioactivity of the ochre, those measurements resulting from selective dissolution gave values in good agreement with the analysis of the pure white lead (5).

I applied the newer analytical methods to approximately 30 of the artists' white lead samples previously analyzed (1) and, in all but one or two cases, obtained good agreement with the previous results. In no case was the basic premise refuted, that is, that modern lead contains Po^{210} (as a measure of Pb^{210}) in excess of Ra^{226} whereas old lead does not.

In the hope that slightly more definitive dating might be obtained, particularly for 19th-century paintings, I applied the method to approximately 30 additional samples between 65 and 140 years old. The results of these analyses were similar to those few previously obtained for this period (1).

A convenient means of depicting the results as a function of age is represented in Fig. 1. The ordinate of the graph is the quantity $[1 - (Ra)/(Po)]$, where the symbols in the parentheses represent the concentration of the radioactive species Ra^{226} or Po^{210} per unit mass of lead. This quantity is a function of age and "separation factor" and is equal to

$$\frac{(SF - 1)e^{-\lambda t}}{(SF - 1)e^{-\lambda t} + 1} \quad (1)$$

where SF is the "separation factor" defined as the ratio of Pb^{210} to Ra^{226} at the time the lead was refined, λ is the disintegration constant for Pb^{210} , and t is the time elapsed since the lead was refined. This relationship is readily derived from the equation relating the radioactivity of Pb^{210} and Ra^{226} given previously (1).

In Fig. 1, the solid line represents the calculated values of $[1 - (Ra)/(Po)]$ for a separation factor of 100, which is the approximate geometric mean (6) for all samples less than 80 years old. The circles represent the results obtained for new as well as previously analyzed samples. Uncertainties are not indicated, although these become quite large for the older samples, where $[1 - (Ra)/(Po)] \cong 0$, and for those of very low radioactivity (7). The results obtained for a few samples were not plotted because the uncertainties led to completely indeterminate values.

For older samples, the values for $[1 - (Ra)/(Po)]$ tend to be more diverse and fall below the solid line (drawn for

$SF = 100$). This indicates that the separation factors obtained for samples older than 80 years are lower and, as expected, exhibit greater uncertainties than those obtained for more modern material.

Based on the data obtained, a sample of any given date may be assigned a certain probability of exhibiting a value for $[1 - (Ra)/(Po)]$ within any defined limit. The dashed and dotted lines in the figure represent such limits for probabilities of 0.68 (1 standard deviation) and 0.95 (2 standard deviations), respectively. These curves were constructed in the following manner.

I divided the samples into several groups, each spanning approximately 20 years, beginning with the present. For each group, I then calculated the mean (and its standard deviation) of the quantity $[1 - (Ra)/(Po)]$ as it varies over the time span of the group. For the more modern samples, the arithmetic mean of $[1 - (Ra)/(Po)]$ was computed as if it were constant because of the relative insensitivity of the value of this quantity to the age of a modern sample. For the groups of older samples, geometric means of the separation factors were computed which, in turn, were used to calculate means and stand-

ard deviations of $[1 - (Ra)/(Po)]$ as a function of age for the appropriate time spans. The dashed and dotted curves shown in Fig. 1 were then drawn to smoothly fit values obtained by adding and subtracting one and two standard deviations, respectively, from the mean value for each group. For the portion of the graph representing the period prior to 1830, I used the mean separation factor and its deviation for the period 1830 to 1850.

The utility of the method for distinguishing between "old" and "modern" white lead is readily apparent from this graph and essentially confirms the conclusions reached previously (1). The graph also shows, however, that the method may supply further information. For example, samples exhibiting values for $[1 - (Ra)/(Po)]$ between approximately 0.4 and 0.8 would almost certainly date from the 19th century (any uncertainties in such individual measurements being taken into account).

I have applied the method to a number of paintings of questioned or questionable authenticity. Table 1 shows the results of analyses of samples of paint weighing 30 mg or more taken from unimportant areas at the edges of the paintings. The concentrations of Po^{210} and Ra^{226} are given in disintegrations per minute per gram of lead, and the computed values of $[1 - (Ra)/(Po)]$ are also given. The uncertainty shown in each case is the standard deviation. These values may be compared with the curves in Fig. 1.

The story of the Van Meegeren paintings, representing probably the most spectacular series of forgeries of all time, can be found elsewhere (8). As a result of a thorough investigation some 20 years ago (8), international opinion generally holds that the first five paintings listed here are indeed forgeries painted by Van Meegeren in the late 1930's and the early 1940's. There remain at this time, however, some persons who still believe "Disciples at Emmaus," "discovered" in 1937, to be a genuine Vermeer. My results, however, conclusively confirm that all of these five paintings are modern and, hence, probably correctly attributed to Van Meegeren. For these results to have been derived from 300-year-old white lead samples would require the originals to have been produced from an incredible, uranium-rich ore (~25 percent uranium) (9). The Hals-style painting of unknown authorship, "discovered" in 1924, has been shown by others to be a

Description	Po^{210} concentration (dpm/g of Pb)	Ra^{226} concentration (dpm/g of Pb)	$[1 - (Ra)/(Po)]$
Van Meegeren,* "Washing of Feet," Vermeer style	12.6 ± 0.7	0.26 ± 0.07	0.98 ± 0.01
Van Meegeren,* "Woman Reading Music," Vermeer style	10.3 ± 1.2	$.30 \pm .08$	$.97 \pm .01$
Van Meegeren,* "Woman Playing Mandolin," Vermeer style, pigment sample	8.2 ± 0.9	$.17 \pm .10$	$.98 \pm .02$
"Woman Playing Mandolin," ground and pigment sample	7.4 ± 1.5	$.55 \pm .17$	$.93 \pm .03$
Van Meegeren,* "Woman Drinking," Hals style	8.3 ± 1.2	$.1 \pm .1$	$.99 \pm .01$
Van Meegeren,† "Disciples at Emmaus," Vermeer style	8.5 ± 1.4	$.8 \pm .3$	$.91 \pm .04$
Unknown,‡ "Boy Smoking," Hals style	4.8 ± 0.6	$.31 \pm .14$	$.94 \pm .02$
Vermeer,§ "Lace-maker"	$1.5 \pm .3$	$1.4 \pm .2$	$.07 \pm .23$
Vermeer,§ "Laughing Girl"	$5.2 \pm .8$	$6.0 \pm .9$	$-.15 \pm .25$

* Courtesy of the Rijksmuseum, Amsterdam, Netherlands; Dr. A. van Schendel, Director-General.
 † Courtesy of the Museum Boymans-van Beuningen, Rotterdam, Netherlands; Dr. J. C. Ebbinge Wubben, Director.
 ‡ Courtesy of the Gröninger Museum, Gröningen, Netherlands; Dr. A. Westers, Director.
 § Courtesy of the National Gallery of Art, Washington, D.C.; Dr. J. Walker, Director.

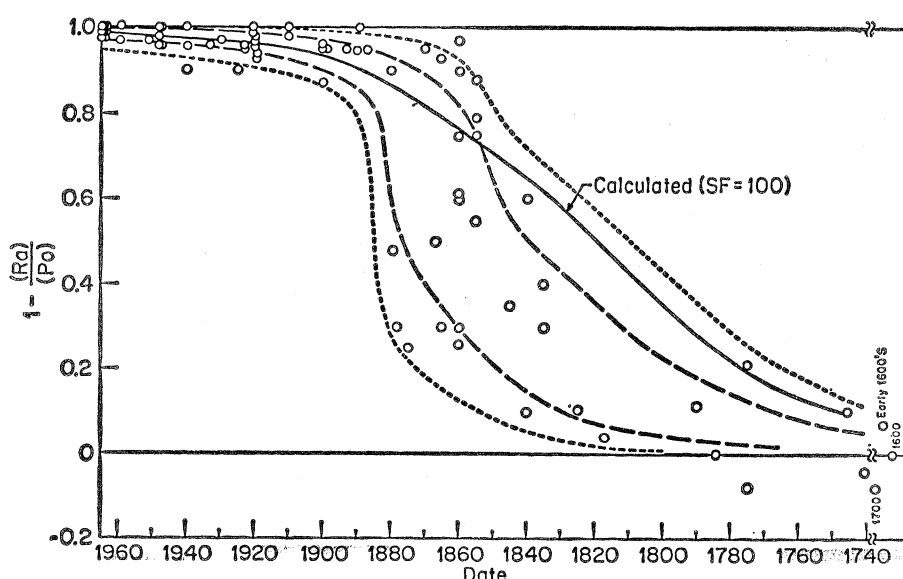


Fig. 1. A "dating curve" for white lead. Circles indicate values of $[1 - (Ra)/(Po)]$ for samples of known age. Such values may be used to discern old and modern white lead and might be used to discern white lead of the 20th century, 19th century, and 18th century or earlier. SF , "Separation factor."

modern forgery (10); and the results confirm this fact also.

The authorship of the two remaining paintings, ascribed to Vermeer, has been questioned (11). Since these paintings first appeared in the art market in the early 1920's, the method was applied to them. The results indicate that it is unlikely that these paintings are 20th-century forgeries. The method, of course, cannot prove that any one painter was the author of a particular work. It does indicate that in these two cases the lead in the paintings was refined at least 100 years ago.

The analyses of the last two paintings were completed, using our older procedure (12), before we fully realized the possible compromising effect of the large amounts of natural earth pigments in the samples. In this case, I believe we circumvented this potential difficulty by analyzing the material for uranium. The reasoning is that any significant quantity of radium and radiolead from the natural iron ochre present, made by grinding rock, must be accompanied by an equivalent quantity of uranium, their ultimate precursor. Fluorometric analyses, of the solutions remaining after our radium analysis, and neutron activation analyses of small samples (less than 1 mg) of the original materials, failed to detect uranium. For these two independent methods, I estimate (13) the uranium content to be less than 1 (fluorometry) and 0.9 (activation analysis) disintegration per minute per gram of Pb for "Laughing Girl," and less than 0.1 (fluorometry) and 0.1 (activation analysis) disintegration per minute per gram of Pb for "Lace-maker." These limits are well below the concentrations of Ra²²⁶ and Pb²¹⁰ activity found in the respective samples (Table 1); and, therefore, the results appear to be valid. It would, of course, be ideal if additional samples could be examined by the new method; but, unfortunately, obtaining further samples of sufficient size from these two paintings would be extremely difficult.

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References and Notes

1. B. Keisch, R. L. Feller, A. S. Levine, R. R. Edwards, *Science* **155**, 1238 (1967).
2. For example, one series of experiments in which 11 disintegrations per minute (dpm) of Ra²²⁶ were added to a sample of white lead, previously found to contain approximately 0.5 dpm, resulted in radium recoveries of 11, 11, and 10 dpm with corrections for chemical yields based on Ba¹³³ measure-

- ments of 74, 46, and 85 percent, respectively.
3. The procedure incorporates parts of the procedure given by D. N. Sunderman and C. W. Townley, *Nat. Acad. of Sci.-Nat. Res. Council Rep.* **3010**, 47 (1960).
4. The filter support used and the results obtained with a similar quantity of barium sulfate as a carrying precipitate are described by B. Keisch and A. S. Levine, *Anal. Chem.* **38**, 1969 (1966).
5. For the Ra²²⁶ (which is most affected by the presence of impurities), the measured concentration in the white lead used was 0.4 ± 0.2 dpm per gram of lead. Analysis of the mixture by the new method gave 0.6 ± 0.2 dpm per gram of lead, while the old method resulted in 1.4 ± 0.4 dpm per gram of lead. The latter result compares with the value of 2.6 ± 0.8 dpm per gram of lead calculated as the total contribution from the other and the white lead.
6. The logarithms of the calculated separation factors exhibit a normal distribution (1).
7. For uncertainties in the measurements of Ra²²⁶ and Po²¹⁰ of 10 percent (one standard deviation), which is typical for these low-level determinations, the uncertainties in $[1 - (Ra)/(Po)]$ at values of 0.9, 0.5, and 0.1 are approximately 1.6, 14, and 130 percent, respectively.
8. P. Coremans, *Van Meegeren's Faked Vermeers and De Hooghs* (Meulenhoff, Amsterdam, 1949).

9. Such an ore would also require the large uranium content to be homogeneously mixed with the lead because heterogeneities containing the entire uranium series would have been removed during ore beneficiation. Needless to say, such an ore is unknown, particularly in the lead mines of 17th-century Europe.
10. W. Froentjes and A. M. de Wild, *Burlington Mag.* **92**, 297 (1950).
11. A. B. de Vries, *Jan Vermeer van Delft* (Batsford, London, 1948), pp. 64-65, and supplement.
12. These results, as well as all of the results reported previously (1) and used here in Fig. 1, were obtained at Nuclear Science & Engineering Corporation.
13. For the fluorometric analyses, we would have been able to measure these quantities with an estimated uncertainty of approximately 50 percent. For the activation analyses, the quantities represent an uncertainty of 1 standard deviation in the comparison of the actual samples with blank samples.
14. I thank E. R. Feidler, J. Walker, and the National Gallery of Art, Washington, D.C., for supporting this work; J. H. Leopold, P. J. J. van Thiel, H. Kühn, and E. Hulmer, in addition to those shown in Table 1, for aid in obtaining samples; R. L. Feller for his valuable advice and criticism; and C. Sizemore for her assistance with the analyses.

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Optical Pulse of a Periodic Radio Star

Abstract. *The pulsating radio star reported by Hewish et al. (1) has been studied in the blue region of the optical spectrum and found to have a pulse amplitude less than 10 percent of the photon count expected for 18th magnitude. No upper limit to a sinusoidal oscillation less than or equal to a complete modulation can be set.*

A rapidly pulsating radio star, observed at 81 Mhz, has been reported by Hewish *et al.* (1). An optical identification of the source (2) suggests that it is associated with a blue star of magnitude 18. The principal radio feature is a recurrent sharp pulse with a duration of a few tens of milliseconds and a repetition period of $1.3372795 \pm .0000020$ seconds. The object has also been seen by Davies *et al.* (3) at 151, 240, and 408 Mhz.

Models for these objects have been put forward by Saslaw *et al.* (4) and by Ostriker (5). In one model, the pulsations arise from a gravitational lens effect around a neutron star binary. In the other, radio emission arises from active regions on a rapidly rotating white dwarf. Clearly more experimental observations are needed to constrain the classes of possible mechanism, and a search for periodic behavior at optical wavelengths is called for in particular. Observation of optical pulsation in the blue object tentatively associated with the radio signals would provide conclusive confirmation of that identification. To this end we have constructed a system which searches specifically for periodic fluctuations of the light intensity from the blue star at

the frequency of the pulsating radio source. We have taken preliminary observations and can report seeing no pulsations. Upper limits to optical pulsations in several possible modes are presented.

Our experimental technique relies heavily on the precision with which Hewish *et al.* (1) have quoted the periodicity of the radio source. Figure 1 is a schematic diagram of the system we use. A 1-Mhz quartz crystal forms a clock which matches the radio peri-

Table 1. The duration of hypothetical optical burst within the 1.337-second cycle is represented by Δt . The mode limited is the 95 percent confidence level upper limit to the number of photons associated with such bursts accumulated over a 10-minute observation time.

k (channels)	Δt (msec)	Mode limits (counts)
1	4.4	53
2	8.8	84
3	13.2	88
4	17.6	98
5	22	116
6	26.4	126
7	30.8	144
8	35.2	151
9	39.6	168
10	44.0	158
15	66	173
20	88	206