Reports

Dating and Authenticating Works of Art by Measurement of Natural Alpha Emitters

Abstract. *A method for distinguishing between modern and old samples of lead has been used to analyze certain works of art. The basis of the method is the detection of radioactive lead-210, which decays with a 22-year half-life when it is unsupported by its long-lived precursor, radium-226. The latter is separated chemically from lead when lead and lead products are prepared from the ore.*

Scientific tools of increasing sensitivity and sophistication have been used to examine the materials of art and archeology. Such tools frequently support and render more reliable the judgment of experts in questions of authenticity. The quality of forgeries, however, has the tendency to improve as forgers become acquainted with new methods of examination and in turn learn to circumvent or confound them. We here describe a new method which should be of value in distinguishing paintings of the 18th century and earlier from forgeries made in the 20th century. Under certain circumstances, the results of an analysis may provide an unambiguous distinction.

The method described here is based upon the following principle. White lead is a pigment of major importance in painting and it has been used by artists for many centuries. Lead metal is also an important constituent of other works of art, such as pewter and lead-bearing bronzes. Lead is extracted from ores which contain a quantity of uranium and its several descendants (*1*) which are in radioactive secular equilibrium with it. The radioactive equilibrium is disturbed in the series of chemical processes associated with the extraction of lead metal from the ore and with the production of lead compounds. The radium, and most of its descendants, is preferentially removed during processing, while the radioactive lead-210 accompanies the stable isotopes of lead. The lead-210 in the metal extracted from the ore is thus no longer supported by its relatively long-lived ancestor, radium-226, and it begins to decay with a half-life of 22 years. This process continues until the lead-210 activity is once more in equilibrium with the much smaller quantity of radium that survived the chemical fractionation process.

One can exploit these relationships to determine the age of a sample by using the equation

$$[\mathrm{Pb}]_t - [\mathrm{Ra}] = \Big([\mathrm{Pb}]_0 - [\mathrm{Ra}] \Big) e^{-\lambda t} \quad (1)$$

where $[\mathrm{Pb}]_t$ is the lead-210 concentration in the sample at present, [Ra] is the radium-226 concentration in the sample, λ is the disintegration constant for lead-210, t is the time since separation of the lead from its ore, and $[\mathrm{Pb}]_0$ is the lead-210 concentration at the time of separation (*2*). The original lead-210 concentration cannot be determined experimentally but it can be presumed to be equal to the concentration of uranium in lead ores, or it can be calculated from the radium concentration of a sample and a known separation factor, defined as $[\mathrm{Pb}]_0/[\mathrm{Ra}]$. Therefore, the utility of the equation in calculating age would be reduced by the occurrence of a wide range of values of either the original uranium concentrations or the separation factors. Nevertheless, valuable deductions may still be possible when large differences in time are being considered (for example, 20th century versus 18th century).

The method was evaluated by determining the concentrations of lead-210 and radium-226 in a variety of lead metals and their compounds in order to compute the range of original concentrations and the range of separation factors. To estimate the age of an unknown sample one must determine the concentrations of these two nuclides in the sample. The method described below is primarily limited to paintings; its extension to other objects follows readily.

The principle was tested in 1928 on a pair of samples, one old and the other recent (*3*). Approximately 25 years ago, a more extensive study was made to demonstrate the low radioactivity of old lead; the study was based upon the measurement of alpha emission (*4*). No suitable method was then available, however, with adequate sensitivity and selectivity to distinguish between the concentrations of radium-226 and those of its descendants. As a result, only a rather ambiguous comparison of gross alpha emission rates could be made, which proved useless.

In contrast, modern methods of radiochemistry make it possible to measure both radium-226 and polonium-210 with a relatively high degree of accuracy in a small sample. Also, if one uses the small size and high energy resolution of solid-state detectors, very low backgrounds are produced, of the order of 0.001 count per minute, a factor which contributes to the sensitivity of the analysis. This is accom-

Table 1. Ore and ore-concentrate samples.

Sample No.	Description and source	Concentration (dpm per gram of Pb)	
		Po^{210}	Ra^{226}
M-12	Chunk galena (Oklahoma-Kansas)	0.03 ± 0.04	0.00 ± 0.25
M-13	Ore concentrate (Oklahoma-Kansas)	5.8 ± 1.3	4.5 ± 1.2
M-6	Crushed raw ore (S.E. Missouri)	4.3 ± .8	2.4 ± .6
M-5	Ore concentrate (S.E. Missouri)	1.7 ± .2	0.7 ± .4
M-17	Ore concentrate (Idaho)	2.5 ± .4	2.2 ± .8
M-18	Ore concentrate (Idaho)	0.27 ± .17	0.18 ± .18
M-19	Ore concentrate (Washington)	170 ± 20	140 ± 20
M-20	Ore concentrate (British Columbia)	3.5 ± .2	1.9 ± 1.1
M-21	Ore concentrate (British Columbia)	0.9 ± .2	0.4 ± .2
M-22	Ore concentrate (Peru)	1.5 ± .4	.0 ± .3
M-23	Ore concentrate (Bolivia)	1.5 ± .4	1.6 ± .5
M-24	Ore concentrate (Australia)	0.8 ± .2	1.1 ± .7

plished by measuring only alpha particles having the energy or energies characteristic of the nuclide to be determined.

The best method to determine the concentration of lead-210, therefore, involves determining the concentration of its alpha-emitting descendant, polonium-210. There are numerous ways to separate polonium-210 and to prepare it for counting (*5*). In brief, the sample (paint, metal, chemical, or ore) is dissolved in dilute nitric acid, and the polonium is eventually plated on silver counting-planchets. The overall efficiency, the product of the chemical yield and the counting yield, was 30 percent for the counting system used. This corresponds to a chemical yield of nearly 100 percent.

The solution remaining after the polonium has been removed is then analyzed for radium. After macroscopic quantities of lead have been removed (used later for a gravimetric lead analysis) and the radium-bearing solution has been purified, radium is eventually carried on a minute precipitate of $BaSO_4$ ($\sim$0.1 mg of barium) which is mounted on a filter for counting (*6*). The overall efficiency for the radium measurement was 85 percent after 2 weeks were allowed for ingrowth of radon and its short-lived descendants. This corresponds to a chemical yield of greater than 95 percent.

The accuracy and reproducibility of the analytical procedures for polonium-210 and radium-226 were established by repeatedly applying the procedures to samples of typical materials having known concentrations of these nuclides. Such samples were prepared by the addition of standardized solutions, in known quantities, sufficient to overwhelm the natural concentrations of the radium nuclides in the starting materials. As a check for reproducibility, duplicate determinations were made on several of the samples of known age.

The results of the analyses of white lead and related lead-bearing materials are given in Tables 1–5. Table 1 gives the polonium-210 (equivalent to lead-210) and the radium-226 concentrations in a variety of lead ores from various regions. The concentrations of polonium and radium are nearly equal in most cases, as they should be, though there seems to be a slight bias in favor of lower radium values. There may be a systematic experimental error due to difficulties in the dissolution

Table 2. Processed material: lead metal or lead compounds.

Sample No.	Description and source	Date of manufacture	Concentration (dpm per gram of Pb) Po^{210}	Ra^{226}	Po^{210} at date of manufacture	Separation factor†
M-7	Lead metal (U.S.)	Recent	1.5 ±0.2*	0.06±0.30	1.5 ±0.2	25
M-16	Lead metal (U.S.)	Recent	6.8 ±1.2*	1.2 ± .6	6.8 ±1.2	5.7
M-15	Basic lead sulfate (U.S.)	Recent	0.06 ± .08	0.0 ± .3	0.06± .08	
M-92-H	Lead metal (U.S.)	1965	4.40 ± .39	.02± .02	4.4 ± .4	220
M-91-H	Lead metal (U.S.)	1963	3.48 ± .39	.23± .07	3.6 ± .4	16
M-3	Lead chloride (U.S.)	1962	46 ±4*	.5 ± .4	50 ±4	100
M-4	Lead nitrate (U.S.)	1962	20 ±2*	1.8 ± .8	22 ±2	12
M-1	Lead acetate (U.S.)	1961	30 ±4*	0.2 ± .4	33 ±5	165
M-2	Lead subacetate (U.S.)	1958	12 ±3*	.0 ± .3	14 ±4	>47
M-8	Lead metal (U.S.)	1914–39	2.5 ± .4*	.0 ± .2	8.7 ±1.4	>43
M-9	Lead metal (U.S.)	1914–39	14 ±1*	5.9 ±1.2	34 ±4	5.8
M-10	Lead metal (U.S.)	1914–39	0.7 ± .1	0.2 ± .3	2.0 ± .4	10
M-29	Spanish lead	1700	.01 ± .03	.05± .04		
M-73-H	Old pipe (England)	16th c.	.039± .041	.08± .03		
M-30	Roman lead	50 B.C.	.002± .008	.02± .01		

*Average of two measurements. †Expressed as ratio between Po^{210} at date of manufacture and Ra^{226}.

Table 3. Artists' white lead (20th century). P, pigment; G, ground.

Sample No.	Description and source	Date of manufacture	Concentration (dpm per gram of Pb) Po^{210}	Ra^{226}	Po^{210} at date of manufacture	Separation factor†
M-76-H	White lead (England) P	1965	2.0±0.3	0.00±.01	2.0±0.3	>200
M-71-H	Cremnitz white (Holland) P	1965	36 ±2	.05±.04	36 ±2	720
M-72-H	White lead (England) P	1965	1.7± .3	.04±.02	1.7± .3	42
M-85-H	Quick process (Australia) P	1965	2.4± .3*	.06±.06*	2.4± .3	40
M-84-H	White lead (Holland) P	1965	16 ±1	.11±.03	16 ±1	150
M-90-H	White lead (U.S.) P	1965	153 ±6	.15±.04	153 ±6	1000
M-82-H	Silver white (France) P	1965	3.4± .4	.06±.02	3.4± .4	57
M-39	Flake white (U.S.) P	1965	15.5±1.8	.00±.2	16 ± .2	>80
M-2-H	White lead (Germany) P	1959	22 ±4	.6 ±.5	26 ±5	43
M-3-H	White lead (Holland) P	1959	3.2± .8	.4 ±.2	3.8±1.0	9.5
M-70-H	Preprimed canvas (U.S.) G	1955	5.1± .7	.02±.05	7.0±1.0	350
M-67-H	Preprimed canvas (U.S.) G	1952	7.2±1.2	.03±.05	11 ±2	370
M-68-H	Preprimed canvas (England) G	1948	3.1± .5	.14±.03	5.1± .8	36
M-5-H	Cremnitz white (England) P	1948	2.4± .5	.4 ±.2	3.8± .9	9.5
M-6-H	Flake white (England) P	1948	2.8± .8	.0 ±.2	4.7±1.4	>24
M-87-H	Stack process (Australia) P	1948	5.2± .5	.1 ±.02	8.6± .9	86
M-86-H	Stack process (Australia) P	1945	1.4± .3	.02±.02	2.7± .5	130
M-1-H	Cremnitz white (Germany) P	1940	0.4± .1	.1 ±.1	0.8± .3	8
M-61-H	Landscape (U.S.) G	1940	7.0± .7	.09±.04	15 ±1	170
M-35-H	Landscape by Lieb (U.S.) G	1940	28 ±2*	.02±.02	61 ±4	3000
M-65-H	Still life (U.S.) G	1933	4.9± .6	1.5 ±.3	11 ±2	7.3
M-74-H	White lead (England) P	1930	3.2± .4	0.08±.02	9.4±1.0	120
M-52-H	Landscape by Vernon (England?) P	1920–30	1.7± .4	.19±.06	5.6±1.3	30
M-8-H	Cremnitz white (Germany) P	1923	12.3±2.3	.62±.50	44 ±9	71
M-18-H	Portrait by Resco (U.S.) G	1923	9.2±1.2	.36±.40	30 ±5	83
M-17-H	Portrait (U.S.) G	1921	6.3±1.3	.0 ±.3	25 ±5	>83
M-29-H	From stretcher of painting by John Kane (U.S.) P	1921	6.7±1.0	.03±.07	26 ±4	90
M-69-H	Landscape (U.S.) G	1912–28	7.0±1.1	.42±.08	27 ±4	64
M-62-H	Landscape (U.S.) G	1910–30	6.5± .9	.23±.11	26 ±4	110
M-30-H	Flowers by Speicher (U.S.) G	1920	3.3± .6	.12±.05	13 ±3	110
M-66-H	Street scene (U.S.) G	1920	6.8±1.2	.36±.11	27 ±5	75
M-58-H	Flower study (U.S.) P	1920	2.9± .4	.03±.03	11 ±2	370
M-28-H	Landscape by C. Hassam (U.S.) P	1919	3.4± .9	.2 ±.5	14 ±4	70
M-40-H	Portrait by Logan (U.S.)	1908–13	2.2± .2	.0 ±.2	13 ±2	>65
M-63-H	Landscape by J. Sloane (U.S.) G	1910	7.3± .8	.13±.07	40 ±4	310

*Average of two measurements. †Expressed as ratio between initial Po^{210} and Ra^{226}.

Table 4. Artists' white lead (19th century). P, pigment; G, ground.

Sample No.	Description and source	Date of manufacture	Concentration (dpm per gram of Pb)			Separation factor†
			Po^{210}	Ra^{226}	Po^{210} at date of manufacture	
M-4-H	Stack process (England) P	1884–94	2.8 ±0.2*	0.0 ±0.1*	30 ± 2	>300
M-51-H	Cavalry scene by deLaunay (France) P	1880	1.8 ± .2	.12± .03	24 ± 3	200
M-41-H	Landscape by Innes (U.S.) P	1850–70	5.5 ±2.0	2.9 ±2.1	70 ± 80	24
M-59-H	Landscape (U.S.) G	1850–60	8.7 ±1.6	2.2 ± .5	210 ± 50	95
M-53-H	Landscape (England) G	1850–60	2.1 ± .3	0.62± .15	48 ± 11	77
M-56-H	Itinerant portrait (U.S.) G	1830–50	0.28± .08	.10± .03	9.5± 4.4	95
M-60-H	Portrait (France) P	1830–40	5.3 ±2.3	3.9 ±1.4	90 ±180	23
M-42-H	Portrait (U.S.) P	1830–40	1.3 ± .10	0.8 ± .1	29 ± 16	36
M-31-H	Primitive (France) P	1830	0.51± .10	.03± .02	32 ± 8	1000
M-12-H	Female saint (Italy?) P	1800–50	.87± .21	.50± .11	29 ± 19	58
M-39-H	Eicholz (U.S.) G	1817	.35± .08	.13± .03	22 ± 8	170

*Average of two measurements. †Expressed as ratio between initial Po^{210} and Ra^{226}.

of the ore samples. The observed wide range of radium-226 and lead-210 concentrations, from essentially zero to nearly 200 disintegrations per minute per gram of lead, precludes one use of Eq. 1, wherein one must assume that the original uranium concentrations in lead ores are reasonably consistent.

The remaining tables present the results obtained for samples of material that had been subjected to chemical separation processes. The tables include lead metal or chemical compounds (Table 2) and white lead. The latter is further divided into groups corresponding to the 20th century (Table 3), the 19th century (Table 4), and the 18th century or earlier (Table 5).

The 20th-century samples listed in Table 3 consisted of two types: painting grounds (G) and relatively pure white-lead pigments (P). The latter were pigments taken either from tubes of paint or from manufacturers' dry colors of artists' grade.

The samples from painting grounds were obtained by scraping the paint from the tacking edge of canvases. Artists' canvases in the 19th and 20th centuries were often preprimed with a coat of glue size and a coat of white-lead paint before the artists purchased them. Canvases were tacked to the sides of a stretcher, with the result that an excess of primed but unpainted canvas is usually found on all edges. The white-lead paint "ground" thus exposed provided us with many of the samples in Tables 3–5. In a few cases, primarily in Tables 4 and 5, actual samples of the artist's white paint were used where the painting itself was of such minor value or in such deteriorated condition that a small sample could be taken. The approximate date of manufacture of the pigment in the paint and ground was considered to be the date of the painting, although it is realized that the pigment could be several years older.

In Tables 2–4, the observed polonium and radium concentrations are given with standard deviations. Also, the computed concentration of polonium for the date of manufacture and a computed separation factor (*7*) are given. The two computed quantities are omitted in Table 5 because they would be meaningless for old samples. It is apparent that the separation factors cover a wide range, from about 6 to more than 1000. Since neither the separation factor nor the original uranium content of the ore is restricted to a narrow range of values, the concept of precisely calculating ages from Eq. 1 must be discarded (*8*).

For the oldest samples (Table 5), in contrast to the more modern samples of the other tables, there are essentially no deviations from equilibrium between the polonium and radium concentrations within the indicated uncertainties. Therefore, the method should be useful in determining if a given sample is "old" or "modern."

To show how this information may be used, we here evaluate results obtained for two fictitious samples of unknown age. These results represent those obtained from samples of two hypothetical paintings purported to have been produced in the 17th century but which might have been forged in 1922, approximately two lead-210 half-lives (44 years) ago.

Let us assume that white lead from painting A is analyzed for polonium-210 and for radium-226. The concentration of polonium-210 is 2.0 ± 0.2 disintegrations per minute (dpm) per gram of Pb, and that of radium-226 is 0.1 ± 0.1. This white lead could not have been produced in the 17th century, since the concentration of polonium-210 in the paint at that time would have been on the order of 10^5 to 10^6 dpm per gram of Pb, an absurd concentration.

Our second sample, hypothetical painting B, is assumed to have been likewise sampled and analyzed. The concentration of polonium-210 is 1.5 ± 0.2 dpm per gram of Pb and that of radium-226 is 1.4 ± 0.2. Since the polonium and radium values are the same within the uncertainties, the sample would appear to be significantly older than 44 years; no such equilibrium has been observed in any samples from the 19th and 20th centuries.

Therefore, given the premise that the paintings were painted either in the 17th century or in the 20th, one could say with great certainty that hypothetical painting A was produced in the 20th century, and hypothetical painting B was produced in the 17th.

It is also possible to draw further conclusions concerning the ages of

Table 5. Artists' white lead (18th century or earlier). P, pigment; G, ground.

Sample No.	Description and source	Date of manufacture	Concentration (dpm per gram Pb)	
			Po^{210}	Ra^{226}
M-15-H	Portrait by Ralph Earl (U.S.) P	1780–1801	1.75±0.62	1.57±0.50
M-43-H	Portrait (France) P	1780–88	2.4 ± .6	1.3 ± .4
M-11-H	Female saint (Italy?) P	1750–1800	3.8 ± .7	3.0 ± .4
M-9-H	Saint (Spanish style) P	1750–1800	3.0 ± .6	2.8 ± .4
M-13-H	Portrait by Claypoole (U.S.) P	1746	1.96± .46	1.82± .43
M-16-H	Portrait by Badger (U.S.) P	1730–50	2.58± .81	2.70± .29
M-57-H	Still life (Holland) P	1700	2.34± .72	1.60± .39
M-20-H	Dogs (Holland) P	1600–60	0.23± .27	0.40± .47
M-10-H	Painting (Italy?) P	Early 1600's	2.81± .57	2.56± .47
M-22-H	Portrait (Italy) P	1600	0.21± .10	0.21± .29

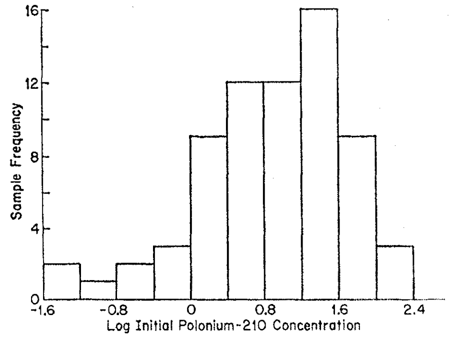

Fig. 1. The distribution of observed initial polonium-210 concentrations, corrected for decay where appropriate.

these two samples. The logarithms of the initial polonium concentration for all materials (some 68 values from Tables 1–4) show a distribution skewed toward the low values, with a mode at about 16 dpm per gram of Pb, and the highest values 100 to 200 dpm per gram of Pb (Fig. 1). The latter would correspond to a uranium content, in an ore containing 50 percent lead, of approximately 0.01 to 0.02 percent. This is a fairly high value for uranium content, since the expected average value for uranium in rocks of the earth's crust is $\sim$2.7 parts per million (*9*), although there are some lead ores in the Western Hemisphere (*10*) which contain as much as a few percent uranium (*11*). Therefore, it is highly unlikely that painting A was produced before the middle of the 19th century, since a decay correction to that time, or earlier, yields an improbably high value for the initial lead-210 concentration in the sample.

The logarithms of the calculated separation factors for more than 50 samples (Tables 2–4) exhibit a normal (*12*) distribution (Fig. 2) with log$_{10}$ of the geometric mean, 1.92, and log$_{10}$ of the geometric standard deviation, 0.59 (*13*). Values of the separation factor for sample B for certain dates in the past were obtained by applying corrections for radioactive decay. These values exhibit increasing uncertainties (*14*) as the magnitude of the decay correction increases. The computed separation factors and uncertainties for sample B at various dates may be statistically compared with the mean and standard deviation of the population of known separation factors by means of a *t*-test (*13*). This test suggests that the odds against hypothetical painting B having been painted later than 1900 are better than 100 to 1. The odds ($\sim$3 to 1) are also against production of the painting later than the early part of the 19th century, but they are not sufficiently high as to rule out this period for the date of production.

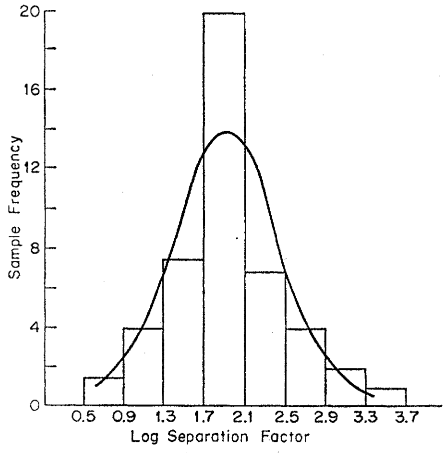

Fig. 2. The distribution of experimentally determined separation factors with a fitted normal curve.

In practice, it is possible to obtain results leading to less positive conclusions, for example, if low levels of radioactivity are encountered. There are also possible sources of interference which may affect the analysis in such a way so as to make old paint appear modern and vice versa. For example, the presence of an acid-soluble sulfate such as gypsum ($CaSO_4 \cdot 2H_2O$), a colorless pigment commonly used in painting grounds and sometimes as an extender in paints, may lead to a low value for the radium analysis and to the conclusion that the sample is modern. Powdered gypsum (10 percent) mixed with white lead was found to lower the apparent concentration of radium in a sample to approximately one fourth of its actual value.

A second potential source of interference is the presence in a paint sample of a relatively large proportion of natural mineral pigments that have high natural radioactivity. Analyses of a selection of five such pigments showed that concentrations of radium and radiolead in these materials may range up to approximately 6 dpm per gram of pigment. The presence of this material could mask a disequilibrium between low concentrations of lead-210 and radium-226 in a modern white-lead component in a mixture. Thus, the sample could erroneously appear old even though the white-lead component exhibited modern disequilibrium values.

Maximum concentrations of radioactivity in the nonwhite-lead portions of over 30 samples of impure white lead (those in Tables 3–5 with less than 50 percent lead) were calculated and found to be generally less than 0.6 dpm per gram of material (*15*). Experimentally, therefore, the effect of contamination of white lead samples appears to be unimportant with lead concentrations greater than approximately 30 percent; but the interpretation of results obtained for paint samples of lower lead content may become questionable.

To avoid these particular analytical difficulties, the painting must be sampled selectively so as to obtain white lead of high purity. The development and use of adequate sampling techniques or, alternatively, the perfection of separation methods to assure a true white-lead analysis are important for full use of the method.

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2. The decay of the radium is assumed to be negligible in the time scale considered here. In 150 years the activity of the radium would decrease by approximately 7 percent if unsupported by its immediate precursor, 7.5 × 10^4-year thorium-230.
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7. When radium was not detectable, one standard deviation was used as its concentration for purposes of computing a lower limit of the separation factor.
8. Note that the range of calculated initial polonium-210 concentrations for the processed material (Tables 2–4) corresponds roughly to the range of values observed for the ore samples (Table 1).
9. S. R. Taylor, *Geochim. Cosmochim. Acta* **28**, 1273 (1964).
10. H. Faul, Ed., *Nuclear Geology* (Wiley, New York, 1954), pp. 284–292; H. D. Wright, C. M. Smith, J. J. Hutta, *Intern. Geol. Congr. 21st Copenhagen 1960 Rept. Session Norden*, part 16, p. 248 (1960).
11. High uranium concentrations were found in samples in which uranium was not homogeneously distributed in the galena. Presumably, these inhomogeneities (and the entire uranium series in them) would be removed during ore beneficiation.
12. Tests for skewness and kurtosis (*13*) were applied. While skewness can be shown to be absent, there is a slight, but statistically insignificant, tendency for the distribution to be leptokurtic.
13. F. E. Croxton, *Elementary Statistics with Applications in Medicine* (Prentice-Hall, New York, 1953).

14. Note that the standard deviations in the values for any one sample are chiefly derived from the statistical nature of the counting process.
15. Maximum values for radium content of impurities were computed by assuming that all of the measured radium in the sample was contributed by the impurities.
16. Samples were obtained from six companies: The Eagle-Picher Co., St. Joseph Lead Co., The Bunker Hill Co., Siegle Co., National Lead Co., and Associated Lead Manufacturers Ltd.; and from E. C. Hulmer, G. L. Stukenbroeker, H. Kühn, W. Bousted, and A. W. deWild. We thank these companies and individuals, as well as R. F. Weise, T. H. Davies, T. G. Fox, T. P. Kohman, and J. Walker and E. R. Feidler for valuable assistance. The work was carried out at the Nuclear Science and Engineering Corporation, Pittsburgh, in association with the National Gallery of Art Research Project, at Mellon Institute. The National Gallery of Art, Washington, D.C., is currently supporting further study of the method at Mellon Institute.

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Natural Displacement of Pollution from the Great Lakes

Abstract. *A simplified mathematical model of a lake system indicates that, if the pollution of the Great Lakes were discontinued, the natural flow through the lower Great Lakes would be sufficient to remove about 90 percent of the waste in about 20 years. On the other hand, hundreds of years would be required to displace the pollution from Lake Michigan and Lake Superior.*

Approximately 30,000,000 people dump their waste into and drink water from the Great Lakes. During the last few years, the rapidly increasing pollution has become a matter for serious concern. The water in the lower lakes has become offensive, and the cost to the public is tremendous for the increased amount of water treatment required, the loss of recreational use, and the decreased number of fish that are caught (*1*, *2*). Multibillion-dollar programs are being proposed to decrease the pollution and to clean up the lake water (*2*). Many recent publications review the problem of contamination and eutrophication and methods for their control, but none have been found which present quantitative data on the effect of natural displacement by the flow of water through the lakes.

To illustrate the time required for self-purging of the lakes, I have made a mathematical analysis of a simplified model of a lake system. The analysis is predicated upon three assumptions: (i) the precipitation on the lake just equals the evaporation; therefore, the flow rate (R) to and from the lake is the same; (ii) the concentration of pollutants in the streams entering the lake (C_1) is constant; and (iii) the pollutants are added to the lake itself at a constant rate (Q) and are distributed so that their concentration (C_2) is uniform throughout the volume (V) of the lake. A material balance around this lake system gives the relationship of the change in the concentration of pollutants in the lake with time (T):

$$C_2 = C_2^0 \exp(-RT/V)$$
$$[C_1 + (Q/R)]\,[1 - \exp(-RT/V)] \quad (1)$$

where C_2^0 is the concentration of pollutants in the lake at the initial time ($T = 0$).

A graph of this function illustrates the rate of buildup of pollutants in an initially uncontaminated lake, $C_2/[C_1 + (Q/R)]$ (curve A, Fig. 1), or the rate of recovery of a contaminated lake when the addition of pollutants is discontinued, C_2/C_2^0 (curve B of Fig. 1). In either case, 90 percent of the final concentration is reached when the volume of water that has flowed through the lake is 2.3 times the volume of water in the lake.

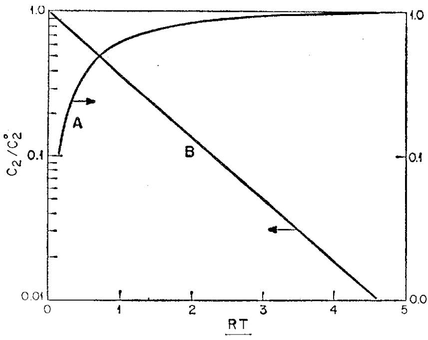

Fig. 1. Effect of water displacement rate (RT/V) of lake on the concentration of material in the lake. Curve A shows the rate of buildup of pollutants in an initially uncontaminated lake ($C_2^0 = 0$); Curve B shows the rate of recovery of a lake when addition of pollutants is discontinued ($C_1 = 0$ and $Q = 0$).

The lower Great Lakes have a relatively high flow-to-volume ratio. The flow through Lake Erie is 0.38 volume per year (Table 1). The concentration of pollutants would, therefore, reach a nearly steady state in about 6 years if the rate of addition of pollutants to the lake were constant. (The concentration continues to increase largely because of the continuing increase in the rate at which pollutants are added to the lake.) If the addition of pollutants were completely discontinued, 90 percent of the waste would be carried from Erie in about 6 years.

Since the wastes from Lake Erie flow into Lake Ontario, no program for cleaning up Lake Ontario alone can be effective. Lake Ontario contains about four times as much water as Erie but has only about 20 percent more flow rate. If the addition of pollutants to both lakes were discontinued, approximately 20 years of series flow would be required to remove 90 percent of the pollution from Ontario.

Because of the low flow ratio of the upper lakes, Lake Michigan would require about 100 years to deplete its contamination by 90 percent through natural flow; Lake Superior would require more than 500 years.

The mathematical relationship used in these estimates ignores many of the factors which influence the contamination of lakes. In actual lake systems, the flow of water through the lake is modified by wind and eddy currents, by the bypassing of bays, by channeling, by thermal stratification, by bot-

Table 1. Data on the Great Lakes system (*1*).

Characteristic	Lake Superior	Lake Michigan	Lake Erie	Lake Ontario
Length (km)	560	490	385	309
Breadth (km)	256	188	91	85
Area (km²)				
Water surface, United States	53,618	58,016	12,898	9,324
Water surface, Canada	28,749		12,768	10,360
Drainage basin land, United States	43,253	117,845	46,620	39,370
Drainage basin land, Canada	81,585		12,224	31,080
Drainage basin land, total	124,838	117,845	58,793	70,448
Drainage basin (land and water), total	207,200	175,860	87,434	90,132
Maximum depth (m)	406	281	60	244
Average depth (m)	148	84	17	86
Volume of water (km³)	12,221	4871	458	1636
Average annual precipitation (mm)	736	787	863	863
Mean outflow (liter/sec)	2,067,360	5,012,640	5,550,720	6,626,880
Average retention time of water (yr)	189	30.8	2.6	7.8