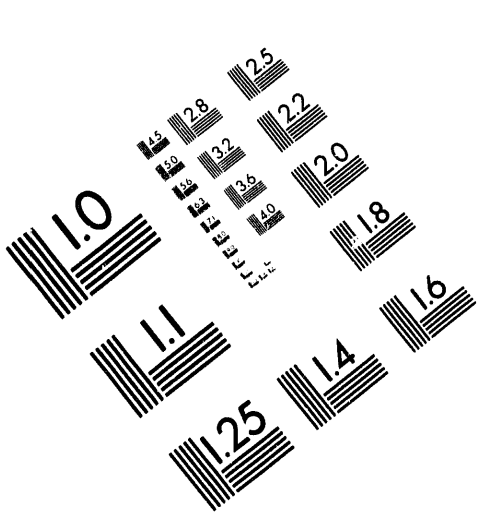

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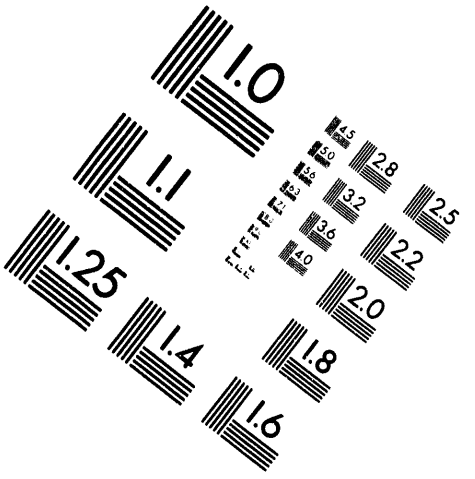

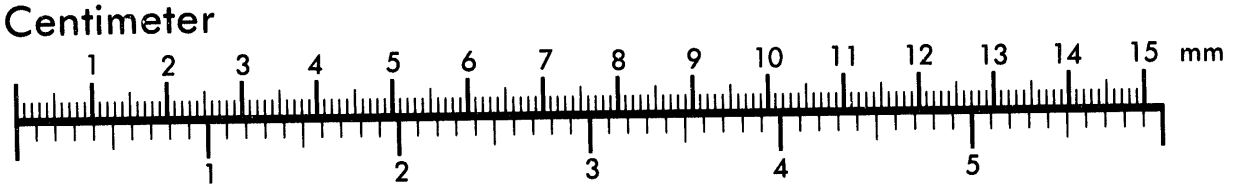

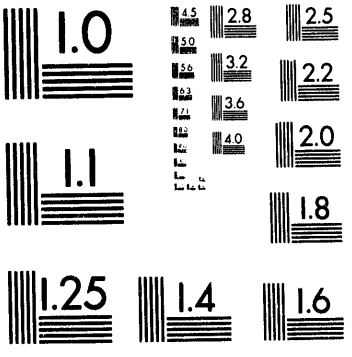

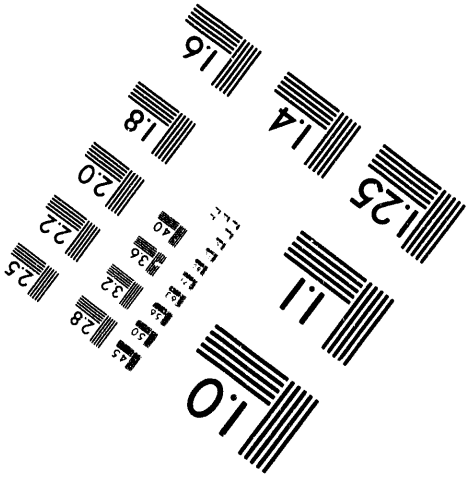

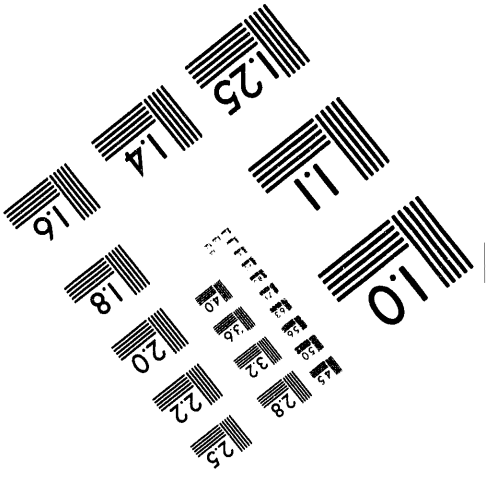

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PREVALENCE OF TECHNICAL MESOTHORIUM IN SELF-LUMINOUS COMPOUNDS USED BY NEW JERSEY RADIUM DIAL WORKERS*

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ABSTRACT

Forty-five sealed glass ampoules containing samples of radium dial paint prepared by the U.S. Radium Corporation (USRC) and used by New Jersey dial workers in the period 1915–1928, were analyzed for radium-226 and radium-228 activity by high-resolution gamma-ray spectrometry. Radium-228 was found to be the dominant activating agent at the probable time of use in most of the sampled paints in which the ratio of radium-228 to radium-226 activity was determinable, the calculated radium-228 to radium-226 activity ratio in 1920 in these ranging from 7.2 to 10 (median 8.4), indicating that radium element chemically separated from commercial thorium ores (technical mesothorium) was used as the activator. Published isotopic activity ratios in USRC dial-paint samples that were appreciably in excess of those we found are shown invariably to be due to errors in calculation. Our results and information in the early literature suggested the hypothesis that dial paints used at USRC before July 1919 were activated with isotopically pure radium-226 whereas compounds used thereafter until the year 1925 were activated with technical mesothorium. Isotopic activity ratios predicted by the hypothesis compared well with median ratios observed in two groups of former workers. We conclude that inaccuracies in dates of hire and termination at USRC might well be the principal source of uncertainty in estimates of skeletal dose for former workers in whom the isotopic activity ratio has not been measured.

1. Introduction

Former dial workers employed by the United States Radium Corporation (USRC) in the period 1915–1926 constitute a major cohort of radium-exposed persons until recently studied for health effects of radiation at Argonne National Laboratory (ANL)[1,2]. Aub *et al.*[3] interpreted early published accounts by Martland *et al.*[4-8] of health effects and measurements of radioactivity in these workers to indicate poisoning by technical mesothorium, a by-product of the thorium-gas-mantle industry obtained by chemically extracting

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radium element from thorium ore. Technical mesothorium was often substituted for radium-226 as the activator in dial paints after a shelf-life of 2 to 3 years to allow for growth of the alpha-emitting decay products of radium-228[3]. According to microfilmed Company records on file at ANL, USRC received its first supply of mesothorium in the year 1917, and court transcripts in 1930[9] indicated that mesothorium was first added to USRC dial paints around June of 1919.

The relative proportions of radium-228 and radium-226 activity at the time of use in dial paints activated with 3-year-old technical mesothorium would lie in the range of 6:1 to 13:1, based on typical isotopic compositions of technical mesothorium reported by Aub *et al.*[3] However, a study of former USRC workers conducted by the Radium Research Project of the New Jersey State Department of Health (NJRRP)[10,11] reported that relative proportions of radium-228 and radium-226 activity calculated to the year 1920 ranged as high as 140:1 in analysed samples of USRC dial paint and as high as 200:1 in former workers. The NJRRP concluded that the dial paints used by the workers probably contained random and highly variable proportions of the two radium isotopes[10,11].

Samples collected by the NJRRP of USRC dial paints that were prepared or used principally before 1926 were made available to us for radioactivity analysis by the Bureau of Radiation Protection, Division of Environmental Quality, Department of Environmental Protection of the State of New Jersey. In this paper, we present the results of our measurements of radium-226 and radium-228 activity in the paint samples, we compare these results and those of others who analysed USRC paints of similar vintage, and we discuss the development and testing of an hypothesis that the relative intakes of radium-228 and radium-226 by former USRC workers are dependent on their dates of hire and termination.

2. Materials and Methods

2.1. Dial-Paint Samples

The 48 sealed glass ampoules containing samples of dial paint that we received from the Bureau of Radiation Protection were originally collected more than 30 years ago by the NJRRP and were recovered from a bank vault in Washington, D. C. in 1982. The dates of preparation or use of 45 of the 48 samples were listed in a NJRRP inventory supplied by the Bureau of Radiation Protection. Three of the 48 samples may have been intended as measurement blanks, no place or date of use having been indicated for these in the inventory.

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Many of the sample numbers were paired or grouped in the inventory, possibly indicating replicate sampling.

2.2. Radioactivity Analyses

Forty-five of the 48 sealed ampoules were analyzed by a gamma-ray spectrometry system comprising a high-resolution, lithium-drifted germanium detector, a multichannel pulse-height analyzer, an on-line minicomputer, and a commercial software package (Spectra-F Version 2.07, Canberra Industries, Inc.). Thorium-228 activity (half-life 1.91 y) was determined from the counting rates of gamma rays emitted in the decay of thallium-208 (half-life 3.1 min). Radium-228 activity was estimated by multiplying the measured thorium-228 activity by the radium-228 to thorium-228 transient radioactive equilibrium ratio of 0.668. Radium-226 activity was determined from the counting rates of gamma rays emitted in the decay of lead-214 (half-life 26.8 min) and bismuth-214 (half-life 19.7 min).

3. Results

For 18 of the 45 paint samples, the radium-228 to radium-226 activity ratio at the time of preparation or use was indeterminate (the radium-226 contents of these samples were <40 Bq). For most of the samples that were paired or grouped in the NJRRP inventory, the radium-226 and radium-228 contents were similar to those of other samples in the pair or group. Of the 27 samples with determinate isotopic activity ratios, 19 fell into 7 pairs or groups. Sample-average radium-226 and radium-228 activities were calculated for each pair or group on the assumption that each pair or group comprised replicate samplings of a single paint. Thus, results are reported in Table 1 for a total of 15 samples or sample groups. No formal analysis of uncertainties was made, but an interlaboratory comparison discussed below of results for some of the paint samples indicates that the overall relative standard errors of results that were significantly different from zero are generally no more than ±10%.

In nine of the thirteen paints prepared in the period 1915-1925 for which an isotopic activity ratio was determined (Table 1), radium-228 activity was clearly dominant at the time of preparation or use. In these, the calculated ratio of radium-228 to radium-226 activity in 1920 averaged 8.4 ± 0.82 (S.D.) and all were within the range expected for samples of three-year-old technical mesothorium. The paints used in 1928 (none of which contained detectable radium-228 activity) probably were activated with isotopically pure radium-226.

Table 1. Radium-226 content and isotopic activity ratio in 1920 for 15 USRC dial-paint samples or sample groups by date of preparation or use.

Date of Preparation or Use	Sample No.	Sample-average Ra-226 in 1920 (kBq)	Ra-228/Ra-226 activity ratio in 1920
1915-1920	48,80	4.4	8.8
	49	0.81	8.2
	50,77	1.1	7.4
	95	210	<0.2
	104	0.92	7.4
	141	7.4	8.2
1919	93	1.9	<0.3
	97	9.6	(1)[a]
1920-1922	86	2.3	9.3
	126	36	7.2
"before 1925"	45,53,54	3.3	9.4
	63,96	2.3	<0.4
	89,105	0.7	10
1928	46,52,61	2.3	<0.4
	88,100,101, 119,132	48	<0.3

a Uncertain

4. Discussion

4.1. Paint-sample analyses by others

The isotopic activity ratios found in other studies of USRC paints are similar to those found in the dial paints in our study in which radium-228 was the dominant radium isotope at the time of preparation or use. In a 1924 industrial hygiene study of the USRC plant by C. K. Drinker[12], in which samples of dial paint were administered to experimental animals by lung instillation, the radium-228 to radium-226 activity ratio calculated to 1920 in sampled tissues averaged 8.2 ± 0.8 (S.E.)[13]. Analyses *postmortem* of bones of 21 former Connecticut dial workers who used paint prepared by USRC[14] showed a weighted mean radium-228 to radium-226 activity ratio in 1920 of 8.4 with a coefficient of variation of 0.17.

Goldin and Drew[15] at New York University measured isotopic activity ratios in 25 USRC paint samples of vintage similar to ours. When we reduced their reported radium-228 to radium-226 activity

ratios by a factor of 1.5 to account for the transient equilibrium ratio (no mention had been made of this ratio), the results were similar to those obtained on our samples, except for two samples for which they calculated radium-228 to radium-226 ratios in 1921 of 36 and 100. The measured radium-226 and radium-228 activities for those two samples were below the activities Goldin and Drew reported for a blank ampoule and below their stated detection limits.

Sharpe[11] published radium-228 to radium-226 ratios calculated to 1920 for 11 samples or sample groups of USRC dial paints, most dated to the period 1915-1920 in the NJRRP inventory. These data originally appeared in the Final Report of the NJRRP[10]. The paint-sample measurements were attributed to Corcoran at ANL *ca* 1961, who reported his thorium-series results to the NJRRP as "the amount in grams of thorium-232 in equilibrium with its daughters that would give the same number of counts as the sample in the 2.62-MeV thorium-C photopeak"[10]. In converting Corcoran's results to radium-228 activity, the NJRRP apparently implicitly assumed that radium-228 and thorium-228 were at equal activities in the paint samples. Moreover, for four of the paint samples, an order of magnitude error apparently was introduced in making the conversion to activity units (if there were no typographical errors in the published thorium-232 gamma ray equivalents). Thus, the radium-228 to radium-226 ratios reported by the NJRRP[10] and Sharpe[11] appear to have been overestimated by factors of 1.5 to 15. Thus, for example, six of the seven highest radium-228 to radium-226 activity ratios in 1920 calculated by the NJRRP[10,11] from dial-paint measurements *ca* 1961 at ANL have been revised downward from published values of 142, 138, 70.5, 15.6, 14.1, and 12.2 to values of 9.3, 7.4, 4.5, 9.7, 8.9, and 7.4, respectively.

Thirteen of the samples analysed by Corcoran[10] were among the samples sent to us by the Bureau of Radiation Protection. Our results and those recalculated from Corcoran's radium-226 and thorium-232 equivalent results as reported by the NJRRP[10] are compared in Table 2 for these samples. The comparison shows that the one atypically-high recalculated isotopic activity ratio remaining, the ratio of 88 in paired Sample Nos. 48 and 80, was apparently the result of a decimal-point error in the reported or published radium-226 activity.

4.2. Isotopic activity ratios in former workers

In its Final Report[10], the NJRRP listed radium-228 to radium-226 activity ratios at time of exposure for 11 former USRC workers calculated from whole-body counting results obtained at New York University. The ratios for four of the former workers, three of whom were employed at USRC exclusively in the extraction of radium from

Table 2. Comparison of the results of our analyses of 7 USRC paint samples or sample groups and Corcoran's analyses of these same samples at ANL *circa* 1961[10].

Sample No.	Sample-average Radium-226 in 1920 (kBq)		Radium-228 to Radium-226 Activity Ratio in 1920	
	Corcoran	This Study	Corcoran	This Study
49	0.60	0.81	9.7	8.2
48,80	0.45	4.4	88	8.8
50,77	1.0	1.1	8.0	7.4
95	250	210	1.3	<0.2
104	0.91	0.92	8.7	7.4
126	38	36	5.8	7.2
88....132	45	48	<0.3	<0.4

uranium ores, ranged from 24 to 204. For two of these four, radiochemical analyses of bone at ANL showed that skeletal radium-226 was more than an order of magnitude below the minimum detectable by whole-body gamma-ray spectrometry and skeletal radium-228 was within the range of environmental levels. For a third former worker, the reported radium-228 body content was below the stated limit of detection. The fourth former worker was employed at a thorium extraction plant at the time of his whole-body measurement. Of the remaining seven former workers who retained detectable radium-228 activity when measured at NYU, six, all dial painters, were measured subsequently at the Massachusetts Institute of Technology (MIT)[16] or at ANL and the presence of radium-228 was corroborated.

Evans *et al.*[16] at MIT measured the isotopic activity ratio in 15 former dial workers who had been employed at USRC. The data for the former workers, all of whom were hired before 1920, suggested at least a 20- to 30-fold increase circa 1919-1920 in the average ratio of radium-226 to radium-226 activity taken up by the workers. The ratio of radium-228 to radium-226 activity corrected for radioactive decay to 1919 was about 2-3 in workers principally exposed after 1919. Only 6 of the 15 former workers had significant periods of exposure after 1919. After 1920, dial-paint application work at the USRC plant declined and most of the USRC self-luminous compound was produced for sale to watch and clock manufacturers[9], and applicationwork at the plant had practically ceased (the plant closed in 1926), so employment before 1925 is of principal concern.

4.3. Isotopic-Composition Hypothesis

The dial paint results and information in the early literature[4-9] led to the development of the following hypothesis regarding the isotopic composition of USRC dial paints: (1) all paint used in application work at USRC before 1 July 1919 was activated with isotopically pure radium-226; (2) all paint used in application work at USRC from 1 July 1919 to 31 December 1924 was activated with technical mesothorium obtained in a single extraction from thorium ore; and (3) the combined activity of radium isotopes in dial paint was on average the same whether the activator was isotopically pure radium-226 or technical mesothorium.

The hypothesis can be expressed to a close approximation by:

$$IR = (f r_0 \exp[-\lambda(t_2-t_1)/2])/(1+(1-f)r_0), \qquad (1)$$

where IR is the ratio of the total intake of radium-228 activity to the total intake of radium-226 activity during the work period, f is the fraction of the work period falling within the period 1 July 1919 to 31 December 1924, r_0 is the radium-228 to radium-226 activity ratio in USRC technical mesothorium on 1 July 1919 (estimated to be 9), λ is the difference between the radioactive decay rate constants of radium-228 and radium-226 (0.12 y^{-1}), t_1 is the time from 1 July 1919 to the date of hire of the worker or zero if the date of hire preceded 1 July 1919, and t_2 is the time from 1 July 1919 to the termination of the work period or to 31 December 1924, whichever was earlier.

4.4. Tests of hypothesis

In the hypothesis expressed by Eq. 1, the estimation of the Intake Ratio depends solely on the dates of USRC employment, which typically are not known to a high degree of accuracy because USRC employment records generally are unavailable. Provisional tests of the hypothesis are afforded by the above-mentioned sets of determinations of whole-body radium in the six former USRC dial workers measured at New York University in whom the presence of radium-228 was corroborated by follow-up measurements at other laboratories and in six former USRC dial workers measured at MIT who had significant periods of exposure after 1919.

Five of the six NYU subjects were hired at USRC in the period 1916-1917 and one was hired in 1918. The six allegedly were employed for a median duration of 3 y and terminated USRC employment in the period 1919-1924. The range of observed Intake Ratios was 0.1-1.1 and the median was 0.38. The median date of hire was 1 February 1917 and the median date of termination was 30 June 1920, so in Eq. 1, t_1=0,

t_2=1y, and f=1y/3.3y, i.e., 0.30. The Intake Ratio predicted by the equation for the median dates of hire and termination of the NYU subjects is 0.35, which compares favorably with the observed median.

Two of the six MIT subjects were hired in 1917 and four were hired in 1919. The six were employed for a median duration of 2.3 years. All had significant periods of exposure after 1919. The range of observed Intake Ratios was 0.33–3.4 and the median was 2.1. The median date of hire was 1 November 1918 and the median date of termination was 31 January 1921, so in Eq. 1, t_1=0, t_2=1.6y, and f=1.6y/2.3y, i.e., 0.70. The Intake Ratio predicted by the equation is 1.5, not too different from the observed median.

5. Conclusion

Encouraged by the results of the tests of the hypothesis against the grouped data, we conclude that inaccuracies in dates of hire and termination at USRC (rather than large day-to-day variations in the isotopic composition of the dial paint[11]) might well be the principal source of uncertainty in estimates of skeletal dose for former workers in whom the isotopic activity ratio has not been measured.

6. Acknowledgments

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