

# PAPER

## Long-Term Stability of Carrier-Free Polonium Solution Standards

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The long-term solution stability of trace quantities of polonium in dilute hydrochloric acid has been investigated. Polonium solutions at trace concentrations, under various alkaline, neutral, or weakly acidic conditions are known to be unstable: being readily hydrolyzed, chemically deposited, or volatilized; exhibiting "radiocolloidal" behavior; and undergoing "plate-out" or adsorption onto glass surfaces. Although stored polonium solutions are generally considered to be stable in the acid range of 0.1 to 1.0 normality (*N*), scant data exist on any possible long-term effects, particularly for very dilute, aged solutions. In this study, previously standardized carrier-free solutions of  $^{208}\text{Po}$  activity concentration, (ranging in age from 1.2 to nearly 9 years, and with acid concentrations from about 0.1 to 2.0 *N* HCl) were re-assayed to determine the remaining soluble fraction of polonium. The results indicate that at acid concentrations of a few tenths of 1 *N*, the solutions are clearly unstable. In the range of 0.3 to 0.5 *N*, the results are somewhat equivocal. Only in the range at or above 1 *N* do the solutions appear to be stable over many years, approaching a decade. All measurements were performed by  $4\pi\text{-}\alpha$  liquid scintillation counting of gravimetrically-determined aliquots of the standardized, aged solution samples. This study also validated the long-term integrity of  $^{208}\text{Po}$  Standard Reference Material SRM 4327.

### Introduction

In 1984, the National Institute of Standards and Technology (NIST, formerly the National Bureau of Standards) prepared, calibrated, and made available for dissemination carrier-free solution standards of 2.9-year  $^{208}\text{Po}$ . These standards (issued as Standard Reference Material SRM 4327) consisted of approximately 1.1 g of 1 *N* hydrochloric acid (HCl) solution in 2-mL flame-sealed borosilicate-glass ampoules, and were certified to contain a  $^{208}\text{Po}$  activity concentration of  $76.6 \pm 1.1 \text{ Bq} \cdot \text{g}^{-1}$  on 20 June 1984.<sup>(1)</sup> In the intervening years, these SRMs have had a great popularity in laboratories throughout the world—being used primarily as low-level tracers to determine recoveries or yields in radiochemical procedures. Over this same time, considerable interest and demand has been

expressed for having available similar standards of the longer-lived 102-year  $^{209}\text{Po}$ .

As a result of the oft perplexing chemistry of polonium [refer to Abstract; and *cf.* Bagnall,<sup>(2,3)</sup> Figgens,<sup>(4)</sup> and references therein], it was deemed advisable to more seriously evaluate the long-term stability of polonium solutions, particularly in terms of validating the integrity of the existing  $^{208}\text{Po}$  solution standards, prior to issuing any further polonium standards; *viz.*,  $^{209}\text{Po}$ .

For this study, three series of previously standardized, carrier-free, dilute acidic solutions of  $^{208}\text{Po}$  were re-assayed to determine the remaining soluble fraction of polonium in the aged solutions. They were: (i) three 7.0-year solutions in 1.0 *N* HCl used in the preparation of SRM 4327, and standardized in June 1984 (see Figure 1); (ii) three 8.8-year

solutions in 0.3 and 1.5 N HCl, standardized in September 1982 (see Figure 2); and (iii) five 1.2-year solutions, ranging in acid concentration from 0.09 to 2.0 N HCl, standardized in March 1990 (see Figure 3). All of the original assays were performed by  $4\pi$ - $\alpha$  liquid scintillation (LS) counting of gravimetrically-determined aliquots of the solutions, using PCS\* (a xylene-surfactant-based LS cocktail) and compared with matched blanks of nearly identical composition. All subsequent assays, conducted to determine the polonium recoveries after aging, were similarly performed by LS counting using sources matched to the original aqueous phase/cocktail composition ratios.

### 7.0-year solutions of $^{208}\text{Po}$ in 1.0 N HCl

The origin and devolution of the 7-year solutions (A, M, and S) are illustrated in the schematic of Figure 1. Solution A was an aliquot of part of the original stock material used to prepare SRM 4327, and consisted of approximately 2.5 g of 1.0 N HCl solution and stored in a flame-sealed 2-mL borosilicate-glass ampoule since 1984. Solution M was an aliquot of a prepared master solution based on a dilution of the stock material. It consisted of approximately 0.5 g of 1.0 N HCl solution and stored since 1984 in a similar flame-sealed 2-mL ampoule. Solution S, a representative sample of the dispensing solution, was a randomly selected ampoule from the SRM 4327 series that was described in the Introduction.

The results of the original 1984 assays for these solutions, based on LS measurements of gravimetrically-related LS-counting sources, are given in Table 1. The inferred decay corrected, 1991

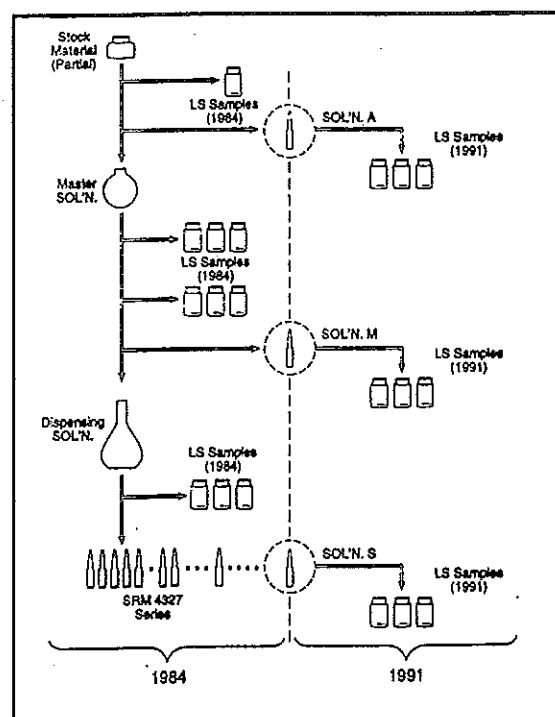


Figure 1 Origin and devolution of the 7-year solutions A, M, and S used in the standardization and preparation of SRM 4327 and as subsequently re-assayed in 1991.

total  $\alpha$ -particle emission rates per gram of solution, based on the 1984 results, are given in Table 2. The results of Table 2 require not merely a decay correction for  $^{208}\text{Po}$ , but also a correction for the known  $^{209}\text{Po}$  impurity in the solutions. The corrections were based on an assumed  $^{209}\text{Po} : ^{208}\text{Po}$  impurity ratio of  $0.0065 \pm 0.0026$  (as obtained from the original NBS (i.e., NIST) certificate<sup>(1)</sup> for SRM 4327) using half lives<sup>(5)</sup> of  $2.898 \pm 0.002$  years and

\* Amersham Corp., Arlington Heights, Illinois. In the interests of accuracy and clarity in describing various items of equipment or apparatus, occasional mention has been made of commercial sources or brand names. This in no way implies endorsement of such products by the U.S. Government.

| Solution <sup>(a)</sup>      | Number of LS samples <sup>(b)</sup> | LS sample composition                             | Total $\alpha$ -particle emission rate per gram solution<br>(as of 1200 EST 29 June 1984) |                          |
|------------------------------|-------------------------------------|---|---|--------------------------|
|                              |                                     |   | Mean ( $\alpha \cdot \text{s}^{-1} \cdot \text{g}^{-1}$ ) <sup>(c)</sup>                  | $s_m$ (%) <sup>(d)</sup> |
| Stock material (A)           | 1                                   | 15 mL PCS<br>0.07 g sol'n.                        | 905.9   | —                        |
| Master (M)                   | 3                                   | 15 mL PCS<br>0.04 to 0.13 g sol'n.                | 3617.   | 0.19                     |
|                              | 3                                   | 15 mL PCS<br>0.04 to 0.13 g sol'n. + 1 mL 1 N HCl | 3611.   | 0.20                     |
| Dispensing (S)<br>(SRM 4327) | 3                                   | 15 mL PCS<br>1.1 g sol'n.                         | 78.00   | 0.22                     |

(a) All solutions are 1.0 N HCl.  
(b) Each sample was LS counted twice.  
(c) Assuming a  $4\pi$ - $\alpha$  LS counting efficiency of 100 percent after corrections for extrapolations to zero energy.  
(d) Relative standard deviation of the mean.

Table 1 Original 1984 liquid scintillation (LS) counting results for the solutions (A, M, and S) used in the preparation of  $^{208}\text{Po}$  SRM 4327.

102 ± 5 years for  $^{208}\text{Po}$  and  $^{209}\text{Po}$ , respectively. The propagated uncertainty due to the effect of the  $^{209}\text{Po}$  impurity on the decay correction is a substantial contributor to the overall estimated uncertainties listed in Table 2. Refer to note (c) in Table 2.

One may observe that the  $\alpha$ -particle emission rate per gram for solution S listed in Table 1 (78.0  $\alpha \cdot \text{s}^{-1} \cdot \text{g}^{-1}$ ) differs from the certified  $^{208}\text{Po}$  activity concentration (76.7  $\text{Bq} \cdot \text{g}^{-1}$ ) for SRM 4327 by 1.7 percent. This difference arises from three factors: (1) SRM 4327 was originally standardized by defined-geometry  $\alpha$ -particle scintillation counting of evaporated sources, while the 1984 LS

counting results given in Table 1 served as confirmatory measurements; (2) the  $\alpha$ -particle emission rate per gram includes the additional contribution from the  $0.5 \pm 0.2 \text{ Bq} \cdot \text{g}^{-1}$  of  $^{209}\text{Po}$  impurity; and (3) a small 0.6 percent decay correction between the reference time for the LS results and the reference time for SRM 4327. The 1.7 percent difference is embodied within the 1.4 percent certified overall uncertainty.<sup>(1)</sup>

The results of the present 1991 re-assays of solutions A, M, and S are summarized in Table 3. The matched composition of the LS counting sources between the 1984 and 1991 assays is demonstrated by comparison of Tables 1 and 3.

| Total $\alpha$ -particle emission rate per gram solution ( $\alpha \cdot \text{s}^{-1} \cdot \text{g}^{-1}$ ) (as of 1800 EST 5 July 1991) |                     |                                      |
|--|---------------------|--------------------------------------|
| Solution <sup>(a)</sup>  | Mean <sup>(b)</sup> | Estimated uncertainty <sup>(c)</sup> |
| A  | 174.7               | 3.1                                  |
| M  | 697.1               | 12.5                                 |
| S  | 15.05               | 0.27                                 |

(a) All solutions are 1.0 N HCl.  
 (b) Based on the decay-corrected 1984 LS counting results of Table 1 assuming a  $^{209}\text{Po} : ^{208}\text{Po}$  impurity ratio of  $0.0065 \pm 0.0026$  at the 1984 standardization time.  
 (c) Assumed to correspond to an approximate relative standard deviation ( $u = 1.8\%$ ) comprised of the following components propagated in quadrature: LS counting precision (0.2%); LS efficiency, including extrapolation to zero energy (1.2%); gravimetric measurements (0.1%);  $^{208}\text{Po}$  decay correction (0.1%); effect of  $^{209}\text{Po}$  on decay correction (1.3%).

**Table 2** Inferred (as of 1991) total  $\alpha$ -particle emission rates per gram for the 1984 solutions A, M, and S.

| Solution <sup>(a)</sup> | Number of LS samples <sup>(b)</sup> | LS sample composition                                     | Total $\alpha$ -particle emission rate per gram solution (as of 1800 EST 5 July 1991) |                          | Recovery <sup>(e)</sup> of polonium from solution after approximately 7.0 years | Estimated overall uncertainty <sup>(f)</sup> in recovery $3u$ (%) |
|-------------------------|-------------------------------------|---|---|--------------------------|---|---|
|                         |                                     |   | Mean ( $\alpha \cdot \text{s}^{-1} \cdot \text{g}^{-1}$ ) <sup>(c)</sup>              | $s_m$ (%) <sup>(d)</sup> |   |   |
| A                       | 3                                   | 15 mL PCS<br>0.5 to 1.0 g sol'n. + 1 N HCl <sup>(g)</sup> | 174.4   | 0.02                     | 0.998   | 6.0   |
| M                       | 3                                   | 15 mL PCS<br>0.05 to 0.11 g sol'n.                        | 688.4   | 0.06                     | 0.987   | 6.0   |
| S                       | 3                                   | 15 mL PCS<br>0.2 to 0.5 g sol'n. + 1 N HCl <sup>(g)</sup> | 14.76   | 0.29                     | 0.980   | 6.1   |

(a) All solutions are 1.0 N HCl.  
 (b) Each sample was LS counted twice with multiple replicates for each of the two independent counts.  
 (c) Assuming a  $4\pi$ - $\alpha$  LS counting efficiency of 100 percent after corrections for extrapolations to zero energy.  
 (d) Standard deviation of the mean.  
 (e) Based on the inferred 1991 solution contents given in Table 2.  
 (f) Assumed to correspond to three times an approximate relative standard deviation ( $u$ ) comprised of the following components propagated in quadrature: LS counting precision (given  $s_m$ ); LS efficiency including extrapolation to zero energy and dead-time corrections (0.9%); gravimetric measurements (0.05%); and the inferred emission rate concentration from Table 2 (1.8%).  
 (g) Adjusted to obtain a total solution mass of 1.1 g.

**Table 3** Present LS counting results for the 1984 solutions A, M, and S indicating the polonium recovery from solution after 7.0 years.

Therefore, differences due to quenching and detection efficiencies between the two assays were minimized. As indicated in Table 3, the recovery of polonium from all three solutions was complete (i.e.,  $\approx 100\%$ ) within statistical variability. The mean recovery was 0.988 with a standard deviation of the mean ( $s_m$ ) of 0.44 percent. The overall relative uncertainty in the polonium recovery is estimated to be 6 percent. By convention of the NIST Radioactivity Group, this overall uncertainty is defined as three times an estimated propagated standard deviation where all of the individual uncertainty components in the propagation are expressed in terms of estimated (experimental) standard deviations (or standard deviations of the mean where appropriate) or uncertainty quantities assumed to correspond to standard deviations, irrespective of the method used to evaluate their magnitude. The overall uncertainty is assumed to provide an uncertainty interval having a high level of confidence of roughly 95 to 99 percent. The substantial magnitude of the six percent relative overall uncertainty in the polonium recovery is due in large measure to the uncertainty in the originally determined  $^{209}\text{Po} : ^{208}\text{Po}$  impurity ratio following a 7-year decay correction.

This 1991 re-assay not only verified the integrity of the solution stability of SRM 4327, but also reconfirmed the original certified  $^{208}\text{Po}$  calibration. Despite the passage of approximately 2.4 half-lives during which the  $^{208}\text{Po}$  decayed by a factor of 0.1867 while the  $^{209}\text{Po}$  contribution to the  $\alpha$ -particle emission rate (with an originally estimated uncertainty of 40%) changed from 0.65 to 3.3 percent, the overall agreement in the  $^{208}\text{Po}$  activity concentration is still within 1.2 percent of the original certified value. A slight elaboration may help to clarify this.

The total  $\alpha$ -particle emission rate per gram of solution at time  $t$ ,  $E_t$ , is just the sum of the contributions from the  $^{208}\text{Po}$  activity concentration and that of the  $^{209}\text{Po}$  impurity. Hence, the  $^{208}\text{Po}$  activity concentration at time  $t=0$ ,  $C_{t=0}$ , is related to a presently determined emission rate  $E_t$  by

$$C_{t=0} = \frac{E_t}{e^{-\lambda_{208}t} + I_{t=0} e^{-\lambda_{209}t}}$$

where  $\lambda_{208}$  and  $\lambda_{209}$  are the decay constants for  $^{208}\text{Po}$  and  $^{209}\text{Po}$ , respectively, and where  $I_{t=0}$  is the

$^{209}\text{Po} : ^{208}\text{Po}$  activity concentration ratio at time  $t=0$ . The relative uncertainties in each of these quantities are:

$$u_{E_t} = 1.0\% ;$$

$$u_{I_{t=0}} = 40.0\% ;$$

$$u_{\lambda_{208}} = 0.069\% ; \text{ and}$$

$$u_{\lambda_{209}} = 4.9\% ;$$

which may be used to obtain the propagated relative uncertainty in  $C_{t=0}$  (see equation below) assuming the uncertainty in the decay time  $t$  is negligible. The  $^{208}\text{Po}$  activity concentration at the original 1984 calibration reference time ( $t=0$ ) determined in this way using the data of Table 3 is  $C_{t=0} = 76.6 \text{ Bq} \cdot \text{g}^{-1}$  with an overall estimated relative uncertainty of approximately  $3u_{C_{t=0}} = 4.9$  percent. This may be compared with the 1984 certified values of  $76.7 \text{ Bq} \cdot \text{g}^{-1}$  with an overall uncertainty of 1.4 percent, or perhaps more consistently with the 1984 LS result of  $78.0 \alpha \cdot \text{s}^{-1} \cdot \text{g}^{-1}$ . The close 1.8 percent agreement between the LS results for the 1991 re-assay and the 1984 value suggests that the estimated 5 percent uncertainty is somewhat overestimated, which may in turn be due to an original overestimate in the uncertainty in the  $^{209}\text{Po} : ^{208}\text{Po}$  impurity ratio. Nevertheless, the agreement confirms the 1984 calibration within its stated uncertainty; and clearly indicates that the given impurity ratio is also well within its stated uncertainty.

### 8.8-year solutions of $^{208}\text{Po}$ in 0.3 and 1.5 N HCl

The origin of the three aged 8.8-year solutions of  $^{208}\text{Po}$  is illustrated in Figure 2. These solutions had  $^{208}\text{Po}$  activity concentrations in the range of 0.1 to  $1 \text{ Bq} \cdot \text{g}^{-1}$  after aging, and were used to evaluate the recovery at very trace levels, although it was known a priori that they would challenge the detection limit capability of the LS measurements. The solutions (labelled CB, CC, and CA in Figure 2) were originally assayed at NBS/NIST in September 1982 by LS counting, and aliquots of the solutions were stored and aged in flame-sealed 5-mL borosilicate-glass ampoules. The aged, stored portions of the original solutions are labelled CB2, CC1, and CA1, respectively. Ampoules CB2 and CC1 were 0.31 N HCl solutions containing

$$u_{C_{t=0}} = \sqrt{u_{E_t}^2 + \frac{\lambda_{208}^2 t^2 (e^{-\lambda_{208}t})^2 u_{\lambda_{208}}^2 + (I_{t=0} e^{-\lambda_{209}t})^2 [u_{I_{t=0}}^2 + \lambda_{209}^2 t^2 u_{\lambda_{209}}^2]}{(e^{-\lambda_{208}t} + I_{t=0} e^{-\lambda_{209}t})^2}}$$

approximately 5.8 and 3.6 g, respectively. Ampoule CA1 was a 1.48 N solution containing approximately 4.5 g.

Table 4 contains the results of the original 1982 assays on the three solutions. The inferred total  $\alpha$ -particle emission rates per gram of solution (as of 1991) for them is given in Table 5. It was assumed that  $^{208}\text{Po}$  was the only  $\alpha$ -emitting radionuclide contributing to the emission rate. The uncertainty estimates provided in the tables were similarly treated as that described in the previous section of this paper. The results of the current re-assay of the solutions for each prepared LS counting source are summarized in Table 6. As before, the LS sample compositions were matched as closely as possible to the conditions of the original 1982 assays. As indicated, the recovery of polonium, in terms of the remaining soluble fraction in solution, is equivocal at first appearance for solutions CB2 and CC1 at 0.31 N, while the recovery is complete (i.e.,  $\cong 100\%$ ) for the 1.48 N solution CA1. The 1 percent and 3

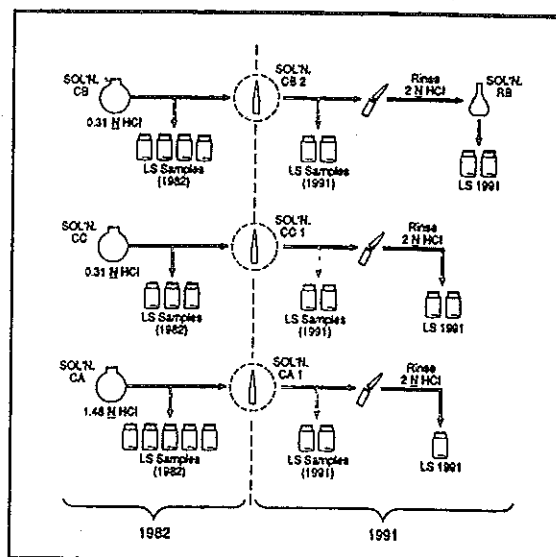


Figure 2 Origin and devolution of the 8.8-year solutions CB2, CC1, and CA1 as assayed in 1982 and re-assayed in 1991.

| Total $\alpha$ -particle emission rate per gram of solution<br>(as of 1200 EST 17 September 1982) |               |                      |                                  |  |                          |                       |
|---|---------------|----------------------|----------------------------------|--|--------------------------|-----------------------|
| 1982 solution   | HCl normality | Number of LS samples | LS sample composition            | Mean ( $\alpha \cdot \text{s}^{-1} \cdot \text{g}^{-1}$ ) <sup>(c)</sup> | $s_m$ (%) <sup>(b)</sup> | 3u (%) <sup>(c)</sup> |
| CB  | 0.31          | 4                    | 15 mL PCS<br>0.8 to 3.4 g sol'n. | 0.6083   | 0.39                     | 2.2                   |
| CC  | 0.31          | 3                    | 15 mL PCS<br>1.6 to 4.0 g sol'n. | 0.6165   | 0.15                     | 1.9                   |
| CA  | 1.48          | 3                    | 15 mL PCS<br>0.4 to 0.9 g sol'n. | 8.900  | 0.10                     | 1.9                   |

(a) Assuming a  $4\pi$ - $\alpha$  LS counting efficiency of 100 percent after corrections for extrapolations to zero energy.  
 (b) Standard deviation of the mean for the precision in LS counting.  
 (c) An overall uncertainty assumed to correspond to three times an approximate relative standard deviation (u) comprised of the following components propagated in quadrature: LS counting precision (given  $s_m$ ); gravimetric measurements (0.1%); dead-time corrections (0.19%); background subtraction (0.13%); detection efficiency (0.5%); count-rate-versus-energy extrapolation to zero energy (0.32%); and decay corrections (0.01%).

Table 4 Original 1982 LS counting results for the solutions CB, CC, and CA.

| Total $\alpha$ -particle emission rate per gram of solution (As of 1200 EST 9 July 1991) |  |                      |
|--|--|----------------------|
| Solution   | Mean ( $\alpha \cdot \text{s}^{-1} \cdot \text{g}^{-1}$ ) <sup>(a)</sup> | u (%) <sup>(b)</sup> |
| CB2  | 0.07397  | 0.75                 |
| CC1  | 0.07497  | 0.66                 |
| CA1  | 1.082  | 0.65                 |

(a) Decay corrected from the results of Table 1 assuming no  $\alpha$ -emitting radionuclides other than  $^{208}\text{Po}$  are present.  
 (b) Estimated relative uncertainty assumed to correspond to an approximate relative standard deviation (u) derived by propagating in quadrature the uncertainty components listed in note (c) of Table 4 and the additional uncertainty in the decay correction (0.16%). No uncertainty contribution due to the possible presence of an  $\alpha$ -emitting impurity was considered.

Table 5 Inferred (as of 1991) total  $\alpha$ -particle emission rates per gram of the 1982 solutions CB2, CC1, and CA1.

percent positive deviations from unity for the two LS counting sources of solution CA1 are well within expected measurement uncertainty intervals, and may also be influenced in part by other longer-lived  $\alpha$ -emitting impurities (e.g.,  $^{209}\text{Po}$ ) which were assumed to be absent. For solution CB2, the one remaining LS sample (a second one was broken and thereby lost during preparation) showed a very low recovery ( $\approx 11\%$ ), although it has a large statistical variability. For solution CC1, the two LS samples were in considerable disagreement. One gave a fractional recovery of approximately 0.85 with an estimated overall relative uncertainty of about 10 percent; the second had almost a negligible recovery ( $\approx 7\%$ ). It should be emphasized, however, that the two LS samples for solutions CB2 and CC1 that had  $\alpha$ -particle emission rate concentrations of  $<0.01 \text{ Bq} \cdot \text{g}^{-1}$  were at or near the limit of detection. Yet, the averaged net LS responses were positive in both cases. These two samples had net counting rates of only between 2 and 5 percent of background for a matched blank; and required a cumulative counting time for each sample of 6 to 8 days in order to be determined to the given statistical precision.

A second series of experiments were performed with the aged solution ampoules in an attempt to account for the unrecovered  $^{208}\text{Po}$ , even if the "missing" or insoluble fraction could only be determined semi-quantitatively. For this attempt, the emptied ampoules that had contained the aged solutions CB2, CC1, and CA1 were rinsed with

warmed 2 N HCl, and the resulting rinse solutions were used to prepare a new set of LS samples (refer to Figure 2). The purpose was to determine if one could recover the insoluble polonium still retained within the ampoules, and thereby account for the "missing" polonium through a material balance. To this end, the following definitions will be helpful for understanding the analysis. The total amount of polonium (in terms of the  $\alpha$ -particle emission rate) contained within each aged ampoule is just  $m_0E$  where  $m_0$  is the total mass of solution in the original sealed ampoule and where  $E$  is the inferred  $\alpha$ -particle emission rate per unit mass as of the 1991 reference time and as given in Table 5. The total amount that was previously recovered (called here the "soluble  $^{208}\text{Po}$ ") from the solution aliquots used to prepare the LS samples is  $R_s = \sum m_{s(i)} E_{s(i)}$  where  $m_{s(i)}$  is the solution aliquot sample mass for the  $i^{\text{th}}$  sample and  $E_{s(i)}$  is the assayed  $\alpha$ -particle emission rate per unit mass given in Table 6. The "recovered soluble fraction" is then just  $f_{\text{sol}} = R_s/m_0E$ . The difference  $D = (m_0E - R_s)$  is called here the total "insoluble  $^{208}\text{Po}$ " and is the quantity of  $^{208}\text{Po}$  still remaining in the emptied open ampoule. This, of course, is an over-simplification. It neglects the amount of soluble  $^{208}\text{Po}$  that is not physically transferred during preparation of the LS sample set. Typically,  $\leq 0.1 \text{ g}$  of solution would remain and be unaccountable after "emptying" an ampoule and transferring its contents with a plastic, aspirating pycnometer. This simplification is not likely to

| Solution | HCl normality | Sample mass in 15 mL PCS (g) | Total $\alpha$ -particle emission rate per gram solution (as of 1200 EST 9 July 1991) |                          | Recovery <sup>(c)</sup> of polonium from solution after approx. 8.8 years | Estimated overall uncertainty in recovery <sup>(d)</sup> 3 $\sigma$ (%) |
|----------|---------------|------------------------------|---|--------------------------|---|---|
|          |               |                              | Mean ( $\alpha \cdot \text{s}^{-1} \cdot \text{g}^{-1}$ ) <sup>(a)</sup>              | $s_m$ (%) <sup>(b)</sup> |   |   |
| CB2      | 0.31          | 3.1602                       | (0.0078) <sup>(e)</sup>   | 8.9                      | (0.11)  | 27.   |
|          |               | 2.5939                       | -lost-  | —                        | —   | —   |
| CC1      | 0.31          | 1.7927                       | (0.0054)  | 6.7                      | (0.07)  | 20.   |
|          |               | 1.7517                       | 0.0634  | 3.1                      | 0.85  | 9.9   |
| CA1      | 1.48          | 1.7393                       | 1.091   | 0.38                     | 1.01  | 3.5   |
|          |               | 2.5464                       | 1.117   | 0.26                     | 1.03  | 3.4   |

(a) Assuming a  $4\pi$ - $\alpha$  LS counting efficiency of 100 percent after corrections for extrapolations to zero energy.  
 (b) Standard deviation of the mean for the precision in LS counting.  
 (c) Based on the inferred 1991 solution contents given in Table 5.  
 (d) Assumed to correspond to three times an approximate relative standard deviation ( $u$ ) comprised of the following components propagated in quadrature: LS counting precision (given  $s_m$ ); LS efficiency including extrapolation to zero energy and dead-time corrections (0.9%); gravimetric measurements (0.05%); and the inferred emission-rate concentration from Table 5 (0.65–0.75%).  
 (e) Values in parentheses indicate results that were at or near the limit of detection. Refer to text for details.

**Table 6** Present LS counting results for the 1982 solutions CB2, CC1, and CA1 indicating the polonium recovery after 8.8 years.

introduce errors of greater than 3 percent for any of the sample masses covered here. If the emptied ampoule is then rinsed with a total mass of solution  $m_R$  of which a sample aliquot of  $m_{a(j)}$  is used in preparing an LS counting source, then the potentially available "insoluble  $^{208}\text{Po}$ " concentration that could be recovered with the rinse is  $D/m_R$ , and  $(m_{a(j)}/m_R)D$  "insoluble  $^{208}\text{Po}$ " could be expected to be present in the  $j^{\text{th}}$  sample of the rinse solution. If we let  $R_{a(j)}$  represent the measured  $\alpha$ -particle emission rate in the  $j^{\text{th}}$  sample, then the "insoluble  $^{208}\text{Po}$ " recovered with the rinse in the  $j^{\text{th}}$  sample is  $(R_{a(j)}/m_{a(j)})/(D/m_R)$ . Summing  $R_{a(j)}$  over all  $j$  samples gives the total "insoluble  $^{208}\text{Po}$ " recovered by the rinse,  $R_a$ . The "rinse recovered insoluble fraction" is therefore,

$$f_{\text{insol}} = R_a/D, \text{ or alternatively, } f_{\text{insol}} = [\sum_j R_{a(j)}/m_{a(j)}](D/m_R) \text{ since it was assumed that } \sum_j m_{a(j)} \approx m_R \text{ to within a few percent. The total fraction of } ^{208}\text{Po} \text{ recovered from both the soluble samples plus that from the rinse solutions is then } f_{\text{tot}} = (R_s + R_a)/m_0E \text{ or } f_{\text{tot}} = f_{\text{sol}} + f_{\text{insol}} (1 - f_{\text{sol}}).$$

The results of this rinse and material balance analysis is given in Table 7. Unfortunately, because of the previously lost LS sample for solution CB2, only lower bounds can be placed on the material balance for this solution. Each emptied ampoule was rinsed with  $m_R$  grams of warmed 2 N HCl. The choice of solvent was based on the author's experience in recovering carrier-free, insoluble polonium from glass vessels. The LS counting results for each sample of mass  $m_{a(j)}$  is given in Table 7 as  $R_{a(j)}$ . The results were decay corrected and referenced to the 1991 assay time given in Table 6. For solutions CB2 and CC1, which were initially

of 0.31 normality, the calculated insoluble fractions recovered by the rinse,  $(R_{a(j)}/m_{a(j)})/(D/m_R)$ , were highly variable. For CB2, the two rinse samples differed by 60 percent (i.e., a fraction of  $\geq 0.78$  compared to  $\geq 0.49$  where the  $^{208}\text{Po}$  quantity comprising the missing part of the bounded limits is invariable in both cases). For CC1, the differences in the two LS samples were even more extreme. The observed  $^{208}\text{Po}$  concentration  $R_{a(j)}/m_{a(j)}$  compared to the potentially available concentration in the rinse  $D/m_R$  was nearly negligible in one LS sample (0.04) and the other contained over 132 percent of  $D$ . Similar sampling differences with solution CC1 were previously seen in the original solution (see Table 6). This, of course, strongly suggests that the polonium in this solution ampoule was highly inhomogeneous and remained so even after the rinse. Several possibilities present themselves: part of the polonium may have precipitated, and thereby have been fractionated unevenly in the various samples; or part of the polonium may have been adsorbed or "plated" onto the glass walls of the ampoule, and differentially released and non-uniformly recovered by the rinse; or part of the polonium may have been present as inhomogeneous colloidal suspensions. The overall total recovery  $f_{\text{tot}}$  from both the original solution and the rinse solution was  $\geq 0.66$  and 0.74 for solutions CB2 and CC1, respectively. Not much can be said about the lower bound for CB2, but its initial behavior (Table 6) seems consistent (in terms of its irregularity) with that for CC1. That only 74 percent of CC1 was recoverable even with the rinse was a surprise based on the author's experience, yet, polonium solutions aged to nearly 9 years were

| Solution Identity   | CB2           | CC1             | CA1            |
|---|---------------|-----------------|----------------|
| Total mass of original solution in ampoule, $m_0$ (g)   | 5.8026        | 3.6012          | 4.4728         |
| Total $^{208}\text{Po}$ in ampoule, $m_0E$ ( $\alpha\text{-s}^{-1}$ )   | 0.4292        | 0.2700          | 4.840          |
| Total $^{208}\text{Po}$ recovered in soluble samples, $R_s = \sum_j m_{s(j)} E_{s(j)}$ ( $\alpha\text{-s}^{-1}$ )   | $\geq 0.0246$ | 0.1207          | 4.742          |
| Recovered soluble fraction of total $^{208}\text{Po}$ , $f_{\text{sol}} = R_s/m_0E$   | $\geq 0.06$   | 0.45            | 0.98           |
| Remainder $^{208}\text{Po}$ in ampoule, $D = (m_0E - R_s)$ ( $\alpha\text{-s}^{-1}$ )   | $\leq 0.405$  | 0.149           | 0.098          |
| Total mass of rinse solution, $m_R$ (g)   | 9.83          | 5.22            | 5.01           |
| Mass of LS sample aliquot of rinse solution, $m_{a(j)}$ (g)   | 5.166         | 4.593           | 3.108          |
| $^{208}\text{Po}$ recovered in rinse by LS counting, $R_{a(j)}$ ( $\alpha\text{-s}^{-1}$ )  | 0.165         | 0.0927 (0.0035) | 0.076 (0.0042) |
| Insoluble fraction of $D$ recovered by rinse, $(R_{a(j)}/m_{a(j)})/(D/m_R)$   | $\geq 0.78$   | $\geq 0.49$     | 0.04           |
| Total insoluble $^{208}\text{Po}$ recovered in rinse, $R_a$ ( $\alpha\text{-s}^{-1}$ )  | 0.258         | 0.080           | (0.0042)       |
| Rinse recovered insoluble fraction $f_{\text{insol}} = R_a/D$   | $\geq 0.64$   | 0.53            | (0.04)         |
| Total fraction $^{208}\text{Po}$ recovered in soluble samples and rinse, $f_{\text{tot}} = (R_s + R_a)/m_0E = f_{\text{sol}} + f_{\text{insol}} (1 - f_{\text{sol}})$ | $\geq 0.66$   | 0.74            | 0.98           |

(a) Refer to text for definitions and nomenclature.

Table 7 Material balance for the recovery of polonium from the 1982 solutions CB2, CC1, and CA1.<sup>(a)</sup>

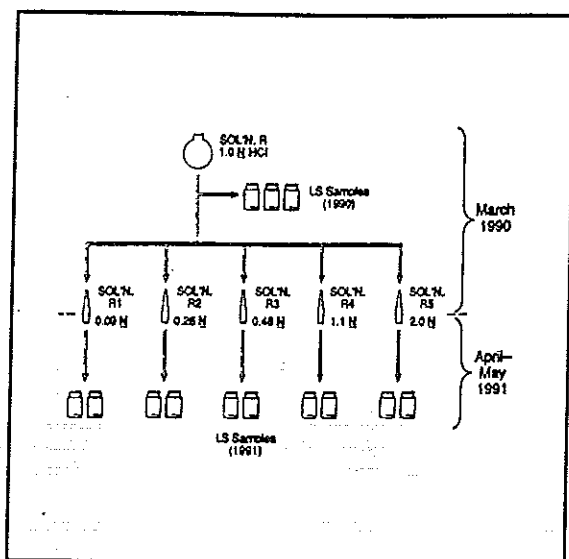
never a part of this experience. The material balance for solution CA1 was only included for completeness. The differences between  $f_{\text{tot}} = 0.98$  of Table 7 and the recoveries of 1.01 and 1.03 of Table 6 are well within the sampling assumptions (e.g., ignoring the trace volumes of solution not transferred in preparing the LS samples) and the expected variations for the measurement uncertainty.

### 1.2-year solutions of $^{208}\text{Po}$ in 0.1 to 2 N HCl

Five carrier-free  $^{208}\text{Po}$  solutions (labelled R1 through R5) were prepared with acid concentrations ranging from 0.09 to 2.0 N HCl (Figure 3). The master solution R from which the five solutions were prepared was assayed by LS counting in March 1990. Solution R consisted of about 5 kBq of  $^{208}\text{Po}$  in approximately 12 g of 1.0 N HCl. Three LS counting sources were prepared such that each source contained a gravimetrically-determined aliquot of R of about 0.2 - 0.5 g in 15 mL PCS, but the cocktail was further diluted with 4 N HCl and distilled water to give a total aqueous phase volume of 5 mL and a HCl normality of 2 N in each cocktail. The total  $\alpha$ -particle emission rate per unit mass for the mean of the three sources was  $430.7 \alpha \cdot \text{s}^{-1} \cdot \text{g}^{-1}$  with a standard deviation of the mean  $s_m = 0.17$  percent (as of 1200 EST, 11 March 1990). The decay-corrected, inferred value as of 1200 EST, 22 May 1991 is  $323.5 \alpha \cdot \text{s}^{-1} \cdot \text{g}^{-1}$ , assuming that the total  $\alpha$ -particle emission rate is due exclusively to  $^{208}\text{Po}$  and has no contribution from any  $\alpha$ -emitting impurity. The estimated overall uncertainty for an assumed 3 standard deviation interval is

approximately 2.0 percent following an uncertainty analysis similar to that given in note (c) of Table 4.

Solutions R1 through R5 were prepared from solution R as given in Table 8. Aliquots of solution R varying from 1.8 to 2.2 g were added with appropriate quantities of 4 N HCl and distilled water to adjust and provide acid normalities from 0.09 to 2.0 N in the five solutions. The solutions were prepared by dilution directly into 5-mL glass ampoules, which were subsequently flame sealed and stored for aging. The total mass of each solution  $m_T$  (obtained independently from mass measurement differences between the final ampoule mass after dilution and the initial tare mass) could also be obtained from the sum of the mass of solution R ( $m_R$ ) plus the masses of the 4 N HCl ( $m_A$ ) and water ( $m_W$ ) dilutions, where  $m_R$ ,  $m_T$ , and  $m_W$  were obtained from pycnometer-dispensed mass differences. In all cases, the mass difference  $m_T - (m_R + m_A + m_W)$  was less than 0.07 mg which in a total mass of about 5 g corresponds to  $\approx 0.001$  percent difference. This type of sample mass verification was employed throughout the preparation of all samples given in this paper, and



**Figure 3** Preparation and devolution of the five 1.2-year solutions R1 through R5 ranging in acid normality from 0.09 to 2.0 N HCl.



has mass uncertainties typical for the routine gravimetric procedures used in our laboratory.

The resulting five solutions with an  $\alpha$ -particle emission rate per unit mass of  $C_0$  given by  $(m_R/m_T)(323.5 \alpha \cdot s^{-1} \cdot g^{-1})$  were aged for approximately 1.2 years and subsequently re-assayed in April and May of 1991. Two LS counting sources were prepared from gravimetrically-determined aliquots of each solution. As before, to match the LS sample composition and thereby match the counting characteristics (i.e., detection efficiency and quenching), the source cocktails were appropriately diluted so that each source consisted of a total aqueous phase mass of about 5 g at 2 N HCl in 15 mL of PCS scintillation fluid.

The re-assayed  $\alpha$ -particle emission rates per unit mass  $C$  for each of the two LS sources for each solution is exhibited in Table 8. The recovery, in terms of the remaining soluble fraction of polonium in the solution,  $C/C_0$ , for each sample is also given in the table. The overall uncertainties

(3u) in the recoveries are estimated to be approximately 3.5 percent, (except for solution R1 with  $3u = 4.4$  to 7.4%) following an uncertainty analysis similar to that in note (d) of Table 6. For solutions R4 and R5 at 1.1 and 2.0 N, respectively, the recoveries were complete with values of  $C/C_0$  between 1 to 2 percent above unity. It is quite conceivable that the values are above unity because of the presence of an  $\alpha$ -emitting impurity that is longer lived than  $^{208}\text{Po}$ . Solutions R2 and R3 at 0.26 and 0.48 N, respectively, have values of  $C/C_0$  very near unity. Yet, their results are somewhat suspiciously peculiar. First, they are low with respect to that of solutions R4 and R5. The mean value of  $C/C_0$  for R3 is nearly 3 percent less than the averages of solutions R4 and R5. Solution R2 has a mean  $C/C_0$  that is 5 percent less. Second, the dispersion in the two results for the two LS samples of solutions R2 and R3 are somewhat greater (4.7 and 3.4%) than those for R4 and R5 (0.7 and 0.3%). The overall uncertainties (3u) in the recoveries between samples have many common terms, and

| Solution Identity | Mass of solution aliquot, $m_R^{(a)}$ (g) | Total mass of solution, $m_T^{(b)}$ (g) | HCl normality (M) | $\alpha$ -particle emission rate per gram $C_0$ (as of 1200 EST 22 May 1991) $(\alpha \cdot s^{-1} \cdot g^{-1})$ | Mass of solution in LS sample $(g)$ | $\alpha$ -particle emission rate per gram $C^{(e)}$ (as of 1200 EST 22 May 1991) |                          | Recovery $C/C_0$ | Estimated overall uncertainty in recovery, $3u^{(g)}$ (%) |
|-------------------|---|---|-------------------|---|-------------------------------------|--|--------------------------|------------------|---|
|                   |   |   |                   |   |                                     | mean $(\alpha \cdot s^{-1} \cdot g^{-1})$  | $s_m$ (%) <sup>(f)</sup> |                  |   |
| R1                | 1.8543                                    | 5.0058                                  | 0.09              | 119.8   | 2.4173                              | 12.22  | 0.93                     | 0.102            | 4.4   |
|                   |   |   |                   |   | 2.3044                              | 0.73   | 2.2                      | 0.0061           | 7.4   |
| R2                | 2.0894                                    | 5.0794                                  | 0.26              | 133.1   | 2.4801                              | 125.6  | 0.21                     | 0.944            | 3.5   |
|                   |   |   |                   |   | 2.4916                              | 131.5  | 0.08                     | 0.988            | 3.5   |
| R3                | 2.2448                                    | 5.1046                                  | 0.48              | 142.2   | 2.1024                              | 138.5  | 0.04                     | 0.974            | 3.5   |
|                   |   |   |                   |   | 2.8414                              | 143.2  | 0.11                     | 1.007            | 3.5   |
| R4                | 2.0186                                    | 4.9831                                  | 1.1               | 131.0   | 1.9505                              | 132.6  | 0.09                     | 1.012            | 3.5   |
|                   |   |   |                   |   | 2.9366                              | 133.5  | 0.24                     | 1.019            | 3.5   |
| R5                | 1.9365                                    | 5.0377                                  | 2.0               | 124.3   | 2.3098                              | 126.9  | 0.06                     | 1.021            | 3.5   |
|                   |   |   |                   |   | 2.6457                              | 126.5  | 0.12                     | 1.018            | 3.5   |

(a) Solution R consists of carrier-free  $^{208}\text{Po}$  in 1 N HCl.  
 (b) Appropriately adjusted with quantities of 4 N HCl and distilled water to obtain the given HCl normality in approximately 5 g.  
 (c) Obtained from the 1990 assay of solution R by LS counting, followed by a decay correction for  $^{208}\text{Po}$  (assuming no other  $\alpha$ -emitters are present in solution) and by a dilution of factor  $m_R/m_T$ . Refer to text.  
 (d) Appropriately adjusted with quantities of 4 N HCl and distilled water to obtain a total aqueous phase mass of about 5 g at 2 N HCl in each LS cocktail (matching the sample composition for the 1990 assay).  
 (e) Obtained from the present 1991 assay by LS counting.  
 (f) Standard deviation of the mean in percent for the precision in the LS measurements.  
 (g) Assumed to correspond to three times an appropriate relative standard deviation (u) following an uncertainty analysis similar to that in note (d) of Table 6.

Table 8 LS counting results for the 1990  $^{208}\text{Po}$  solutions indicating the polonium recovery after 1.2 years.

on excluding them, the differences between solutions R2 and R3 compared to solutions R4 and R5 seem to lie outside the range of expected statistical variations. Yet, the differences are sufficiently small that it is difficult to be definitive. Solution R1 was clearly unstable with the two samples recovering only 10 percent and 0.6 percent of the available  $^{208}\text{Po}$ .

### Summary

Table 9 contains a summary and tabulation of the results from all three recovery experiments. All of the results for solutions with acid normalities of 1.0 *N* and above appear to have complete recoveries (i.e.,  $\approx 100\%$ ) within experimental uncertainties. For more weakly acidic solutions below  $\approx 0.3$  *N* the solutions are unstable in terms of the soluble fraction of  $^{208}\text{Po}$  recovered from sample aliquots of the solutions. In the range around  $\approx 0.3$  up to  $\approx 0.5$  *N*, the results are somewhat more equivocally subject to interpretation, exhibiting wide sample-to-sample variations within the same solution, and between 8.8-year solutions at 0.31 *N* and 1.2-year solutions at 0.26 *N*.

Thus, for purposes of insuring long-term polonium solution stability, it would appear that solutions should be maintained at HCl normalities of at least 1 *N*. It is the author's conviction, however, that to be conservative, the solutions perhaps should be closer to 2 *N* unless there are some specific application requirements that would dictate more dilute solutions.

In regard to the solution stability of SRM 4327

and the validity of its 1984 calibration as confirmed by the 1991 re-assay, the soluble fraction of polonium has remained stable over the intervening seven years and the 1984 calibration is well within its stated uncertainty. One should note, however, that when the SRM is employed for applications involving gross  $\alpha$ -particle emission-rate measurements, it is necessary to adequately correct the  $\alpha$ -particle emission rate for both decay of  $^{208}\text{Po}$  and the decay of the  $^{209}\text{Po}$  impurity. With increasing passages of time, the  $^{209}\text{Po}$ : $^{208}\text{Po}$  impurity ratio will not only continue to increase (from 0.0065 in June 1984 to 0.033 in July 1991), but the overall uncertainty in the  $\alpha$ -particle emission rate will as well (from approximately 1.7% in 1984 to over 6% in 1991 at an assumed three standard deviation uncertainty interval).

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| Solution Identity | Solution age (years) | HCl normality (M) | Approximate range of $^{208}\text{Po}$ activity concentration before and after aging ( $\text{Bq} \cdot \text{g}^{-1}$ ) |  | Recovery range <sup>(a)</sup> | Estimated overall uncertainty in recovery <sup>(a)</sup> 3 $\sigma$ (%) |
|-------------------|----------------------|-------------------|--|--|-------------------------------|---|
|                   |                      |                   |  |  |                               |   |
| A                 | 7.0                  | 1.0               | 900 - 175  |  | 1.00                          | 6.0   |
| M                 | 7.0                  | 1.0               | 3600 - 690   |  | 0.99                          | 6.0   |
| S                 | 7.0                  | 1.0               | 80 - 15  |  | 0.98                          | 6.1   |
| CB2               | 8.8                  | 0.31              | 0.6 - 0.07   |  | 0.1 <sup>(b)</sup>            | 27. <sup>(b)</sup>  |
| CC1               | 8.8                  | 0.31              | 0.6 - 0.07   |  | 0.07 - 0.85 <sup>(b)</sup>    | 20. - 9.9 <sup>(b)</sup>  |
| CA1               | 8.8                  | 1.48              | 9 - 1.   |  | 1.01 - 1.03 <sup>(b)</sup>    | 3.5 <sup>(b)</sup>  |
| R1                | 1.2                  | 0.09              | 160 - 120  |  | 0.006 - 0.1 <sup>(b)</sup>    | 7.4 - 4.4 <sup>(b)</sup>  |
| R2                | 1.2                  | 0.26              | 170 - 130  |  | 0.93 - 0.98 <sup>(b)</sup>    | 3.5 <sup>(b)</sup>  |
| R3                | 1.2                  | 0.48              | 190 - 140  |  | 0.97 - 1.01 <sup>(b)</sup>    | 3.5 <sup>(b)</sup>  |
| R4                | 1.2                  | 1.1               | 170 - 130  |  | 1.01 - 1.02 <sup>(b)</sup>    | 3.5 <sup>(b)</sup>  |
| R5                | 1.2                  | 2.0               | 160 - 120  |  | 1.02 <sup>(b)</sup>           | 3.5 <sup>(b)</sup>  |

(a) Refer to Tables 3, 6, and 8.

(b) Assuming the  $\alpha$ -particle emission rate per unit mass in the solutions is due exclusively to  $^{208}\text{Po}$  and has no contribution from any  $\alpha$ -emitting impurity.

Table 9 Summary of the recovery experiments for the aged, carrier-free  $^{208}\text{Po}$  solutions.

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#### References

1. National Bureau of Standards, Certificate for Standard Reference Material SRM 4327, Polonium-208, issued January 1985.
2. Bagnall, K.W., *Chemistry of the Rare Radioelements*, Academic Press, New York (1957), pp. 1-94.
3. Bagnall, K.W., *Chemistry of Polonium*, Quart. Rev. 11, 30-48 (1957).
4. Figgins, P.E., *The Radiochemistry of Polonium*, National Academy of Sciences, National Research Council, Nuclear Science Series NAS-NS-3037, Washington, DC (1961).
5. Lederer, C.M. and Shirley, V.S. (eds.), *Table of Isotopes*, 7th Ed., Wiley Interscience, New York (1978).

#### Biography

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