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Contract Title: Decay of Th-234 and Daughter Pa-234m in Secular Equilibrium: Resolution of Observed Anomalies

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SUMMARY

Recent gamma-ray spectroscopy measurements have highlighted problems in determining the Pa-234m and Th-234 content of environmental samples. These radionuclides are daughters of U-238 and should rapidly reach secular equilibrium, and maintain this balance between their measured activities. A detailed evaluation of the relevant nuclear decay data by Nichols and Toole (1) has resulted in a significant revision of the recommended emission probability of the 1001 keV gamma ray of Pa-234m from 0.00590 ± 0.00010 to 0.00835 ± 0.00011. However, intercomparison exercises between laboratories have continued to indicate a discrepancy between the measured activities of Th-234 and Pa-234m, and hence a detailed study of the decay data for Th-234 has been undertaken. This re-evaluation had generated a recommended value for the emission probability of the 63.3 keV gamma ray of Th-234 of 0.037 ± 0.002, compared with values between 0.040 and 0.048 from previous evaluations.

A detailed examination has been made of the gamma-ray spectroscopic methods adopted for low-energy gamma-ray measurements as applied to Th-234. Such quantitative studies are relatively difficult, and therefore a recommended procedure is given in this paper, together with experimental and computer-modelling validations. Measurements were undertaken on four silt samples from the Ribble Estuary using this procedure and the recommended emission probability data: such a combination of improvements resulted in good agreement between the Th-234 and Pa-234m activities in secular equilibrium.

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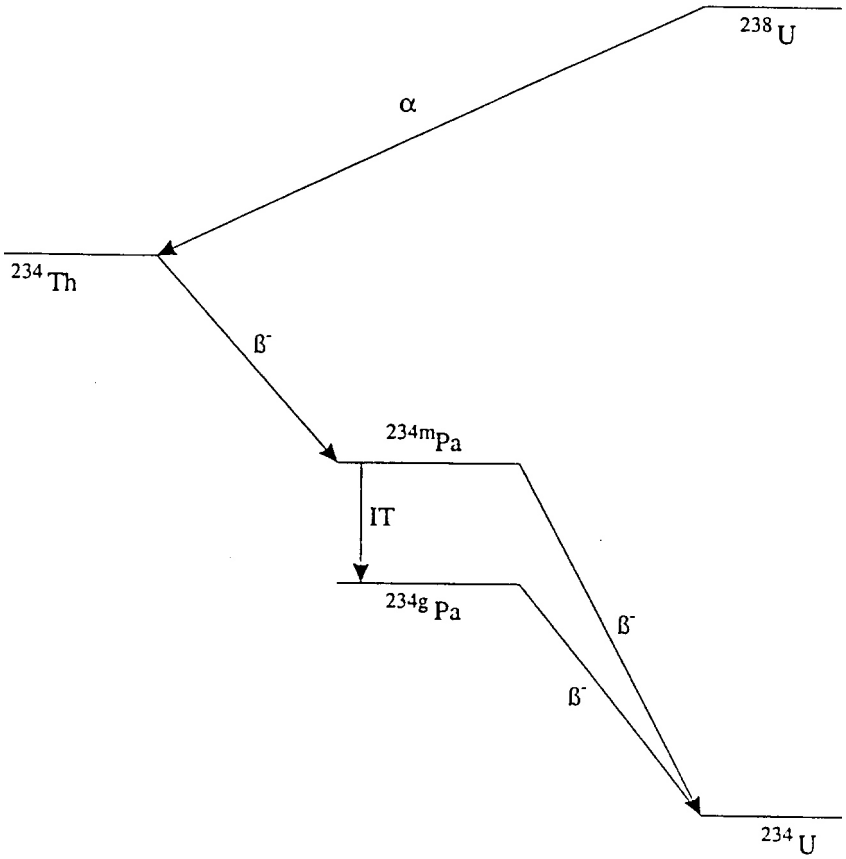
1 INTRODUCTION

The manufacturing plant at BNFL Springfields is primarily concerned with the preparation of uranium hexafluoride for enrichment purposes and the production of fuel elements for thermal reactors. Th-234 and Pa-234m constitute the principal radionuclides discharged to the environment as the major disintegration products of natural uranium, with smaller quantities of Th-228, Th-230, Th-232 and uranium. While the radiological impact of these discharges is low, local monitoring is obligatory to quantify and guarantee discharge authorisations under the Radioactive Substances Act, 1960.

Uranium-238 undergoes alpha-particle decay ($t_{1/2}$ = 4.468 × 10^9 years) to daughter thorium-234 ($t_{1/2}$ = 24.1 days) to give secular equilibrium in less than 1 year; thorium-234 decays to protactinium-234m by beta-particle emission:



The half-life of Pa-234m is short (1.17 min), and this radionuclide is in secular equilibrium with parent Th-234. However, problems have been experienced in quantifying these radionuclides on the basis of their decay parameters. Significant doubts have been placed on the validity of the gamma-ray emission probabilities used to quantify the Th-234 and Pa-234m contents of samples by spectral analysis (previously recommended values: Th-234, Pγ (63.30keV) of 0.045 ± 0.007, Pγ (92.38 keV) of 0.026 ± 0.006 and Pγ (92.80 keV) of 0.026 ± 0.007; Pa-234m Pγ (1001keV) of 0.00590). Sutton et al (1) observed an apparent excess of 80% Pa-234m over Th-234 when the recommended decay data from UKHEDD-1 were adopted (2). As a consequence of this significant discrepancy, the gamma-ray emissions of

Pa-234m were measured at a number of laboratories and a re-evaluation was undertaken to produce a well-defined absolute emission probability for the 1001 keV gamma ray (3). When the newly-recommended value of 0.00835 ± 0.00011 was applied to a set of laboratory intercomparison data from reference 4, the measured Th-234 content of a series of silt samples from the Ribble estuary were still estimated to be deficient relative to the corrected Pa-234m content. These studies implied that the Th-234 measurements were low as a consequence of either the adoption of an incorrect abundance for the 63.3 keV gamma ray or undercorrection of the self-absorption of this low-energy emission by the sample (or a combination of both). A comprehensive evaluation has been carried out on the basis of the above anomaly to produce a new set of recommended decay data for Th-234. The gamma-ray abundance of the 63.3 keV line in particular has been carefully re-assessed from a series of measurements carried out over the previous 25 years.

Gamma-ray spectrometers are usually calibrated using multi-radionuclide standards whose emission energies cover the range 60 keV to 2 MeV. At energies > 200 keV the dominant interaction mechanism is Compton scattering, which is largely independent of the material matrix. However, at lower energies the transport of gamma rays through the sample is highly dependent upon the matrix type and density. At these lower energies, the principle interaction method is photoelectric absorption which has a cross section proportional to the fourth power of the atomic number. Thus, the gamma-ray transport characteristics between the 4M HCl based multi-radionuclide solution used for calibration and the dried river mud samples from the Ribble Estuary may be expected to be significantly different. Two methods can be adopted to correct results for this difference in attenuation. Firstly, to measure directly the attenuation coefficient of samples and correct accordingly, or secondly, to model the response for a particular matrix using computer codes. Both of these approaches have been considered in this work programme.

The studies fall into two distinct work programmes:

(a) an assessment of the published nuclear decay data to evaluate recommended emission probabilities for the gamma-ray emissions of Th-234

(b) a study of the practical aspects of undertaking accurate gamma-ray spectroscopy measurements for the determination of Th-234 in samples.

The report is presented in two main parts on the basis of these two fields of study . Section 2 deals with the data evaluation aspects of the study; Section 3 is devoted to the application of gamma-ray spectroscopy and the newly recommended decay data to the measurement of Th-234.

2 EVALUATION OF PUBLISHED NUCLEAR DECAY DATA FOR Th-234

Although Th-234 and Pa-234m are in secular equilibrium, the recommended decay data for Th-234 are believed to be inconsistent in this respect when compared with recently measured and evaluated decay data for short-lived, daughter Pa-234m. Values between 0.040 and 0.048 have been adopted in previous evaluations for the absolute emission probability of the 63.30 keV gamma ray of Th-234. The current re-evaluation has generated a recommended value of

0.037 ± 0.002, based on the most recent measurements in the late 1980s and a re-assessment of earlier studies described below.

2.1 LITERATURE REVIEW

Laboratory studies in the 1960s and 70s focussed on measuring the energies and emission probabilities of the primary beta particles and gamma rays of Th-234 (denoted originally as uranium X_1 (UX_1)). Godart and Gizon (5) undertook the first comprehensive and consistent study of the decay parameters of Th-234, and reported on the properties of the gamma-ray transitions in conjunction with the beta-particle emission probabilities. While these measurements have been augmented by the work of Chu and Scharff-Goldhaber (6) and Scott and Marlow (7), detailed studies are lacking to assist in producing a recommended data set with high confidence.

The contents of the relevant references are described below. Half-life measurements are given in Table 1, while the beta-particle and gamma-ray emission probabilities are listed in Tables 2-4.

2.1.1 Curie et al (1931), Reference 8

Tables of radioactive constants were formulated by the Radium-Standards Commission for worldwide adoption. These data included a recommended value of 24.5 d for the half-life of Th-234, based on measurements by Rutherford and co-workers. A value of 23.8 d was also noted, but not preferred.

2.1.2 Sargent (1939), Reference 9

Studies of the beta-spectra of Th-234 furnished a series of half-life values for Th-234. An ionisation chamber was used to follow the decrease in beta-particle activity, and corrections were applied for the decay of Pb-210 and actinium-based impurities. Semi-logarithmic plots of the resulting data were used to determine a value of 24.1 ± 0.2 d.

2.1.3 Knight and Macklin (1948), Reference 10

Two Th-234 samples free from U-235, U-234 and other radionuclidic impurities were obtained by a series of precipitations and dissolutions. Thin-walled Geiger counters were used to follow the radioactive decay of these samples over at least 1700 h immediately after preparation. All data were corrected for counter shift, coincidence losses and background. Half-lives were obtained from the slope of the decay curve to give an average value of 24.101 ± 0.025 d.

2.1.4 Stoker et al (1953), Reference 11

Mixed samples of Th-234/Pa-234m were prepared from kilograms of uranyl nitrate using ether-water extraction and passage through an ion-exchange column; the mean thickness of the active material was 0.3 mg cm^{-3}. Beta spectra of these samples were studied by means of a double-focusing spectrometer: sixteen of the electron emissions were ascribed to eight gamma rays of Th-234, while others were identified with Auger lines. A Fermi-Kurie analysis

of the continous beta spectrum resulted in two Th-234 components with end points of 103 and 193 keV and relative intensities of 33% and 67% respectively.

2.1.5 Johansson (1954), Reference 12

Mixed samples of Th-234/Pa-234m were prepared from natural uranium by ether-water extraction and fluoride precipitation with lanthanum carrier. Sodium iodide and anthracene spectrometers were used to generate beta-gamma coincidence spectra, while a sodium iodide scintillation counter measured the gamma-ray spectrum. Two major gamma-ray emissions were detected at 64 and 94 keV, and two weaker transitions at 17 and 30 keV. Although the mean energy of the uranium K x-ray is 96 keV, the 94 keV peak was determined to be sufficiently large to contain a significant gamma-ray component. Some interference from an escape peak also occurred in the case of the 30 keV transition, while the 17 keV emission was attributed to L x-rays of protactinium.

The coincidence spectra implied that the gamma-ray transitions at 29, 63 and 93 keV are in coincidence with a beta group (end point ~100 keV). Both the 29-keV gamma ray and the L x-rays were found to be in coincidence with the 63-keV gamma ray. Beta endpoints of 101 and 193 keV were determined with relative emission probabilities of 28% and 72% respectively.

2.1.6 de Haan et al (1955), Reference 13

Measurements of the Th-234 and Pa-234 decay data were reviewed, and studies carried out using a magnetic coincidence spectrometer, with and without a Bi-shield. A beta spectrum was found with an endpoint energy of 100 ± 2 keV. On the assumption that the 91 keV gamma-ray transition can be correlated with this beta-particle emission, a maximum energy of 191 keV was derived. Thus, beta endpoints of 100 and 191 keV were determined, with emission probabilities of 35 ± 3% and 65 ± 3% respectively.

2.1.7 Deutsch and Nikolic (1955), Reference 14

A purified sample of Th-234 was used to determine whether this radionuclide undergoes alpha-particle decay. An upper limit of $(1.6 \pm 0.3) \times 10^{-6}$ was measured for the alpha branching fraction.

2.1.8 Ong Ping Hok et al (1956), Reference 15

A combination of a double-focusing beta-ray spectrometer and NaI(Tl) scintillation counter were used to study the emissions from mixed samples of Th-234/Pa-234m, as an extension of earlier work by Stoker et al and de Haan et al (11, 13). The emission probability of the 30 keV gamma ray was observed to be much lower than measured by Johansson (12).

Conversion electron emissions were re-interpreted in terms of a 29 and 62.8 keV gamma-ray cascade and a 91.4 keV gamma-ray crossover transition. The two beta-particle transitions with endpoints of 103 and 193 keV were estimated to have emission probabilities of 21% and 79% respectively.

2.1.9 Geiger et al (1961), Reference 16

Gamma-gamma coincidence measurements were briefly reported in a laboratory progress report. The total internal conversion coefficients for the 29 and 63 keV gamma-ray transitions were ≥ 200 (M1 + E2 multipolarity) and 0.8 (E1 multipolarity) respectively. More importantly, the 92 keV gamma-ray emission was found to be a doublet consisting of a 92.26 keV M1 component and a less well-defined 92.69 keV transition. Furthermore, these studies also suggested that the 62 keV gamma-ray emission constitutes a doublet (62.78 and 63.2 keV components). Energy considerations imply that there are two levels in Pa-234 separated by only 0.45 keV, with parallel cascades involving the 29.48 and 63.24 keV transitions and the 29.48 and 62.78 keV transitions.

2.1.10 Foucher et al (1962), Reference 17

Conversion electron studies were used to derive the multipolarity of the gamma-ray transitions: 29.88 keV (E2), 43.89 keV (E2), 63.21 keV (M1 + E2), 63.64 keV (E1), 93.08 keV (M1), 93.52 keV (E1), 102 keV (E2) and 228 keV (M1). Beta spectra were also analysed in terms of three transitions involving the Pa-234 nuclear levels of 163.3 keV (6.5%), 162.9 keV (12.5%) and 69.8 keV (81%), with the latter defined as the Pa-234m state.

2.1.11 Adamson et al (1962), Reference 18

Coincidence techniques were used to determine the internal conversion coefficients of the 29 keV ($\alpha_{tot} > 130$) and 63 keV ($\alpha_L = 0.32 \pm 0.03$) gamma-ray transitions.

2.1.12 Bjornholm and Nielsen (1963), Reference 19

A Th-234 sample was prepared by dissolving 3 kg of uranyl nitrate in ether, and extracting the solution with water. The aqueous thorium phase was back-extracted several times with ether, and absorbed onto an anion-exchange column to remove any residual uranium before eluting with 0.1M nitric acid. Finally, the source was concentrated on a sulphonated polystyrene-VYNS foil (thickness of 10 to 30 $\mu g\ cm^{-2}$). Various detectors were used to monitor the resulting activity, including a six-gap beta spectrometer, scintillation counters, and conversion electron-gamma and beta-gamma coincidence systems.

The continuous beta spectrum was measured over the energy range from 50 to 2350 keV. Two beta groups were detected for Th-234 with endpoints of 100 keV (33%) and 193 keV (67%), in accord with the measurements of Stoker et al (11). Various conversion electrons were also observed in coincidence with the 64 keV gamma ray.

2.1.13 Foucher et al (1965), Reference 20

Nuclear levels at 167 and 184 keV were postulated from an extended series of gamma-ray measurements. However, these levels were effectively normalised with respect to the Pa-234m nuclear state, and therefore will have energies relative to this metastable state. The transitions evolve from a highly questionable analysis of the upper energy of the unresolved spectrum, and their existence within the decay scheme of Th-234 can be challenged.

2.1.14 Godart and Gizon (1973), Reference 5

The decay data of Th-234 were investigated by means of two iron-free double-focusing spectrometers and several Ge(Li) detectors. Samples were purified from 20 kg of uranium trioxide using a Dowex resin column. Beta spectra were analysed and found to consist of four components: 22 keV (1.3%), 60 keV (5.4%), 104 keV (20.7%) and 198.5 keV (72.5%). The conversion-electron spectra were reasonably complex, with over 60 identifiable transitions that could be related to the various gamma-ray emissions. These data were used to assist in the calculation of the multipolarities of the gamma-ray transitions as listed in Table 3. A decay scheme to Pa-234m was proposed, with eleven gamma-ray transitions.

The study of Godart and Gizon represents the most comprehensive set of measurements undertaken to the present date (January 1995). Subsequent studies have tended to focus on specific aspects of the decay scheme proposed in their publication, particularly the emission probabilities of the 63.3 and 92.4 keV gamma rays.

2.1.15 Sampson (1973), Reference 21

A thin-window Ge(Li) detector was used with a resolution of 536 eV at 122 keV to undertake precise measurements of the three most prominent gamma rays in the beta-decay of Th-234. Various calibrants were used, including Co-57, Cd-109, Am-241 and the x-rays of Au, Pb and U. The energies of the 63.3 keV singlet and 92.3 keV doublet were determined to a high accuracy, and the relative emission probabilities of the resolved doublet (92.37 and 92.79 keV) were quantified.

2.1.16 Taylor (1973), Reference 22

A high-resolution Si(Li) detector was used to determine with precision the energies of the gamma-ray emissions of Th-234 below 120 keV. The energy resolution of the system was 285 eV at 6.4 keV, and some compromise had to be made between the sample activity and self-absorption of the gamma rays below 100 keV. X-ray emissions were used to calibrate the system.

The composite emission at 92 keV was resolved into a doublet at 92.47 and 92.82 keV (total relative intensity defined as 100%), while the 63.25 keV peak was analysed in terms of two transitions with energies of 62.97 and 63.35 keV (total relative intensity of 77%). Both doublets were identified with the beta-decay of Th-234 feeding excited levels of protactinium leading to Pa-234m.

2.1.17 Chu and Scharff-Goldhaber (1978), Reference 6

A relatively detailed study was made of the low-energy portion of the gamma-ray spectrum of Th-234. These data confirmed the postulated decay scheme of Godart and Gizon (5), and generated a reasonably comprehensive set of relative emission probabilities for the gamma rays.

Carrier-free Th-234 was prepared by passing 0.5M nitric acid containing 300 g uranyl oxide through a Dowex-50 cation exchange column. Th-234 was absorbed on the column, and

washed and eluted with 0.5M oxalic acid in 2M nitric acid. Thorium was coprecipitated with ferric hydroxide, and separated from iron and any remaining uranium by loading onto a Dowex column and washing with 8M hydrochloric acid. A Ge(Li) detector was calibrated with a series of standards (Ti-44, Co-57, Cd-109, Ce-139 and Am-241) prior to and during the measurements undertaken at monthly intervals. Gamma-ray intensities were normalised with respect to the combined intensity of the 62.9 and 63.3 keV transitions. The intensity of the 73.7 keV transition in the decay of daughter Pa-234m was observed to be much lower than the value reported by Godart and Gizon (5), and effectively eliminated the need to postulate the existence of a significant 74 keV transition within the Th-234 decay scheme. Interferences involving $U_{K\alpha}$ and $U_{K\beta}$ x-rays were also noted (regions around 92-94 and 111-113 keV). These relative intensity data along with those of Godart and Gizon (5) are particularly important in the evaluation of a comprehensive and consistent decay scheme for Th-234.

2.1.18 Momeni (1982), Reference 23

A Ge(Li) detector with a resolution of 1.8 keV at 1330 keV and a peak-to-Compton ratio of 44:1 was incorporated into a dedicated counting system for the study of the complex spectra of the uranium, actinium and thorium series. Software control included zero channel and gain, and a detailed procedure for deconvolution of the resulting spectra. Gamma-ray standards included Co-57, Co-60, Se-75, Hg-203, Am-241, thorium ore and uranium pitchblende.

Absolute emission probabilities were reported for the 63.34 and 92.75 keV gamma-ray lines (0.0405 and 0.0163 respectively, with uncertainties of approximately 5%). There is a significant amount of interference due to the complexity of the spectra, although the nature of this study implies that the high resolution of the system achieved separation of any overlapping doublets prior to statistical analysis.

2.1.19 Pik-Pichak (1986), Reference 24

A theoretical analysis was made of the natural emission of light nuclei from a series of transactinium nuclides, including Th-234. These calculations implied the existence of such a decay, albeit via an extremely low branching fraction that results in the emission of Ne-26. While this decay mode is feasible and has been noted during the evaluation of the decay scheme, any contribution to such parameters as the mean alpha and beta energies will be negligible and is not included in the final set of recommended data.

2.1.20 Scott and Marlow (1990), Reference 7

Uranium samples of known mass and radionuclidic concentration were dissolved in aqueous solution and analysed with a high-purity Ge spectrometer. Calibrants included Co-60, Ba-133, Eu-152, Th-228 and U-235. This detector system had an energy resolution of 1.74 keV at 1332 keV, and a relative efficiency of 35.7%. Spectra were recorded for periods of 200000 secs for each of six sources in an exercise spanning approximately one month, followed by a two-month waiting period and another month-long set of measurements. The results were combined to give a weighted average for an extensive range of gamma rays emitted in the U-238 decay chain. Unfortunately, only the (63.24 ± 0.10) keV gamma ray of Th-234 is included in this study, with an emission probability of 0.036 ± 0.001, which represents the most precise absolute value reported in the open literature.

2.1.21 Lin and Harbottle (1992), Reference 25

The emission probabilities of a limited number of gamma rays in the Th-232, U-235 and U-238 decay chains have been determined using a high-purity Ge detector and various standards covering the energy range from 59 to 1836 keV. The U-238 source consisted of a metal foil (92.8% enriched, and thickness of 72.10 mg cm^{-2}) mounted in a lucite disk.

Approximate gamma-ray energies are listed for identification purposes. Thus, a gamma-ray energy of 92.38 keV is given, which is assumed to be the 92-93 keV doublet of Th-234 with an absolute emission probability of 0.0557 ± 0.0028.

2.2 Th-234 DECAY SCHEME

Despite the significant number of papers describing studies of the decay scheme data of Th-234, a high degree of uncertainty still remains. These difficulties can be identified with the nature of the decay which involves a high-intensity beta branch to daughter Pa-234m and a number of important low-intensity, low-energy gamma-ray emissions (see Figure 1). The gamma-ray transitions represent the principal means of detecting and quantifying Th-234 directly by means of gamma-ray spectroscopy. Any significant uncertainties in these data (and particularly the absolute emission probabilities of the 63.30, 92.38 and 92.80 keV transitions) represent a major difficulty in any such assay.

There is good agreement between the half-life measurements reported by Sargent (9) and Knight and Macklin (10). A recommended half-life value of

$$24.10 \pm 0.03 \text{ days}$$

has been derived from the data listed in Table 1 on the basis of a weighted mean analysis (excluding Curie et al (8) in which a half-life is proposed with no associated uncertainty).

Both the beta-particle and gamma-ray studies from the early 1950s exhibit a number of inconsistencies that have proved difficult to resolve. A significant amount of effort was expended to quantify the beta-particle energies and emission probabilities, despite problems of inadequate spectral resolution (Table 2). While the beta branch to Pa-234m was defined with reasonable confidence, the population of a series of nuclear levels between 170 and 195 keV above the ground state (Pa-234g, see Figure 1) has proved considerably more problematic. The main beta branch directly to Pa-234m can be assumed to be 0^+ - 0^- (first forbidden non-unique), and is estimated to undergo this form of decay with a transition probability of approximately 0.75 (75%); all remaining beta branches will sum to a transition probability of 0.25 (25%). These data are supported to a reasonable degree by subsequent gamma-ray measurements with high-resolution detectors, from which gamma-ray emission probabilities can be used to calculate these beta branches with greater confidence and resolution. Although Godart and Gizon (5) postulated the existence of additional beta-particle transitions to even higher nuclear levels of Pa-234, there is no experimental evidence from any of the other studies to support this proposal.

Gamma-ray studies proved particularly valuable with the advent of the Ge(Li) and high-purity Ge detectors. Measurements from the 1960s onwards have resolved a number of issues associated with nuclear levels separated by as little as 1 or 2 keV by detecting and quantifying the emission probabilities of overlapping gamma-ray lines. However, these data have proved to be rather sketchy from the point of view of consistency and completeness. Efforts have tended to focus on specific transitions (i.e. 63.30 keV, and 92.38 - 92.80 keV doublet), apart from the more comprehensive studies of Godart and Gizon (5) and Chu and Scharff-Goldhaber (6). Godart and Gizon measured the relative emission probabilites of 13 gamma rays (with a number of unresolved doublets quantified as single peaks), and assessed the transition probabilities of 18 gamma transitions. A number of these transitions have been rejected in the evaluation because of their questionable existence and close proximity to various uranium x-rays (i.e. 57.75, 92.0, 103.7, 132.9 and 184.8 keV). There is reasonable agreement between the resulting data set and the equivalent measurements of Chu and Scharff-Goldhaber, and therefore weighted mean values were derived for the relative emission probabilities of the 83.3, 103.35, 108.0 and 112.8 keV transitions based on $P\gamma$(92.38 + 92.80 keV) of 100, as listed in Table 3. Relative emission probabilities for all of the other gamma rays were calculated from a combination of theoretical considerations and population/depopulation of the various nuclear levels. The multipolarities of the gamma transitions have been assigned on the basis of the studies by Godart and Gizon (5), while their internal conversion coefficients were derived from the theoretical tabulations of Hager and Seltzer (26) and Rösel et al (27). All of these relative emission probabilities were adjusted to be expressed in terms of $P\gamma$(63.29 keV) of 100, as listed in column 9 of Table 3. Two gamma-ray emission are included in the final data set that cannot be incorporated in the proposed decay scheme (87.02 and 108.00 keV transitions), while the 73.92 keV transition has been assigned to the isomeric decay of daughter Pa-234m.

Absolute gamma-ray emission probabilities have been measured with their associated uncertainties by Momeni (23), Scott and Marlow (7), and Lin and Harbottle (25). These studies focussed on the 62-63 and 92-93 doublets, as listed in Table 4. The data presented in Table 3 of the publication by Godart and Gizon (5) can also be used to derive absolute emission probabilities from their reported transition probabilities (combination of both the gamma-ray and conversion-electron emissions) and theoretical internal conversion coefficients. Hence, the absolute emission probability of the 63.30 keV gamma ray was calculated from the following data:

Godart and Gizon (5)	0.033 ± 0.003
Momeni (23)	0.0405 ± 0.0020
Scott and Marlow (7)	0.036 ± 0.001

The uncertainty of the value reported by Scott and Marlow was adjusted to $\pm$ 0.002, and the above data were then used to give a weighted mean of 0.037 ± 0.002. Equivalent data for the 92.38 and 92.80 keV gamma rays proved more difficult to manipulate because of a lack of spectral resolution.

2.3 RECOMMENDED DECAY DATA FOR Th-234

The recommended decay data for Th-234 are listed in Tables 5 and 6 for the beta-particle and gamma-ray emissions respectively. These data were derived as described in Section 2.2

above, using a combination of the gamma-ray measurements and assuming that the direct beta branch to the Pa-234m nuclear level is approximately 0.75 (75%).

Other decay-data evaluations have also been assessed (Table 7). Duchemin et al (31) appear to have assigned an absolute emission probability of 0.047 ± 0.004 to the 63.30 keV gamma ray on the basis of the measurements by Godart and Gizon (5), although the original authors defined this value as the transition probability (inclusive of internal conversion) that they had used to estimate the beta branches. If this value of 0.047 is linked to their quoted total internal conversion coefficient of 0.421, an absolute emission probability of 0.033 ± 0.003 can be calculated. Akovali (29) derived decay-scheme data from an absolute emission probability of 0.0557 ± 0.0028 for the unresolved gamma-ray doublet of 92.38 + 92.80 keV, as measured by Lin and Harbottle (25).

The newly recommended data have been processed using the COGEND computer programme (32) to generate the data file in ENDF-6 format. This exercise resulted in the following consistency check for the proposed decay scheme compared with previous evaluations by the author:

Th-234 (ref 2)	+0.2140%
Th-234 (ref 33)	+0.2141%
Th-234 (present evaluation)	+0.1140%

The new data set is of the desired quality and completeness for incorporation in the UK Heavy Element and Actinide Decay Data Library (UKHEDD-2.1 (33)). Nevertheless, comprehensive decay data are lacking for Th-234, and further gamma-ray and conversion-electron measurements are required to resolve the difficulties in defining a consistent decay scheme. These emissions are relatively low-energy transitions, and some care needs to be taken in preparing the sources to minimise self-absorption. A high-resolution system is recommended in order to generate accurate emission probabilities for the individual components of the 62-63 and 92-93 keV doublets as well as the lower-energy transitions (20.02 and 29.5 keV).

3 DETERMINATION OF THE ACTIVITIES OF Th-234 AND Pa-234m IN ENVIRONMENTAL SAMPLES

A validated experimental procedure has been developed for determination of Th234 in environmental samples. This procedure is based upon measuring the absorption of low-energy gamma rays from Th234 to enable compensation to be made for differences in gamma attenutation and transport in different sample types. This method has been demonstrated to yield consistent activity results between Th-234 and Pa-234m in dried river silt samples using the newly recommended values for the emission probabilities of Th-234 and Pa-234m (see Section 2.3 and reference 3, respectively). An appropriate methodology is described below.

A numerical modelling approach using the Monte Carlo code EGS4 has also been used to provide a correction factor to compensate for differences in gamma-ray transport properties in various sample types and standards. This process also provides good agreement between the estimated activities of Th-234 and Pa-234m in these samples.

3.1 LOW-ENERGY GAMMA-RAY SPECTROSCOPY

Gamma-ray spectroscopy is a comparative technique: quantification of the radioactivity in a sample is determined by direct comparison with known standards in a similar geometry. The problems of conducting gamma-ray spectroscopic measurements at low-energies are well known (34), and arise because gamma transport within the samples (and standards) is critically affected by the matrix density and elemental content. The absorption cross-section of the matrix is a critical factor in gamma transport that can be easily corrected if determined independently.

The energy of the main gamma-ray emission from Th-234 is 63.3 keV. Together with Pb-210 (46.5 keV), Am-241 (59.6 keV) and Eu-155 (86.4 keV), these nuclides form the main set of low gamma-ray emitting radionuclides found in nuclear waste streams and in the environment that require special consideration. A simple experimental method to correct for self-attenuation of low-energy gamma-rays within samples has been established, as described in Section 3.2. This procedure has been developed using Am-241, which has the advantage over Th-234 of being readily available as both a solution and point source. The difference in detection efficiency between Am-241 (59.6 keV) and Th-234 (63.3 keV) is less than 1% on the detectors used in these studies, and thus the approach is readily transferable between these two radionuclides.

A computer modelling approach using the Monte Carlo code EGS4 has also been examined. While the results are consistent with the experimental data, this approach would probably be of more value in modelling complex situations i.e. in-situ response for portable gamma-ray measurements. The results of the computer modelling are given in Section 3.2.

Details of the measurements and computed results are given in Section 3.3 for four silt samples supplied by HMIP from the Ribble Estuary.

3.1.1 Theory of Gamma-ray Absorption

When the matrix and geometry of the sample and the standard are the same, the activity in the sample is given by the equation:

$$A_{SA} = A_{ST} \times \frac{C_{SA}}{C_{ST}} \qquad (1)$$

where A_{SA} is the activity of the sample,
A_{ST} is the activity of the standard,
C_{SA} is the count-rate in the photopeak of the sample, and
C_{ST} is the count-rate in the photopeak of the standard.

However, if there is a difference in attenuation properties between the sample and the standard, a correction factor needs to be determined by undertaking additional transmission measurements on the sample and standard.

Consider a standard counting geometry (Figure 2) in which the measured count-rate in the photopeak is given by:

$$C = k.a\int_{o}^{H} e^{-\mu x} \, dx \qquad (2)$$

where C is the measured count rate,
k is a constant factor dependent upon sample-detector geometry,
a is the activity per incremental volume disc,
μ is an attenuation factor, and
the exponential attenuation factor $e^{-\mu x}$ represents the attenuation of gamma rays that originate at a height x in the sample (in reality, the attenuation factor is averaged over a range of path lengths as shown in the Figure 3.2, and discussed in detail later).

Integrating equation (2) yields:

$$C = \frac{k.a}{\mu}\left[1 - e^{-\mu.H}\right] \qquad (3)$$

The resulting equations for a sample and a standard are:

$$C_{SA} = \frac{k\,a_{SA}}{\mu_{SA}}\left[1 - e^{-\mu_{SA}H}\right] \qquad (4)$$

and

$$C_{ST} = \frac{k\,a_{ST}}{\mu_{ST}}\left[1 - e^{-\mu_{ST}.H}\right] \qquad (5)$$

Division of equation (5) by equation (4), and assuming that the incremental activities summed over the whole sample volume give the total activity:

$$\frac{C_{ST}}{C_{SA}} = \frac{k\,\mu_{SA}\,A_{ST}}{k\,\mu_{ST}\,A_{SA}}\frac{\left[1 - e^{-\mu_{ST}.H}\right]}{\left[1 - e^{-\mu_{SA}.H}\right]} \qquad (6)$$

and if this is re-arranged:

$$A_{SA} = A_{ST}\,\frac{C_{SA}}{C_{ST}}\,\frac{\mu_{SA}}{\mu_{ST}}\,\frac{\left[1 - e^{-\mu_{ST}.H}\right]}{\left[1 - e^{-\mu_{SA}.H}\right]} \qquad (7)$$

When compared with equation (1), the extra terms form the correction for the differences in gamma transport between the sample and standard matrices.

The attenuation factors for the sample and standard matrices can be measured directly by transmission measurements as shown in Figure 4. However, in reality an averaged attenuation factor over a range of path lengths is determined as shown in Figure 5.

Using a simple exponential attenuation model, the transmitted intensity is given by:

$$I = I_o\, e^{-\mu.H} \qquad (8)$$

For the sample and standard matrices this equation becomes:

$$I_{ST} = I_o \quad e^{-\mu_{ST}.H} \tag{9}$$

$$I_{SA} = I_o \quad e^{-\mu_{SA}.H} \tag{10}$$

I_{ST} and I_{SA} are the contributions from the transmission measurement alone, and any significant contribution from the sample must be subtracted from these terms.

Using the relationships that

$$\frac{I}{I_o} = e^{-\mu.H} \tag{11}$$

$$\text{and} \qquad \mu = \frac{1}{H} \cdot \text{Ln} \left(\frac{I_o}{I}\right) \tag{12}$$

and substituting in equation (7):

$$A_{SA} = A_{ST} \quad \frac{C_{SA}}{C_{ST}} \quad \frac{\left[\frac{1}{H} \quad \text{Ln} \frac{I_o}{I_{SA}}\right]}{\left[\frac{1}{H} \quad \text{Ln} \frac{I_o}{I_{ST}}\right]} \quad . \quad \frac{\left[1 \quad - \quad \frac{I_{ST}}{I_o}\right]}{\left[1 \quad - \quad \frac{I_{SA}}{I_o}\right]}$$

$$A_{SA} = A_{ST} \quad \frac{C_{SA}}{C_{ST}} \quad \frac{\left[\text{Ln} \frac{I_o}{I_{SA}}\right]}{\left[\text{Ln} \frac{I_o}{I_{ST}}\right]} \quad . \quad \frac{\left[I_o - I_{ST}\right]}{\left[I_o - I_{SA}\right]} \tag{13}$$

This equation represents the correction which must be applied to the measurement of sample activity to compensate for differences in the attenuation properties of the sample and standard matrices.

It should be noted that in reality the model is more complex than presented above. The attenuation factors for both the normal and transmission measurements are averaged over a range of path lengths. However, providing that the attenuation factors derived from the transmission measurements are a constant ratio to those relating to the normal gamma-ray measurements, μ will become kμ (where k is a constant) and k will cancel from both the standard and sample responses to give the same result (equation 13).

3.1.2 Experimental Measurements

A standardised solution of Am-241 was prepared in 4M HCl, and 10 ml aliquots of this solution were used to dope carrier matrices of a variety of materials (Table 8). The 4M HCl

sample was used as the standard for calibration purposes. Sufficient of the carrier matrix was used in each case to make a total volume of 100 ml. Solid samples were dried, ground, mixed and transferred to 150 ml capacity Perspex 'polypots'. Each sample was counted for 3600 seconds, and the area of the Am-241 photopeak was recorded (column a in Table 8). A transmission measurement was also conducted on each sample (column b in Table 8) by collecting, in turn, the counts transmitted through the 4M HCl standard, the sample material and an empty container using an Am-241 source mounted in a special rig.

From Table 8 it can be seen that there is a general fall in the measured signal count rate with increasing sample density. There is also clear evidence of the dependence on matrix type: although the clay and glycerol samples have similar densities, there is significantly more attenuation in the clay than the glycerol (i.e., the average atomic number of the aluminosilicate clay is greater than the carbon, hydrogen, oxygen of the glycerol).

Using the transmission measurements, the correction factors for each sample can be determined relative to the 4M HC1 as given in column c of Table 8. The normalised results are listed in column d, and the percentage difference (with respect to the 4M HCl standard solution) is given in column e. This method of compensation works well, with the uncorrected gamma-ray measurements for identical quantities of Am-241 in the various samples covering the range from -16% to +35% relative to the standard, whereas the corrected measurements range from -2.3% to 3.8%.

3.2 COMPUTER MODEL

Several computer codes have been developed over the years to model gamma-ray transmission, interaction and detection. Monte Carlo codes are able to simulate such gamma-ray interaction processes, and EGS4 (Electron-Gamma-Shower, Version 4) is of particular interest in this respect. The code is 'user friendly' and can be easily adapted to the measurements considered in the Th-234/Pa-234m studies.

Key parameters that need to be fed into the program include the detector and sample dimensions and constituent materials, together with the gamma-ray energies of interest. This information is used to calculate the interaction cross-sections for the sample and detector materials, along with the detection efficiency for the specified sample types. Typical computer run-times for each matrix on a 486PC are a few minutes.

Elemental constituencies of the various materials used in the study are given in Table 9. Output data from the computer modelling are the effective detector efficiencies for the respective material types. These results are directly comparable with the experimental data (Table 10), which can be normalised to a total Am-241 emission rate of 28.964 gammas/sec/10 ml of solution.

3.3 DATA COMPARISON

Both methods appear to compensate for the self-attenuation of low-energy gamma rays within environmental samples. The overall errors associated with the direct measurement of the attenuation coefficient of the sample has an rms error of 1.0% (sd 0.8% and bias 0.2%), whereas the computer modelling approach results in an rms error of 3.8% (sd 2.5% and bias

+1.3%). This observation is not surprising since the elemental constituencies of some of the samples (soil and clay) are not well known, and average values had to be used.

4 MEASUREMENTS ON SILT SAMPLES FROM THE RIBBLE ESTUARY

4.1 GAMMA-RAY SPECTROSCOPY MEASUREMENTS

The experimental method described in Section 3.1.2 is directly applicable to the measurement of Th-234. Although a Th-234 point source should be used for the transmission measurements, this type of sample is not commercially available, and therefore Am-241 was used for the transmission measurements on both the standard and the sample. Any systematic error should be largely cancelled because the gamma-ray emission energies of Am-241 and Th-234 are reasonably close (59.6 and 63.3 keV, respectively).

The four silt samples were weighed, dried, re-weighed, crushed, ground and homogenised. 100 ml sub-samples of each were taken and transferred to 150 ml polypots. Two detectors were used for the experimental measurements, these are referred to as POP1 and POP2. Both detectors are n-type hyperpure germanium, manufactured by EG&G^{TM} with efficiencies of ~25%. Spectra were accumulated for 14 h periods for each sample on two detectors (eight measurements in all). A transmission measurement was also made on each sample, using a point source of Am-241 that could be accurately positioned above the sample and detector. Transmission data from the 4M HCl standard and an empty polypot container were also obtained. The resulting data listed in Table 11 show that the measurements for Th-234 need correcting by factors that vary between 7 and 15%. Equivalent Pa-234m activities were derived using conventional gamma-ray spectroscopy.

All of the decay data were corrected to mid-day on the 1 January 1996, using a half-life of 24.1 days for Th-234 (see Section 2.2 of this report). Pa-234m activity results were also corrected with the same half-life (24.1 days), assuming secular equilibrium between daughter and parent. The emission probabilities of 0.037 for the 63.3 keV gamma ray of Th-234 (see Section 2.2 of this report) and 0.00835 for the 1001 keV gamma-ray of Pa-234m (3) were used to give the calculated activities listed in Table 12. Counting statistics were less than 0.5%.

Differences in the results for Th-234 and Pa-234m with detector POP1 are all less than 3%, while the data for detector POP4 exhibit more significant deviations with a maximum deviation of 6.6%. Given that the uncertainties in the emission probability data for Th-234 is 5% and for Pa-234 is 1.3%, and that there are associated measurement and geometry errors of approximately 2%, the results can be defined as being in good agreement.

4.2 MONTE CARLO-BASED ACTIVITY ASSESSMENT FOR Th-234

The EGS4 code was applied to the four matrices, assuming a standard aluminosilicate composition and corresponding detection efficiencies. Monte Carlo-based efficiency corrections were used to derive the Th-234 data listed in Table 13. The correlation between the corrected Th-234 activities and Pa-234m was found to be better when adopting this approach, with the differences for POP1 being typically 1% and the maximum deviation reduced to 5.1% for POP4. Some reservation should be placed upon these figures because the

precise elemental constituents and consistency of the aluminosilicate were not known, and an "average" composition had to be assumed for the matrix.

5 CONCLUSIONS

When the newly-recommended value of 0.00835 ± 0.00011 for the 1001 keV line of Pa-234m was applied to laboratory-intercomparison data from reference 4, the measured Th-234 content of silt samples remained deficient relative to the corrected Pa-234m content. These Th-234 measurements are believed to be low because of a combination of factors:

(a) the gamma-ray abundance adopted for the 63.30 keV transition was too high (value of 0.040 was used),

(b) self-absorption of the low-energy 63.30 keV gamma ray by the samples was under-corrected.

A re-evaluation of all available data has resulted in a new value being recommended for the gamma-ray abundance (Tables 6 and 7):

$$P\gamma\,(63.30\ \text{keV}) = 0.037 \pm 0.002$$

Although this extensive evaluation was undertaken to determine a newly-recommended set of gamma-ray and beta-particle decay data, further measurements are merited to resolve a number of uncertainties involving the low-energy gamma-ray emissions, as noted in Section 2.3.

From the laboratory studies with Am-241 doped matrices, it can be concluded that low-energy gamma-ray spectroscopy measurements will be in error unless some compensation is made for the differences in gamma-ray transmission properties between the calibration standards and samples. The magnitude of the error will be dependent upon the sample type, particularly the density and elemental constituents of the sample. Two methods of compensating for the differences in attenuation between the standard and samples have been considered in this report: one approach was based on an experimental correction method and the other method involved Monte Carlo modelling of the gamma transport processes in the sample. Both methods significantly improved the associated uncertainty with the activity determinations, typically by one order of magnitude. Both types of analysis produced consistent results for the activities of these radionuclides in samples taken from the Ribble Estuary when used in conjunction with the newly recommended data for the emission probabilities of Th-234 and Pa-234m.

Although both the experimental and computer modelling methods of compensating for the absorption of the low-energy Th234 gamma-ray have been demonstrated to valid, it is more practical to use the experimental method to determine this correction. The experimental measurement is direct and does not rely on any estimate of the elemental composition, and it also does not require any use of additional technical capabilities such as computer based modelling. However, the demonstration that this type of modelling is useful as it is of advantage when there is only a small amount of sample, insufficient for a reasonable

transmission measurement, or when a different geometry is used and modelled e.g. a small vial within a well-type detector.

A comprehensive assessment has been made of the gamma-ray spectroscopic methods adopted for low-energy gamma-ray measurements of Th-234. Such quantitative studies are difficult, and a suitable procedure has been outlined in this report, together with experimental and computer-modelling validations. Measurements were undertaken on four silt samples from the Ribble Estuary using this procedure in conjunction with the re-evaluated and recommended emission probabilities for the prominent gamma rays: such a combination of improvements produced good agreement between the Th-234 and Pa-234m activities and unambiguous evidence of secular equilibrium.

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Table 1: Half-life of Th-234 (days)

Curie et al (8)	Sargent (9)	Knight and Macklin (10)	Recommended
24.5 (also value of 23.8)	24.1 (2)	24.101 (25)	24.10 (3)

Table 2: Beta-particle Decay Data Published for Th-234

E_β^{max}	Stoker et al (11)	Johansson (12)	de Haan et al (13)	Ong Ping Hok et al (15)	Foucher et al (17)	Bjornholm and Nielsen (19)	Godart and Gizon (5)
22(3)	-	-	-	-	-	-	0.013(7)
60(3)	-	-	-	-	-	-	0.054(10)
98	0.33	0.28	0.325 – 0.38	0.21	0.065	0.33	0.207(10)
99					0.125		
192	0.67	0.72	0.65(3)	0.79	0.81	0.67	0.725(2)

Table 3: Gamma-ray Decay Data Published for Th-234 - Relative Emission Probabilities

Eγ (keV)	Godart and Gizon (5)		Sampson (21)	Taylor (22)	Chu and Scharff-Goldhaber (6)		Recommended*	
							$P\gamma^{rel}$ (92.38+92.80 keV)	$P\gamma^{rel}$ (63.29 keV)
20.02(2)	-	-	-	35?	-	-	[0.22(2)]	[0.31(3)]
29.49(2)	-	-	-	-	-	-	[0.024(2)]	[0.034(3)]
57.75(10)	1.0(6)	0.10(6)	-	-	-	-	-	-
62.86(2)	736	71	-	77	736	87	[0.09(1)]	[0.13(1)]
63.29(2)			-				71(4)	100
73.92(2)	9.6(5)	0.92(5)	-	-	2.6(2)	0.31(2)	Pa-234m	Pa-234m
74.0(1)			-	-			[0.05(2)]	[0.07(3)]
83.30(5)	13.5(6)	1.30(6)	-	-	12.0(6)	1.42(7)	1.36(6)	1.92(8)
87.02(6)	1.4(2)	0.13(2)	-	-	2.9(5)	0.34(6)	[0.13(2)]	[0.18(3)]
92.38(1)	1041(6)	100.0(6)	50.3(7)	100	846(43)	100(5)	50.3(7)	70.8(10)
92.80(2)			49.7(7)				49.7(7)	70.0(10)
103.35(10)	1.31(10)	0.126(10)	-	-	0.8(1)	0.095(12)	0.11(2)	0.15(3)
103.71(6)			-	-			-	-
108.00(5)	1.14(10)	0.11(1)	-	-	1.6(2)	0.19(2)	0.15(4)	0.21(6)
112.81(5)	46.5(5)	4.47(5)	-	-	42(3)	5.0(4)	4.7(3)	6.6(4)

* Data are weighted-mean values from the measurements of Godart and Gizon (5) and Chu and Scharff-Goldhaber (6), apart from those in square parenthesis derived from population/depopulation considerations of the nuclear levels.

Table 4: Gamma-ray Decay Data Published for Th-234 - Absolute Emission Probabilities

Eγ (keV)	Johansson (12)	Ong Ping Hok et al (15)	Momeni (23)	Scott and Marlow (7)	Lin and Harbottle (25)	Recommended
29.49(2)	0.065	0.05	-	-	-	-
62.86(2)	0.065	0.05	-	-	-	-
63.29(2)			0.0405(20)	0.036(1)	-	0.037(2)
92.38(1)	0.148	0.16	-	-	0.0557(28)	-
92.80(2)			0.0163(8)	-		-

Table 5: Recommended Beta-particle Energies and Emission Probabilities of Th-234

E_β (keV)	P_β	log ft	Transition type
78(5)	0.028(5)	6.7	Allowed
88(5)	0.0006(2)	9.0	First forbidden non-unique
98(5)	0.058(5)	6.6	Allowed
99(5)	0.174(5)	6.2	First forbidden non-unique
192(5)	0.739(5)	6.5	First forbidden non-unique
BF_β	0.9996		

Table.6: Recommended Gamma-ray Energies and Emission Probabilities of Th-234

Eγ (keV)	$P\gamma^{rel}$ (*)	Multipolarity	α_K	α_L	α_{M+}	α_{tot}
20.01(4)	0.31(3)	99.15% M1 + 0.85% E2	-	99	109	208(20)
29.50(4)	0.034(3)	E2	-	3700	600	4300(200)
62.88(4)	0.13(1)	89.5% M1 + 10.5% E2	-	20	8	28(3)
63.30(4)	100	E1	-	0.310	0.100	0.410(2)
73.85(7)	0.07(3)	98.8% M1 + 1.2% E2	-	8.4	3.1	11.5(5)
83.31(4)	1.92(8)	E1	-	0.147	0.052	0.199(2)
87.02(6)+	0.18(3)	?				
92.38(4)	70.8(10)	M1	-	4.2	1.4	5.6(1)
92.80(2)	70.0(10)	E1	-	0.112	0.037	0.149(2)
103.35(7)	0.15(3)	M1	-	3.05	1.02	4.07(5)
108.00(5)+	0.21(6)	?				
112.81(5)	6.6(4)	E1	0.287	0.067	0.021	0.375(5)

* Normalisation factor of 0.037(2)

+ Not incorporated into the proposed decay scheme

Table 7: Absolute Gamma-ray Emission Probabilities: Comparisons With Other Evaluations

Eγ (keV)	Ellis-Akovali (28)	Akovali (29)	Coursol et al (30)	Duchemin et al (31)	Current Evaluation
63.30	0.045(9)	0.048(8)	0.045(7)	0.041(7)	0.037(2)
92.38	0.026(6)	0.028(4)	0.0261(15)	0.0242(15)	0.0262(18)
92.80	0.026(7)	0.028(4)	0.0258(15)	0.0239(15)	0.0259(18)
112.81	0.0026(7)	0.0028(4)	0.00257(20)	0.0024(6)	0.0024(3)

Table 8: Experimental Measurements on Matrices Spiked with Am-241

Matrix	Mass (g) of 100ml Volume	a	b	c	d	e
Silica	29.2	13863	53016	0.73	10128	-1.4%
Peat	31.7	13579	50698	0.74	10040	-2.3%
Graphite	75.1	11008	32374	0.92	10091	-1.8%
Talc	78.6	10873	30071	0.95	10293	+0.1%
Ethanol	84.9	11543	35877	0.88	10109	-1.6%
4M HCl	105.7	10280	26464	1	10280	-
Clay	125.7	8610	16160	1.22	10509	+2.2%
Glycerol	127.1	10114	26120	1.01	10170	+1.1%
Soil	150.5	8404	14563	1.27	10672	+3.8%
Sand	152.9	8618	16448	1.21	10440	+1.6%
Empty pot			67176			

a: Uncorrected Am-241 photopeak, counts per 3600 sec
b: Am-241 transmission count rate per 100 sec
(after subtracting the contribution in the sample from Am-241)
c: Correction factor based on equation (13)
d: Corrected Am-241 photopeak, counts per 3600 sec
e: Percentage difference from 4M HCl standardised solution of Am-241

Table 9: Elemental Composition of Matrices

Matrix	Mass (g)	Composition (average atoms per molecule)
Silica	29.2	Si (1), O(2)
Peat	31.7	C (3), N (1), O (1), H (1)
Graphite	75.1	C
Talc	78.6	Mg (3), Si (4), O (18), H (2)
Ethanol	84.9	H (8), C (3), O (1)
4M HCl	105.7	H (2.07), O (1), Cl (0.07)
Clay	125.7	Al (4), Si (4), O (18), H (8)
Glycerol	127.1	H (8), C (3), O (2)
Soil	150.5	Si (21), Al (4.3), Ca (4), Mg (0.24), Fe (2.3), H (13.9), O (41.6)
Sand	152.9	Si (1), O (2)

Table 10: Comparisons of the Measured and Calculated Detector Efficiencies for Am-241 in Various Matrices

Matrix	Mass (g)	a	b	c
Silica	29.2	4.90	4.95	+1.0
Peat	31.7	4.86	5.08	+4.5
Graphite	75.1	4.89	4.58	-6.3
Talc	78.6	4.98	4.93	+1.0
Ethanol	84.9	4.89	5.13	+4.9
4M HCl	105.7	4.98	5.26	+5.6
Clay	125.7	5.08	4.63	-8.8
Glycerol	127.1	4.92	5.27	+7.1
Soil	150.5	5.17	5.65	+9.2
Sand	152.9	5.05	5.36	+6.1

a: Efficency derived from experimental measurements

b: Efficiency derived from Monte Carlo model

c: Percentage difference

Table 11: Transmission Measurements On Four Silt Samples, 4M HCl Standard, and Empty Polypot: Correction Factors

Sample	Mass (g)	Transmitted Counts	Correction Factor
G13284	103.02	22282	1.15
G13285	102.56	23045	1.13
G13286	88.09	26583	1.07
G13287	96.70	24514	1.11
standard		31253	
empty pot		77806	

Table 12: Th-234 and Pa-234m Activities Using Transmission Method to Correct for Gamma-ray Attenuation

Sample	Mass (g)	POP1 Bq/g 12:00:00, 1 Jan 1996			POP4 Bq/g 12:00:00, 1 Jan 1996		
		Th-234	Pa-234m	% diff	Th-234	Pa-234m	% diff
G13284	103.02	17.82	17.45	-2.1	17.82	17.14	-3.8
G13285	102.56	51.95	50.56	-2.7	53.10	49.60	-6.6
G13286	88.09	61.82	61.60	-0.4	63.37	61.59	-2.8
G13287	96.70	54.91	54.17	-1.3	55.52	55.75	+0.4

Table 13: Th-234 and Pa-234m Activities Using Monte Carlo Method to Correct for Gamma-ray Attenuation

Sample	Mass (g)	POP1 Bq/g 12:00:00, 1 Jan 1996			POP4 Bq/g 12:00:00, 1 Jan 1996		
		Th-234	Pa-234m	% diff	Th-234	Pa-234m	% diff
G13284	103.02	17.24	17.45	+1.2	17.24	17.14	-0.6
G13285	102.56	51.12	50.56	-1.1	52.25	49.60	-5.1
G13286	88.09	61.53	61.60	+0.1	63.08	61.59	-2.3
G13287	96.70	54.01	54.17	+0.3	55.61	55.75	+0.3

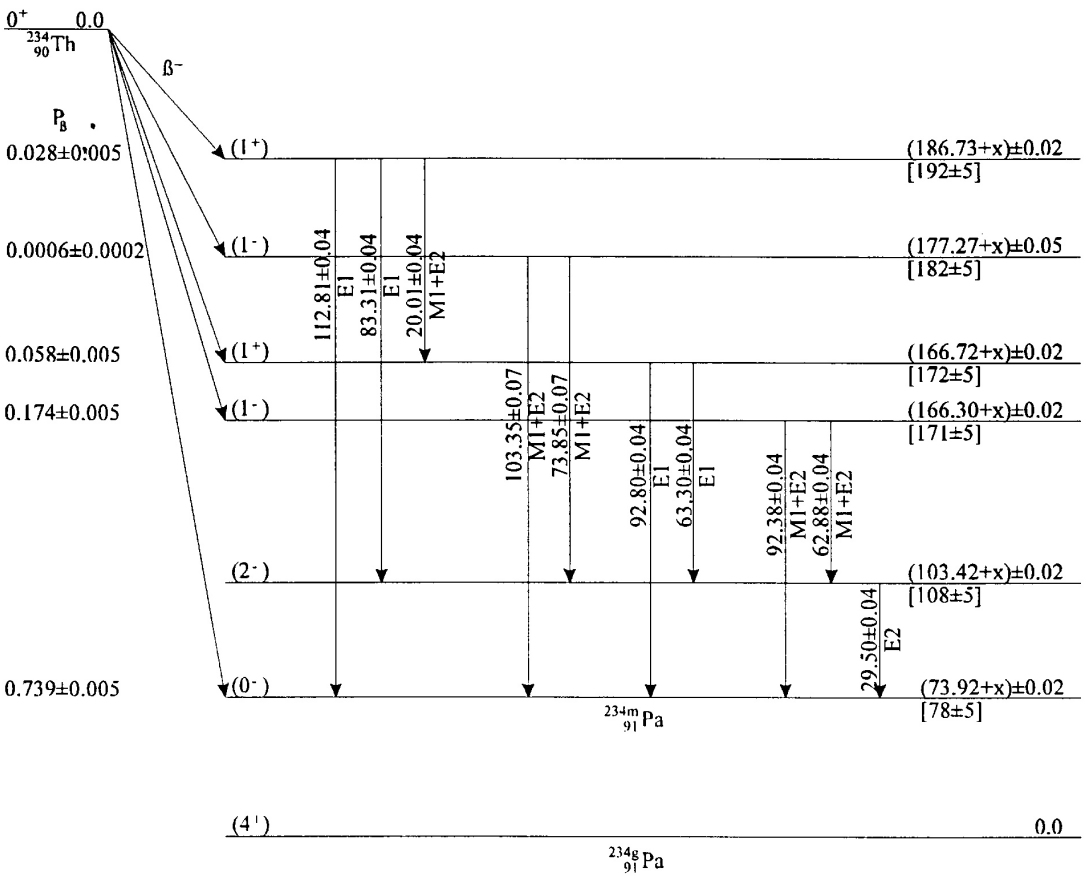

Figure 1: ${}^{234}_{90}\mathrm{Th}(\beta){}^{234m}_{91}\mathrm{Pa}$, $\mathrm{Q} = (192 \pm 10)\mathrm{keV}$

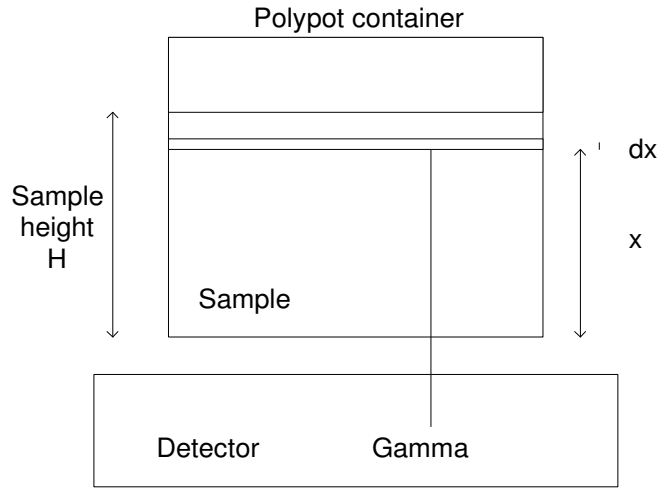

Figure 2 – Standard counting geometry

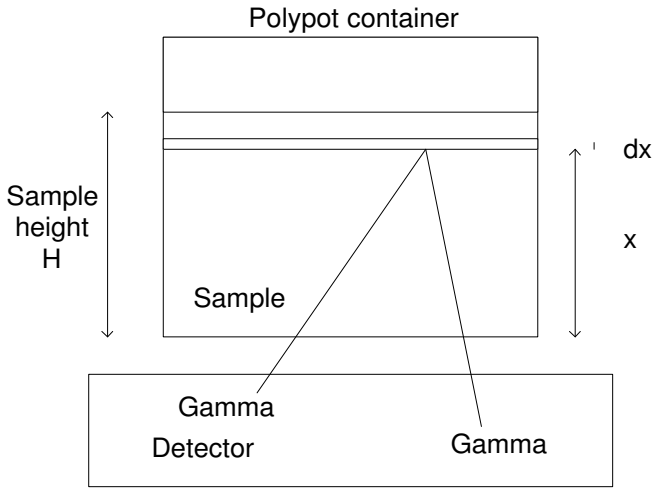

Figure 3 – Different gamma-ray path lengths within the sample

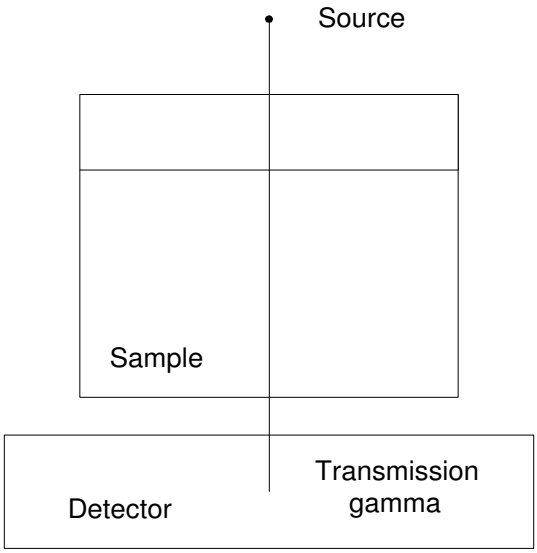

Figure 4 – Gamma-ray transmission

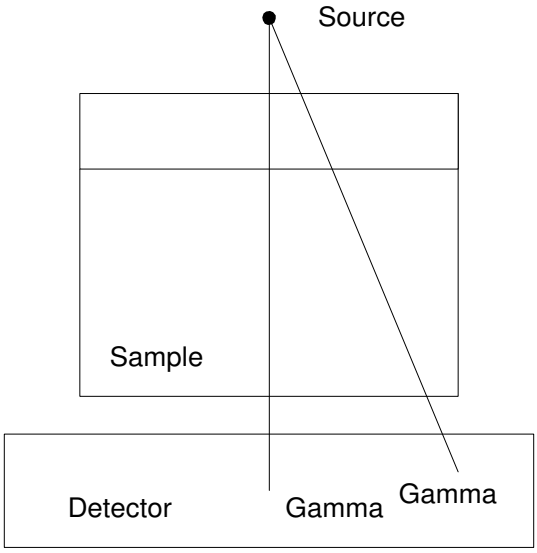

Figure 5 – Different gamma-ray transmission path lengths