APPENDIX 1

PREPARATION AND PURIFICATION OF THE SPIKES ^{229}Th, ^{233}Pa AND ^{232}U

^{229}Th ($7,3 \times 10^3$ y)

This is not a naturally occurring radioactive isotope and is therefore a very convenient one to use. All the other thorium isotopes are either found naturally or their half-lives are too short to be used. The ^{229}Th spike obtained from Harwell in the UK was not pure for it also contained ^{228}Th, which is naturally occurring. Fortunately this did not interfere with the determinations as ^{228}Th was not being sought. A correction nevertheless had to be applied to the total α-activity of the spike so as to eliminate it from the calculation.

Before ^{229}Th could be calibrated it was purified in the usual manner to remove any daughter products that had grown in. (For example ^{224}Ra and ^{220}Rn from ^{228}Th, and ^{225}Ac from ^{229}Th). Calibration was done on the same day as purification, otherwise the calibrated value would also include the α-activities of the daughters. Experimentation showed that ^{224}Ra could be detected after six hours.

^{233}Pa (27,4 d)

^{233}Pa was a synthetically prepared radioactive isotope and was produced by irradiating about 10 mg of purified reagent-grade thorium nitrate for 20 minutes in the

pneumatic facility (the method of purification was similar to that used in Table 9). Purification of the ^{233}Pa was necessary to remove all ^{232}Th remaining. The method used was exactly the same as for the general purification of protactinium. A milking procedure was used whenever ^{233}Pa was required. A new sample had to be prepared after two weeks because of the relatively short half-life of ^{233}Pa and the production of ^{233}U. About 70 µℓ of the ^{233}Pa solution was added to the sample and exactly the same volume evaporated to dryness on a separate disc. The γ-count of this disc was used as the initial ^{233}Pa activity, to which the yield correction was normalized.

^{232}U (71,7 y)

^{232}U does not occur naturally. It is, however, useful because it is mono-energetic and does not have other uranium isotope contaminants. The radiochemical centre, Amersham, UK, were the suppliers. Calibration was done after the ^{232}U had been purified using anion exchange in the chloride form (Table 9) from which ^{228}Th and ^{226}Ra daughters were removed.

APPENDIX 2

CALCULATIONS FOR THE DETERMINATION OF CHEMICAL YIELD FOR THORIUM, PROTACTINIUM AND URANIUM ISOTOPES

Nomenclature:

$(Ao)_{230}$ - actual activity of ^{230}Th

A^{m}_{234} - measured activity of ^{234}U

$(Ao)^{STD}_{231}$ - actual activity of ^{231}Pa in standard

A^{STD}_{231} - measured activity of ^{231}Pa in standard

A^{S}_{231} - measured activity of ^{231}Pa in sample

λ_{235} - decay constant of ^{235}U ($9,76 \times 10^{-10}$)

λ_{238} - decay constant of ^{238}U ($1,54 \times 10^{-10}$)

N_{235} - number of atoms of ^{235}U

N_{238} - number of atoms of ^{238}U

E_{α} - efficiency of α detector (i.e. geometry)

E_{γ} - efficiency of γ detector (i.e. geometry)

Y - chemical yield

Activity values are given per unit counting time, per unit weight. In this work the values were usually given as counts per hour per gram. The actual activity of the spike was corrected for weight, as the calibrated activity was quoted as counts per second per gram in the cases of ^{229}Th and ^{232}U only.

Uranium:

$$(Ao)_{234} = A^{m}_{234} . E_{\alpha} . Y \qquad (1)$$

$$(Ao)_{232} = A^{m}_{232} . E_{\alpha} . Y \qquad (2)$$

As uranium only was involved, the chemical yield (Y) and geometry (E_{α}) was constant for both ^{234}U and ^{232}U respectively. The same applies to ^{238}U.

$$\frac{(Ao)_{234}}{(Ao)_{234}} = \frac{A^{m}_{234}}{A^{m}_{232}} \qquad (3)$$

$$(Ao)_{234} = \frac{A^{m}_{234} \cdot (Ao)_{232}}{A^{m}_{232}} \qquad (4)$$

$$\text{Similarly } (Ao)_{238} = \frac{A^{m}_{238} \cdot (Ao)_{232}}{A^{m}_{232}} \qquad (5)$$

The $^{234}U/^{238}U$ ratio is derived from equations (4) and (5).

Thorium

The thorium spike was a mixture of ^{229}Th and ^{228}Th. A correction must be applied to remove the ^{228}Th activity contribution.

$$(Ao)_{TOTAL} = (Ao)_{229} + (Ao)_{228} \qquad (6)$$

$$(Ao)_{228} = A^{m}_{228} . E_{\alpha} . Y \qquad (7)$$

$$(Ao)_{229} = A^{m}_{229} . E_{\alpha} . Y \qquad (8)$$

$$\frac{(Ao)_{228}}{(Ao)_{229}} = \frac{A^{m}_{228}}{A^{m}_{229}} = R \qquad (9)$$

$$(Ao)_{228} = R(Ao)_{229} \qquad (10)$$

$$(Ao)_{TOTAL} = (Ao)_{229} + R(Ao)_{229} = (Ao)_{229}(1 + R) \qquad (11)$$

$$(Ao)_{229} = \frac{(Ao)_{TOTAL}}{(1 + R)}$$

$$= \frac{(Ao)_{TOTAL}}{1 + \frac{A^m_{228}}{A^m_{229}}} \qquad (12)$$

The value of (1 + R) should be constant for the spike solution. Using the samemethod of calculation, the activity of ^{230}Th is determined as follows:

$$(Ao)_{230} = \frac{A^m_{230} \cdot (Ao)_{229}}{A^m_{229}} \qquad (13)$$

The $^{230}Th/^{234}U$ ratio is derived from equations (4) and (13).

Protactinium

The calculation of the $^{231}Pa/^{234}U$ ratio is slightly more complicated because both isotopes come from different decay chains, the ^{235}U and ^{238}U chains respectively.

$$Pa: \quad (Ao)^{STD}_{231} = (Ao)^{STD}_{235} = \lambda_{235} \cdot N_{235} \qquad (14)$$

$$U: \quad (Ao)^{STD}_{234} = (Ao)^{STD}_{238} = \lambda_{238} \cdot N_{238} \qquad (15)$$

$$\left[\frac{(Ao)_{231}}{(Ao)_{234}}\right]^{STD} = \left[\frac{\lambda_{235}}{\lambda_{238}} \cdot \frac{N_{235}}{N_{238}}\right]^{STD} \qquad (16)$$

Relationships in equation (16) were determined from a standard uranothorianite sample from Phalaborwa which was in radioactive equilibrium. The atom ratio (N_{235}/N_{238}) is determined by mass spectrometer.

Pa:

$$\left.\begin{aligned}(Ao)^{STD}_{231} &= A^{STD}_{231}.Y^{1}.E_{\alpha}\\ (Ao)^{S}_{231} &= A^{S}_{231}.Y.E_{\alpha}\end{aligned}\right\} \quad (\alpha\text{-spectrometer}) \qquad (17)$$

$$\left.\begin{aligned}(Ao)^{STD}_{233} &= A^{STD}_{233}.Y^{1}.E_{\gamma}\\ (Ao)^{S}_{233} &= A^{S}_{233}.Y.E_{\gamma}\end{aligned}\right\} \quad (\gamma\text{-spectrometer}) \qquad (18)$$

$$\frac{A^{STD}_{231}}{A^{S}_{231}} = \frac{(Ao)^{STD}_{231}}{(Ao)^{S}_{231}}.\frac{Y}{Y^{1}} \qquad (19)$$

$$\frac{A^{STD}_{233}}{A^{S}_{233}} = \frac{(Ao)^{STD}_{233}}{(Ao)^{S}_{233}}.\frac{Y}{Y^{1}} \qquad (20)$$

Combine equations (19) and (20),

$$\frac{A^{STD}_{231}}{A^{S}_{231}}.\frac{A^{STD}_{233}}{A^{S}_{233}} = \frac{(Ao)^{STD}_{231}}{(Ao)^{S}_{231}}.\frac{(Ao)^{STD}_{233}}{(Ao)^{S}_{233}} \qquad (22)$$

U:

$$\left.\begin{aligned}(Ao)^{STD}_{234} &= A^{STD}_{234}.Y^{11}.E_{\alpha}\\ (Ao)^{S}_{234} &= A^{S}_{234}.Y^{11}.E_{\alpha}\end{aligned}\right\} \quad (\alpha\text{-spectrometer}) \qquad (23)$$

$$\frac{A^{STD}_{234}}{A^{S}_{234}} = \frac{(Ao)^{STD}_{234}}{(Ao)^{S}_{234}}.\frac{Y^{11}}{Y^{11}} \qquad (24)$$

$$\left.\begin{aligned}(Ao)^{STD}_{232} &= A^{STD}_{232}.Y^{11}.E_{\alpha}\\ (Ao)^{S}_{232} &= A^{S}_{232}.Y^{111}.E_{\alpha}\end{aligned}\right\} \quad (\alpha\text{-spectrometer}) \qquad (25)$$

$$\frac{A^{STD}_{232}}{A^{S}_{232}} = \frac{(Ao)^{STD}_{232}}{(Ao)^{S}_{232}} \cdot \frac{Y^{111}}{Y^{11}} \qquad (26)$$

Combine equations (24) and (26)

$$\frac{A^{STD}_{234}}{A^{S}_{234}} \cdot \frac{A^{STD}_{232}}{A^{S}_{232}} = \frac{(Ao)^{STD}_{234}}{(Ao)^{S}_{234}} \cdot \frac{(Ao)^{STD}_{232}}{(Ao)^{S}_{232}} \qquad (27)$$

Now

$$\frac{A^{S}_{231}}{A^{S}_{234}} = \frac{A^{S}_{231}}{A^{STD}_{231}} \cdot \frac{A^{STD}_{231}}{A^{STD}_{234}} \cdot \frac{A^{STD}_{234}}{A^{S}_{234}} \qquad (28)$$

Substitute equations (16), (22) and (27) into (28)

$$\frac{A^{S}_{231}}{A^{S}_{234}} = \frac{\left[\frac{\lambda_{235}}{\lambda_{238}} \cdot \frac{N_{235}}{N_{238}}\right]^{STD} \cdot \frac{(Ao)^{STD}_{234}}{Ao)^{S}_{234}} \cdot \frac{A^{STD}_{232}}{A^{S}_{232}} \cdot \frac{(Ao)^{STD}_{233}}{(Ao)^{S}_{233}}}{\frac{(Ao)^{STD}_{232}}{(Ao)^{S}_{232}} \cdot \frac{A^{STD}_{233}}{A^{S}_{233}} \cdot \frac{(Ao)^{STD}_{231}}{(Ao)^{S}_{231}}} \qquad (29)$$

$$= \frac{^{231}Pa}{^{234}U} \quad \text{in sample} \qquad (30)$$