RiO5 METHOD (3)

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Determination of particulate and dissolved thorium-234
30L water samples

The following is a historical internal technical manual from the Woods Hole Oceanographic Institution, 1980. Further information and descriptions for this method may be found in the following publication:

Anderson, R.F. and A.P. Fleer (1982) Determination of natural actinides and plutonium in marine particulate material. *Anal. Chemistry,* v54, 1142-1147.

Disclaimer

It is the responsibility of the analyst to follow established safety and health practices. Although each laboratory identified as the source has tested the methods, each user should perform an individual validation procedure.

DETERMINATION OF
PARTICULATE AND DISSOLVED THORIUM-234

The determination of particulate and dissolved ^{234}Th is similar to the procedure of *Anderson and Fleer* (1982). Samples are collected using 30-liter Niskin bottles with teflon or epoxy-coated internal springs. On deck, the sample is pumped with delrin impeller pump through a 0.45-μm pore size 147-mm diameter Millipore filter and into a pre-rinsed 6-gallon plastic cubitainer held in a plastic milk crate. An inline plastic water meter records volumes in gallons. The particulate sample filter is folded twice and stored in a polyethylene sample bag. To the ~20-liter dissolved sample is added: 30 mls reagent grade 16$\underline{N}$ HNO$_3$; 500 μl of ^{230}Th tracer of ~30 dpm/ml; and 5 mls of 50 mg/ml iron carrier previously cleaned by extraction into isopropyl ether from an 8$\underline{M}$ HCl solution and back extracted into 0.1$\underline{M}$ HCl. The acidified sample is allowed to equilibrate for a day to a maximum of a few days. The sample is weighed on a Heathkit digital scale and the pH is adjusted to approximately 8 with about 40 mls of 10$\underline{M}$ NH$_4$OH to precipitate iron hydroxide containing all the thorium and uranium from the solution. The precipitate is allowed to settle for 12 to 24 hours. The supernate is drawn off, the precipitate is decanted and then spun down in a centrifuge tube to about an 8 ml volume. The precipitate is resuspended in a distilled water and spun down again, then dissolved in three times its volume with 12$\underline{N}$ HCl to make a 9$\underline{N}$ HCl solution. A 1.5-cm x 12-cm ion exchange column is filled with AG1 x 8 100–200 mesh resin and conditioned with 9$\underline{N}$ HCl. The sample solution is run slowly through. The iron and uranium are retained on the column; the thorium passes through in the effluent and collected in a teflon beaker. An additional 30 mls 9$\underline{N}$ HCl are used to rinse the centrifuge tube and resin. The collected thorium containing effluent is evaporated to near dryness, cooled slightly and 3–4 times that volume of conc. HNO$_3$ is added. After an initial effervescence subsides, the sample is heated, rinsing down the beaker twice with conc. HNO$_3$ until all the HCl has evaporated and before precipitates begin to form. While still hot, the sample, now in conc. HNO$_3$, has an equal volume of distilled water added, resulting in an 8$\underline{N}$ HNO$_3$ solution. If the solution is not perfectly clear, more 8$\underline{N}$ HNO$_3$ can be added and/or the solution heated slightly.

A 0.7-cm x 12-cm ion exchange column is filled with AG1 x 8 100–200 mesh resin and conditioned with 8$\underline{N}$ HNO$_3$. The sample solution is run through, plus an additional 20 mls 8$\underline{N}$ HNO$_3$ to rinse the beaker and resin. The effluent is discarded and the thorium is eluted with three 10-ml portions of

$9\underline{N}$ HCl. The eluate is collected in a teflon beaker. The solution is heated to near dryness with the addition of a few mls. conc. HNO_3. If the final single drop of sample can become very small before becoming solid, as it starts to solidify, 1 ml of $0.01\underline{M}$ HNO_3 is added. If the sample begins to solidify as a drop sized or larger mass, a repeat of the second nitrate column will be necessary to purify the sample sufficiently. To the sample in $0.01\underline{M}$ HNO_3 is added 1 ml of $2\underline{M}$ NH_4Cl. An additional 2 mls of $2\underline{M}$ NH_4Cl is used to transfer the sample to the electroplating cell of the following characteristics: 1-in diameter polished silver plancet as the cathode with $\frac{3}{4}$-in diameter center portion exposed, teflon walls, a coiled platinum anode $\frac{3}{16}$-in from silver disk, and a teflon stir bar above the anode to prevent bubble formation on the electrodes. A 0.8 amp current at 6 volts is applied while stirring. The potential may initially drop but will begin to rise to 6 volts. As the electroplating nears completion, the current will drop. The procedure is complete when the current reaches 0.2 or 0.3 amp, usually after one hour. However, if the current drops and then begins to rise, the platinum anode is dissolving and plating on the sample and plating should be terminated. To end the plating, add a few drops conc. NH_4OH to the plating cell and disconnect the leads to the electrodes. Rinse out the plating cell, remove the silver disk, rinse and gently flame the silver plancet, being careful not to melt the silver.

To the particulate sample in a teflon beaker add 1 ml of 50 mg/ml iron carrier, 0.5 ml of ^{230}Th tracer, 10 mls HNO_3, 3 mls conc. $HClO_4$, and 2 mls HF. Heat the sample and evaporate to dryness, redissolve in $2\underline{N}$ HCl, and precipitate the iron with conc. NH_4OH. Spin down the iron, decant the supernate, redissolve with $9\underline{N}$ HCl, reprecipitate with conc. NH_4OH, spin down and decant to remove any traces of $HClO_4$ in the sample. The procedure from this point on is the same as the dissolved thorium samples except that a smaller 0.7 cm x 12 cm first column can be used due to the smaller amount of iron added to the sample.

The recovery of the ^{230}Th tracer is measured by alpha counting in a Nuclear Measurements Corporation 2π gas flow proportional counter at 1100 volts bias. A ^{230}Th standard is counted between samples to correct for short-term variations in counting efficiency.

^{234}Th is measured as the beta activity of ^{234}Th and its short-lived beta emitting daughter ^{234}Pa ($t\frac{1}{2} = 1.18$ min). Beta activities are measured in low background gas flow beta detectors with lead shielding and anti-coincidence counting as per the design of *Lal and Shink* (1960). The higher energy beta particles of ^{234}Pa are counted with about 50% efficiency, and the lower energy betas of ^{234}Th with less than 5% efficiency. The sample plancets are held in a delrin ring with a plastic window of about 10 mg/cm^2. Backgrounds ranged from 0.2 to 0.8 cpm and were measured weekly. An electroplated ^{238}U standard was counted weekly to correct for short-term variations in counting efficiency. For every

sample set, two or more ^{234}Th standards were run to determine overall beta counter efficiencies. ^{234}Th standards were prepared by separation from a ^{238}U primary standard solution by the same separation procedures discussed above and by using the same ^{230}Th tracer as in the samples.

A series of counts on a single sample are related by plotting $e^{-\lambda t}$ vs. net cpm. Net cpm is background corrected and also related to the ^{238}U standard countings to correct for differences in efficiencies among the different detectors, and $e^{-\lambda t} = 1$ on the plating date. Three fits to the data are made and in all the points are weighted according to their statistical errors. The first fit allows a y intercept other than zero. The second forces the fit through the origin. The third is a weighed average of the counts decay corrected to the plating date. Since there is no significant ingrowth of beta emitters from the ^{230}Th tracer, and uranium has been removed and there is no significant beta activity from other thorium isotopes due to sample size; the three fits are essentially the same for these samples. The value of y in cpm at $x = e^{-\lambda t} = 1$ is the net cpm.

For dissolved thorium samples, a correction is made for the ingrowth of ^{234}Th from ^{238}U between sampling and separation. Uranium concentrations are calculated from salinity as shown by *Chen, Edwards, and Wasserburg* (1986).

The activities are calculated in the following manner for dissolved ^{234}Th samples:

$$^{234}Th\ dpm/kg = \frac{\left[\frac{net\ cpm\ t_3}{e^{-\lambda(t_3-t_2)}(Beta\ efficiency)(^{230}Th\ recovery)}\right] - \left[[^{238}U](volume)(1 - e^{-\lambda(t_2-t_1)})\right]}{e^{-\lambda(t_2-t_1)}(volume)}$$

where

t_1	=	time of sampling
t_2	=	time of separation = time of first column
t_3	=	time of plating
$[^{238}U]$	=	(salinity %‰)(0.0660) dpm/kg
λ	=	0.028755
volume	=	weight of sample in kg

For particulate ^{234}Th samples:

$$^{234}Th\ dpm/kg = \frac{(\text{net cpm } t_3)}{e^{-\lambda(t_3 - t_1)}(\text{Beta efficiency})(^{230}Th\text{ recovery})(\text{volume})}$$

where

t_1 $\quad = \quad$ time of sampling

t_3 $\quad = \quad$ time of plating

volume $\quad = \quad$ weight of volume filtered in kg

REFERENCES

Anderson, R. F. and A. P. Fleer (1982) Determination of natural actinides and plutonium in marine particulate material. *Analytical Chemistry*, 54, 1142–1147.

Lal, D. and D. R. Shink (1960) Low background thin-wall flow counters for measuring beta activities of solids. *Review of Scientific Instruments*, 31, 395–398.

Chen, J. H., R. L. Edwards, and G. J. Wasserburg (1986) ^{238}U, ^{234}U and ^{232}Th in seawater. *Earth and Planetary Science Letters*, 80, 241–251.