Division Control No. ECD-106

This manuscript has been submitted to
Health Physics
and the contents are subject to change.

This copy is to provide information
prior to publication.

NON-DESTRUCTIVE DETERMINATION OF SELECTED URANIUM AND THORIUM-SERIES RADIONUCLIDES IN BIOLOGICAL SAMPLES

S.R. Joshi

NWRI Contribution No. 86-68

Environmental Contaminants Division
National Water Research Institute
Canada Centre for Inland Waters
Burlington, Ontario, Canada L7R 4A6

• Environment Canada

NONDESTRUCTIVE DETERMINATION OF SELECTED URANIUM- AND THORIUM-SERIES RADIONUCLIDES IN BIOLOGICAL SAMPLES

S.R.Joshi

Paper submitted to Health Physics

MANAGEMENT PERSPECTIVE/EXECUTIVE SUMMARY :

This paper describes the development of a nondestructive technique for the measurement of lead-210,radium-226,thorium-228 and uranium-238 in biological samples.The radioisotope concentrations are derived from the measurements on the low-energy gamma-rays emitted by these radionuclides or their progenies.The technique has been extensively and satisfactorily used in establishing the levels of these radionuclides in fish samples from the Great Lakes and Langley Bay/Lake Athabasca.

The major advantage in using this method is the complete elimination of chemical steps requiring sample decomposition using strong mineral acids.This feature alone improves safety aspects,reduces corrosion of expensive laboratory fixtures and equipment,and saves time involved in sample processing.Furthermore,the nondestructive nature of the method permits determination of other constituents such as heavy metals.

DETERMINATION NON DESTRUCTIVE DE CERTAINS RADIONUCLIDES CHOISIS DE LA SERIE URANIUM ET THORIUM DANS DES ECHANTILLONS BIOLOGIQUES

S.R.Joshi

Mémoire présenté à Health Physics

PERSPECTIVE DE GESTION/RESUME :

Ce mémoire décrit la mise au point d'une méthode non destructive pour mesurer le plomb-210, le radium-226, le thorium-228 et l'uranium-238 présents dans les échantillons biologiques. Les concentrations de radioisotopes sont dérivées des mesures des rayons gamma de faible énergie émis par ces radionuclides ou leurs parents. La méthode a été largement utilisée avec succès pour établir les teneurs de ces radionuclides dans des échantillons de poissons provenant des Grands lacs et de la baie Langley/lac Athabasca.

Le principal avantage de cette méthode est d'éliminer complètement les étapes chimiques nécessitant la décomposition de l'échantillon à l'aide d'acides minéraux forts. Cette seule caractéristique améliore la sécurité du procédé, réduit la corrosion du matériel de laboratoire et permet de gagner du temps dans le traitement des échantillons. En outre, la nature non destructive de cette méthode permet de déterminer d'autres constituants tels que les métaux lourds.

Introduction

Il est essentiel de connaître les teneurs des divers radionuclides de la série uranium et thorium dans les matériaux biologiques pour bien comprendre leur évolution dans l'environnement. Certaines des études les plus courantes dans ce domaine établissent les teneurs de ces radionuclides dans les poissons en vue soit de dériver la dose radiative reçue par le poisson ou par les humains consummant le poisson contaminé, soit de comprendre le rôle du poisson dans le cycle biogéochimique des radionuclides dans le milieu aquatique (Wo74; Sw83; Jo84). En général, ces mesures sont effectuées à l'aide de méthodes chimiques par voie humide (Sw83; Jo84) qui prennent beaucoup de temps, nécessitent l'emploi de produits chimiques coûteux et demandent un personnel hautement qualifié. En outre, utilisation de grandes quantités d'acides minéraux concentrés pour solubiliser l'échantillon présente certains dangers en laboratoire. Dans les cas (comme dans celui de ^{210}Po) où aucune émission de rayons gamma n'accompagne la décroissance radioactive, l'analyste n'a d'autre choix que de dissoudre l'échantillon et d'isoler le radionuclide qui l'intéresse avant d'effectuer les mesures. La décroissance de plusieurs radionuclides importants de la série uranium or thorium ou de leurs dérivés de courte vie est toutefois accompagnée d'émissions de rayons gamma caractéristiques. La mesure de ces émissions au moyen d'un détecteur planaire au germanium constitue une approche distincte et non destructive dans les essais de plusieurs radionuclides de ce genre présents dans les matériaux biologiques et fait l'objet de la présente communication.

Introduction

A knowledge of the levels of various uranium- or thorium-series radionuclides in biological materials is essential in understanding their behaviour in the environment. Some of the most common of such studies involve establishing the levels of these radionuclides in fish with the view of either deriving the radiation dose received by fish or by humans consuming contaminated fish or in understanding the role of fish in the biogeochemical cycling of radionuclides in the aquatic environment (Wo74; Sw83; Jo84). Generally, these measurements are carried out using wet chemical methods (Sw83; Jo84) that are time consuming and require expensive chemicals and highly skilled technical staff. Furthermore, the consumption of large amounts of concentrated mineral acids in bringing the sample into solution form compromises the laboratory safety aspects. In cases (such as ^{210}Po) where no gamma emissions accompany radioactive decay, the analyst has no choice but to dissolve the sample and isolate the radionuclide of interest prior to measurement. The decay of several important uranium- or thorium-series radionuclides or their short-lived daughters, however, is accompanied by the emission of characteristic γ-rays. The measurement of such γ-emissions with a germanium planar detector constitutes an independent, non-destructive approach to the assay of several such radionuclides in biological materials and is the subject of this communication.

Materials and Methods

Following collection and dissection in the field, the samples were weighed and stored at or about 4°C until freeze-drying in the laboratory. The dried and weighed samples were ground to a fine powder and stored sealed in polypropylene counting vials for at least four months to ensure equilibrium between ^{238}U and ^{234}Th ($T_{1/2}$ = 24.1 d). The storage time is significantly decreased if a determination for ^{238}U is not desired. Thus, for ^{226}Ra and ^{228}Th measurements, a storage time of only about 3-4 weeks is sufficient to ensure equilibrium with daughter nuclides.

The γ-ray spectra of the samples were accumulated for up to 2.5×10^5 s by placing the counting vial directly on a germanium planar detector. The detector characteristics and computational procedure have been described earlier (Jo85). The critical issue in the direct γ-ray spectrometric determination of radionuclides in biological materials involves efficiency calibration of the detector. We calibrated our detectors first by using sawdust and bentonite carefully spiked with ^{210}Pb (46.5 keV), ^{241}Am (59.6 keV), ^{57}Co (122 keV), ^{228}Th (239.6 keV), and ^{226}Ra-^{214}Pb (186.2, 295.2 and 351.9 keV). Both pelletized (using a hydraulic press) and powdered materials were used. The efficiency calibration curve obtained using the pelletized sample was very similar to the one obtained using spiked sediments and certified uranium ore and other solid materials

for which we have very reliable efficiency measurements (Jo85). The curve, however, was significantly different from the one derived from measurements on powdered samples, illustrating the density effects on the self-absorption of low-energy γ-rays.

Following Cutshall et al. (Cut83), a normalization technique was used to account for the self-absorption effects. The technique relates the net count rate for the sample(S) to that expected for material identical to that used for efficiency calibration (C) in similar geometry by the expression

$$C = S \cdot \frac{\ell n(C'/S')}{1 - S'/C'} ,$$

where C' and S' are photon emission rates of disc sources containing radionuclides of interest through the unspiked calibrating material and sample, respectively. We have evaluated this technique by analyzing samples of widely different composition and known radionuclide content as 'unknowns' and found the technique to give very reliable measurements. The technique also established that our efficiency measurements made using samples spiked in our laboratories are also reliable. In our experience, the above normalization technique virtually eliminates the need for separate detector efficiency calibration for each matrix provided accurate efficiency measurements for one matrix are available. Uranium ores, sediments

and soils are the preferred materials for detector calibration since, unlike other matrices, many certified reference materials are available for cross-checking. Even if reliable biological matrix standards were available, each measurement should be corrected for the attenuation of low-energy (up to 300 keV) γ-rays as described above since this attenuation is very dependent on sample composition (Wi80; Cut83).

Results and Discussion

The low-energy γ-ray spectra of composited Langley Bay (Lake Athabasca) pike bone, muscle and kidney samples, obtained at about 0.2 keV/channel, are shown in Fig. 1. The spectra reveal that suitable γ-emissions from ^{210}Pb, ^{226}Ra (^{214}Bi), ^{228}Th (^{212}Pb) and ^{238}U (^{234}Th) are all located in the regions relatively free from interferences due to X-rays or emissions from other major radionuclides. Special caution, however, must be exercised in employing the 63.3-keV ^{234}Th photoemission (3.9%) for deriving the concentration of ^{238}U. This photoemission includes contributions from the newly-discovered (Ro83) 63.9-keV emission from ^{232}Th (0.255%), 63.9-keV emission from ^{231}Th-^{235}U (0.023%), and the 62.9-keV emission from ^{234}Th (0.018%). Of these, only emissions from ^{231}Th and ^{232}Th constitute potential interferences. The former will have significant contribution only for samples relatively rich in ^{235}U. In such a situation, correction can

easily be applied since ^{235}U has a clean photoemission at 143.8 keV. Similarly, the magnitude of the ^{232}Th contribution can be estimated using the 238.6-keV ^{212}Pb gamma-emission assuming secular equilibrium between ^{232}Th and its daughters. The use of the 93-keV ^{234}Th γ-emission (not listed in Fig. 1), which is actually a doublet comprising the 92.4- and 92.8 keV gammas, should be avoided in deriving levels of ^{238}U since this region is crowded by numerous X-rays and γ-emissions (Er79).

The technique was used to assay some samples of biological or plant origin portions of which were previously assayed for ^{226}Ra using wet chemical procedures. The results are given in Table 1 which also compares the results for ^{238}U for several fish organs analyzed by instrumental neutron activation analysis. The latter analyses were performed, under contract, by Becquerel Laboratories, Inc., Mississauga, Ontario. Good agreement is found among the values obtained by different techniques. The non-availability of suitable certified reference materials, unfortunately, precludes the possibility of further evaluation for these low-energy γ-emitters.

Since its adaptation in early 1981, we have used the technique for analyzing over 100 samples of biological or plant origin. In almost all cases, we were able to derive meaningful information on the distribution of radionuclides, for example, in various fish organs as shown in Table 1. The minimum detectable activity (MDA) values (Cur68) obtainable with the detector system we use generally vary

between about 5 and 10 mBq/g dry for a 2.5×10^5 s count on a 15-g sample, though on occasion we were able to measure levels as low as about 0.5 mBq/g dry. The MDA values vary significantly with the radionuclide and the sample type. The lowest values are obtained with ^{228}Th and ^{226}Ra; for ^{210}Pb and ^{238}U, the lowest values are obtained for tissue samples relatively free of high-energy γ-emitters. This is because of the higher Compton background prevailing in the lower energy regions.

Standard methods must still remain the choice in cases where maximum sensitivity is required, though for many situations involving concentrations and sample sizes suitable for low-energy photon analysis, the described technique offers a very attractive alternative. The nondestructive technique also offers another advantage in that it may lead to information on other constituents of the sample. Thus, the low-energy spectra shown in Fig. 1 led us to the reckoning that more cesium and/or barium is present in the pike muscle than in the other two samples. Subsequent analyses of the γ-ray spectra taken on a germanium coaxial detector revealed that the levels of ^{137}Cs, in Bq/kg fresh weight, were indeed higher in pike muscle (6.45) when compared with pike bone (3.2) and pike kidney (1.6); barium concentrations were below the detection limit for instrumental neutron activation analysis technique.

Acknowledgments - The author thanks Mrs. S.P. Thompson for technical assistance. Initial detector calibration measurements using spiked materials were performed by her under the supervision of Dr. R.W. Durham (now retired). Dr. D.T. Waite, Environment Canada (Regina), provided Langley Bay fish samples.

S.R. JOSHI

Environmental Contaminants Division
National Water Research Institute
Canada Centre for Inland Waters
Environment Canada
P.O. Box 5050
Burlington, Ontario L7R 4A6
Canada

References

Cur68 Currie, L.A., 1968, "Limits for Qualitative Detection and Quantitative Determination. Application to Radiochemistry". Anal. Chem. 40, 586.

Cut83 Cutshall, N.H., Larsen, I.L., Olsen, C.R., 1983, "Direct Analysis of ^{210}Pb in Sediment Samples: Self-Absorption Corrections", Nucl. Instrument. Methods 206, 309.

Du79 Durham, R.W., Joshi, S.R., 1979. "Determination of ^{228}Th, ^{230}Th, and ^{232}Th in Environmental Samples from Uranium Mining and Milling Operation", J. Radioanal. Chem. 52, 181.

Er79 Erdtmann, G., Soyka, W., 1979, "The Gamma Rays of the Radionuclides, pp. 388-390 (Weinheim: Verlag Chemie).

Jo76 Joshi, S.R., Durham, R.W., 1976, "Determination of Pb-210, Ra-226, and Cs-137 in Sediments", Chem. Geol. 18, 155.

Jo84 Joshi, S.R., 1984, "^{137}Cs, ^{226}Ra and Total U in Fish from Lakes Ontario, Erie, Huron and Superior during 1976-1982", Water Poll. Res. J. Canada 19, 110.

Jo85 Joshi, S.R., 1985, "Determination of Thorium-228, Thorium-230, and Thorium-232 in Sediments by Anion Exchange and Nuclear Spectrometry", Anal. Chem. 57, 1023.

Ro83 Roy, J.-C., Breton, L., Côté, J.-E., Turcotte, J., 1983, "On the Identification of Gamma Rays from the ^{232}Th Decay", Nucl. Instrument. Methods 215, 409.

Sw83 Swanson, S.M., 1983, "Levels of ^{226}Ra, ^{210}Pb and $TOTAL_U$ in Fish near a Saskatchewan Uranium Mine and Mill", Health Phys. 45, 67.

Wi80 Wilson, W.E., 1980, "Absolute Activity Determinations on Large Volume Geological Samples Independent of Self-Absorption Effects", Nucl. Instrument. Methods 169, 577.

Wo74 Woodhead, D.S., 1974, "The Estimation of Radiation Dose Rates to Fish in Contaminated Environments, and the Assessment of the Possible Consequences", in: Population Dose Evaluation and Standards for Man and his Environment, STI/PUB/375, pp. 555-575 (Vienna: International Atomic Energy Agency).

Table 1. Results of comparative measurements on biological and plant samples.

Sample type	Radionuclide	Concentration (mBq/kg fresh wt.)	
		Wet chemical or INAA	Direct photon counting
Lake Ontario Rainbow trout (posterior section)	^{226}Ra	22.2±0.2[a]	22.4±2.8(powder) 22.8±2.6(pelletized)
Lake Ontario Rainbow trout (posterior section)	^{226}Ra	31.7±0.8[a]	34.7±0.6(powder)
Elliot Lake Uranium Mine Tailings Grass	^{210}Pb	13.9±0.7[b]	14.8±3.6(powder) 13.1±3.4(pelletized)
	^{226}Ra	9.6±0.2[b]	8.9±1.4(powder) 9.1±1.2(pelletized)
	^{228}Th	13.8±0.8[c]	13.9±1.1(powder) 13.6±1.3(pelletized)
Elliot Lake Uranium Mine Tailings Grass	^{210}Pb	17.6±0.9[b]	16.8±2.1(powder) 16.6±1.9(pelletized)
	^{226}Ra	20.8±0.3[b]	21.4±1.9(powder) 19.6±2.1(pelletized
	^{228}Th	6.1±0.8[c]	6.3±1.6(powder) 6.5±1.3(pelletized
Langley Bay Whitefish bone	^{238}U	53.5±1.8[d]	48.9±4.8(powder)[d]
Langley Bay Whitefish kidney	^{238}U	47.4±1.7[d]	44.9±3.1(powder)[d]
Langley Bay Whitefish gut	^{238}U	8.7±1.0[d]	12.0±4.0(powder)[d]
Langley Bay Whitefish male gonads	^{238}U	6.6±0.8[d]	8.3±7.9(powder)[d]
Langley Bay Whitefish liver	^{238}U	13.8±0.9[d]	13.4±2.9(powder)[d]

[a]Values measured by the radon emanation technique (Jo84).

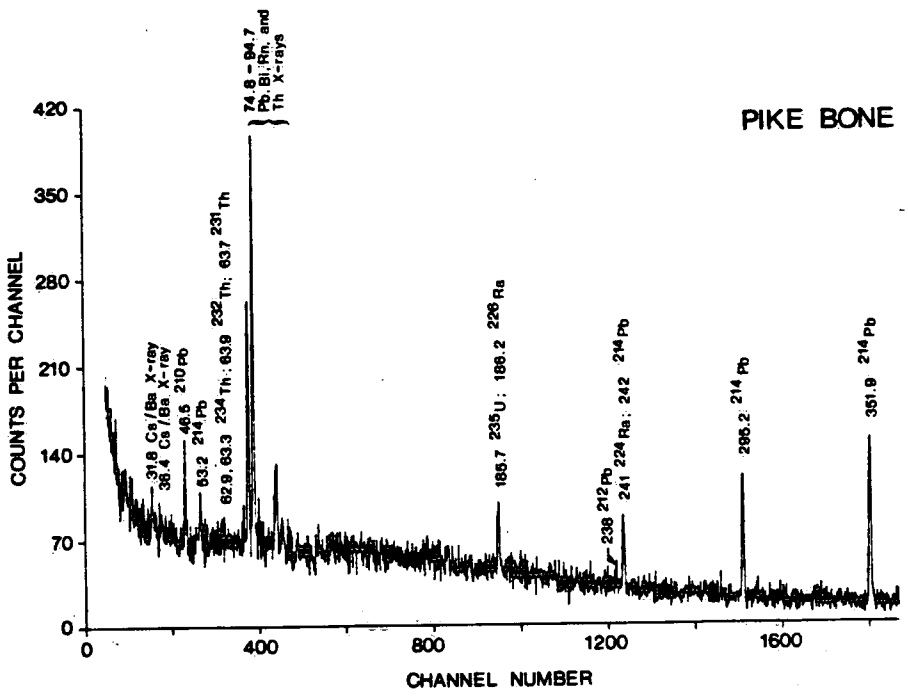
[b]Values measured using variation of the procedure described for sediments (Jo76).

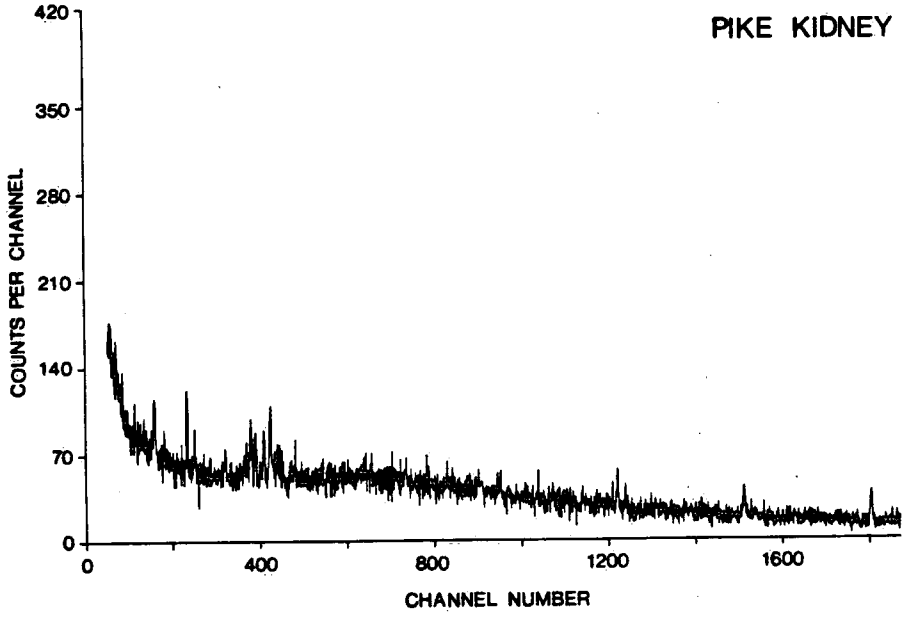
[c]Values measured using ^{234}Th as a yield monitor and a variation of the extraction procedure described earlier (Du79).

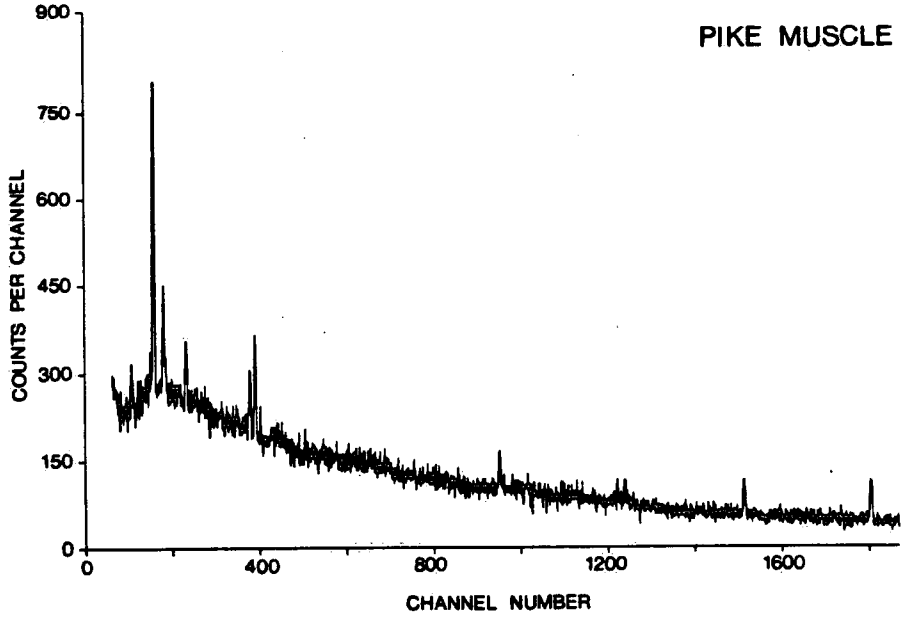
[d]Values in mBq/g dry.

Figure Caption

Fig. 1 The γ-ray spectra (10-370 keV) of pike samples collected from Langley Bay, Lake Athabasca. Each spectrum was accumulated for 2.5×10^5 s. Energies are in keVs.


PIKE BONE
COUNTS PER CHANNEL
CHANNEL NUMBER
0
70
140
210
280
350
420
400
800
1200
1600
74.8 - 94.7 Pb, Bi, Rn, and Th X-rays
31.8 Cs/Ba X-ray
36.4 Cs/Ba X-ray
46.5 210Pb
63.2 214Pb
62.9, 63.3 234Th; 63.8 232Th; 63.7 231Th
185.7 235U; 186.2 226Ra
238 212Pb
241 224Ra; 242 214Pb
295.2 214Pb
351.9 214Pb


PIKE KIDNEY
COUNTS PER CHANNEL
CHANNEL NUMBER
0
70
140
210
280
350
420
400
800
1200
1600


PIKE MUSCLE
COUNTS PER CHANNEL
CHANNEL NUMBER
0
150
300
450
600
750
900
400
800
1200
1600