DRAFT

AECB Contract 87055-9-4070/01-SS

ATOMIC ENERGY OF CANADA LIMITED

MEASUREMENT OF TRITIUM IN CANADIAN FOOD ITEMS
Report of Progress to the end of May 1990

by

R.M. Brown

Environmental Research Branch
Chalk River Nuclear Laboratories
Chalk River, Ontario KOJ 1J0

1990 June

INTRODUCTION

A number of investigators have observed that the specific activity of organically-bound tritium (OBT) is higher than that of the free water tritium (HTO) in most food items at normal environmental levels. This might result in a significantly higher dose than estimated by the currently used ICRP metabolic model.

The objective of the present project is to develop and validate techniques of OBT/HTO measurement and to obtain reliable data on the concentration of organically bound and free water tritium in Canadian diet items, specifically those produced in the vicinity of tritium-emitting facilities and, for comparative purposes, at a control site free of local tritium emissions.

ANALYTICAL TECHNIQUES

The usual technique for OBT measurement is careful drying of the material, combustion in a stream of O_2 or in a pressurized combustion "bomb", recovery of the water of combustion containing the tritium which had been organically bound, and measurement by liquid scintillation counting. The critical step is protecting the dry organic material from adsorption of atmospheric moisture, which may have a significant tritium content, in the course of transferring from drying oven to combustion system. We have used this technique in the past by drying the material in the combustion system itself to avoid any exposure to the atmosphere. The combustion system limits the sample size and hence the sensitivity and makes drying a slow process.

An alternative technique for low level tritium measurement is measurement by mass spectrometry of the amount of decay He-3 produced in a sample in a defined time. W.B. Clarke of McMaster University developed the very specialized He-3/He-4 static-mode mass spectrometer required for this measurement. A copy of his early paper describing the technique is attached. For OBT/HTO measurements the technique involves placing the sample in a flask of aluminosilicate glass (Corning No. 1720) which has low permeability to He, freeze-drying the material collecting the water in a similar flask, thoroughly degassing both the water and the dry organic residue, sealing the flasks, recovering the ingrown He-3 after a defined decay period and measuring it on the mass spectrometer. The He-3 diffuses out of the dry material readily so combustion is not required. The mass spectrometer measurement requires about ½ hour but the ingrowth period must be a month or more depending on the level of activity present. The method is sensitive to any residual or leaked atmospheric He which diffuses through the usual laboratory Pyrex glass readily. To further reduce diffusion, the samples are kept at -20°C during the ingrowth period. The He-4 of atmospheric He serves as a monitor for contamination by He-3 from the atmosphere. Large samples can be handled but size is limited by the time required for freeze-drying. One hundred grams of 80% moisture material requires about 24 hours. Sensitivity can be increased by allowing longer ingrowth periods. One month is an appropriate time for current environmental levels. The technique give a measure of the amount of tritium in the material in the flask. To derive a T/H ratio for comparing OBT and HTO one needs to measure the H content of the material or estimate it from its known chemical composition.

WORK ACCOMPLISHED

Originally it was intended to do the OBT/HTO measurements by the combustion-counting technique using a Parr O_2 combustion "bomb". It was soon realized that multiple combustions would have to be done of materials of low organic content, e.g. fruit, leafy vegetables, to obtain the sensitivity required for present-day environmental levels. Furthermore, high and erratic levels of activity were observed on combusting polyethylene, which should have a low tritium content. Efforts to decontaminate the combustion bomb or its parts by heating and repeated combustion of low-tritium materials brought the "blanks" down somewhat and stabilized them, but it seemed that an analytical blank of about the same level of activity as expected in food items from an uncontaminated environment would persist.

At this point it was decided to explore the possibility of using the He-3 technique and Dr. Clarke was contacted. His measurements in the past have been primarily on water but he had done small samples of freeze-dried tissue and foresaw no problem in doing food materials other than drying and handling the larger samples involved. He expressed interest in participating in the program to the extent of doing the mass spectrometry on about 100 samples at his usual analytical charge. The author visited his laboratory and prepared a few trial samples which were run subsequently and are reported in the attached Table. Sample flasks with a 16 mm filling tube were prepared by the McMaster glassblower from Dr. Clarke's stock of special glass and sent to Chalk River.

A new vacuum line for freeze-drying and sealing-off samples was constructed in the Low Background Laboratory of Environmental Research Branch and a selection of food items prepared. Techniques for filling different materials into the flasks without leaving residues on the wall of the filling tube that must be sealed off were developed. 100 g of wet material was found to be the maximum convenient sample size, requiring about 24 hours for processing and drying. Some samples were filled in a glove bag but this proved to be difficult and time-consuming.

These samples were retained at Chalk River in a deep freeze for the ingrowth period. They were then transported, packed in dry ice, by private car to McMaster University and analyzed by Dr. Clarke. Portions of the water samples were measured by liquid scintillation counting at CRNL for comparative purposes and to give guidance as to the required ingrowth time. These samples were prepared primarily to develop handling and drying techniques and check our ability to properly degas and seal the samples. Satisfactorily low levels of He-4 were found in the samples on mass spectrometer analysis.

Results for samples prepared at McMaster and at CRNL are presented in the Table. Several samples prepared at McMaster were unsatisfactory due to problems with the vacuum pump. The "T-free" waters were higher than expected but could have been contaminated on filling. Drying of the potato indicated that this stip is very, very time-consuming. The samples prepared at CRNL analyzed well as a result of low He-4 content but some of the results are anomalous. The "T-free" water was satisfactorily low. However, the 1951 milk powder, intended as a blank for OBT, showed tritium content which would have been 120 TU when the material was prepared and hermatically sealed in a steel can in the fall of 1951 at Almonte, Ontario. This level seems too high, from our knowledge of the history of bomb tritium releases. Repeat analysis will be done. Levels observed for Deep River potato and tomato are reasonable in view of known levels of reactor tritium in this area. The moose liver was from an animal killed on the CRNL plant highway in 1989 October. Both the He-3 and combustion-counting techniques indicate the OBT and HTO are in equilibrium at a high level. It was expected that the HTO might be high as the result of ingestion of water in the waste disposal areas, but it was not expected that the moose would have been in the area long enough for the OBT to be strongly elevated. In fact, the results indicate that the moose has spent most of its life in the plant area.

Results for the last three samples are anomalous and cannot be explained at the present time. The lettuce, bought in Chalk River and probably imported from California, has a completely unreasonably OBT value, but an expected HTO level. It is difficult to see how the OBT could be contaminated to this extent with no effect on the HTO. Present-day tritium levels in California are 5-10 TU so both the OBT and HTO of the orange are too high. The OBT of the egg from Perth, Ontario, seems high whereas the HTO level is reasonable or slightly low. Further measurements are required to identify the causes of these anamalous results.

FUTURE PROGRAM

The project is reasonably on schedule and within budget. A meeting will be held with Ontario Hydro personnel to arrange sampling at harvest time in the Pickering area and a control site in eastern Ontario will be selected. Dr. Clarke has had storage flasks for 25 OBT and 25 HTO samples prepared. This has used up all his stock of 16 mm glass tubing and the manufacturer indicates that it may be a year before more of this particular glass is produced. Dr. Clarke is looking into other sources such as colleagues in other laboratories. Three or four more drying units will be built on the present vacuum line to accommodate parallel processing of samples. Processing of samples will proceed as they become available. Arrangements have been made for sample handling and filling into flasks to be done at the Petawawa National Forestry Institute which is further removed from CRNL plant and has no local sources of tritium.

A meeting at AECB to discuss progress has been arranged for July 16, 1990.

TRITIUM MEASURED BY He-3 AND COUNTING TECHNIQUES

MATERIALS	OBT (TU)	HTO (TU)	OBT/HTO	COMMENTS
I Prepared at McMaster U., '90 Jan., He-3 measured '90 March				
1. CRNL "T-free" well water, dist'd		5.6 +/- 1.1		
2. CRNL "T-free" well water, undist'd		3.8 +/- 1.4		
3. CRNL pine needles		919 +/- 9		(High He-4 due to
4. Milk powder, sealed since 1951.	---			(pump problems.
5. Potato purchased in Hamilton, 1989.	88 +/- 6	60 +/- 3	1.47	
II Prepared at CRNL Low Level Lab, '90 March, He-3 measured '90 May.				
1. CRNL "T-free" well water, undist'd		0.11 +/- 0.04		Used as blank water for
" By L.S. Counting		0 +/- 8.		liquid scintillation counting
2. Milk powder, sealed since 1951.	13.2 +/-1.1			Unexpectedly high.
3. Potato, Deep River 1989.	412 +/-14	340 +/- 11	1.21	
" By L.S. Counting		355 +/- 13		
4. Moose liver, CRNL 1989	20474 +/-615	21099 +/-635	0.97	
" By L.S. Counting		19794 +/- 92		
" By combustion & L.S. Counting	20468 +/-154	20921 +/-135	0.98	
5. Tomato, Deep River, frozen 1987	298 +/- 23	269 +/- 8	1.11	
" By L.S. Counting		418 +/- 17		
6. Lettuce, California? 1990.	334 +/- 22	10.2 +/- 0.8	32.75	OBT unreasonably high.
" By L.S. Counting		20 +/- 9		
7. Egg, Perth Ont. 1990	76.1 +/- 5.	22.9 +/- 5.5	3.32	
" By L.S. Counting		38 +/- 6		
8. Orange, California, 1990	57 +/- 17	104 +/- 3.6	0.55	High He-4 on OBT
" By L.S. Counting		109 +/- 8		OBT and HTO unreasonably high.

1 Tritium Unit (TU) = 1 T atom per 10^18 H atoms
= 1.08 Bq/Kg H
= 0.120 Bq/L water.