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DEVELOPMENTS AND TRENDS IN LOW-LEVEL TRITIUM MEASUREMENT

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1. Introduction

Tritium concentration in the environment is being measured since about 20 years. The technique of tritium assay was always much more difficult than that of other radioisotopes due to low tritium environmental concentration and very low energy of tritium beta particles. Parallel with the special design of tritium detection instrumentation also the tritium enrichment methods were developed. Early tritium counting method consisted of one or multistage electrolytical enrichment and gas counter (Geiger of proportional) placed in the anticoincidence and heavy metal shield. Low-background gas counters required especially selected low-background construction materials, also as shielding materials, low radio-activity old lead or steel was required. Special design of proportional counters (Oeschger type) eliminated the walls between the main and guard counters thus lowering considerably the background of the system. Electronic circuitry, although simple in principles of operation should assure low noise and absence of spurious pulses.

Liquid scintillation counting was not competitive in the early stage of low-level tritium counting history with gas counting due to low efficiency and higher background. Developments in photomultipliers' technology, in electronic circuitry and in compositions of scintillation cocktails allowing for accommodation up to 50% of water, put at present that method as quite comparable to other systems.

During 20 years of tritium history the environmental concentration has passed its maximum of about 10 000 T.U. in the northern hemisphere precipitation in 1963 and has dropped by two orders of magnitude in present precipitation (Fig. 1). On the other hand the tritium concentration in ocean

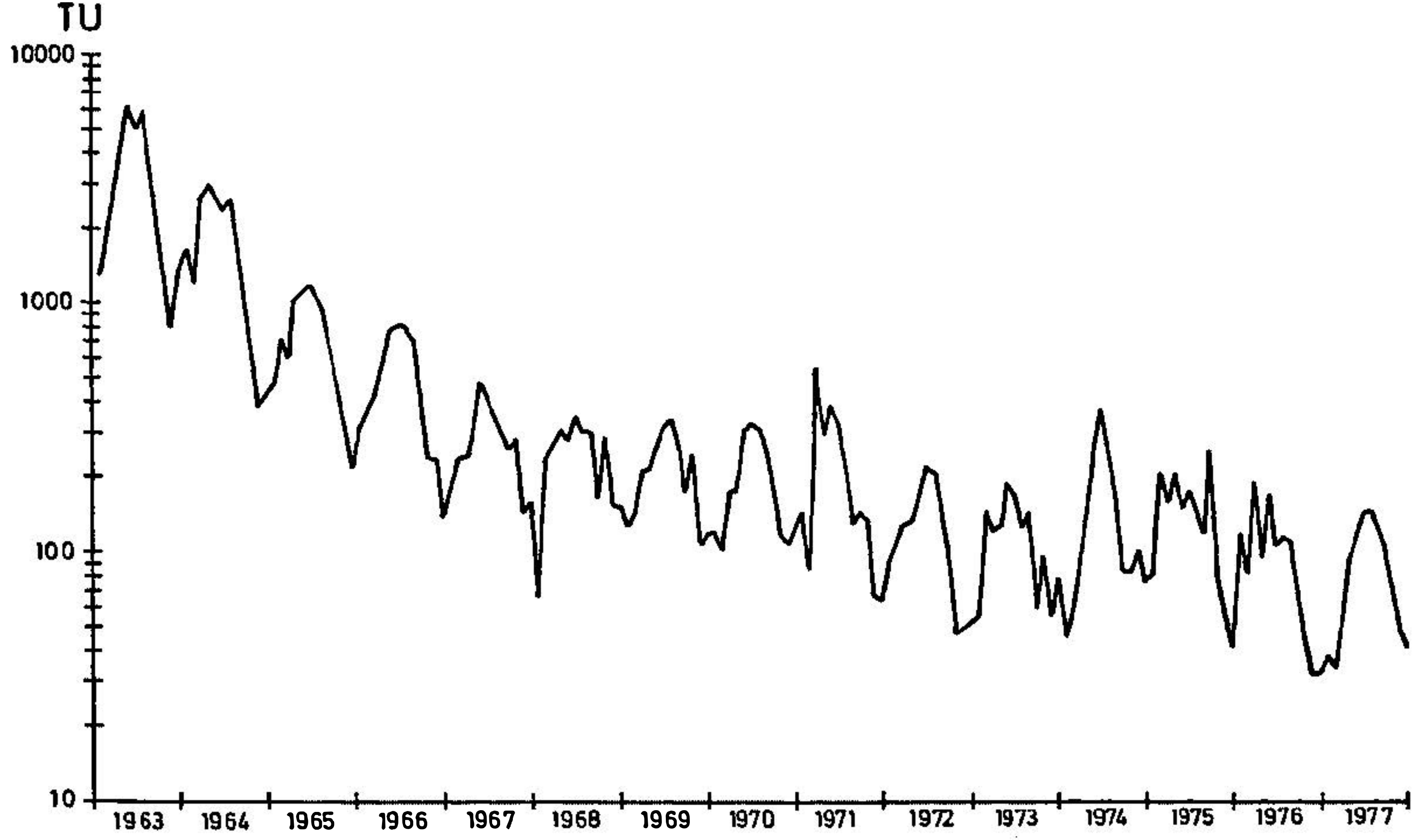

Fig. 1 TRITIUM IN PRECIPITATION, VIENNA

water has increased slightly allowing for unique studies of ocean water dynamics. The meaningfulness of tritium presence in surface, subsurface and groundwater initiated a new hydrological research tool called now isotope hydrology which has expanded with time by adopting further methods as stable isotope ratios, radiocarbon and other radioisotope dating possibilities.

Decrease of tritium concentration in precipitation has required development of better analytical methods of higher sensitivity and precision. Also the number of laboratories for low level tritium measurements in various countries has increased from a few in the early sixties to about fifty at present.

The growing nuclear industry has created a new artifical tritium source. Tritium in the form of hydrogen gas and tritiated vapour and water is being released to the environment. This trend will certainly continue which requires a new approach to observation of tritium input into the environment on the local scale in order to utilise it for hydrological, meteorological and other studies. (see Tables 1 and 2)

2. Progress in gas counting methods

Developments in gas counting methods are directed into following areas:

a) counter construction
b) gas preparation
c) shielding of counters
d) electronic circuitry

Low background counters are made from selected electrolytic copper, stainless steel or quartz. High voltage insulators must be free of gas adsorption which causes tritium memory. Although low-level proportional counters are in general not commercially available due to a very short market,

TABLE 1

Tritium release from nuclear industry

	per 1000 MWe	
	liquid release	atmospheric release
BWR (Boiling Water reactors)	45 Ci/y	20 Ci/y
PWR (Pressurized Water reactors)	800	35
HWR (Heavy Water reactors)	50,000	50,000
FBR (Fast Breeder reactors)	60	60

(Numbers have been taken from NCRP Report No. 62, Tritium in the Environment, National Council for Radiation Protection and Measurements, Washington, 1979).

TABLE 2

Total projected release and accumulation of tritium from all sources

(MCi)

Year	Annual Release		Tritium Accumulated in the Environment				
	Atmospheric	Liquid Release	Atmospheric Weapons Testing	Natural Tritium Production	Nuclear Power	Other Activities	Total
1980	6,1	0,65	1170	70	1	16	1257
1981	6,2	0,75	1110	70	2	17	1199
1982	6,3	0,85	1050	70	4	17	1141
1983	6,4	0,85	990	70	5	18	1083
1984	6,5	0,95	935	70	7	19	1031
1985	6,7	1,0	880	70	8	19	977
1986	6,8	1,2	840	70	10	20	930
1987	6,9	1,4	790	70	12	20	892
1988	7,1	1,6	750	70	15	21	856
1989	7,2	1,7	705	70	17	22	814
1990	8,1	2,0	665	70	20	22	777
1991	8,6	2,2	630	70	24	22	746
1992	9,0	2,4	595	70	29	23	717
1993	9,5	2,6	560	70	34	23	687
1994	10	3,0	530	70	39	24	663
1995	11	3,2	500	70	46	24	640
1996	12	3,4	475	70	52	24	621
1997	12	3,6	450	70	60	25	605
1998	13	4,0	425	70	68	25	588
1999	14	4,2	400	70	77	25	572
2000	12	3,6	380	70	83	25	558

(Table has been taken from NCRP Report No. 62, Tritium in the Environment, National Council for Radiation Protection and Measurements, Washington, 1979).

laboratories are able to build their own counters according to their own construction design. Good counters can work for many years, therefore, no rapid progress in new designs is observed.

Various methods of gas sample preparation have been checked and described. The main consideration in this respect is the relative simplicity and low time consuming system along with negligible possibilities of sample contamination and memory effects in the procedure. Some laboratories routinely use ethane or methane synthesis, others direct hydrogen counting. In the latter case a proper hydrogen/quenching gas mixture (argon-methane or propane) is used in order to minimise the background spectrum component in the tritium energy channel. /1,2/. Increase of sensitivity is achieved by preparing hydrocarbon gases with high hydrogen proportion per mol (e.g. propane C_3H_8) or applying high pressures (up to 5 atm).

In the matter of shielding, a comprehensive study of shielding requirements and shielding composition in different conditions is still missing. Laboratories use their "know-how" in order to reduce the cosmic and material radioactivity background by applying lead and/or steel shields, sometimes additional neutron shield and also in some cases additional shield between the main and guard counters. The main achievement in the field of lowering the counter background is made in recent years in Bern University Laboratory by constructing an underground counting room in the depth equivalent to 70 m of water. Counter backgrounds have been reduced by factor of three in comparison with the ground location of counting room /3/.

It should be stressed here that although the absolute background value in cpm characterizes a good low-level counting system , the more important parameter is the background stability. This stability measured as standard error of repeated background measurement together with the precision resulting from sample preparation, memory in the system, contamination possibility etc, describes fully the usefulness of the system for low-level measurements.

Electronic circuitry used for low-level tritium gas counting is sometimes of own home design (low cost) or consists in some cases of commercial units like Low-level Johnstone Inc Electronic Console (not produced any more). Recently, very often NIM-modules are used to complete the required system. As a rule two or three channel counting is applied. Main tritium channel is accompanied by low amplitude noise rejection channel and higher energy channel for radon monitoring.

The possibility of background reduction in low-level proportional counters by pulse shape discrimination (PSD) was recognised a few years ago and was tested in a few laboratories. Experiments in IAEA laboratories carried out recently indicate that the background count-rate can be reduced by 30 to 40% with negligible loss in efficiency /4/. It seems that even a very good PSD system would not be able to replace the inactive heavy meson shield and anticoincidence guard counter. Use of a PSD system could, however, limit to a certain extent need for a perfectly designed and constructed heavy shield. The last word in this matter has not yet been said and due to a rapid progress in electronics, improvement in this matter can also be expected.

3. Developments in liquid scintillation counting

Liquid Scintillation Spectrometers are produced commercially by a number of companies. Parameters of these counters (efficiency, background, stability) have been noticeably improved during recent years. Modern instruments from all firms represent about the same standard and parameters. As instruments are designed and produced for a wide range of users, for radiotracer work, no extra attention is paid to optimizing the background count rate. Low-level counting laboratories usually remove the external standard radioactive source assembly and apply an additional lead shield above the measuring chamber. These steps reduce the background of instruments by ca 2 cpm.

In the IAEA Laboratory the new 3255 Model Tricarb Spectrometer has efficiency for tritium of 30% (8 ml water + 12 ml Instagel) corresponding to 57 TU/cpm and background of 3,6 cpm with its stability of 0,3 cpm. These figures can be assumed as representing the modern liquid scintillation spectrometers. For a scintillation cocktail, Packard Instagel is mostly used although other firms produce similar water emulsifier under different names. They can incorporate up to 50% of water by volume. Usual and optimal composition is 8 ml of water sample + 12 ml of Instagel. Standard 20 ml polyethylene vials proved to be most economic and of lowest background.

Liquid scintillation technique combined with simple enrichment provides the detection limit of 1 T.U. which is sufficient to most of hydrological application.

Attempts are being made to increase the sample volume in order to lower the detection limit and to use the method for direct counting without enrichment. One instrument of this type is available commercially (ALOKA, Japan). Its sample volume is 100 ml (40 ml of water + 60 ml of Instagel). The sample changer accommodates 15 samples. Anticoincidence plastic scintillator shield is used together with heavy shield for meson flux reduction. The background is 5 cpm and efficiency corresponding to 25 $TU/_{cpm}$ /5/. Sensitivity is still too low to eliminate enrichment procedure. On the other hand, when using enrichment it is more economical to go with the final sample volume lower than 40 ml and to use the much cheaper standard liquid scintillation spectrometer.

Some laboratories have their own design or modification of commercial liquid scintillation counters for accommodation of larger sample volume.

4. Tritium enrichment methods

Electrolysis enrichment

Two kinds of electrolytical cells are routinely used in tritium laboratories at present: glass Ostlund type cells /6/ and metal IAEA-type cells. (Fig. 2 and 3)

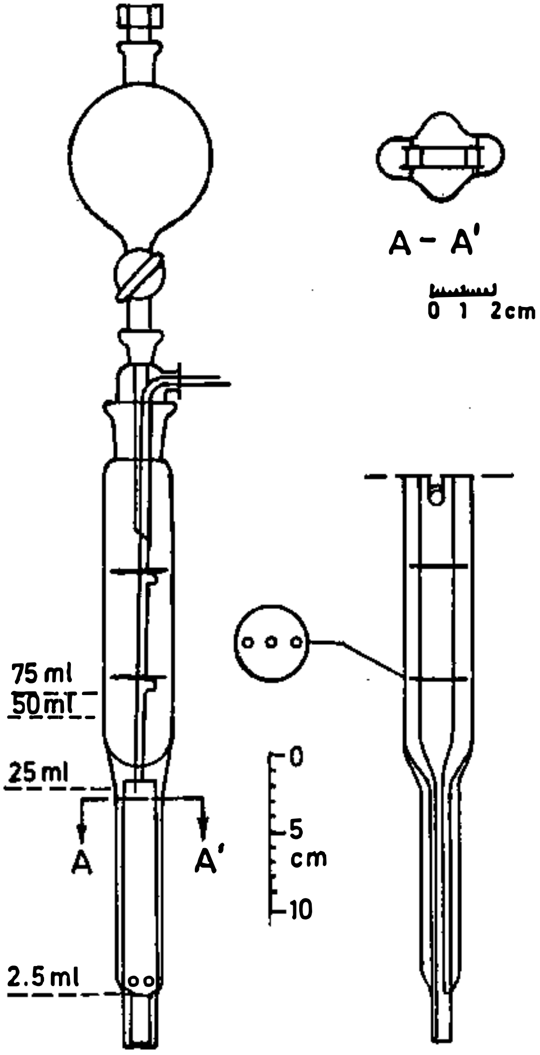

Fig. 2 Modified cell for periodic addition electrolysis

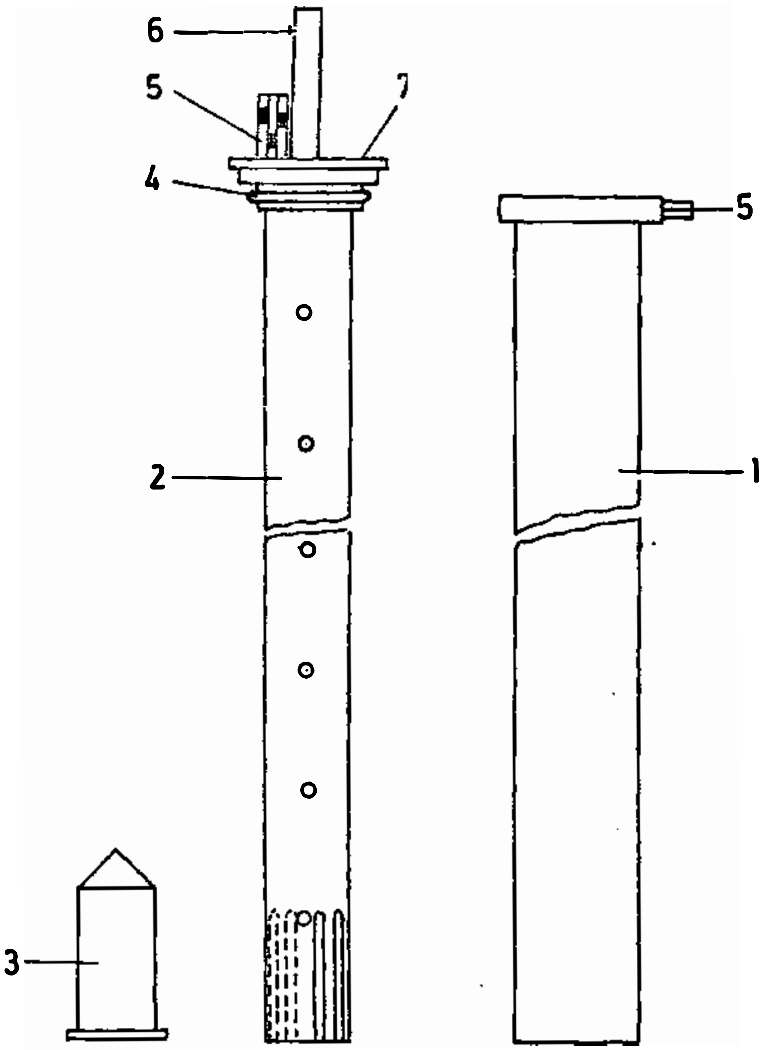

Fig. 3. Sketch of the electrolytical cell:
1-Stainless steel anode, 2-Iron cathode (phosphated), 3-Teflon cork, 4-O-Ring, 5-Electr. contacts, 6-Gas outlet, 7-Plastic shield

Glass cells are of 100 ml volume but usually are equipped with the additional sample container of 400 ml volume allowing for periodic additions. As the current intensity used is 6A, 50 ml of new water sample must be added to the cell each day. In the last stage (last 25 ml) cells are changed from a serial to parallel connection and are stopped automatically when the final volume reaches about 3 ml. The separation factor β is 25 ± 3 and enrichment factor can be up to 200 depending on the initial volume. Typical value for 100 fold mass reduction, of enrichment factor is about 80 with sigma ranging between 2 and 3% /1/. The disadvantage of the glass cells is the need of great care necessary during the whole procedure, the need of the stock of glass breakable parts of cells and the low final volume (below 3 ml). The big advantage is that high enrichment factor can be easily obtained by increassing the initial volume and expanding the electrolysis time.

The IAEA type metal cells are working in many laboratories. The standard cell has initial volume of 250 ml and the final volume of about 10 to 12 ml. Enrichment factor is between 15 and 18 depending on the final volume. If correction is taken forthe mass reduction in each cell by applying "enrichment parameter" /7/, the standard error of the single cell can be reduced to the value between 1 and 2% /8/.

Recently constructed and checked in IAEA "long" cells have the same design except the length. The "long" cell can accommodate 500 ml of water sample. The enrichment parameter up to 35 is obtained with the standard error of 3%.

In some laboratories a new design of metal cells are being proposed allowing for higher enrichment factor /9/, however experimental data about their use are not yet available.

Thermal diffusion enrichment

This method is used in two laboratories as an additional enrichment stage after simple electrolytic enrichment. Water sample has to be converted into hydrogen gas which passes through the diffusion column. The method is quite complex but works reliably and results in enrichment factor of about 16 for one mole of gas /10/.

Enrichment by gas chromatography

The gas-chromatographic method of tritium enrichment is not yet used routinely, however, its potential has already been shown /11/. Experimental work is now continuing and is directed towards the easy routine use of this method /12/.

5. Problems of contamination during sample procedure and storage

Laboratories which use the most sensitive analytical methods for low-level tritium assay, (below 1 T.U.) have experienced cases of sample contamination. The most popular source of tritium contamination in the laboratory are watches with luminous pointers containing appreciable amounts of tritium. Some of the watches of this kind continuously release sufficient flux of tritium to contaminate the laboratory's ambient air and processed samples.

The usual procedure applied in laboratories for monitoring the possible contamination of samples is periodical measurement of tritium content in laboratory air moisture and periodic analysis of "blanks", i.e. tritium free water samples. Systematic observation of both tritium in air and analytical blanks assure the real detection limit of the procedure.

Uptake of tritium from ambient air during the storage of water samples in polyethylene bottles was observed, therefore for longer storage time glass bottles are preferred.

6. Tritium measurements by ^{3}He method

Tritium nucleus decaying creates ^{3}He nucleus, therefore the number of ^{3}He atoms in an isolated system (sealed sample) grows exponentially. The mass of ^{3}He in the sealed sample accumulates according to the formula:

$$M(^3He) = \alpha \cdot m \cdot c\,(1 - e^{-\lambda t})\ cm^3\ STP$$

where m = sample mass (water sample)

c = tritium concentration /TU/

t = integration time

$\alpha = 2{,}48 \times 10^{-15} \cdot \frac{cm^3\ STP}{g\ \ TU}$

λ = tritium decay constant

Helium-3 is extracted from the water sample and is measured by a mass spectrometer especially designed for high accuracy measurements of gases with very low atomic number.

Amount of helium is proportional to the tritium concentration, however, both, mass of the water sample and time of helium growth can be varied in a large range to obtain a required precision and detection limit. Usually a 40 gram water sample is kept for about 6 months and detection limit is then 0,1 T.U. /13/. Experiments with larger sample size (up to 500 g) and longer integration time (up to 1 year) are underway in Woods Hole Oceanographic Institution (USA) /14/. The expected detection limit for tritium should yield then 0,01 T.U. (See Fig. 4).

He-3 method seems to be easy and more precise for low-level tritium assay, however, the main drawbacks being: high investment cost of a mass-spectrometer (about $ 250,000.-) and long waiting time for tritium results. The method is especially attractive for oceanographic studies where the tritium concentration is low and high accuracy of measurements is required. For isotope hydrological investigation this method offers the possibility of determination of determination of $^3He/4_{He}$ and ^{3}He/T and those ratios are of interest

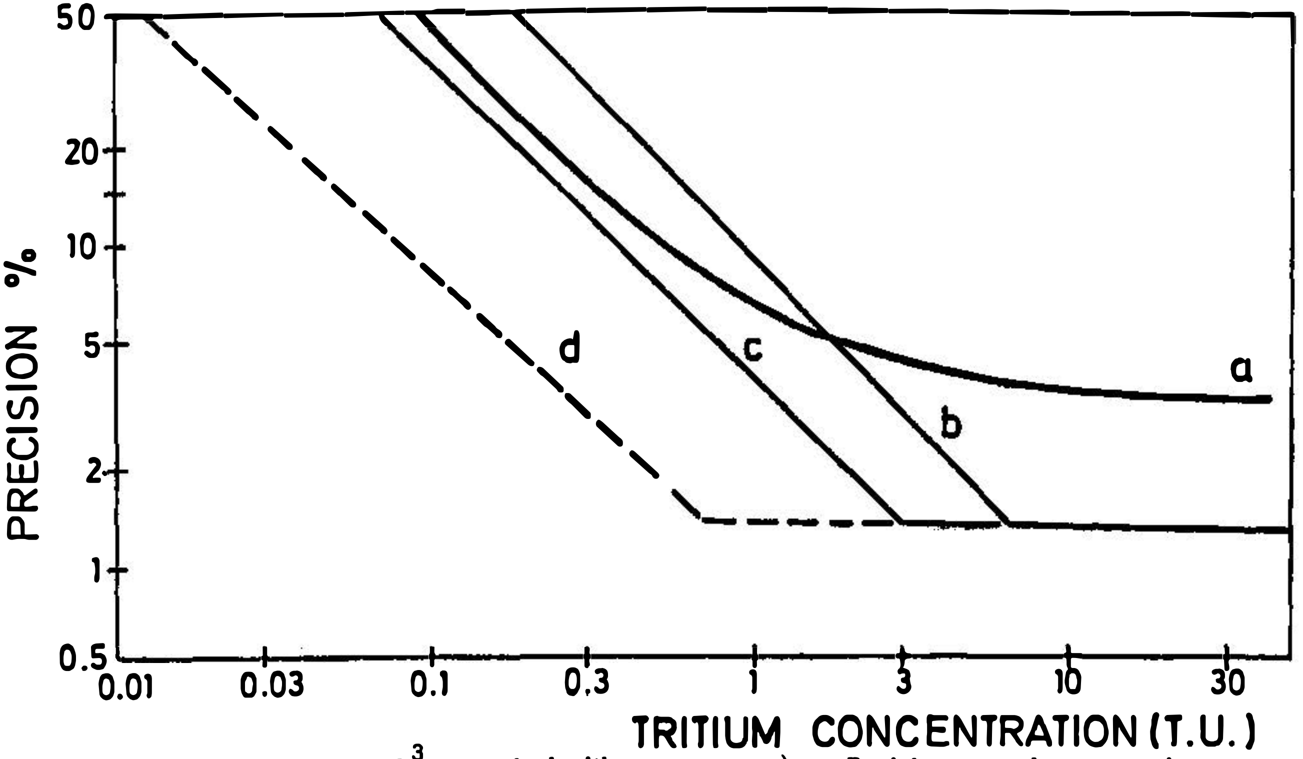

Fig. 4 Comparison of ^{3}He method with gas counting. The graph indicates the precision of measurement for a given tritium concentration using following methods:

a) Enrichment and gas counting;
b) ^{3}He method, sample 45 grams, integration time one year;
c) ^{3}He method, sample 90 grams, integration time one year;
d) ^{3}He method, sample 500 grams, integration time one year (expected).

for age and turn-over time estimation. Table 3 summarizes the advantages of tritium measurements by ^{3}He mass spectrometry /14/.

7. Tritium standards, tritium half-life and interlaboratory comparison

Tritium Standards used in laboratories originate from U.S. National Bureau of Standards. As broadly used tritiated water standard SRM 4926 stock is finished, NBS has prepared a new Standard 4926C in which tritium concentration differs only negligible from the old standard as for 3 September 1978. Recalibration of tritium standards concluded that the half - life of tritium is longer than that commonly adopted (12,262 years) /15/. A new value of 12,350 years has recently been recommended by the IAEA Consultant's Panel. It cannot be excluded that in the near future after repeated accurate measurement a new value of 12,44 years will be adopted, however, the now recommended value of 12,350 years seems to be a good tentative compromise.

The IAEA Consultant's Panel also recommended that the term tritium ratio (TR) should be used rather than tritium unit (T.U.) as the term "unit" should not be applied to the number ratio.

International comparisons of low-level tritium measurements play an important role in the improvement of the quality and accuracy of analysis in laboratories all over the world. Three intercomparisons have been organised by the IAEA, in 1963, 1969 and 1976 /16 - 18/. The number of laboratories taking part in the intercomparisons has increased from 12 in 1963 to 41 in 1976. It was recommended by the recent IAEA Panel that intercomparisons should also be organised in future in every five to six years.

TABLE 3

Advantages of ^{3}He methods against beta counting /from 14/

1. Simpler chemistry
2. Can be applied to any fluid directly
3. Detection limit is essentially open ended
4. Contamination possibility lower
5. Output is high:

   1 mass spectrometer - 1 man-shift operation results in about 2,500 samples/year.
6. High accuracy
7. Primary standard is air, accuracy depends on knowledge of tritium half-life.

Drawbacks

1. High investment cost (mass-spectrometer + sample containers + preparation lines about 300 K$)
2. Waiting time for tritium results (few months till one year).

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