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Abstract

The low-temperature oxidizing plasma technique is a method successfully applied in various chemical and physical analytical fields, and appropriate equipment is available in many laboratories. With a suitable system for trapping the water formed in the oxidation process it can be used to determine tritium bound organically in low-level samples. First, the samples are freeze-dried and the tissue water obtained in this way is measured, after distillation, in a liquid scintillation spectrometer. The residual dry matter is ashed in the reactor chamber of the plasma system. Oxidation takes place at temperatures not exceeding 200 °C in an oxygen flow of about 40 ml/min. The water of oxidation is collected in a cold trap installed behind the reactor chamber. A volume of about 10 ml of water is sufficient to measure the tritium activity without enrichment.

The oxidation behavior of various organic materials has been tested. Some first results of ³H concentrations in tissue water and the organic dry matter from food and plant samples collected in the vicinity of the Nuclear Research Center will be presented. Compared with procedures reported earlier for total ashing of large samples, the method described has the advantage that a commercially available instrument can be used requiring only little additional equipment. Handling is much less dangerous and, furthermore, contamination effects by atmospheric tritium can easily be kept at a minimum.

Die Bestimmung von organisch gebundenem Tritium in Umgebungsproben unter Anwendung der Plasma-Oxidation

Zusammenfassung

Die Tieftemperatur-Plasma-Oxidation ist eine Methode, die bereits erfolgreich auf vielen Gebieten der chemischen und physikalischen Analytik angewendet wird, und entsprechende Einrichtungen sind in vielen Laboratorien vorhanden. Mit einem geeigneten System zur Rückgewinnung des Wassers, das beim Oxidationsprozeß entsteht, ist die Bestimmung von organisch gebundenem Tritium in Low-level-Proben möglich. Die Proben werden zuerst gefriergetrocknet, und das auf diese Weise gewonnene Gewebewasser wird nach Destillation in einem Flüssigszintillationsspektrometer ausgemessen. Die zurückbleibende Trockensubstanz wird in der Reaktorkammer des Plasmaprozessors verascht. Die Oxidation findet bei Temperaturen unterhalb 200 °C bei einem Sauerstoffdurchfluß von etwa 40 ml/min statt. Das Oxidationswasser wird in einer Kühlfalle hinter der Reaktorkammer aufgefangen. 10 ml Wasser sind für die Aktivitätsmessung ohne Anreicherung ausreichend. Das Oxidationsverhalten verschiedener organischer Materialien wurde getestet. Einige erste Resultate der Tritiumkonzentration in Gewebewasser und organischer Trockensubstanz aus Nahrungsmitteln und Pflanzenproben aus der Umgebung des Kernforschungszentrums Karlsruhe werden berichtet. Verglichen mit früher berichteten Verfahren für die vollständige Veraschung von großen Proben hat die beschriebene Methode den Vorteil, daß ein kommerziell erhältliches Instrument mit wenig zusätzlicher Ausrüstung benutzt werden kann. Die Handhabung ist weniger gefährlich und außerdem können Kontaminationseffekte durch atmosphärisches Tritium auf ein Minimum beschränkt werden.

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1. Introduction

Increasing releases of tritium into the environment will enhance the future radioecological significance of this radionuclide by the end of this century. Uses of large amounts of tritiated compounds in the luminous paint industry as well as handling of high tritium activities in nuclear reprocessing plants and in new types of reactors (e. g. fusion reactors) will be connected with unavoidable losses, and significant contaminations of the environment, both worldwide and local, must be taken into account.

At the Karlsruhe Nuclear Research Center, some 2 kCi of tritium are released into the atmosphere per year. This enables us to study the radioecological behavior of tritium under realistic field conditions.

Last year we extended our tritium monitoring program to include the determination of organically bound tritium (OBT). This compartment in biological systems merits increasing attention because of its important rôle in the local ecological cycling of tritium. Furthermore, this fraction of environmental tritium cannot be neglected in the radiation protection of man in cases of major contamination. A rough estimate of the quantities of hydrogen in man is that some 33 % of the total hydrogen is fixed in organic matter, which is a considerable pool for the distribution of tritium.

Another aspect is that autotrophic green plants synthesize their organic matter by using the hydrogen of the H₂O present in the green parts of the plant. In this way,

they can preserve an earlier tritium exposure. If all mechanisms of distribution and retention of tritium in the organic pool leading to a specific OBT concentration in plants were known sufficiently well, OBT measurements in connection with mathematical modeling could serve as a "biological dosimeter" in the future.

2. Materials and Methods

2.1 Freeze-drying and Tritium Measurement

Depending on the water content of the sample, 150 to 600 g of the fresh material were frozen in steel sample boats at $-40\text{ }^{\circ}\text{C}$. The dishes are enclosed in plastic bags to prevent contamination of the samples by tritium in the humidity of the air, which could seriously disturb our low-level measurements.

For drying we use a special system (Dr. Morand AG, Lausanne, Switzerland), which allows the tissue water to be recovered completely. This water is trapped by a condenser ($-80\text{ }^{\circ}\text{C}$) on top of the vacuum chamber and can easily be removed by changing the cooling mixture against hot water. The iceblock will burst in this case and the pieces can be collected on a thin sheet of aluminium, always well protected from humidity of the air.

To measure the tritium activity without electrolytic enrichment a method described by König et al. [1] is applied. For that procedure, 10 ml of sample water are sufficient. The detection limit in this case is about 0.15 pCi/ml and 5.6 mBq/ml, respectively (measuring time: 100 min).

2.2 Plasma Oxidation

To determine tritium bound organically, a commercial Plasma Processor (500 E, Technics, Munich, Fed. Rep. of Germany) is used. The low-temperature oxidizing plasma technique is a method applied successfully in various chemical and physical analytical fields [2]. We use these processors for tritium analysis with an appropriate system for trapping the water formed in the oxidation process. The components of the system are shown in Fig. 1.

For oxidation, the residual dry matter from freeze-drying is pulverized and evenly spread on two flat-bottom boat containers. Sample sizes range between 20 and 40 g. Next, all humidity of the air and traces of tissue water remaining in the sample are removed by establishing a vacuum of 10^{-2} mbar (1.0 Pa). Subsequently, an oxygen flow of about 40 ml/min is established, producing an operating pressure of 1 mbar in the chamber. Finally, the plasma is initiated and maintained at a high frequency (rf) of 27.12 Mhz and some 600 W power. Oxidation then takes place at temperatures not exceeding 200 °C. Oxidation of samples such as leaves leads to operating temperatures ranging between 80 and 120 °C.

The water formed by oxidation of the organic matter of the samples is collected in a trap cooled by an ethanol/dry-ice mixture and by an electric cooling system, respectively, especially when operating over night. The trap is placed into a bypass of the connection between the reaction chamber and the vacuum pump. For interrupting the process, the trap can be sealed hermetically by two bellows-sealed valves. After finishing the oxidation, 10 ml of the trapped water is used for low-level measurement of tritium in the liquid scintillation counter.

Plasma-ashing of one sample takes about 10 hours. However, the oxidation behavior obviously depends on the composition and the surface structure of the samples. High contents of non-oxidizing mineral substances will develop a layer of ash on top of the samples which prevents further oxidation. This layer acts as a catalyst supporting the recombination of atomic oxygen, and the oxidation rates may decrease logarithmically. Therefore, it is necessary to interrupt the process for stirring the samples in order to keep the time for oxidation as short as possible.

Another advantage arises from changing the arrangement of the sample boats in the reaction chamber, because of the heterogeneity of the plasma. Fig. 2 shows the oxidation process of starch powder plotted as a function of the position of the sample boat in the chamber. However, in the case of starch, degradation takes place mostly as a linear function of time, due to the absence of inorganic particles. Fig. 3 shows the oxidation of the protein gelatine in two large sample boats made of aluminium.

Compared with procedures reported earlier for complete ashing of large samples [8, 9], the method described above has the advantage of allowing a commercially available instrument to be used and only requiring little additional equipment. Handling is much less dangerous, because oxidation is well under control and last, but not least, contamination effects by atmospheric tritium can easily be kept at a minimum.

3. Results

3.1 Biological Samples

Our first intention was to obtain a general view of the inventory of OBT in different biological samples collected in the vicinity of the Research Center. In late 1980, leaves from beeches and hornbeams, apples and Brussels sprouts from various locations were analyzed. The results are shown in Table 1.

Tritium activities of HTO were found to range between 0.33 ± 0.17 pCi/ml and 9.00 ± 0.21 pCi/ml, reflecting the wide range of tritium activities in drinking water (median in 1980: 0.36 pCi/ml), precipitation (average in 1980 at KfK: 1.38 pCi/ml, outside KfK: 0.21 pCi/ml) [3] and the tritium concentration varying strongly in the humidity of the air.

Concentrations of OBT range between 0.49 ± 0.18 pCi/ml and 14.9 ± 0.9 pCi/ml of water of oxidation. With only one exception, these concentrations are higher than the corresponding activity of HTO. The medians of all calculated ratios R ($R = [\text{OBT}]/[\text{HTO}]$) are given in Table 2. Each median of R is greater than unity. This result confirms earlier observations in environmental samples [4, 5, 6]. We interpret these findings as implying a retention of tritium in the organic pool in plants under dynamic conditions regarding tritium concentrations in the ambient water phase, particularly since tritium is discriminated in the photosynthetic formation of organic matter in plants by an isotopic effect of about 0.8 (20 % discrimination against protium) [7] and no evidence exists that tritium may accumulate against a concentration gradient. However, a comprehensive model explaining those R-values is still missing.

In the case of Brussels sprouts, the R-values show significant differences in parts of the plant. This may reflect differences in the time of development of those parts. However, for an explanation to be found, these findings first need to be confirmed by further investigations.

3.2 Tritium in Pine Needles

A limited research program on tritium in pine needles was started in the winter of 1980/1981. Needles were collected of several young pine trees (pinus sylvestris) growing in the Research Center. We distinguished needles

developed last year from those developed the year before and those developed two years ago. In this way, tritium concentrations in needles from different locations in the Center grown in 1978, 1979 and 1980 could be studied. To get an idea of ambient tritium concentrations in the atmosphere, humidity of the air was collected at the time of sampling. This was done by a freezing technique using a metal sheet cooled by dry ice.

The results are shown in Fig. 4. Obviously, the highest activities can be found in the immediate surroundings of the MZFR (heavy water moderated reactor, 200 MW thermal power), the main emitter of atmospheric tritium at the Center.

At the time of sampling the tritium concentration in the humidity of the air close to the exhaust stack was clearly enhanced, resulting in a higher specific ^3H concentration in airborne humidity than in the free tissue water of the needles. In all other cases, the contrary was observed, indicating that tritium concentrations in needles are influenced by different sources and equilibration with the humidity in the air is only one cause among others, e. g., precipitation and humidity of the soil.

The ratio between OBT and HTO in almost all samples is greater than unity. In two cases it equals unity and in only one sample a ratio of 0.54 ± 0.23 was found. However, we cannot exclude that this is due to an artifact. Regarding the different types of needles as a function of age, there seems to be a tendency

of the tritium content rising as a function of age. This may be due to a higher tritium exposure of those trees in earlier years. However, further investigations are necessary to clarify whether possible retention mechanisms in metabolic processes are responsible for these findings.

4. Discussion

The data presented in this paper demonstrate that reproducible results of low-level tritium activity measurements can be obtained by the method applied although, at a nuclear research center, contamination effects by atmospheric tritium at the time of sample preparation constitute a serious problem. We are still engaged in optimizing the plasma ashing process, but it is already a valuable instrument to study the behavior of organically bound tritium in environmental samples.

The results of our monitoring programs concerning OBT give a first insight into the situation in the vicinity of the KfK. One critical point in interpreting these data is that all these measurements only show an instantaneous picture, not the development of this compartment under the dynamic conditions existing in natural ecosystems.

Further investigations of OBT of a more systematic and long-term character are already under preparation.

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Table 1: ³H Concentrations in Environmental Samples
in [pCi/ml]

Date	Location	Sample	HTO	OBT	R
10.11.	KfK-N7	Beech Leaves	1.34±0.21	4.10±0.34	3.1 ±0.6
10.11.	KfK-S6		1.34±0.21	3.46±0.36	2.6 ±0.5
10.11.	B-26		9.00±0.21	14.90±0.90	1.66±0.10
15.10.	KfK-M3	Horn- beam L.	4.49±0.34	3.54±0.29	0.79±0.09
29.10.	KfK-M3		2.53±0.26	3.22±0.28	1.21±0.17
10.11.	KfK-M3		1.62±0.22	4.23±0.38	2.61±0.43
11.11.	I*		0.38±0.17	0.76±0.21	2.0 ±1.1
21.11.	L*	Apples	0.37±0.17	0.78±0.27	2.1 ±1.2
12.12.	A*		0.37±0.16	0.53±0.18	1.4 ±0.8
09.12.	F*	B.S.**- Heads	0.47±0.18	1.11±0.19	2.4 ±1.0
11.12.	E*		0.66±0.18	2.10±0.27	3.2 ±1.0
12.12.	Th*		0.23±0.16	0.48±0.17	2.1 ±1.6
09.12.	F	B.S.**- Leaves	0.49±0.18	1.12±0.26	2.3 ±1.0
11.12.	E		0.56±0.18	1.38±0.32	2.5 ±1.0
12.12.	Th		0.34±0.17	0.49±0.18	1.4 ±0.9
09.12.	F	B.S.**- Stems	0.54±0.19	0.63±0.43	1.2 ±0.9
11.12.	E		0.53±0.17	0.83±0.18	2.5 ±1.4
12.12.	Th		0.31±0.17	0.41±0.17	1.5 ±1.0
09.12.	F	B.S.**- Roots	0.41±0.18	0.53±0.20	1.3 ±0.8
11.12.	E		0.40±0.18	0.59±0.21	1.5 ±0.9
12.12.	Th		0.28±0.17	<D.L.***	-

*I = Ittersbach, L = Leopoldshafen, A = Augustenberg,
F = Friedrichstal, E = Eggenstein, Th = Thomashof

**B.S. = Brussels Sprouts

***D.L. = Detection Limit: 0.15 pCi/ml

Table 2: Median of R (1981)

Type of sample	Median of R = $\frac{\text{OBT}}{\text{HTO}}$
Brussels Sprouts	
Heads	2.4
Leaves	2.3
Stems	1.5
Roots	1.4
Apples	1.8
Pine Needles	1.7
Beech Leaves	2.6
Hornbeam Leaves	1.6

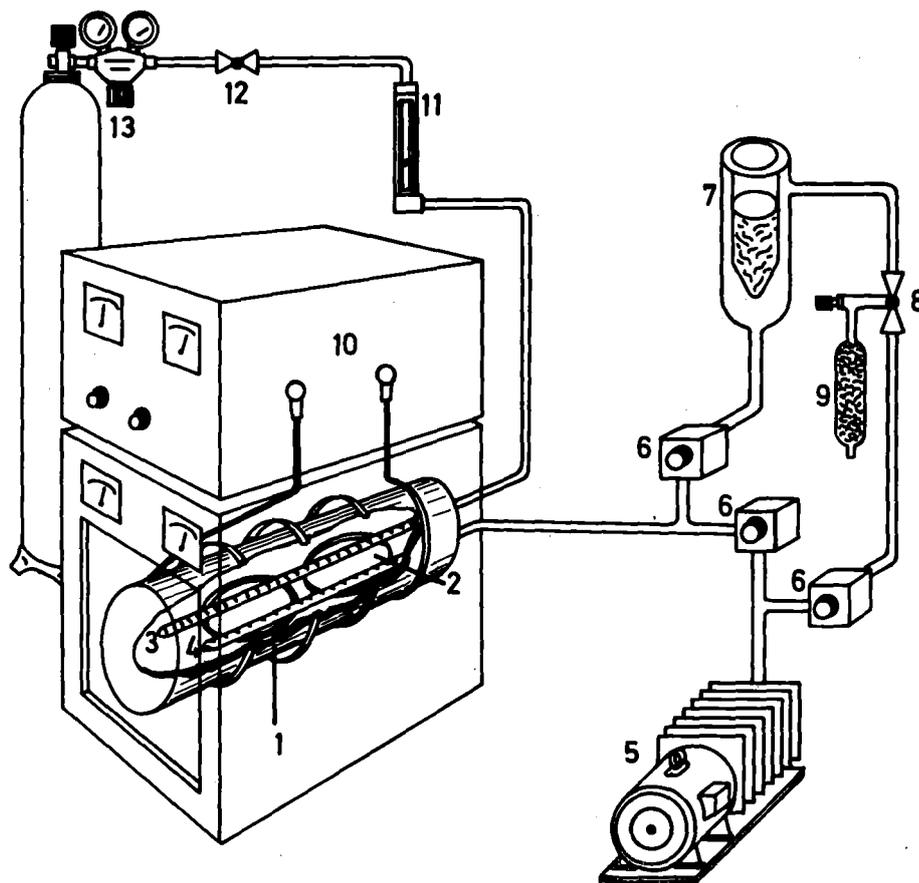


Fig. 1: System for Plasma ashing organic samples

- | | |
|----------------------------|---------------------|
| 1 - Reactor Chamber | 8 - Gas Inlet Valve |
| 2 - Sample Boat | 9 - Molecular Sieve |
| 3 - Gas Inlet Pipe | 10 - RF-Generator |
| 4 - Gas Outlet Pipe | 11 - Flowmeter |
| 5 - Mechanical Vacuum Pump | 12 - Needle Valve |
| 6 - Bellows Sealed Valves | 13 - Oxygen Supply |
| 7 - Cold Trap | |

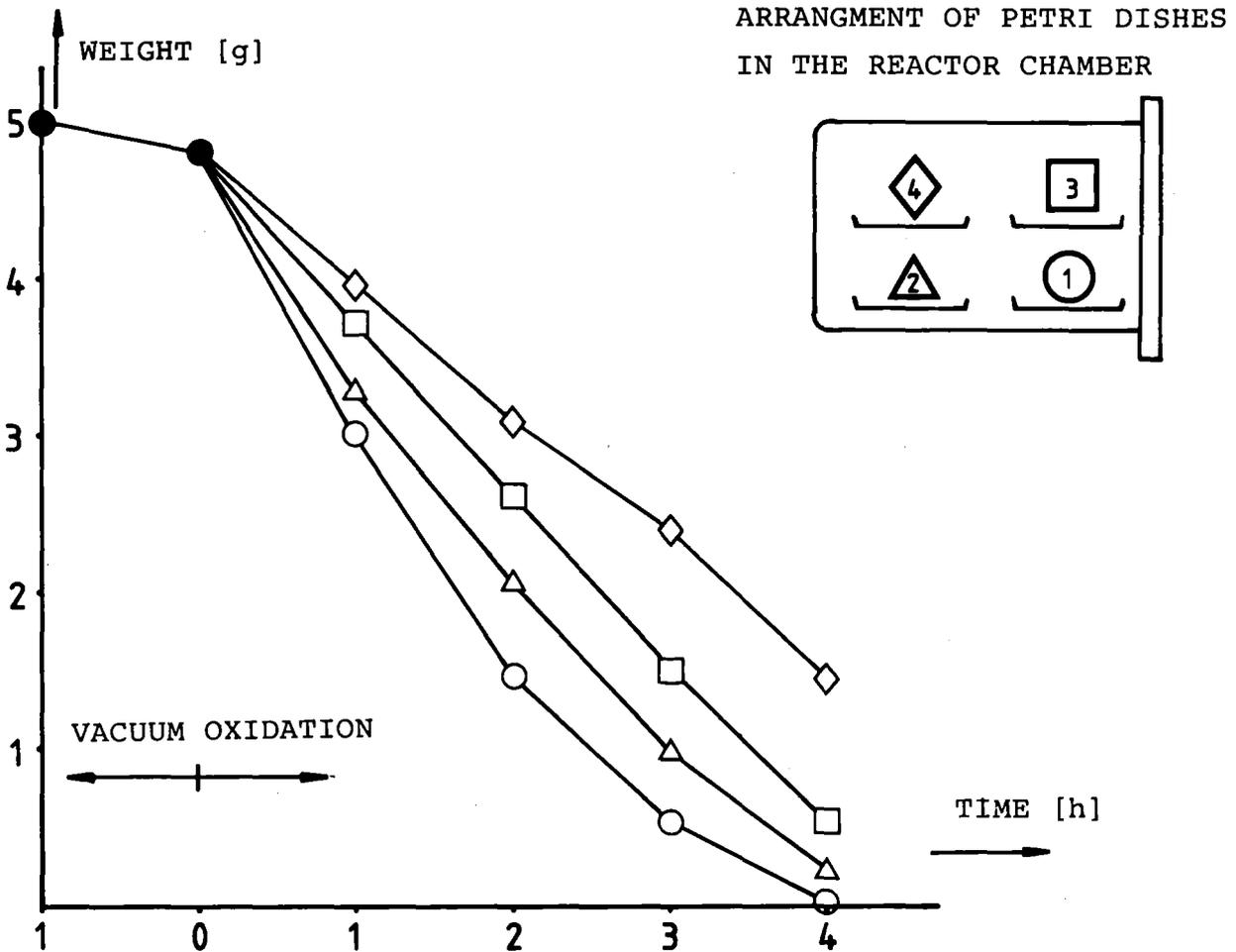


Fig. 2: Development of Plasma Oxidation of Starch Powder as a Function of the Location of Petri Dishes in the Reactor Chamber

(○ - Pos. 1; ▲ - Pos. 2; □ - Pos. 3; ◇ - Pos. 4)

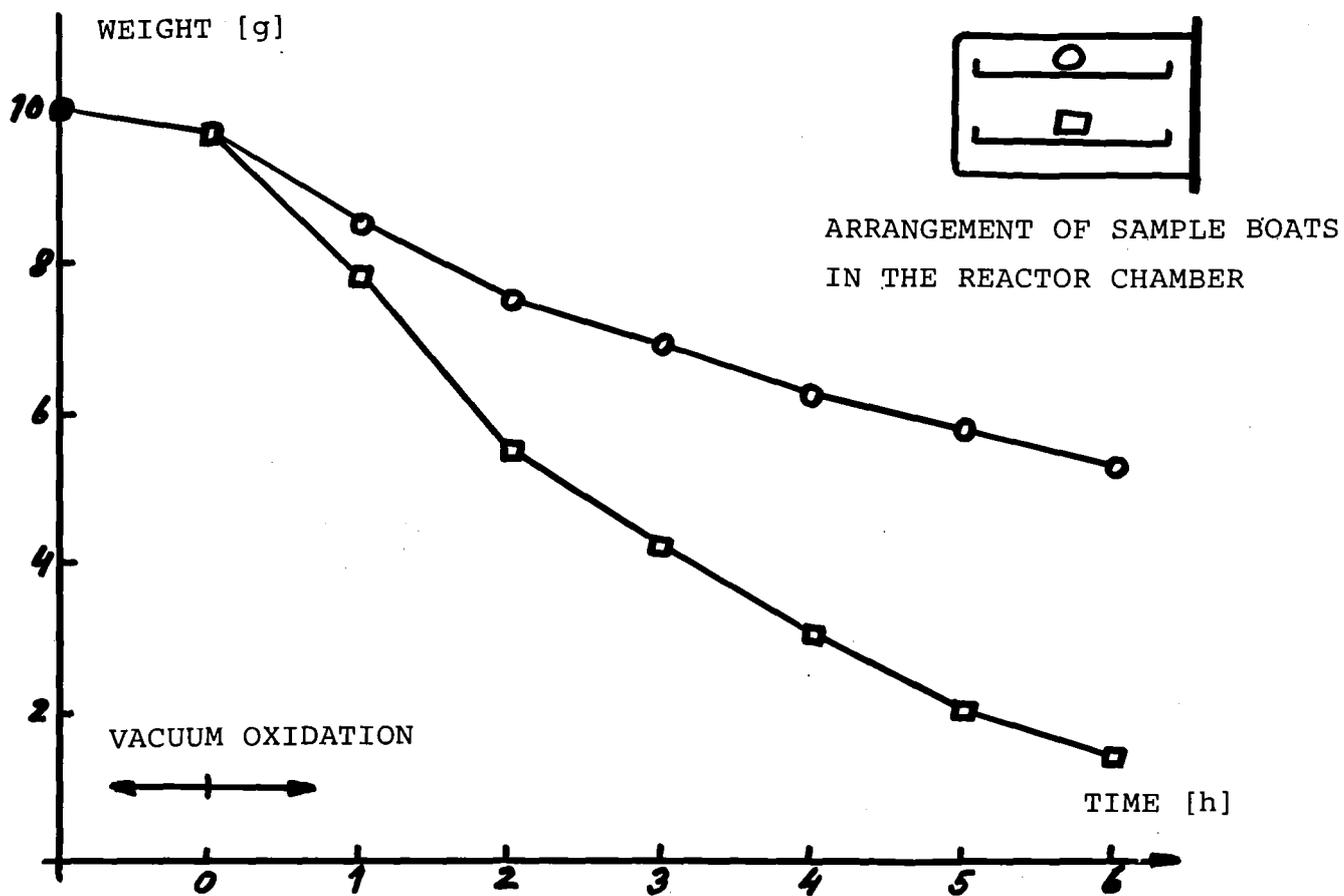


Fig. 3: Plasma Oxidation of Gelatine

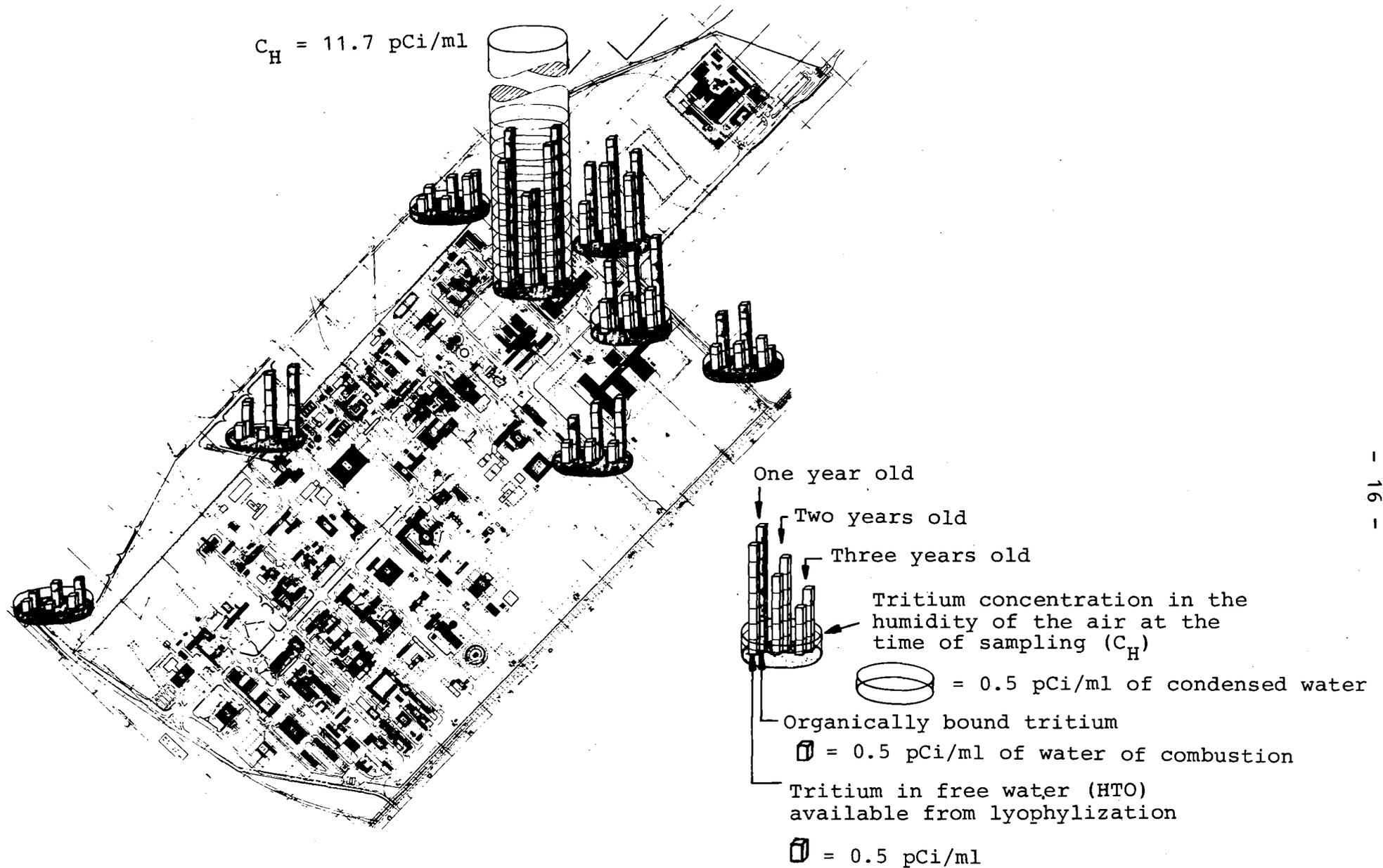


Fig. 4: Tritium Concentrations in Pine Needles from Different Locations in the Karlsruhe Nuclear Research Center