

論 文

高感度熱量計によるトリチウム量の絶対測定 (I) — 熱量測定システムの設計・製作及び性能試験 —

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Absolute Measurement of Tritium by High-Sensitivity Calorimeter (I)
- Construction of Calorimetric System and its Performance Tests -

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Abstract

A calorimetric system for evaluation of the absolute amount of tritium was designed and constructed, and its basic performance was tested. A calorimeter can be used to measure total energy of radiations as a calorific value. The present calorimetric system consists of a twin-type thermal conductivity calorimeter equipped with a vacuum shielding, a tritium container, total pressure gauges, a quadrupole mass spectrometer, and high-vacuum systems. A calibration curve of the calorimeter was prepared at first using two samples enclosed a given amount of Zr-Ni alloy powder only, and the following linear relation was obtained: $E_{\text{out}} = (0.2694 \pm 0.0010) Q_{\text{in}}$, where E_{out} is the output (μV) from the heat sensors and Q_{in} is the input power (μW) by Joule heating to the sample cell. In addition, the lower detection limit was estimated to be $0.15 \mu\text{W}$ from stability of the calorimeter, which corresponds to the tritium amount of 0.16 GBq . As an initial test, Zr-Ni alloy powder loaded with a given amount of tritium was used and the amount of tritium was estimated to be 26.3 GBq , which was slightly less than the tritium activity determined previously by using a small ionization chamber.

1. Introduction

Various kinds of techniques and devices are required for highly precise evaluation and control of the tritium amount in the fuel cycle of a thermonuclear fusion device from viewpoints of safe handling and economy of the large amount of tritium. Those are divided into two groups: one is the relative measuring techniques and the other is the absolute measuring ones. Among the former techniques, ionization chamber, proportional counter, β -ray-induced X-ray counter, mass spectrometer, inorganic scintillation counter and so on play an important role for quantitative measurements of tritium concentration. On the other hand, a pressure-volume-temperature method and a calorimetric method are ascribed to the absolute measuring techniques, whereas the former method additionally needs an equipment to analyze a tritium partial pressure in the measuring gas. The latter calorimetry is a promising method to determine the absolute amount of tritium, while this technique has been mainly applied so far to measurements of a large amount of tritium because of emission of low energy β -rays. Increase in the sensitivity of a calorimeter will result in extension of its availability for the tritium measurements.

Although there are a variety of chemical forms and/or physical states of tritium species, the number of β -rays emitting from the tritium species is dependent on only the number of tritium atoms in a sample and basically independent of the chemical form and physical state of the tritium species. Namely, total energy emitting from a tritium sample is due to the total number of tritium atoms. This is a reason why a calorimetric method is the promising one for evaluation of the absolute amount of various kinds of tritium samples and has high potential as a standard system for the relative measuring devices. Some applications of a calorimeter have been conducted to determine the amount of radioactive materials: for example, measurements of tritium in getter materials^[1-2] and massive carbon tiles exposed to tritium plasmas of the D-T fusion experiments in JET^[3], measurements of tritium^[4] and tritiated

water^[5], measurements of ^{14}C ^[6], and so on. Kinetic energy of β -rays emitting from tritium atoms is as remarkably small as 5.7 keV (=912 aJ) in average energy. For this reason absolute measurement of tritium by a calorimeter needs ample carefulness. The total energy emitting from a given amount of tritium can be numerically calculated using the β -ray spectrum shown in Fig. 1^[7], and for example the amount of tritium of 37 GBq (=1.0 Ci) corresponds to energy emission of 33.8 μW .

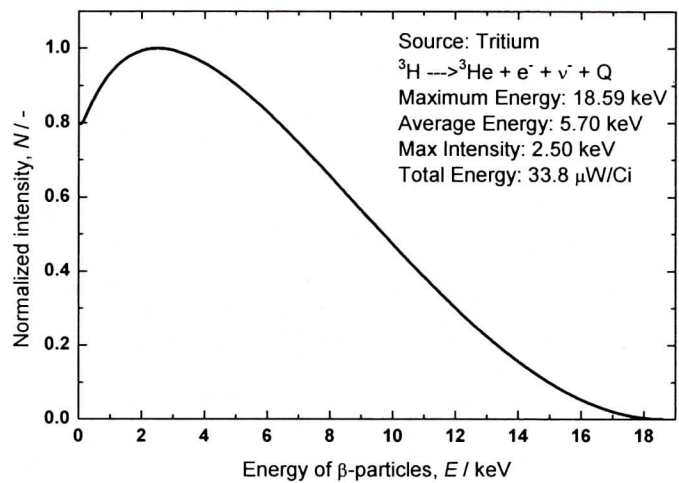


Fig. 1 The calculated spectrum of β -rays emitting from tritium.

If the activity level of tritium is above a few tens Ci, it is relatively easy to measure by using a conventional calorimeter. However, this level is far beyond a detection range of the other devices as mentioned above. To make a standard system of a variety of tritium measuring devices, it is necessary to develop a calorimetric system with high reliability and sensitivity, which is available to an activity level below 1 Ci.

From this viewpoint, a calorimetric system that equipped with a high-sensitivity calorimeter was constructed for measurements of gaseous, liquid and solid tritium. In this paper, schematic of the calorimetric system and basic performance tests used a Zr-Ni alloy sample in which a given amount of tritium was retained will be presented.

2. Construction of a calorimetric system

2.1. Schematic of the designed calorimetric system

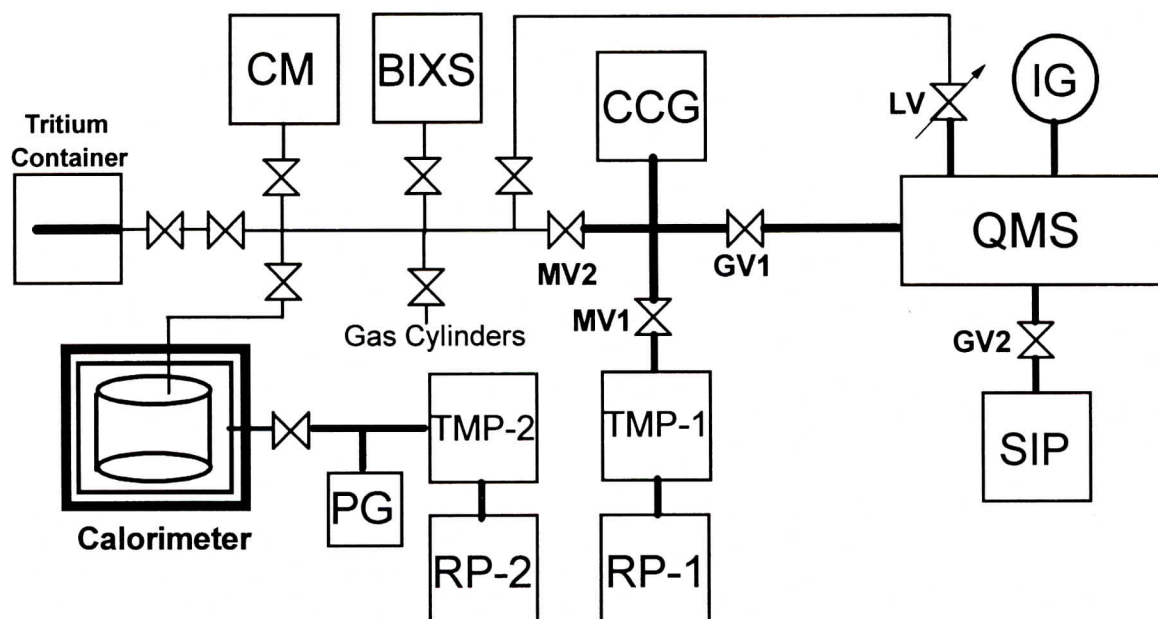


Fig. 2 Schematic drawing of a calorimetric system designed for the absolute measurement of tritium.

Figure 2 shows a schematic diagram of the calorimetric system designed for the absolute measurement of tritium. There are three different physical states of tritium: gaseous, liquid and solid state. Among them, solid state of tritium means the ad/absorption states of tritium on/in solid materials. The calorimetric part consists of vacuum pumps (TMP-2: turbo molecular pump, RP-2: oil-sealed rotary pump) and the high-sensitivity calorimeter (Model: INC-7200) that was purchased from Tokyo Riko Ltd. To measure gaseous tritium, devices for storage and analysis of tritium were also equipped. A total pressure and a partial pressure of tritium can be measured by a capacitance manometer (CM) and β -ray-induced X-ray spectrometer (BIXS), respectively. As a vacuum gauge, a cold cathode gauge (CCG) was employed in this system. Purity of tritium species can be analyzed by a quadrupole mass spectrometer (QMS) equipped with a sputter ion pump (SIP). Tritium gas diluted with hydrogen is stored in the tritium container, which was specially designed to confine safely tritium. An inner tube of the container consists of a stainless steel tube loaded with Zr-Ni alloy powder and a heater with thermocouples at the outer surface. The outer tube is connected with the vacuum pumps (TMP-1 and RP-1) to avoid the increase in a temperature of the outer tube

and to protect from contamination of the ambient air. Figure 3 shows the outlook of the calorimetric system used in this study.

A schematic drawing of a specially designed high sensitivity calorimeter for the present study is shown in Fig. 4. The present calorimeter is a twin type thermal conductivity calorimeter and special improvements were made to measure quite small calorific value. Namely, main parts such as a heat sensor, cell holder and heat

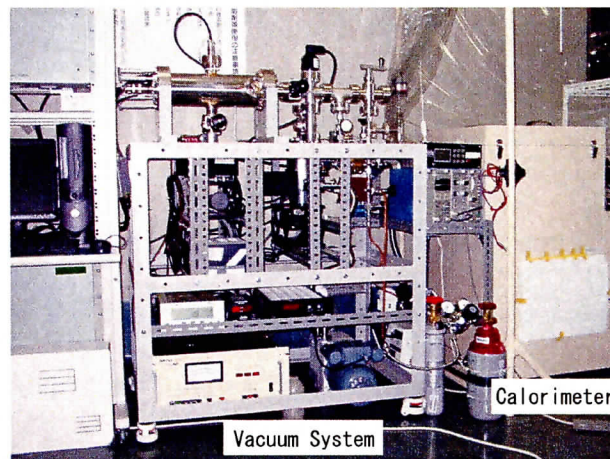


Fig. 3 Outlook of the calorimetric system used in this study.

sink were compactly packed into the vacuum chamber made of stainless steel, which is connected with vacuum pumps and a pressure gauge (PG). To reduce the effects of a temperature change in ambient atmosphere as

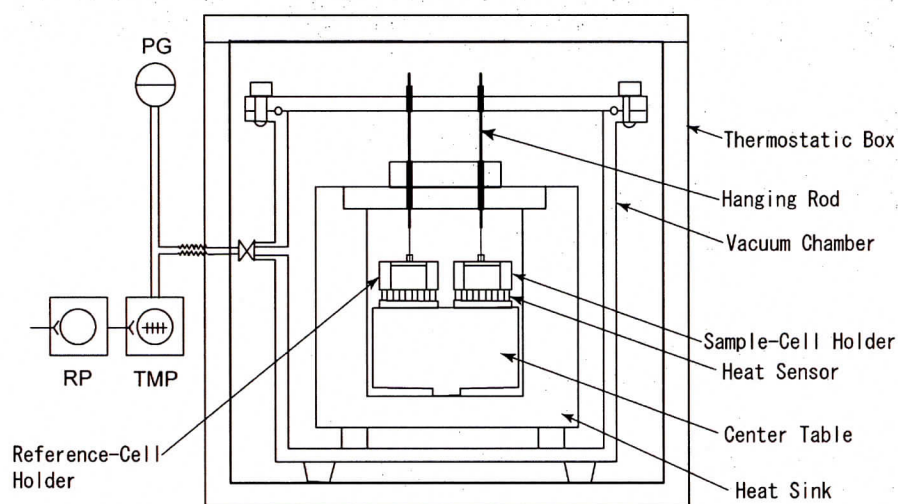
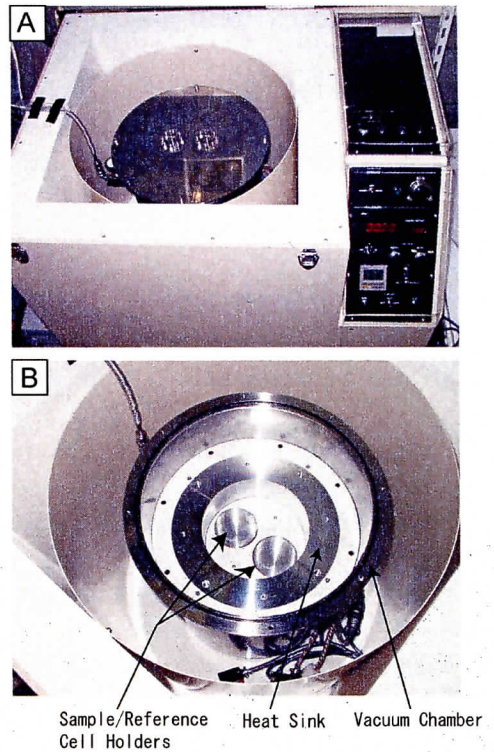


Fig. 4 Schematic drawing of a specially designed high sensitivity calorimeter.

possible, the vacuum chamber was kept in an air-thermostatic box, which was usually operated at a temperature of 300.0 K. Figure 5 is the photographs of the inside arrangement of the present calorimeter.

A thermo module consisting of thermo elements of 254 pairs connected in series was used as a heat sensor of the cell holder. Thermal sensitivity of two thermo modules attached beneath the sample and reference cell holders is about 52 mV/K. Calibration of the thermo

module with Joule heating was carried out using a heater material fixed on the outside of each cell holder. A fine Manganin wire was selected as the heater material, and its resistance was controlled as to be 100.0 Ω . Differential output due to the temperature difference between two thermo modules is amplified through a direct current amplifier, and the amplified output was finally recorded. Since resolution of the amplifier used is 0.1 μV , the present calorimeter is able to measure the temperature difference as quite small as 2×10^{-6} K.



2.2. Design of a cell to measure solid materials absorbed tritium

Fig. 5 Photographs of the high-sensitivity calorimeter: (A) vacuum chamber kept in the air thermostatic box, (B) cell holders and heat sink kept in the vacuum chamber.

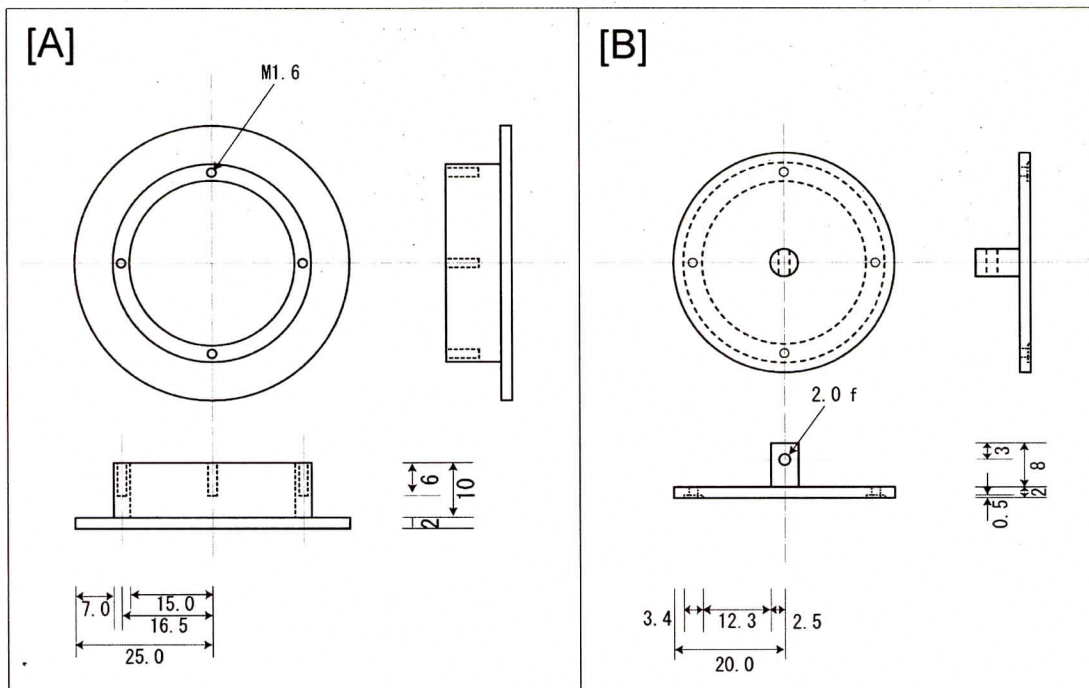


Fig. 6 Detailed drawing of a solid cell used for measuring the tritium amount absorbed in Zr-Ni alloy powder.

Figure 6 shows the detailed design of two cells used for measurement of tritium absorbed in Zr-Ni alloy powder (described as “solid cell”). Two solid cells were used for measurements as reference and sample cell. To lower heat capacity of the solid cell, the body and lid was made of aluminum alloy as small as possible.

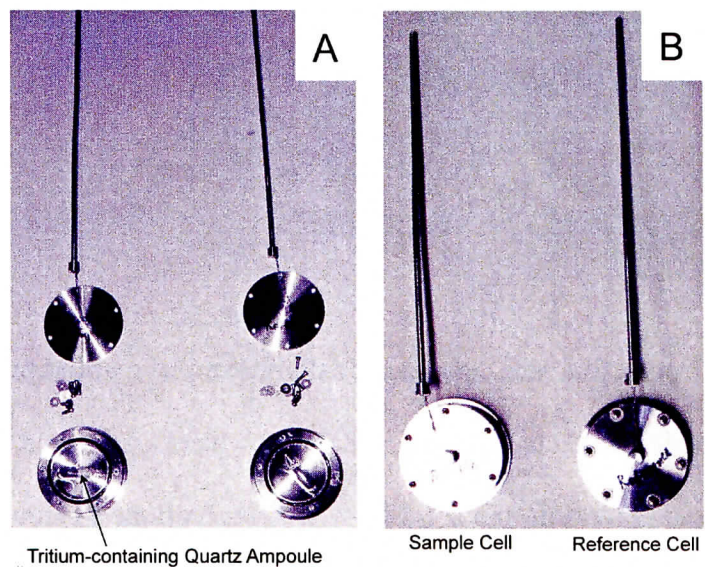


Fig. 7 Photographs of the solid cells before (A) and after (B) construction.

Photographs of the solid cells before and after construction are shown in Fig. 7. Each solid cell was connected with a fine rod through a fine wire in series.

3. Experimental

3.1. Materials

To examine basic performance of the present calorimeter, three quartz ampoules loaded with Zr-Ni alloy powder were prepared as test samples. One of them was loaded with a given amount of tritium gas diluted with hydrogen, which was prepared using a specially designed tritium-handling device. The other two ampoules were loaded with the alloy powder only. Particle size and weight of the powdered Zr-Ni alloy were 300-350 μm and 0.50 g, respectively. Concentration of tritium gas used for loading was evaluated to be 22% by using a small ionization chamber that was preliminarily calibrated^[8]. The total amount of tritium was 33 GBq (determined at April 20, 2004), and the concentration of hydrogen isotopes in Zr-Ni alloy powder was $\text{ZrNiQ}_{0.04}$ ($Q=H + T$). According to the thermodynamic data of a

ZrNi-hydrogen system, it is expected that residual pressure of hydrogen isotopes is below about 5×10^{-6} Pa at 300K.

3.2. Procedures of measurement

As a first step, to make a calibration curve of the present calorimeter, two quartz ampoules loaded with the alloy powder only were packed in both solid cells. To improve thermal conductivity in the solid cells, a given volume of liquid paraffin was additionally introduced in each solid cell. A small hole of lids of the solid cells was connected to a fine rod using fine wires after assembly of the solid cells. Subsequently, they were placed on the sample and reference cell holders, and each fine rod of them was separately fixed to the lid of vacuum chamber through half-cut lids of the heat sink and half-cut copper disks. About 3 cm^3 of liquid paraffin was dropped in the cell holders in advance to improve thermal conductivity between a solid cell and a cell holder. After fixing the lid of vacuum chamber, it was exhausted by vacuum pumps below 1.0×10^{-2} Pa.

Preparation of a calibration curve by means of Joule heating was carried out after the difference in output from two heat sensors was stable. Applied voltage to the resistance attached to the outside of a sample cell holder was changed in the range of 5 to 65 mV, which corresponds to the input power of 0.25 to 42.25 μW .

4. Results and discussion

4.1. Preparation of the calibration curve

Since the original output from the calorimeter during the tritium measurements is remarkably small, the accuracy of calorific measurements strongly depends on stability of a

total calorimetric device including an amplifier. The variations of a background level measured with no tritium-containing samples give indication of the accuracy and stability of the calorimeter. Figure 8 shows an example of change in the background level with time. In this case the background level was evaluated as $-0.293 \pm 0.014 \mu\text{V}$. This indicates that the present calorimeter is able to measure precisely the calorific values if the output above $0.04 \mu\text{V}$ ($3\sigma=0.042 \mu\text{V}$) is taken place by the net temperature difference in both solid cells.

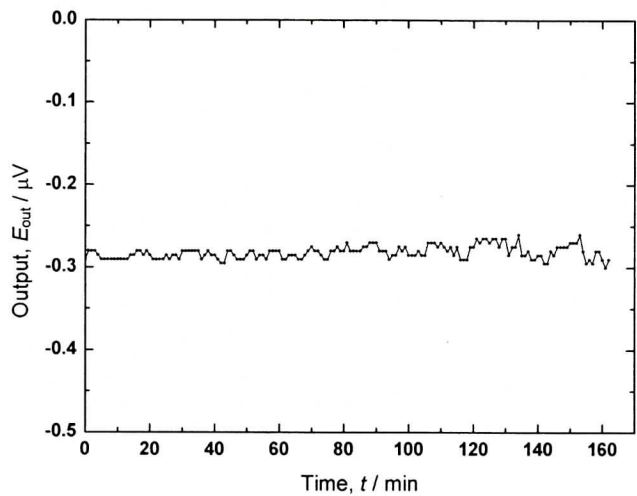


Fig. 8 Background level of the output measured without tritium: both solid cells is contacting with the cell holders.

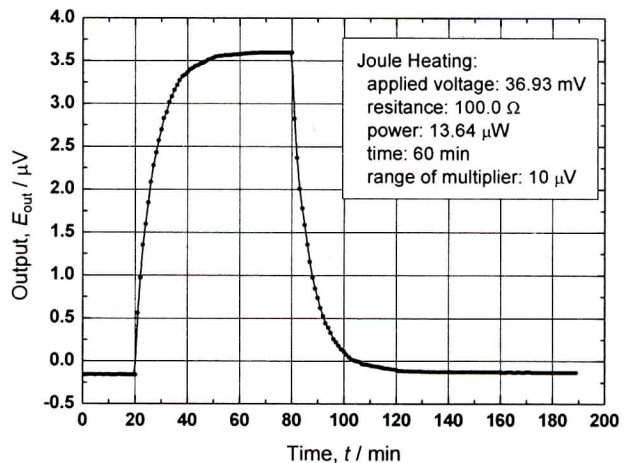


Fig. 9 An example of the output-time curves with Joule heating.

A calibration curve of the present calorimeter was prepared by applying a given voltage to the electric resistance fixed on the outside of the sample cell holder. An example of the changes in the output is shown in Fig. 9. In this case, the input power of $13.64 \mu\text{W}$ was supplied for 1 hour. A rapid increase in the output appears with the input power, and the output reached a given saturation value after about 30 minutes. The difference between the baseline and the saturation value is an equilibrium output depending on the present calorimeter.

When the applied voltage was cut off, the output decreased exponentially to a value of the initial base line. Such behavior is shown in Fig. 10. The linear relation is described in general

by the following equation:

$$\Delta T = (T_2 - T_1) \exp(\sigma t / H), \text{----- (1)}$$

where ΔT is the temperature difference between two heat sensors, T_n ($n=1$ and 2) the temperatures of the reference and sample cell holder, σ the thermal conductivity of a thermo module, H the effective heat capacity of a cell and its holder, and t the time. In this equation, the reciprocal value of σ / H is equivalent to a time constant (τ) of a calorimeter. The time constant is the elapsed time to decrease to $1/e$ of the equilibrium output, which was estimated to be 5.0 min from analysis of the line described in Fig. 10.

Figure 11 describes the calibration

curve determined by applying a variety of input power (Q_{in}) to the sample cell holder loaded with a solid cell. The calibration curve was measured under the condition that a pressure of the vacuum chamber is below 1.0×10^{-2} Pa. As clearly seen from the figure, a good linear relation between the input and output power appeared, and it was found that the linear relation can be reproduced by the following equation in the range of 0.2 to 40 μW :

$$E_{out} [\mu\text{V}] = (0.2694 \pm 0.0010) Q_{in} [\mu\text{W}] \text{----- (2)}$$

Taking account of the standard deviation obtained from the result of Fig. 8, the lower detection limit may be evaluated as 0.15 μW from the above equation, which corresponds to the tritium amount of 0.16 GBq (4.4 mCi).

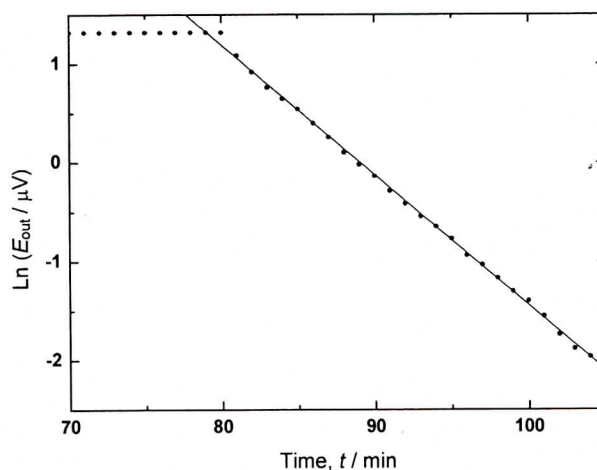


Fig. 10 Plot of $\text{Ln}(E_{out})$ vs. time.

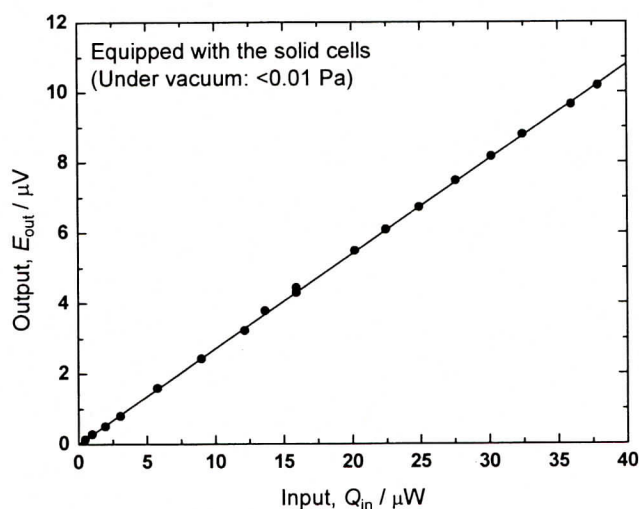


Fig. 11 Calibration curve for the solid tritium measurements.

4.2. Measurement of Zr-Ni alloy powder absorbed tritium

After establishment of the calibration curve, a quartz ampoule in the solid cell of the sample cell holder was taken out, and then the tritium-loaded quartz ampoule was alternatively set to measure a solid tritium sample. Subsequently, the solid cell was put on the sample cell holder, and for several days it has

left until the output become constant. After this, the solid sell was lifted and separated temporarily from the sample cell holder in the vacuum chamber for one night, and then lifted down again on the sample cell holder under the vacuum condition below 1.0×10^{-2} Pa. Figure 12 illustrates change in the output with time. The output increased sharply just after the sample cell was brought into contact with the cell holder, and then it gradually decreased to a constant output. The constant value observed was $6.21 \mu\text{V}$. The net output due to loading with the tritium sample is $6.5 \mu\text{V}$, since the base line was $-0.29 \mu\text{V}$ as shown in Fig. 8. It was seen from the Eq. 2 that this output corresponds to $24.1 \mu\text{W}$.

The present tritium sample was loaded with the tritium amount of 32 GBq, taking into account the elapsed time after the initial tritium loading. The output of the present tritium sample is therefore expected to be $29.2 \mu\text{W}$. Namely, the observed output was 82% of the expected one. It is considered that the difference in output was caused by the calibration curve of the small ionization chamber and/or changes in the base line of the calorimeter. Further investigations about these points are required to establish a calorimetric system for tritium measurements.

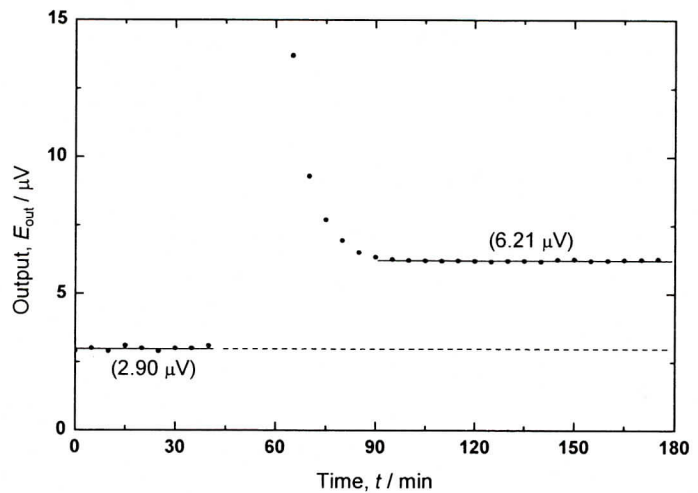


Fig. 12 Change in the output with time before and after lifting down the tritium sample cell on the sample cell holder.

5. Summary

A calorimetric system applicable to measure solid, liquid and gaseous tritium was designed and constructed to evaluate the absolute amount of tritium, and its basic performance has been tested. A twin type thermal conductivity calorimeter set in a vacuum chamber was specially employed for the present purpose. The present calorimetric system consists of a high sensitivity calorimeter, a tritium container, total pressure gauges, a quadrupole mass spectrometer, and high vacuum systems. A calibration curve of the calorimeter has been prepared at first using solid materials absorbed a given amount of tritium, and the following linear relation was obtained: $E_{\text{out}} = (0.2694 \pm 0.0010) Q_{\text{in}}$, where E_{out} describes the differential output (μV) from the thermo modules and Q_{in} the input power (μW) by Joule heating to the sample cell. In addition, the lower detection limit was estimated to be $0.15 \mu\text{W}$ from stability of the calorimeter, which corresponds to the tritium amount of 0.16 GBq . As a first test, Zr-Ni alloy powder loaded with a given amount of tritium was measured by the calorimeter. The observed output was 24.1 mW , which corresponds to 26.3 GBq . It was seen that this activity was slightly less than that expected from the tritium activity evaluated by a small ionization chamber. The difference in activity should be further investigated.

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