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A NEW METHOD OF EXTRACTING TRITIUM PRODUCED  
IN NEUTRON-IRRADIATED LITHIUM-CONTAINING  
PELLETS FOR LIQUID SCINTILLATION COUNTING

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A New Method of Extracting Tritium Produced  
in Neutron-irradiated Lithium-containing Pellets for Liquid Scintillation Counting

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A new method to incorporate inorganic radiochemicals into liquid scintillation cocktail has been developed for measurement of tritium in lithium-containing pellets of  $\text{Li}_2\text{CO}_3$ ,  $\text{LiOH}\cdot\text{H}_2\text{O}$  and  $\text{Li}_2\text{O}$ . This method has the following advantages : 1) high figure of merit, 2) simple chemical treatment and 3) short dissolving time. This was achieved by a systematic study for a relation of chemical treatment of irradiated pellets to the scintillation efficiency and sample compatibility.

Experiments indicated that satisfactory solubility was obtained from a mixture of two acids,  $\text{HNO}_3$  and  $\text{CH}_3\text{COOH}$ . Since  $\text{HNO}_3$  can dissolve a pellet of mass greater than  $\text{CH}_3\text{COOH}$ , this method makes it possible to measure low level tritium activity in the pellet. However,  $\text{HNO}_3$  considerably quenches scintillations of liquid scintillator. In contrast,  $\text{CH}_3\text{COOH}$  doesn't have such a strong quenching effect. Consequently, by using a mixture of two acids, the most part of pellet is dissolved in  $\text{HNO}_3$  and the rest is dissolved in  $\text{CH}_3\text{COOH}$ . The tritium counting efficiency and sample compatibility with scintillation cocktail depends strongly on the volume ratio of the two acids. The optimum mixture of the acids was determined empirically for each type of lithium-containing pellet and for two kinds of cocktails. These experiments indicated that the mass of pellet to be dissolved in the solvent was two times as large as in the Dierckx's method. Compatibility of counting samples and stability of counting efficiency were excellent for a month.

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Keywords: Tritium, Lithium-containing Pellets, Liquid Scintillation Counting, Acid, Optimum Solvent Composition, Sample Compatibility, Low Level Activity, Easy-to-use Method, Tritium Production, Fusion Neutronics.

液体シンチレーション計数のための中性子照射した  
リチウム含有ペレット中のトリチウム抽出の新しい方法

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(1994年11月15日受理)

高いシンチレーション収量を示す無機化学物質の液体シンチレーション溶液への新しい溶解法を $\text{Li}_2\text{CO}_3$ 、 $\text{LiOH}\cdot\text{H}_2\text{O}$ および $\text{Li}_2\text{O}$ のLi含有ペレット中のトリチウム測定のために開発した。この方法は以下のような特長を持っている。即ち、1) 高い有利指数 (Figure of Merit) 2) 化学操作の簡単さ 3) 短い溶解時間、である。この方法は照射ペレットの化学操作とシンチレーション効率および溶解サンプルの共存性の関係を系統的に調べることによって達成された。実験から、 $\text{HNO}_3$ と $\text{CH}_3\text{COOH}$ の2種の混合酸によって満足すべき溶解度が得られた。 $\text{HNO}_3$ は $\text{CH}_3\text{COOH}$ より大きい質量のペレットを解かすことができるのでペレット中の低レベルのトリチウムでも測定することを可能にする。しかし、 $\text{HNO}_3$ はシンチレータに対して強いクエンチング作用があり、一方、 $\text{CH}_3\text{COOH}$ は強いクエンチング作用を持たない。そこで、本方法では2種の混合酸を用い、はじめに少し足りない分量の $\text{HNO}_3$ で溶解し、残存する分を $\text{CH}_3\text{COOH}$ で溶解する。トリチウムの計数効率とサンプルのシンチレータ・カクテルとの共存性はこの2種の酸の混合比に強く依存する。そこで、3種のペレットと2種のシンチレータ・カクテルについてその最適化を行った。これらの実験は従来のDierckx's法と比べてペレットの質量で2倍溶解できることを示し、長時間にわたって測定溶液の安定性も良かった。また、計数効率も一ヶ月にわたって一定であった。

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## 1. Introduction

Measurement of a tritium production rate distribution in a simulated blanket assembly is one of the most important items in the fusion neutronics study. Considerable efforts have been made to obtain absolute values of these distributions<sup>1)</sup>. Tritium production rate is defined in terms of tritium activity generated in neutron-irradiated lithium-containing pellets. During the reasonable irradiation time of assembly by the D-T neutron source (neutron fluence  $\sim 10^{15}$  neutrons/ $4\pi$ ), a small amount of tritium activity ( $\sim 10^9$  nuclei/g), though it is difficult to measure, is produced. The difficulties for measurement are growing especially for the engineering-oriented fusion blanket benchmark experiments with the heterogeneous structure. In such a situation, the great number of lithium-containing pellets are required to obtain detailed distribution of tritium production rates. Thus these severe demands in the experiments lead to select the tritium measurement methods. The demands are concerned with sensitivity, accuracy and speed-up for detector treatment as well as with the possible use of automatic instrumentation.

The most sensitive method for the detection of tritium is liquid scintillation counting<sup>2)</sup>. Due to basic principle of liquid scintillation counting it is necessary to bring tritium that is contained in the pellet in close contact with the scintillator molecules of the scintillation solution because the  $\beta$ -ray energy of tritium decay is very small. On the other hand the tritium extraction technique depends on the material of pellet. The technique for metal lithium is based on the thermal digestion of the pellets in a metered carrier hydrogen stream to convert to HTO and liquid scintillation counting<sup>3)</sup>. However, this technique is difficult for the engineering-oriented fusion blanket benchmark experiments. Therefore the techniques based on the extraction of tritium from pressed-powder pellets of lithium salts by wet-chemistry method were developed<sup>4)-7)</sup>.

In order to prepare the sample for liquid scintillation counting there are three main steps: 1) dissolution of pellet, 2) removal of lithium salts from pellet solution by using hydrofluoric acid or cryo-distillation, 3) incorporation of the pellet solution into the liquid scintillator. These techniques are less laborious and make it possible to treat a large number of pellets, but the lower limit of tritium activity measurement is higher. This is because the weight of the pellet to be solved is limited by the pellet solubility in the diluted acetic acid. According to well known Dierckx's method<sup>4)</sup> this value is about 20 g of  $\text{Li}_2\text{CO}_3$  for 100 ml of the diluted acetic acid. The use of strong acid make it possible to prepare more concentrated solution of the pellet, for example, 50 g of  $\text{Li}_2\text{CO}_3$  can be dissolved in concentrated nitric

acid. However, this benefit is lost after the incorporation of the pellet solution into the liquid scintillator, because the small quantity of free nitric acid considerably quenches scintillations, and it is rarely practical to make the pellet solution without free nitric acid. Therefore, to improve the wet-chemistry method it is necessary to find appropriate solvent acids forming more concentrated solutions without strong quenching. In addition, it is possible to simplify sample preparation technique by reducing the number of steps necessary to prepare the pellet for counting. This can be accomplished by using the appropriate solvent acids and scintillation cocktail. The cocktail contains the surfactant, Triton X-100 or similar chemicals, which makes possible the incorporation of the pellet solution into the scintillation cocktail. By this manner the second step of the wet-chemistry method, removal of lithium salts from pellet solution, can be eliminated.

From the above discussion it is clear that the approach for solving this problem is in search of the pellet solvents which form:

- 1) concentrated solution without strong quenching,
- 2) clear fluid, after the incorporation of the solution into the scintillation cocktail.

Consequently, the objective of the present study is to develop a new acid solvent, which gives more concentrated solution of pellet, for liquid scintillation counting of lithium contained pellets,  $\text{Li}_2\text{CO}_3$ ,  $\text{LiOH}\cdot\text{H}_2\text{O}$  and  $\text{Li}_2\text{O}$ .

A mixture of two different acids,  $\text{HNO}_3$  and  $\text{CH}_3\text{COOH}$ , has been proposed to deal with these problems. The optimum acid volume ratio was determined empirically for each type of pellet. The pellet solubility, the counting efficiency of the mixture of pellet solution and scintillation cocktail and the compatibility were determined with respect to the acid volume ratio. Then the maximum weight for each type of pellet per 20 ml standard vial for scintillation counting was determined for the solvent with the optimum acid volume ratio. For the latter procedure, the counting efficiency of the pellet solution-cocktail mixture and the compatibility were determined with respect to the dissolved pellet weight. These investigations were performed for two kinds of cocktails, Clear-sol and Aquasol-II. Finally the Figure of Merit, which is defined as the product of the pellet weight and tritium counting efficiency, was discussed in comparison with the previous techniques.



## 2. Liquid Scintillation Counting Techniques for Tritium Measurement

Presently, the most reliable method for tritium production measurement is certainly the activation method which measures tritium activity extracted from irradiated lithium salt pellets by using liquid scintillation counting. Lithium salts,  $\text{Li}_2\text{CO}_3$ ,  $\text{LiOH}\cdot\text{H}_2\text{O}$  and  $\text{Li}_2\text{O}$ , are usually used for pellet manufacture. Characteristics of these lithium compounds are given in Table 1.

Table 1. Densities of lithium salts.

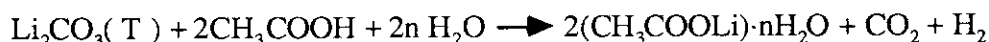
Compound	Density ( $\text{g}/\text{cm}^3$ )		Lithium density ( $\times 10^{22}$ atom/g )
	theoretical	experiment*	
$\text{Li}_2\text{CO}_3$	2.1	1.69	1.63
$\text{LiOH}\cdot\text{H}_2\text{O}$	1.6	1.35	1.45
$\text{Li}_2\text{O}$	2.0	1.47	4.03

\* The pellet was made from powder by cold pressing

During neutron irradiation lithium salts, tritium is generated and stored as  $\text{LiOT}$  in lithium salts<sup>8)</sup>. Therefore, the stability of the tritium stored in the irradiated compounds should be high to keep little chance of escape before dissolution, and the tritium should easily move into solution.

Unfortunately lithium salts are incompatible with the solubility characteristics of scintillation cocktail. To overcome these problems various techniques have been developed. Figure 1 illustrates the sample processing schemes of these techniques. All techniques are similar to one proposed by Diercks and consist of three main steps: 1) dissolution of pellet, 2) removal of lithium salts from pellet solution by using hydrofluoric acid or cryo-distillation, 3) incorporation of the pellet solution into the liquid scintillator.

According to the Dierckx's method, all chemical operations are performed in a standard 20 ml vial. To each vial, 0.7 g of  $\text{Li}_2\text{CO}_3$ , 1  $\text{cm}^3$  of distilled water and 2  $\text{cm}^3$  of  $\text{CH}_3\text{COOH}$  are added and the reaction



is continued to completion. This reaction process takes ~ 1 day. When the solution becomes clear, 0.7 cm<sup>3</sup> of hydrofluoric acid ( 40% ) is added to precipitate lithium fluoride by the reaction:



and so to remove lithium acetate from solution.

This reaction is almost instantaneous, and the amount of HF added is less than that required to remove all the lithium acetate to ensure that no free HF is left. Then another 20 cm<sup>3</sup> of the liquid scintillator is added. The vial is closed and centrifuged. When the LiF forms the white layer on the bottom of the vial the sample is ready for counting.

This technique has the following disadvantages. The pellet solubility in the diluted acetic acid is not so high; about 20 g of Li<sub>2</sub>CO<sub>3</sub> per 100 ml of the solvent. For comparison, 50 g of Li<sub>2</sub>CO<sub>3</sub> can be dissolved in 100 ml concentrated nitric acid. The remaining lithium acetate is liable to make the scintillation solution unstable and to reduce the tritium counting efficiency. To overcome these disadvantages a new extraction method has been developed. The sample processing scheme of this technique is shown in Fig.2. This procedure is simple and does not require to remove lithium salt from the solution. The binary-acid solvent results in lower limit of tritium activity level for measurement because of increases of pellet solubility and counting efficiency, and allows the direct incorporation of pellet solution in the scintillation cocktail.

### 3. Solvent Acids for Pellet Dissolving

#### 3.1 Chemicals

The chemicals used for making inorganic solutions of the pellet were HNO<sub>3</sub> ( 61% ) and CH<sub>3</sub>COOH ( 100% ) in analytical grade. Commercial scintillation cocktails, Aquasol-II ( New England Nuclear ) and Clear-sol ( Nakarai Chemical Co. Ltd. ), were used. Teflon vials were used in all the measurements and the scintillator liquids were dispersed by means of auto burette instrument, having an accuracy less than 1%. Eppendorf micropipettes with a volume accuracy less than 1% were used to incorporate radioactive solution into the scintillator liquid.

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### 3.2 Choice of Pellet Solvent

The ideal solvent for pellet would obviously satisfy the following main requirements:

- high pellet solubility,
- absence of the strong quenchers in pellet solution,
- good compatibility of pellet solution to scintillation cocktail.

From the above point of view, in order to provide high solubility of lithium salt it is best to use an acid<sup>9)</sup>. But the acid may be the strong quencher. Therefore, to examine the influence of the acids incorporated into the scintillator upon the tritium counting efficiency an experiment was carried out. The quenching of light output of the cocktail, Clear-sol, was investigated by the incorporation of weak and strong acids. The measurements of counting efficiency were carried out in 20 ml volume teflon vials. The counting samples were obtained by adding acid volumes to 10 ml of cocktail, because variations in scintillation volume gave an insignificant effect on counting efficiency in the range from 8 to 17 ml, as shown in Fig. 3. Counting efficiency was obtained by spiking 0.1 ml tritiated water corresponding to 13300 dpm in a vial containing the sample of interest. Efficiency (  $\epsilon$  ) was calculated by the following equation:

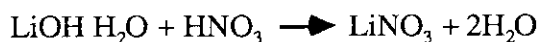
$$\epsilon (\%) = \frac{\text{number of counts per minute ( cpm )}}{\text{number of tritium decay per minute ( dpm )}} \times 100$$

By visually checking homogeneity of sample, the sample holding capacity of cocktail was determined. One is expressed as sample load. Sample load ( SL ) is defined in percentage by

$$SL (\%) = \frac{\text{solute volume}}{\text{solute volume} + \text{cocktail volume}} \times 100$$

Figure 4 shows the relation of counting efficiency to the sample load for different solvents. For reference, quenching effect of water is also plotted in the same figure. From the figure it is seen that the strong acid,  $\text{HNO}_3$ , leads to a rapid decrease in counting efficiency. Therefore, the amount of the strong acid deficient to dissolve the pellet should be used, as the rest part of the pellet can be dissolved by the acetic acid. This binary-acid doesn't have a significant impact on the counting efficiency. Since it is not practical to determine the exact composition of the mixture of two acids by calculation, the mixing ratio of two acids was determined empirically.

In order to dissolve the lithium-containing pellets, as defined above, seven solvent compositions ( A - E ), varying the acid volume ratio, for each type of pellet were prepared. Those characteristics are shown in Fig.5 - 7. Type "A" solvent contained only the nitric acid. Its volume was estimated by calculation according to the chemical reaction. The following reactions take place in the mixture:



Next, types "B" - "G" solvents contained the mixture of two acids varying the acid volume ratio. These solvents were prepared by the following manner: the volume of nitric acid was reduced gradually, but the volume of acetic acid was increased. The amount of acetic acid was determined until the pellet was dissolved completely. Chemical composition of solvent for each type of pellet is given in Table 2.

Table 2. Acid volumes ( ml ) in solvents for dissolving 1 g lithium salt.

Compound	LiOH·H <sub>2</sub> O		Li <sub>2</sub> CO <sub>3</sub>		Li <sub>2</sub> O	
	HNO <sub>3</sub>	CH <sub>3</sub> COOH	HNO <sub>3</sub>	CH <sub>3</sub> COOH	HNO <sub>3</sub>	CH <sub>3</sub> COOH
Solvent type						
A	1.81	0.0	2.10	0.0	5.07	0.0
B	1.74	0.03	2.03	0.08	4.80	0.15
C	1.59	0.16	1.96	0.18	4.02	0.85
D	1.38	0.35	1.81	0.37	3.62	0.97
E	1.16	0.51	1.71	0.61	3.36	1.30
F	1.09	0.62	1.59	0.82	3.10	1.80
G	0.87	0.91	1.38	1.22	2.90	2.10

Based on the experimental data, the solubility of lithium salts was evaluated as summarized in Table 2. Traditionally, the solubility of each substance is expressed in grams of dissolved substance per 100 ml solvent <sup>10)</sup>. Evaluated data are also shown in Fig.8 - 10 as graphical plots. From these figures one can see that the solubility decreases by about 10% with increase of acid volume ratio from 0 to 1.

To observe the effect of varying the chemical composition of pellet solution incorporated into the scintillation cocktail on counting efficiency and sample compatibility, seven samples for each type of pellet and cocktail were prepared from the solvent "A" - "G". Samples "a" - "g" for the examination of  $\text{LiOH}\cdot\text{H}_2\text{O}$  solutions in Clear-sol and Aquasol were obtained by adding 0.5g  $\text{LiOH}\cdot\text{H}_2\text{O}$  dissolved by acid solvent of seven different acid volume ratios "A" - "G" to 10 ml of the corresponding cocktail. Samples "a" - "g" are distinguished by dissolving the pellet from the corresponding solvents of "A" - "G". After shaking the sample thoroughly, a visual assessment of transparency was made. The obtained results are shown in Fig.11 - 12. They show the influence of the solution on the counting efficiency and sample compatibility with its pH value. Curves dropped rapidly for "a" sample because the free nitric acid exists in sample by excess of acid. It is supported by pH value measurements shown together. On the other hand, the influence of the solution on the sample compatibility is difficult to explain and the further consideration is needed. In order to obtain the optimum of acid volume ratio, it is necessary to study the pellet weight dependence on the counting efficiency and sample compatibility.

By the similar way, the examinations of  $\text{Li}_2\text{CO}_3$  and  $\text{Li}_2\text{O}$  solutions were performed for Clear-sol and Aquasol-II. Pellet weights dissolved in both pellets by acid solvent were 0.4 g and 0.2 g, respectively. The influence of the solution on the counting efficiency and sample compatibility was examined for both cocktails and pellets. Figures 13 - 16 show the obtained dependences. They are very similar to the dependences for  $\text{LiOH}\cdot\text{H}_2\text{O}$  solutions.

### 3.3 Optimization of the Solvent

From the above discussion, it appears that the optimum mixture of acids for each type of lithium-containing pellet and for each cocktail should be determined empirically. Thus, the influence of the solution composition on the counting efficiency and sample compatibility was studied as well as the influence of pellet weight. For this purpose, two sets of samples "a" - "g" with different weights were prepared in the same manner as described in

chapter 3.2. The weights of LiOH·H<sub>2</sub>O pellets were 1.0 g and 2.0 g for the Clear-sol mixture, and 1.0 g and 1.5 g for the Aquasol-II mixture. The weights of Li<sub>2</sub>CO<sub>3</sub> pellets were 0.8 g and 1.4 g for the Clear-sol mixture, and 0.6 g and 0.9 g for the Aquasol-II mixture. The weights of Li<sub>2</sub>O pellets were 0.4 g and 0.8 g for the Clear-sol mixture, and 0.35 g and 0.5 g for the Aquasol-II mixture. A comparison between the two sets of the prepared samples was made in terms of Figure of Merit, FOM. The FOM is defined as the product of pellet weight and counting efficiency, and thus it denotes capability for measurement of low level tritium produced. The FOM is written as:

$$\text{FOM} = \epsilon \cdot M$$

where,  $\epsilon$  - counting efficiency (%),

M - mass of pellet (g)

Consequently, the data of three types of samples were arranged in a graph to see the optimum condition of solvent. The optimum implies that the sample has the highest FOM value within the clear fluid region of good compatibility.

The dependences of chemical compositions of samples and pellet weight on the Figure of Merit and the sample compatibility are shown in Fig. 17 - 22. The optimum solvent compositions for all lithium compounds and for cocktail acid combinations are summarized in Table 3.

Table 3. Optimum chemical composition of the solvents for dissolving 1g lithium salt.

Compound	Cocktail	Acid volume ( ml )	
		HNO <sub>3</sub>	CH <sub>3</sub> COOH
LiOH·H <sub>2</sub> O	Clear-sol	1.16	0.51
	Aquasol-II	1.09	0.62
Li <sub>2</sub> CO <sub>3</sub>	Clear-sol	1.81	0.37
	Aquasol-II	1.59	0.82
Li <sub>2</sub> O	Clear-sol	3.36	1.30
	Aquasol-II	3.10	1.80

## 4. Counting of Tritium Activity in Emulsion

### 4.1 Optimization of Emulsion of Pellet Solution and Scintillation Cocktail

The aim of this procedure is to evaluate the optimum pellet weight with respect to the capability for measurement of low level tritium by using 20 ml standard vial. The optimum weight of the lithium salt was determined experimentally, because on the one hand, the counting efficiency in liquid scintillation counting decreases and the sample compatibility impairs with increasing amount of the pellet solution in the cocktail (impurity quench), and on the other hand, FOM increases. To observe this effect, the series samples of optimum chemical composition with different pellet weights were prepared. Figures 23 - 28 demonstrate the results of the optimization procedure for all lithium compounds. The values of optimum pellet weight are shown in Table 4.

Table 4. The optimum weight of lithium salt for measurement of low level tritium by using 20 ml vial.

Compound	Cocktail	Counting efficiency ( % )*	Weight ( g )
LiOH H <sub>2</sub> O	Clear-sol	16.3	2.5
	Aquasol-II	22.7	2.2
Li <sub>2</sub> CO <sub>3</sub>	Clear-sol	21.7	1.4
	Aquasol-II	26.7	0.9
Li <sub>2</sub> O	Clear-sol	15.1	1.1
	Aquasol-II	27.7	0.4

\* Counting efficiency for the optimum pellet solution-cocktail mixture



## 4.2 Stability of Emulsion

Numerous experiments during the present study were carried out to examine the stability of the pellet solution and cocktail mixture and the changes of counting efficiency with time. Stability of the emulsion system was excellent over a long period. No time-dependence was observed in counting efficiency over one month. Reproducibility of counting characteristics for the replicated emulsions with the same composition was excellent within statistics of counting, the initial pipetting accuracy and the long-term stability of the counting system.

## 4.3 Chemical Quenching by Solution Types

During this study numerous quenching curves were obtained for various quenchers. The quenching behavior of eight quenchers was examined using the xylene based cocktail, Clear-sol. The examined substances were  $H_2O$ ,  $HNO_3$ ,  $CH_3COOH$  and the acid solutions of  $Li_2CO_3$ ,  $LiOH \cdot H_2O$  and  $Li_2O$ . All quenchers were the uncolored substances. Normal 20 ml teflon vials were used for 10 ml of scintillation liquid. All samples were kept in equilibrium with air and thus they contain the same amount of oxygen as a quencher. To observe the effect of increase of quenching, a series of samples were prepared with increasing volumes of quencher. External standard ratio method was used for measurement of quenching factor. The results of the measurement are shown in Fig. 29. The significant differences between these curves imply that different chemical quenchers lead to different quenching curves. These differences can be explained as differences in the scintillation pulse shapes.<sup>11)</sup>

Essentially this effect means that in order to eliminate the possibility of systematic errors it is necessary to use the same type of vials, the same scintillation cocktail and the same quencher when the standard and the unknown samples are measured.

## 5. Results and Discussion

### 5.1 Comparison of Scintillation Cocktails

Clear-sol and Aquasol-II were used as the cocktails of scintillation counting. The aim of this comparison is to select the cocktail for each type of the pellet with the highest Figure of Merit, FOM. The FOM data of the optimum samples for both cocktails were shown in Fig. 30-32, for convenience. The optimum samples were prepared with the use of optimum pellet solvent and they were in the clear fluid region of sample holding capacities.

The following observations were obtained:

- 1) Clear-sol has the advantage of large holding capacities of the pellet solution in the clear fluid region;
- 2) Clear-sol provides the highest FOM value for  $\text{Li}_2\text{CO}_3$  and  $\text{Li}_2\text{O}$  pellets;
- 3) Aquasol-II provides the highest FOM value for  $\text{LiOH}\cdot\text{H}_2\text{O}$  pellets;
- 4) Aquasol-II provides the highest FOM value for all pellet types which have the weight of about half of the maximum value.

As the results of these investigations the following combinations can be selected for routine use:

- 1)  $\text{LiOH}\cdot\text{H}_2\text{O}$  solution & Aquasol-II;
- 2)  $\text{Li}_2\text{CO}_3$  solution & Clear-sol;
- 3)  $\text{Li}_2\text{O}$  solution & Clear-sol.

It should be noted that compared to Clear-sol, Aquasol-II with pellet solutions tends to form gel phase of emulsion cocktail. The efficiency of such an emulsion cocktail depends upon the diameter or thickness of the aqueous micellar phase <sup>12)</sup>. If particle size is not controlled, the unknown counting losses due to the self-absorption of low energy  $\beta$ -ray can take place.

### 5.2 Comparison with the Previous Techniques

In order to compare the capability for measurement of low level tritium by various techniques, the Figure of Merit was used. A difference of lithium density for various lithium-containing compounds was taken into account by using the factor  $k_{\text{Li}}$ . This factor is defined as the ratio of the lithium concentration in the lithium-containing pellet to the lithium concentration in the lithium metal pellet. The higher the Figure of Merit is, the lower the

tritium level to be measured is. This value is, of course, based on the instrument used. However, because all the instruments are considered to be similar, this factor can be assumed to be equal.

The main parameters of the techniques and the calculated Figure of Merit are summarized in Table 5.

Table 5. Comparison of measuring techniques.

Organization & technique	Chemical form of pellet	Pellet weight (g)	Lithium ratio, $k_{Li}$	Transfer efficiency * (%)	Counting efficiency (%)	Figure of merit ( $g_{Li} \cdot \%$ )
CEA/Cadarache Dierckx' 2)	$Li_2CO_3$	0.7	0.188	100	26.6	3.50
IGA/EPFL Dierckx' 2)	$Li_2CO_3$	0.7	0.188	100	20.6	2.71
ENEA Dierckx' 2)	$Li_2CO_3$	0.7	0.188	100	22.7	2.99
Osaka Univ. Dierckx' 2)	$Li_2CO_3$	0.5	0.188	100	18.6	1.75
Tokyo Univ. Dierckx' 2)	$Li_2CO_3$	0.6	0.188	100	29.8	3.59
JAERI Present tech.	$Li_2CO_3$	1.4	0.188	100	21.7	5.71
Harwell Technique 6)	$LiOH \cdot 1/17 H_2O$	1.0	0.278	100	20.0	5.56
JAERI Present tech.	$LiOH \cdot H_2O$	2.2	0.167	100	22.7	8.35
JAERI Technique 5)	$Li_2O$	0.4	0.464	75	25.7	4.53
JAERI Present tech.	$Li_2O$	1.1	0.464	100	15.1	7.70

\* Transfer efficiency; ( tritium amount transferred into a vial ) / ( tritium amount produced in a pellet )

Figure 33 shows the comparison of the FOM for each type of lithium-containing pellet. It is clearly demonstrated that the present technique can improve the FOM by a factor of about two for all lithium-containing compounds.

## 6. Conclusion

New acid solvents for dissolving of lithium salts,  $\text{LiOH}\cdot\text{H}_2\text{O}$ ,  $\text{Li}_2\text{CO}_3$  and  $\text{Li}_2\text{O}$ , were developed. The utilization of the combination of acid solvents and the scintillation cocktail containing surfactant created a new efficient technique for measuring the tritium activity in lithium-containing pellets. Characteristics of these solvents and the solution-cocktail mixtures were optimized to obtain the maximum Figure of Merit for the measurement of tritium in the pellets of lithium salts. The Figure of Merit, the product of pellet solubility and counting efficiency of the solution-cocktail mixture, denotes the capability for measurement of low level tritium. The present method improves the previous one by a factor of about two in the FOM.

## Acknowledgment

The authors would like to thank Dr. M. Tanase for his critical reading of manuscript.

## 6. Conclusion

New acid solvents for dissolving of lithium salts,  $\text{LiOH}\cdot\text{H}_2\text{O}$ ,  $\text{Li}_2\text{CO}_3$  and  $\text{Li}_2\text{O}$ , were developed. The utilization of the combination of acid solvents and the scintillation cocktail containing surfactant created a new efficient technique for measuring the tritium activity in lithium-containing pellets. Characteristics of these solvents and the solution-cocktail mixtures were optimized to obtain the maximum Figure of Merit for the measurement of tritium in the pellets of lithium salts. The Figure of Merit, the product of pellet solubility and counting efficiency of the solution-cocktail mixture, denotes the capability for measurement of low level tritium. The present method improves the previous one by a factor of about two in the FOM.

## Acknowledgment

The authors would like to thank Dr. M. Tanase for his critical reading of manuscript.

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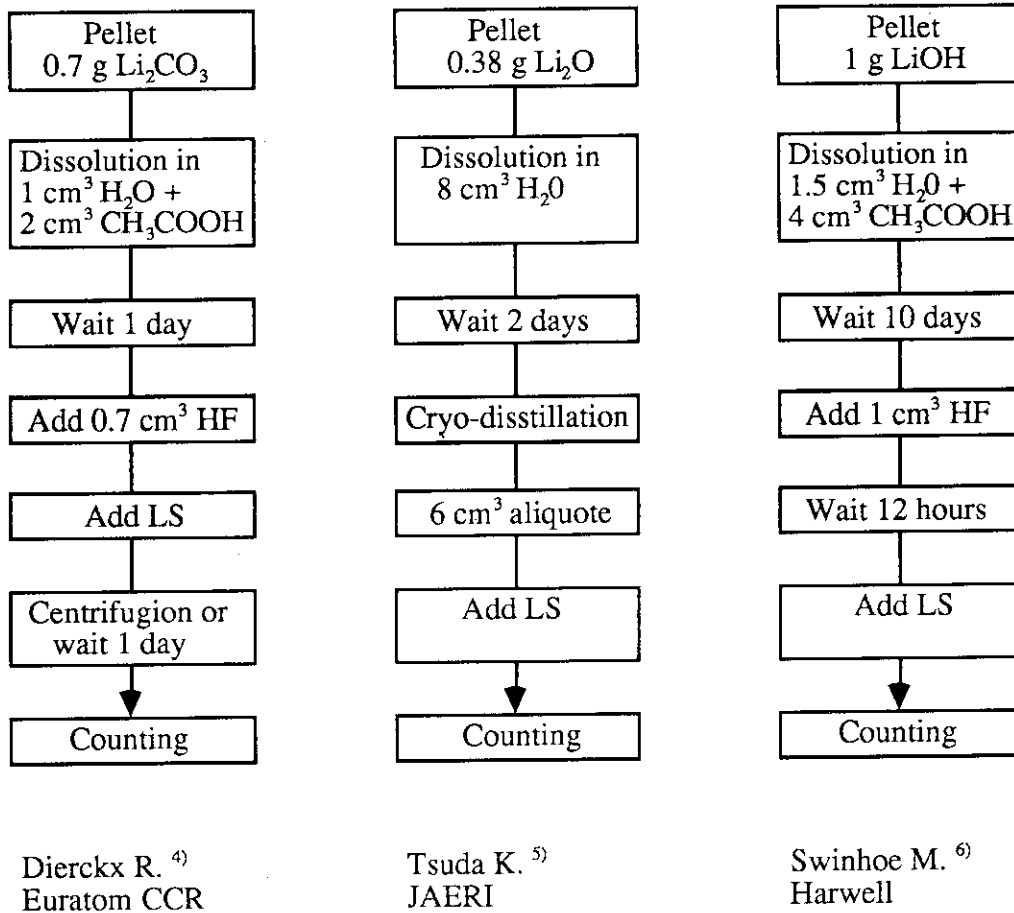
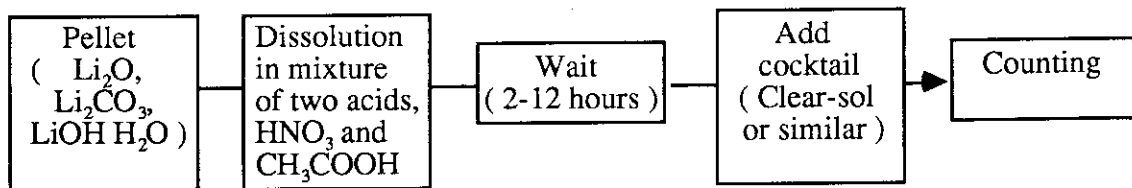


Fig.1 Sample processing schemes.



All the operations are carried out in a scintillation vial

Fig.2 Sample processing scheme of the present technique.

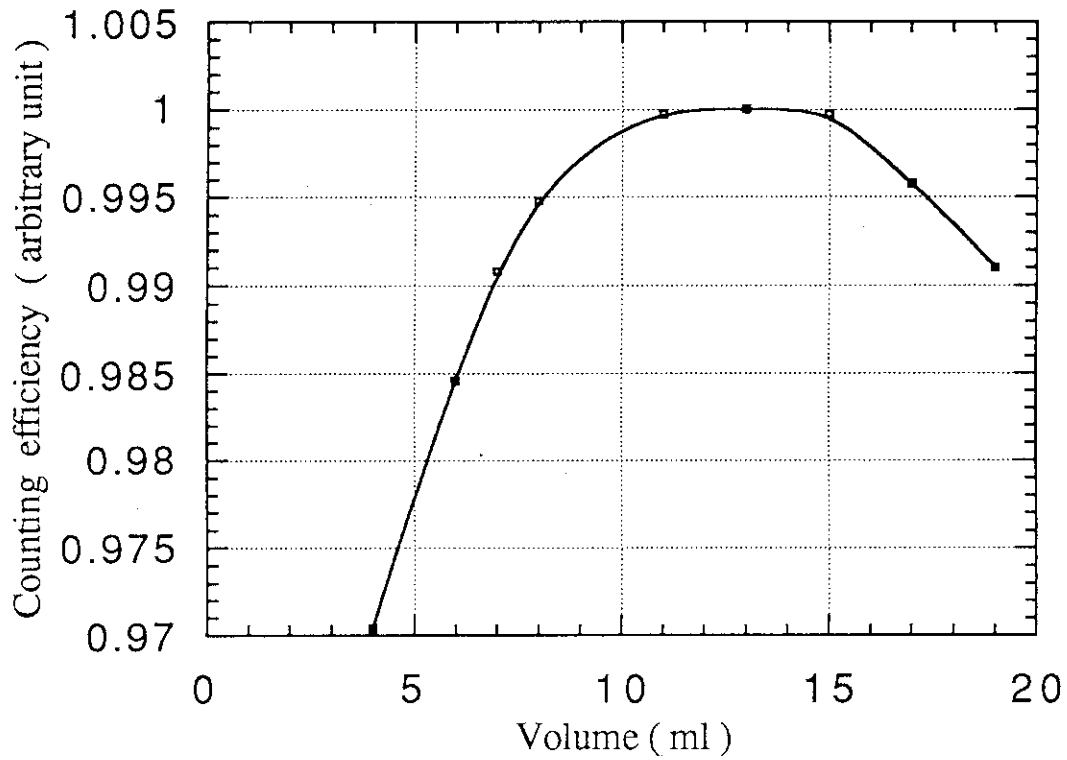


Fig.3 Effect of scintillation cocktail volume on counting efficiency of tritium for Clear-sol in 20 ml teflon vial.

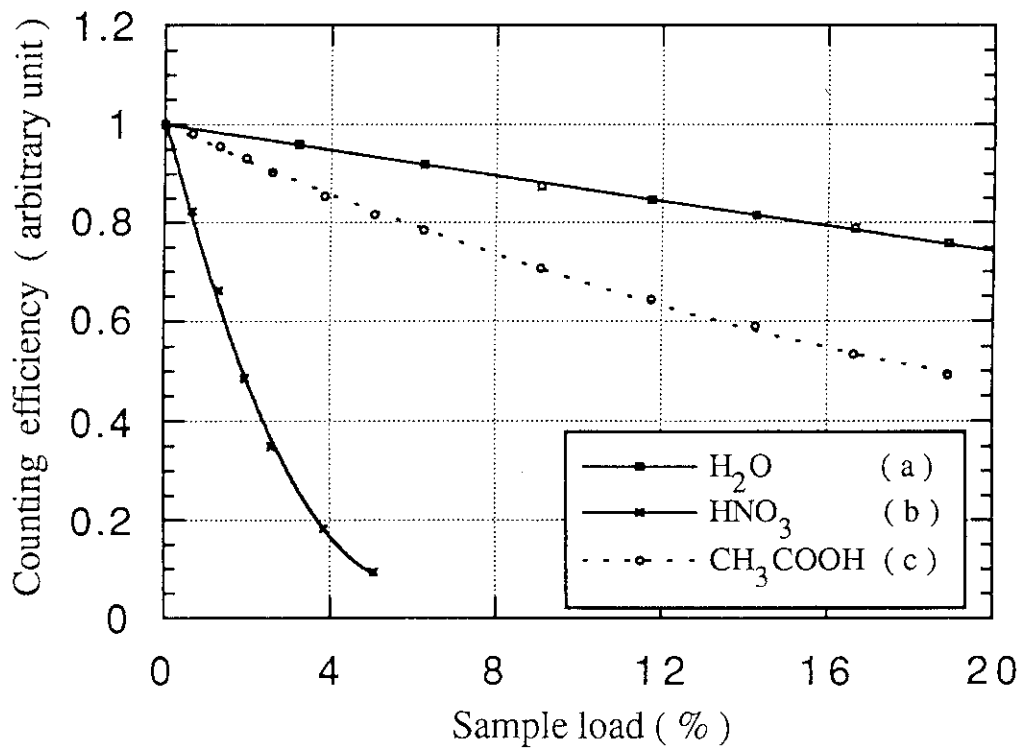


Fig. 4 Effect of varying the sample volume on tritium counting efficiency for Clear-sol. Samples are: a) distilled water, b) nitric acid ( 61% ), c) acetic acid ( 100% ).



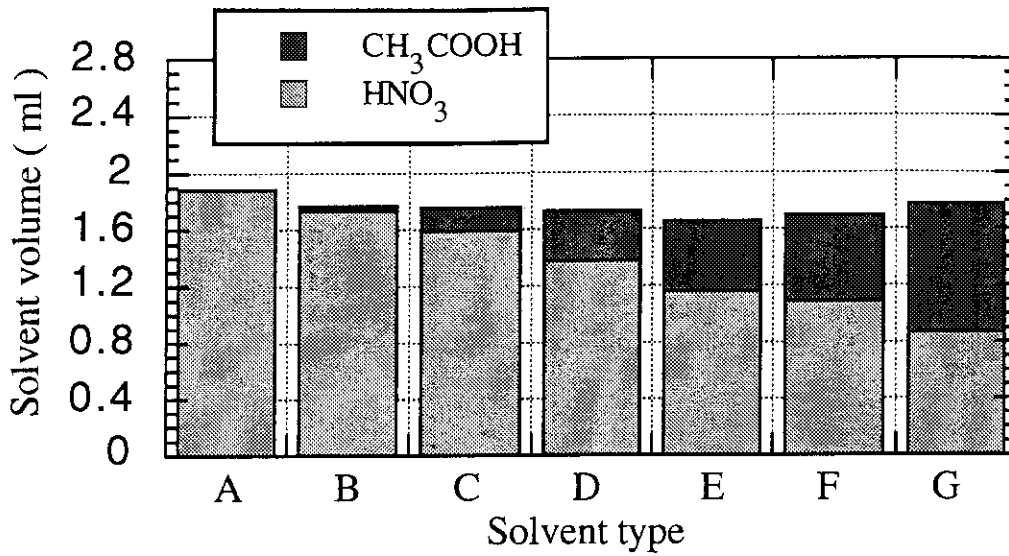


Fig.5 The composition of solvents for dissolution of 1g LiOH·H<sub>2</sub>O by the mixture of acetic and nitric acids.  
( See Table 2 for interpretation of solvent type )

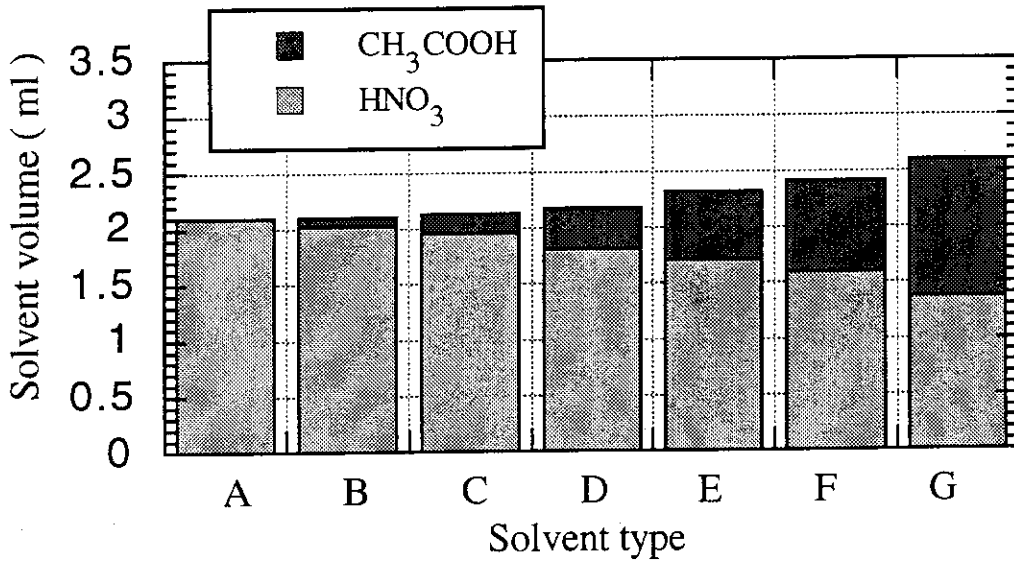


Fig. 6 The composition of solvents for dissolution of 1g Li<sub>2</sub>CO<sub>3</sub> by the mixture of acetic and nitric acids.  
( See Table 2 for interpretation of solvent type )

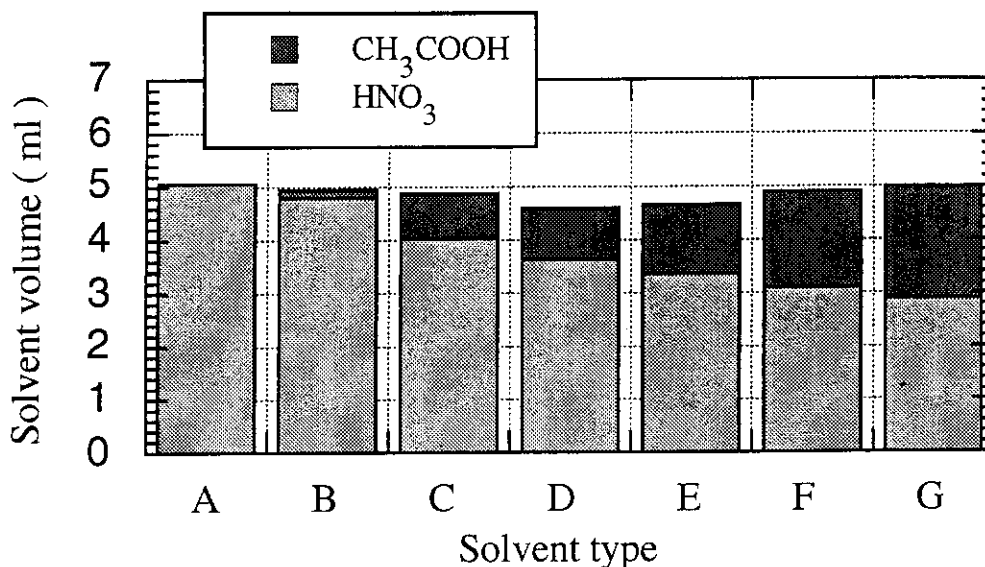


Fig.7 The composition of solvents for dissolution of 1g Li<sub>2</sub>O by mixture of acetic and nitric acids.  
( See Table 2 for interpretation of solvent type )

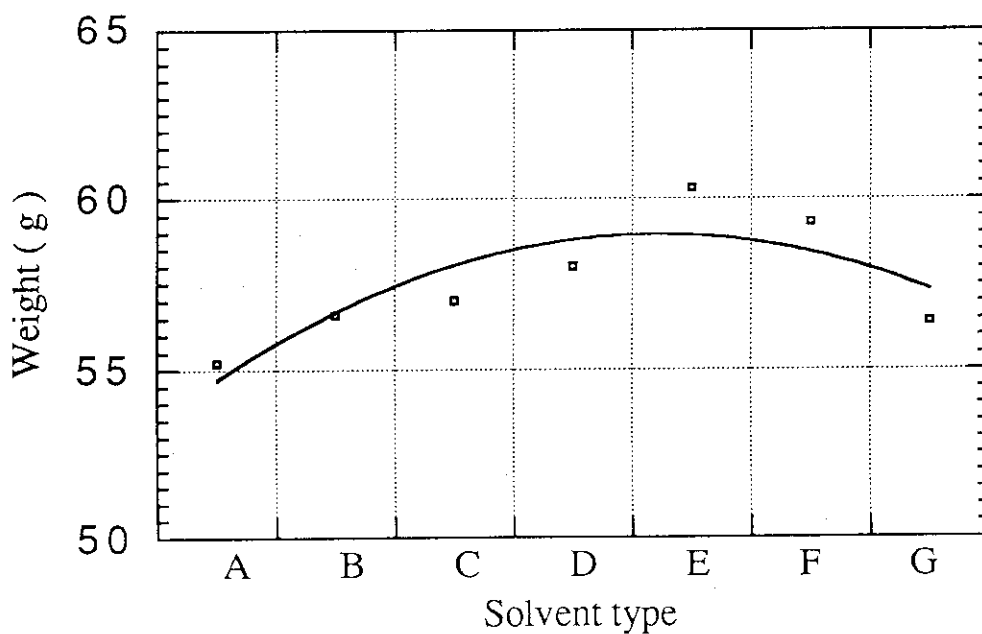


Fig. 8 The influence of the solvent compositions upon the weight of LiOH·H<sub>2</sub>O dissolved by 100 ml of mixture of acids.  
( See Table 2 for interpretation of solvent type )

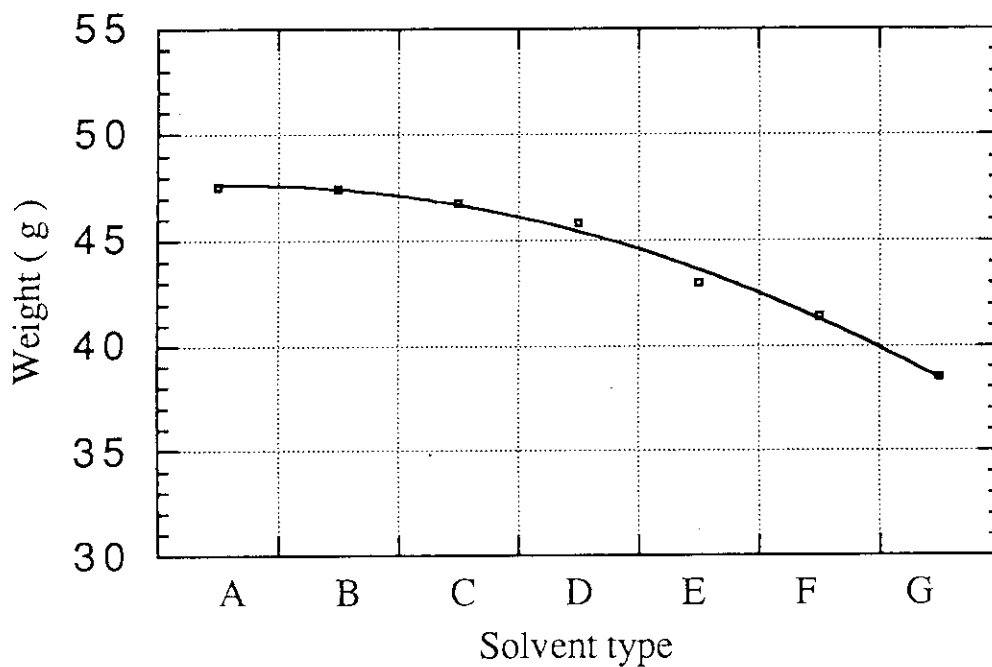


Fig.9 The influence of the solvent compositions upon the weight of  $\text{Li}_2\text{CO}_3$  dissolved by 100 ml mixture of acids.  
( See Table 2 for interpretation of solvent type )

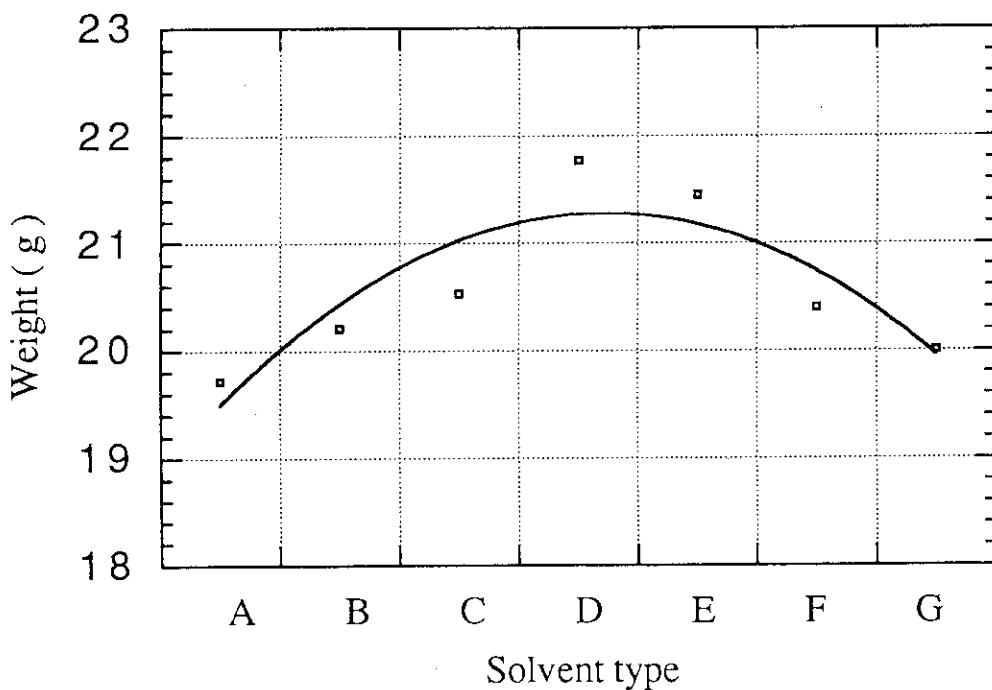


Fig.10 The influence of the solvent compositions upon the weight of  $\text{Li}_2\text{O}$  dissolved by 100 ml of mixture of acids.  
( See Table 2 for interpretation of solvent type )

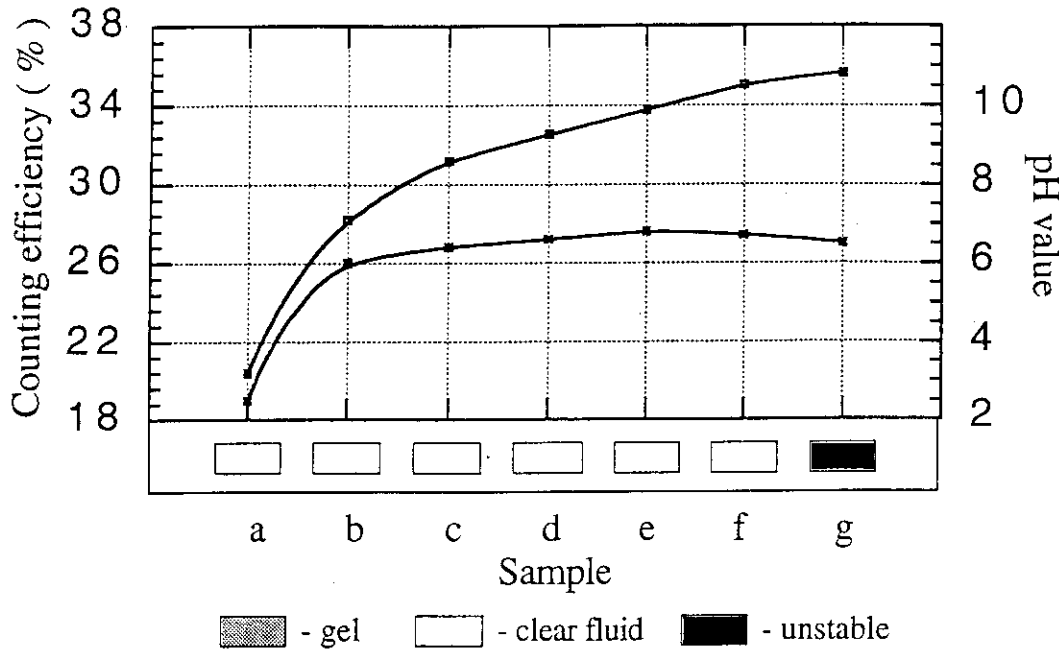


Fig. 11 Effect of the chemical compositions of samples on pH value, counting efficiency and sample compatibility. Samples "a" - "g" denote the solutions with 0.5 g LiOH H<sub>2</sub>O which is dissolved by the acid solvent with seven different acid volume ratios and mixed into 10 ml of Clear-sol.

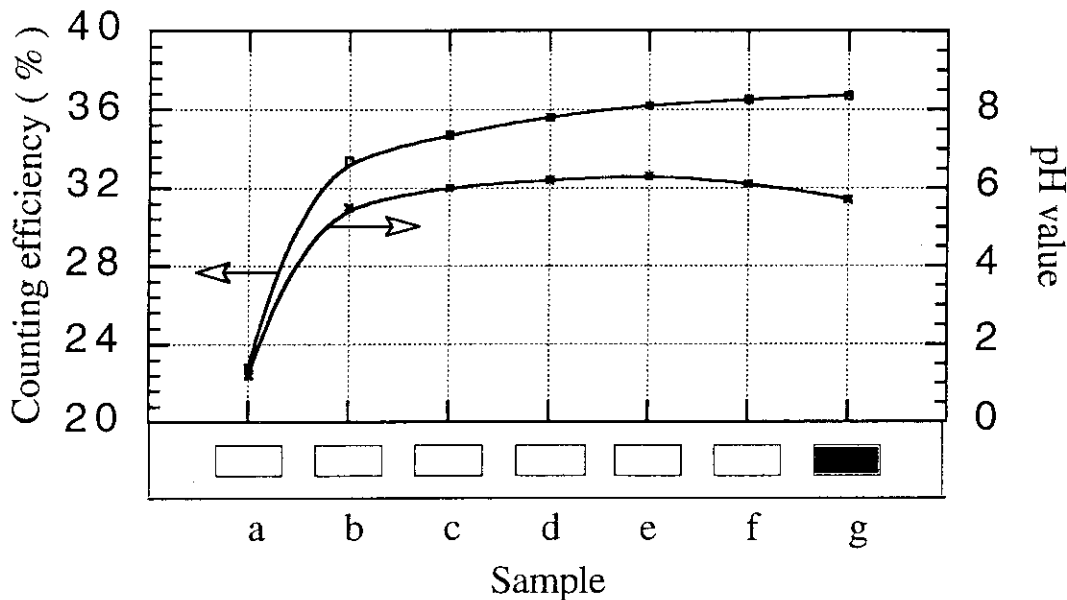


Fig. 12 Effect of the chemical compositions of samples on pH value, counting efficiency and sample compatibility. Samples "a" - "g" denote the solutions with 0.5 g LiOH H<sub>2</sub>O which is dissolved by the acid solvent with seven different acid volume ratios and mixed into 10 ml of Aquasol-II. ( See legends to Fig.11 for interpretation. )

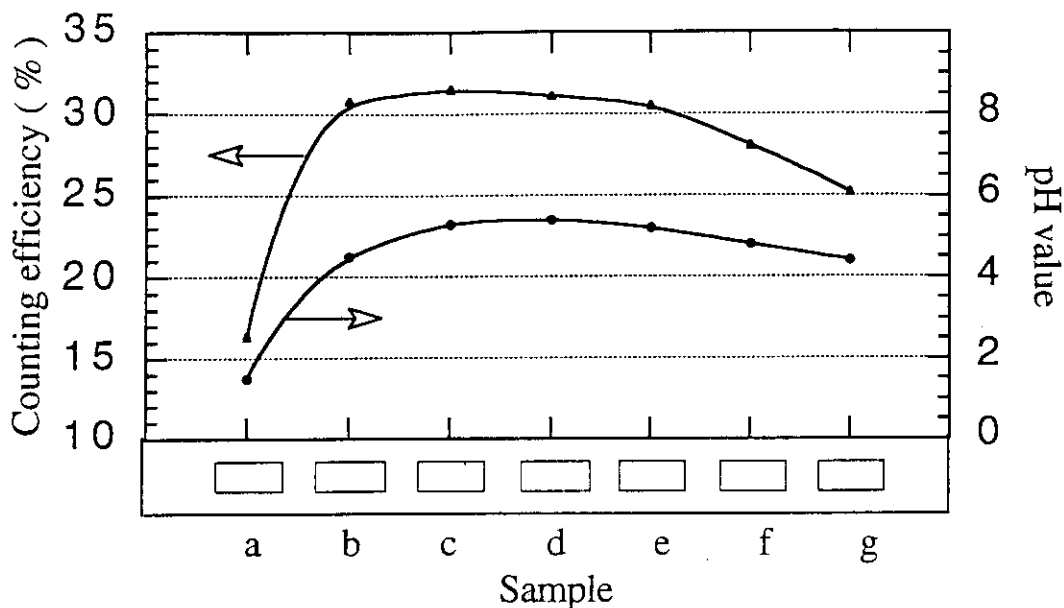


Fig. 13 Effect of the chemical compositions of samples on pH value, counting efficiency and sample compatibility. Samples "a" - "g" denote the solutions with 0.4 g  $\text{Li}_2\text{CO}_3$  which is dissolved by the acid solvent with seven different acid volume ratios and mixed into 10 ml of Clear-sol. ( See legends to Fig.11 for interpretation )

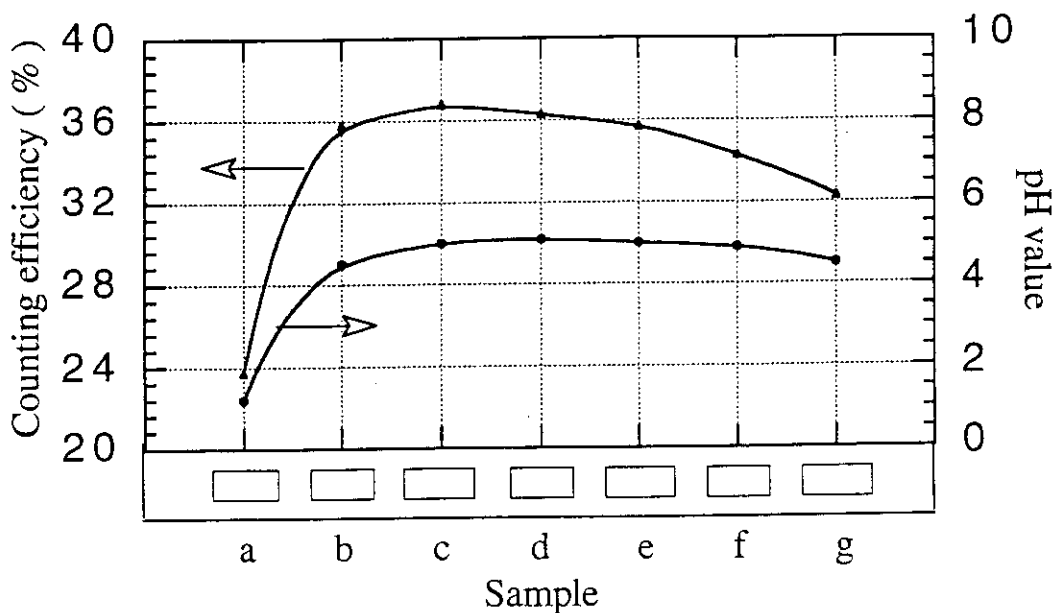


Fig. 14 Effect of the chemical compositions of samples on pH value, counting efficiency and sample compatibility. Samples "a" - "g" denote the solutions with 0.4 g  $\text{Li}_2\text{CO}_3$  which is dissolved by the acid solvent with seven different acid volume ratios and mixed into 10 ml of Aquasol-II. ( See legends to Fig.11 for interpretation )

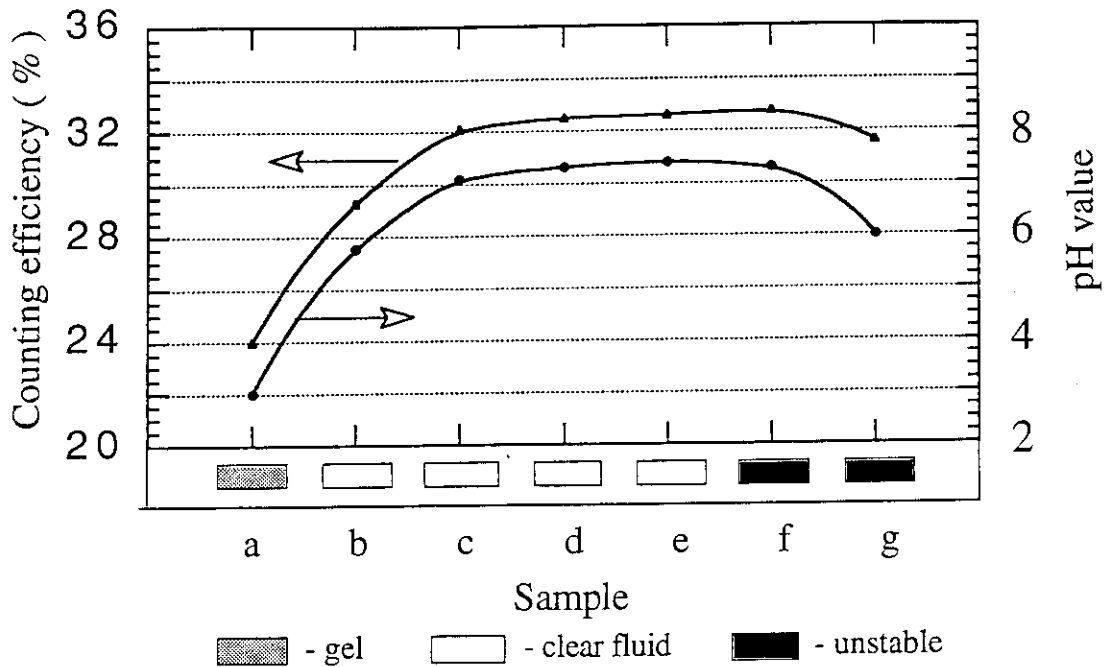


Fig.15 Effect of the chemical compositions of samples on pH value, counting efficiency and sample compatibility. Samples "a" - "g" denote the solutions with 0.2g  $\text{Li}_2\text{O}$  which is dissolved by the acid solvents with seven different acid volume ratios and mixed into 10 ml of Clear-sol.

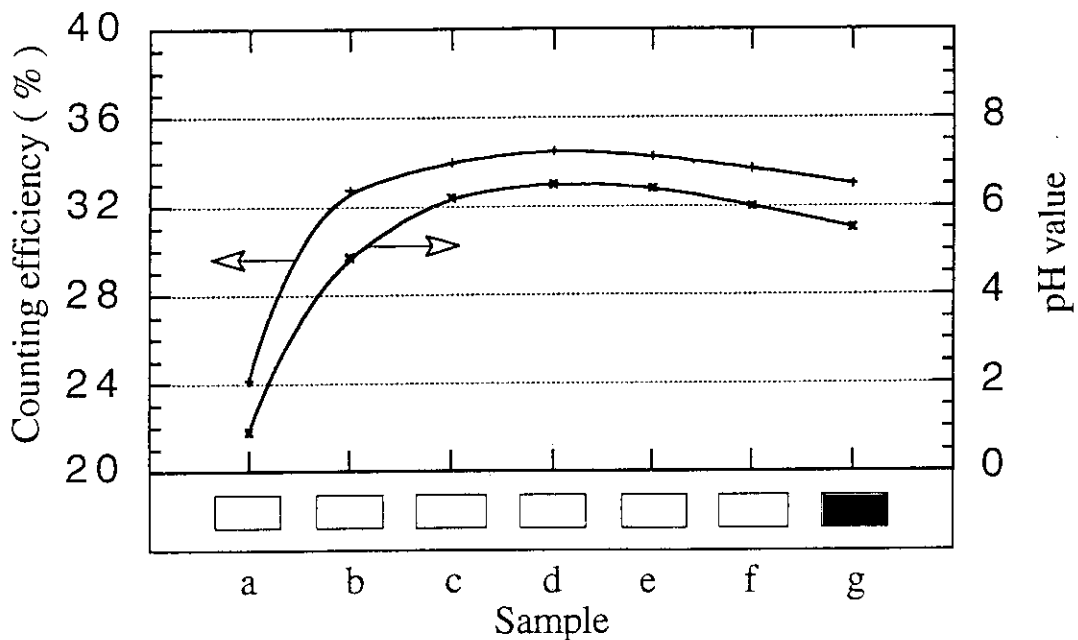


Fig.16 Effect of the chemical compositions of samples on pH value, counting efficiency and sample compatibility. Samples "a" - "g" denote the solutions with 0.2 g  $\text{Li}_2\text{O}$  which is dissolved by the acid solvent with seven different acid volume ratios and mixed into 10 ml of Aquasol-II. ( See legends to Fig.11 for interpretation )

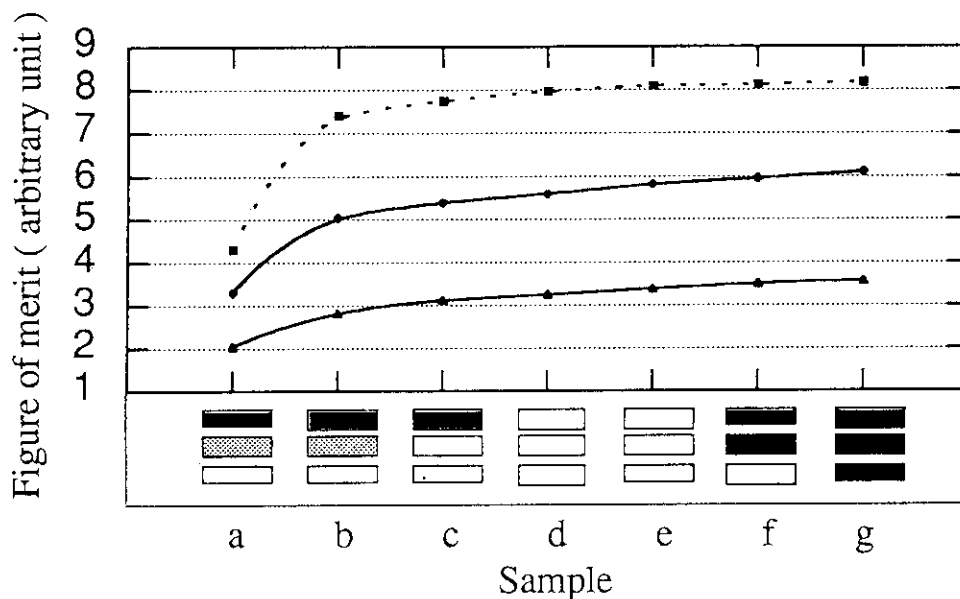


Fig.17 Effect of the chemical compositions of samples and increasing pellet weight on figure of merit and sample compatibility. Samples "a" - "g" denote the solutions with 0.5g (▲), 1.0g (●), and 2.0g (■)  $\text{LiOH}\cdot\text{H}_2\text{O}$  which are dissolved by the acid solvent with seven different acid volume ratios and mixed into 10 ml of Clear-sol. ( See legends to Fig.11 for interpretation )

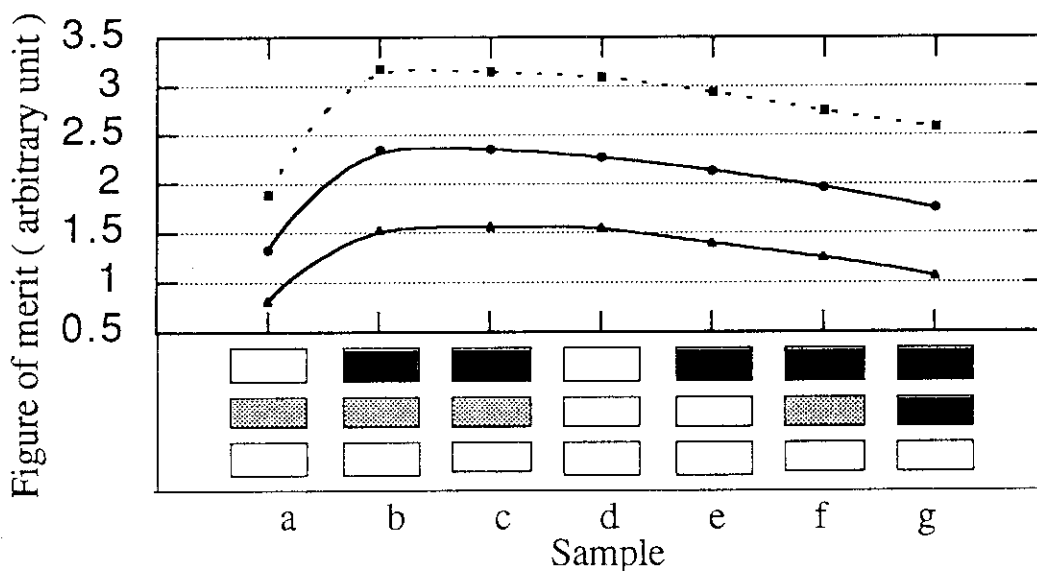


Fig. 18 Effect of the chemical compositions of samples and increasing pellet weight on figure of merit and sample compatibility. Samples "a" - "g" denote the solutions with 0.4g (▲), 0.8g (●) and 1.4g (■)  $\text{Li}_2\text{CO}_3$  which are dissolved by the acid solvent with seven different acid volume ratios and mixed into 10 ml of Clear-sol. ( See legends to Fig. 11 for interpretation )

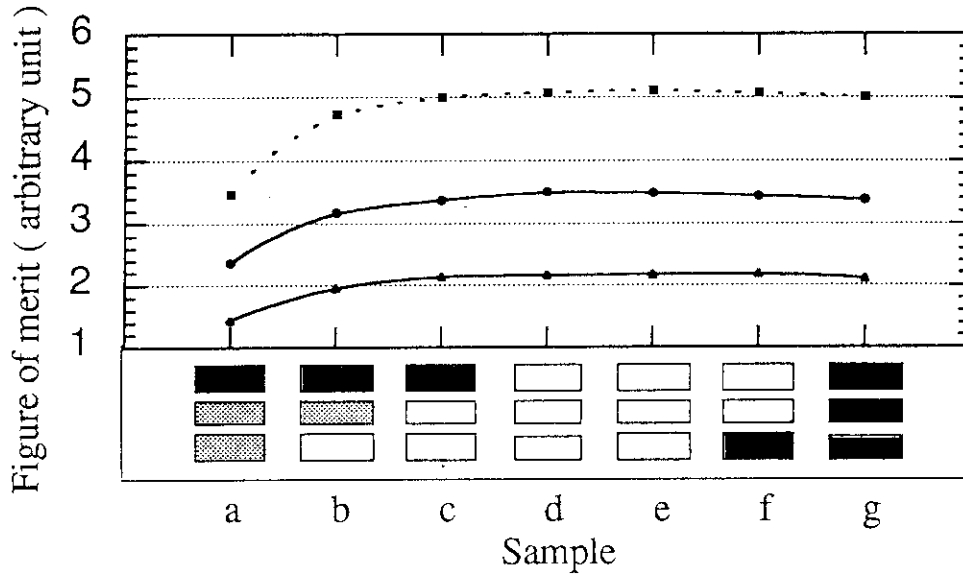


Fig.19 Effect of the chemical compositions of samples and increasing pellet weight on figure of merit and sample compatibility. Samples "a" - "g" denote the solutions with 0.2g (▲), 0.4g (●) and 0.8g (■) Li<sub>2</sub>O which are dissolved by the acid solvent with seven different acid volume ratios and mixed into 10 ml of Clear-sol. ( See legends to Fig.11 for interpretation )

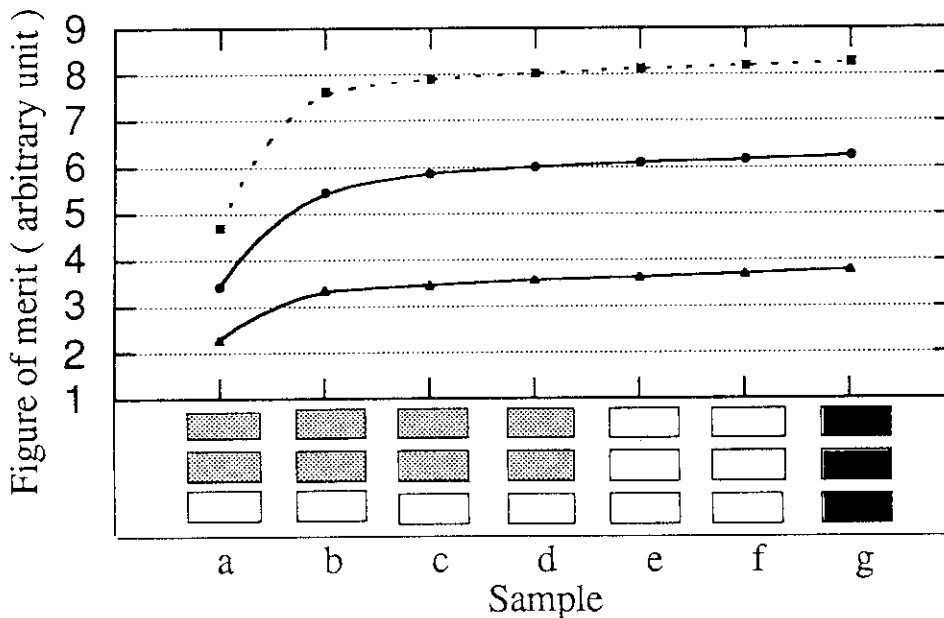


Fig. 20 Effect of the chemical compositions of samples and increasing pellet weight on figure of merit and sample compatibility. Samples "a" - "g" denote the solutions with 0.5 g (▲), 1.0 g (●) and 1.5g (■) LiOH·H<sub>2</sub>O which are dissolved by the acid solvent with seven different acid volume ratios and mixed into 10 ml of Aquasol-II. ( See legends to Fig.11 for interpretation )



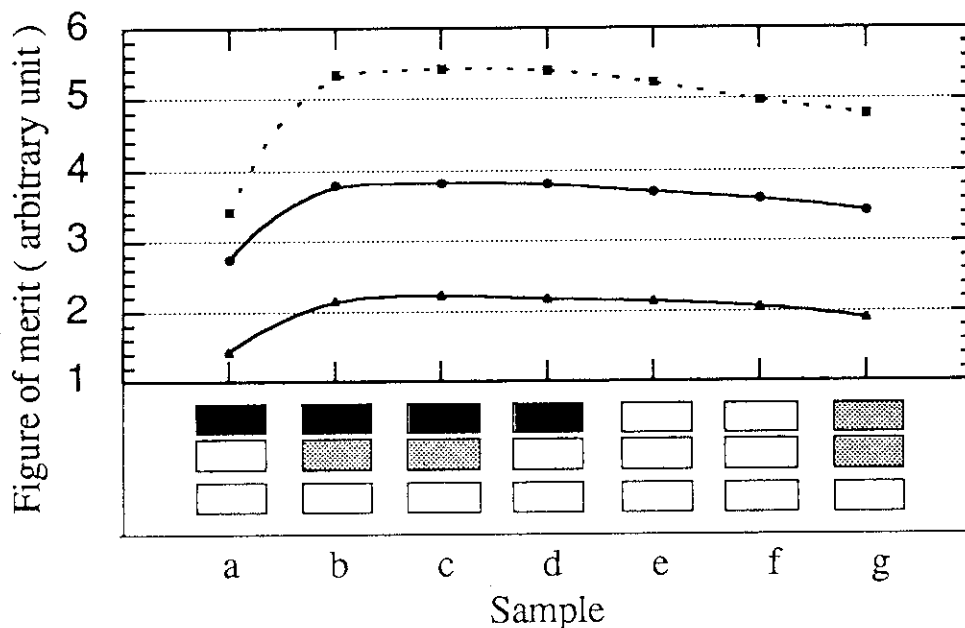


Fig. 21 Effect of the chemical compositions of samples and increasing pellet weight on figure of merit and sample compatibility. Samples "a" - "g" denote the solutions with 0.4 g (▲), 0.6 g (●) and 0.9 g (■)  $\text{Li}_2\text{CO}_3$  which are dissolved by the acid solvent with seven different acid volume ratios and mixed into 10 ml of Aquasol-II. ( See legends to Fig.11 for interpretation )

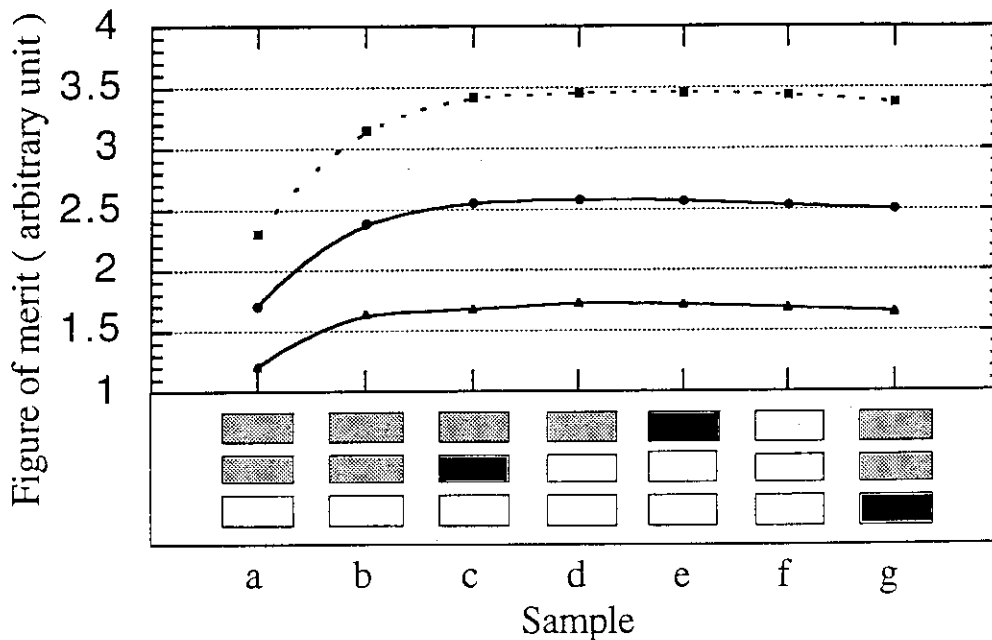


Fig. 22 Effect of the chemical compositions of samples and increasing pellet weight on figure of merit and sample compatibility. Samples "a" - "g" denote the solutions with 0.2 g (▲), 0.35 g (●) and 0.5 g (■)  $\text{Li}_2\text{O}$  which are dissolved by the acid solvent with seven different acid volume ratios and mixed into 10 ml of Aquasol-II. ( See legends to Fig.11 for interpretation )

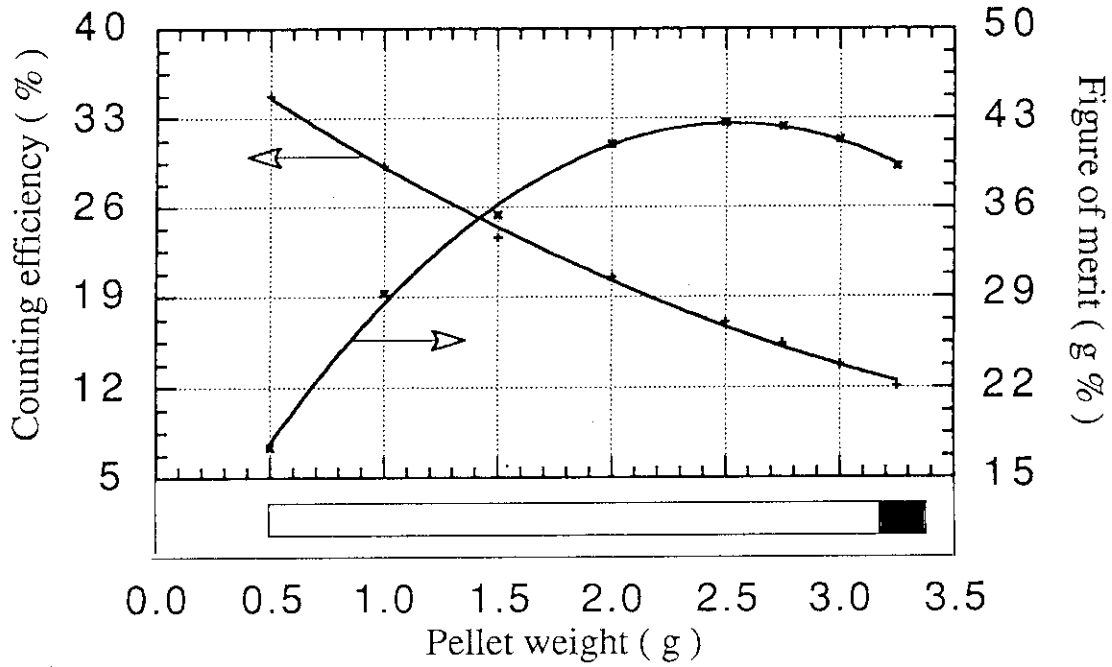


Fig.23 Tritium counting efficiency, figure of merit and sample compatibility versus  $\text{LiOH}\cdot\text{H}_2\text{O}$  weight. The pellet was dissolved by the acid solvent with optimum acid volume ratio and incorporated in 10 ml Clear-sol. ( See legends to Fig.11 for interpretation )

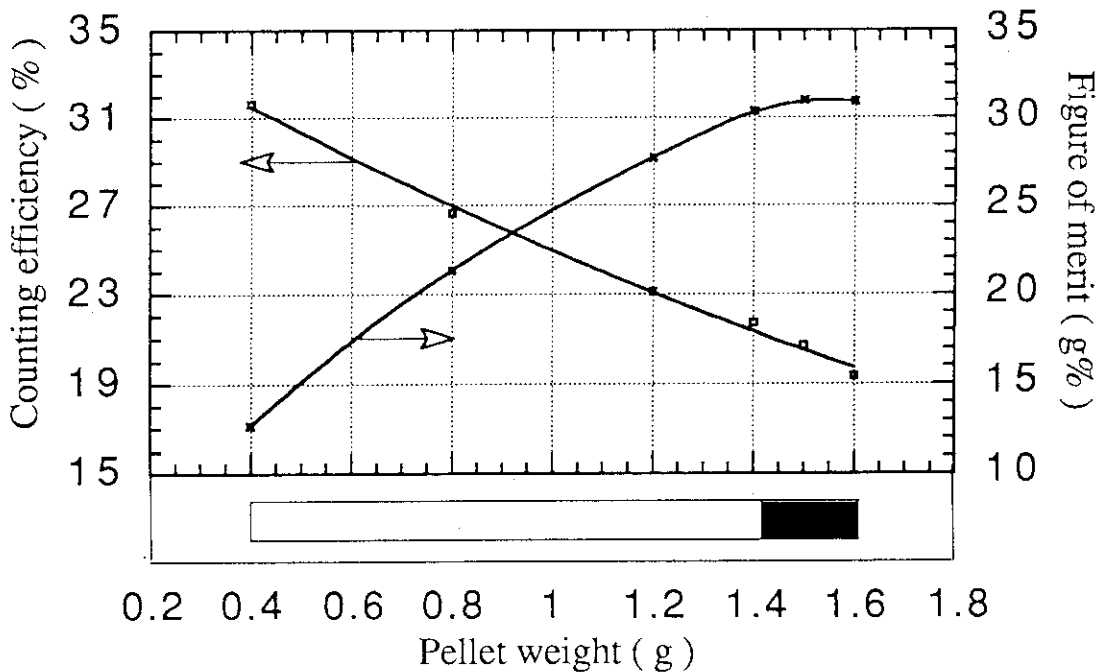


Fig. 24 Tritium counting efficiency, figure of merit and sample compatibility versus  $\text{Li}_2\text{CO}_3$  weight. The pellet was dissolved by the acid solvent with optimum acid volume ratio and incorporated in 10 ml Clear-sol. ( See legends to Fig.11 for interpretation )

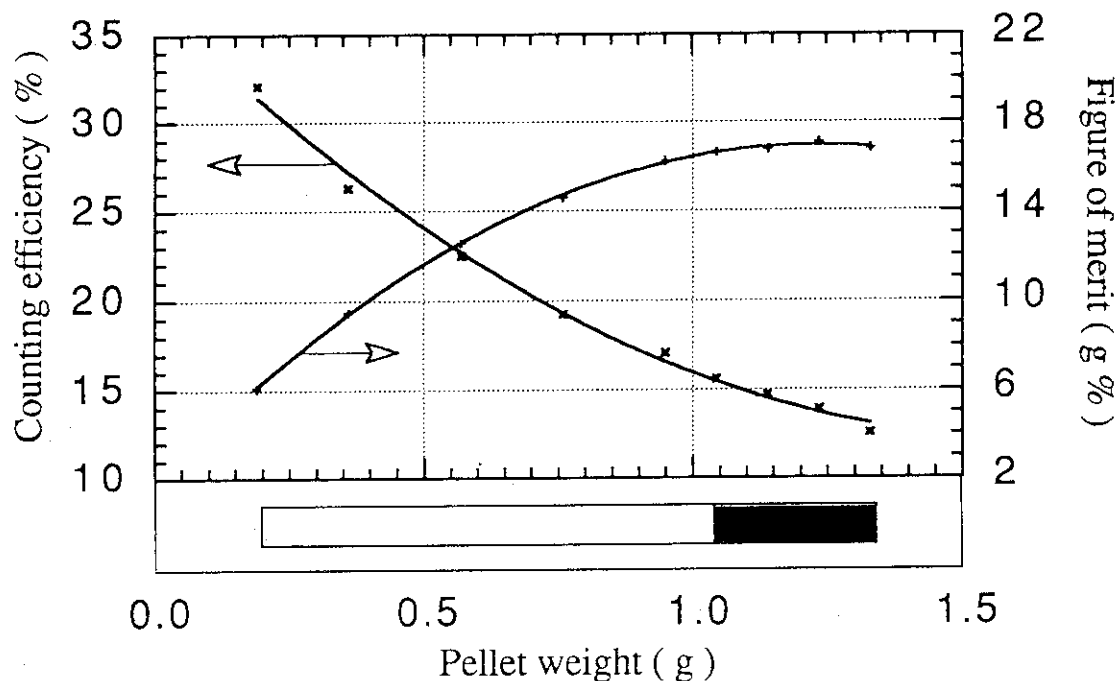


Fig. 25 Tritium counting efficiency, figure of merit and sample compatibility versus  $\text{Li}_2\text{O}$  weight. The pellet was dissolved by the acid solvent with optimum acid volume ratio and incorporated in 10 ml Clear-sol. ( See legends to Fig.11 for interpretation )

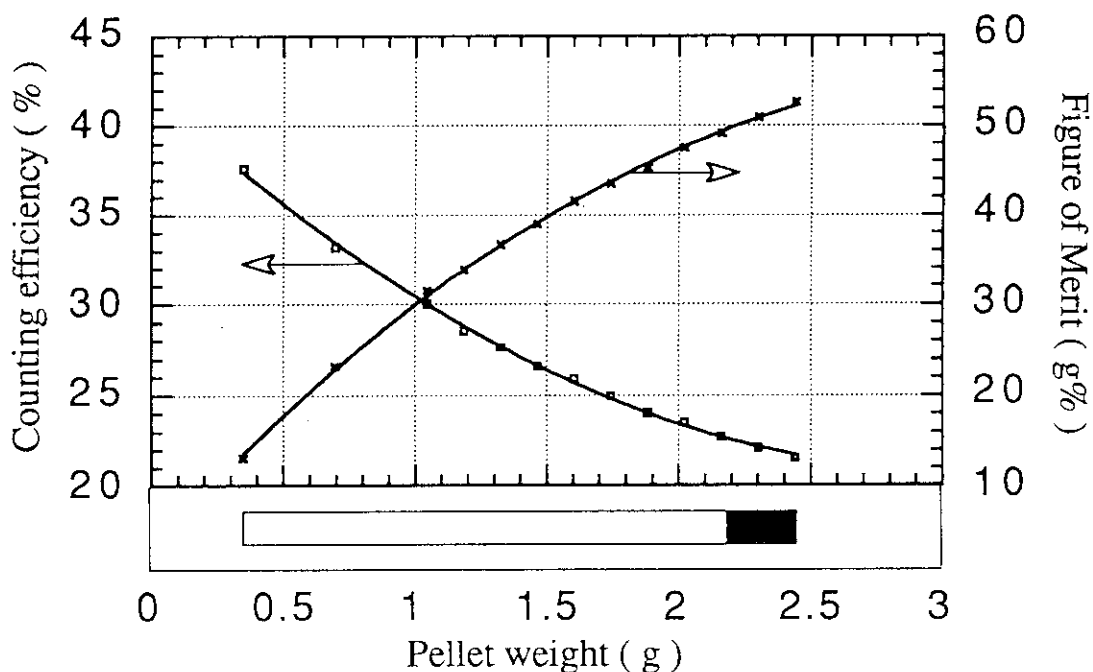


Fig. 26 Tritium counting efficiency, figure of merit and sample compatibility versus  $\text{LiOH}\cdot\text{H}_2\text{O}$  weight. The pellet was dissolved by the acid solvent with optimum acid volume ratio and incorporated in 10 ml Aquasol-II. ( See legends to Fig.11 for interpretation )

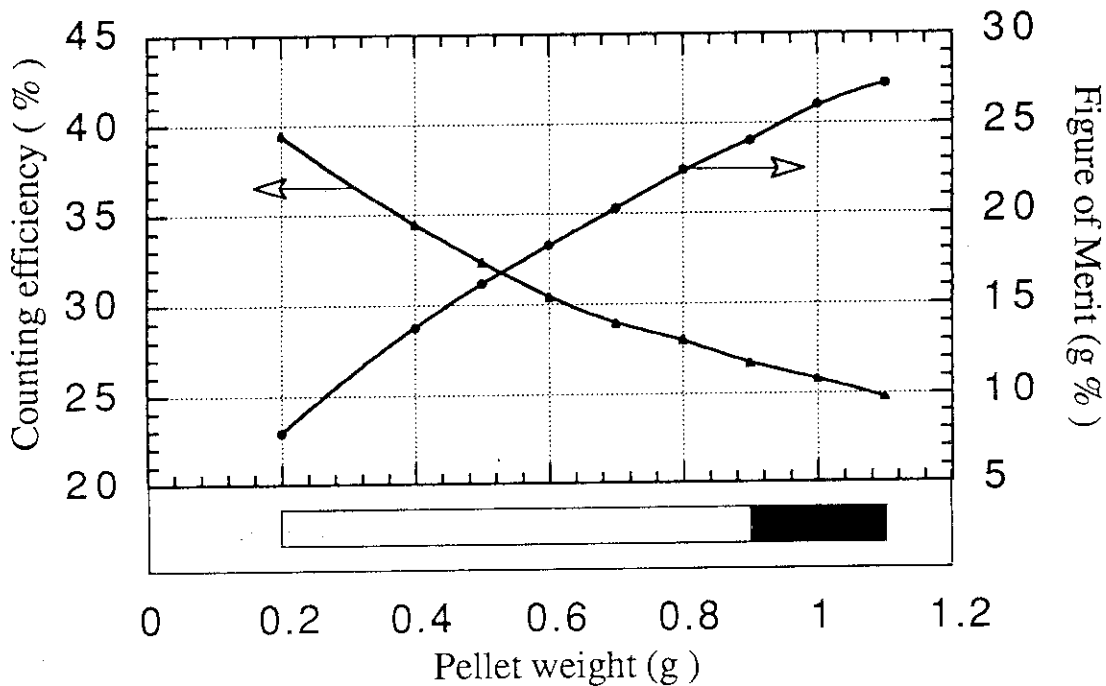


Fig. 27 Tritium counting efficiency, Figure of Merit and sample compatibility versus  $\text{Li}_2\text{CO}_3$  weight. The pellet was dissolved by the acid solvent with optimum acid volume ratio and incorporated in 10 ml Aquasol-II. ( See legends to Fig.11 for interpretation )

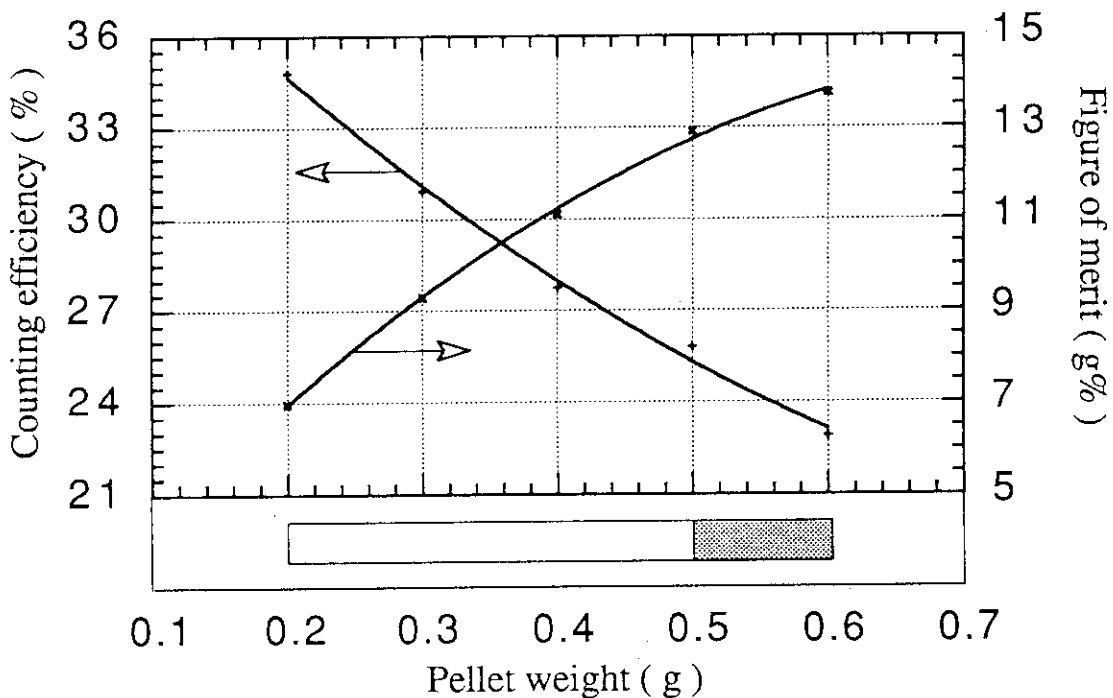


Fig. 28 Tritium counting efficiency, figure of merit and sample compatibility versus  $\text{Li}_2\text{O}$  weight. The pellet was dissolved by the acid solvent with optimum acid volume ratio and incorporated in 10 ml Aquasol - II. ( See legends to Fig.11 for interpretation )

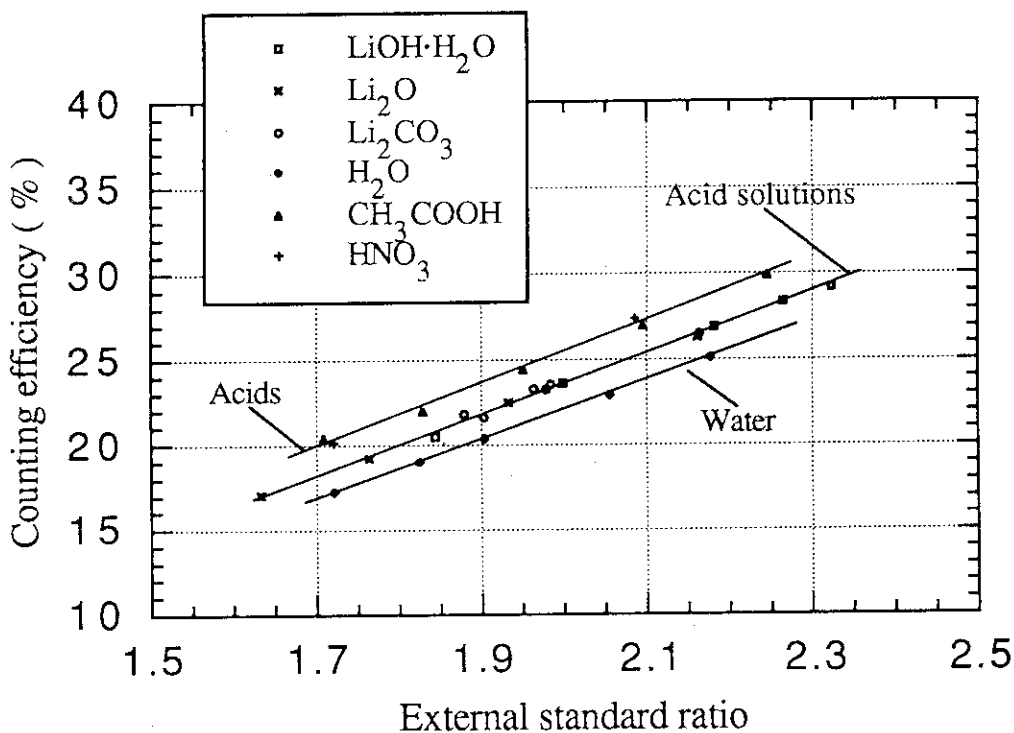


Fig. 29 The influence of the different chemical quenchers incorporated in the Clear-sol upon tritium counting efficiency.

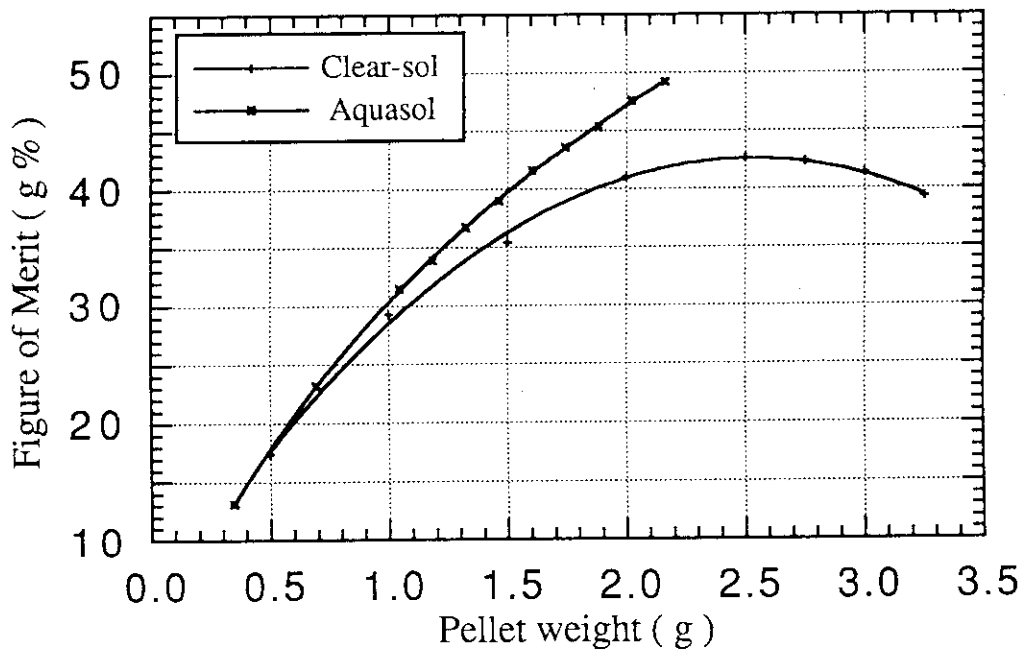


Fig. 30 Figure of Merit in clear fluid region versus  $\text{LiOH}\cdot\text{H}_2\text{O}$  weight. The pellet was dissolved by the acid solvent with the optimum acid volume ratio and incorporated in 10 ml Clear-sol or Aquasol-II cocktails.

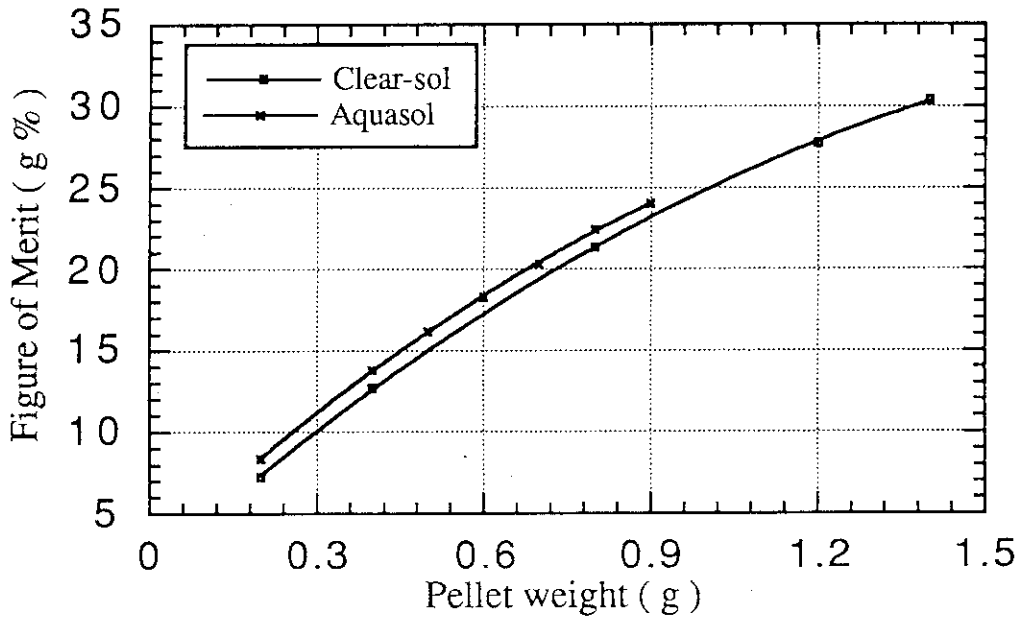


Fig. 31 Figure of Merit in clear fluid region versus  $\text{Li}_2\text{CO}_3$  weight.  
 The pellet was dissolved by the acid solvent with the optimum acid volume ratio and incorporated in 10 ml Clear-sol or Aquasol-II cocktails.

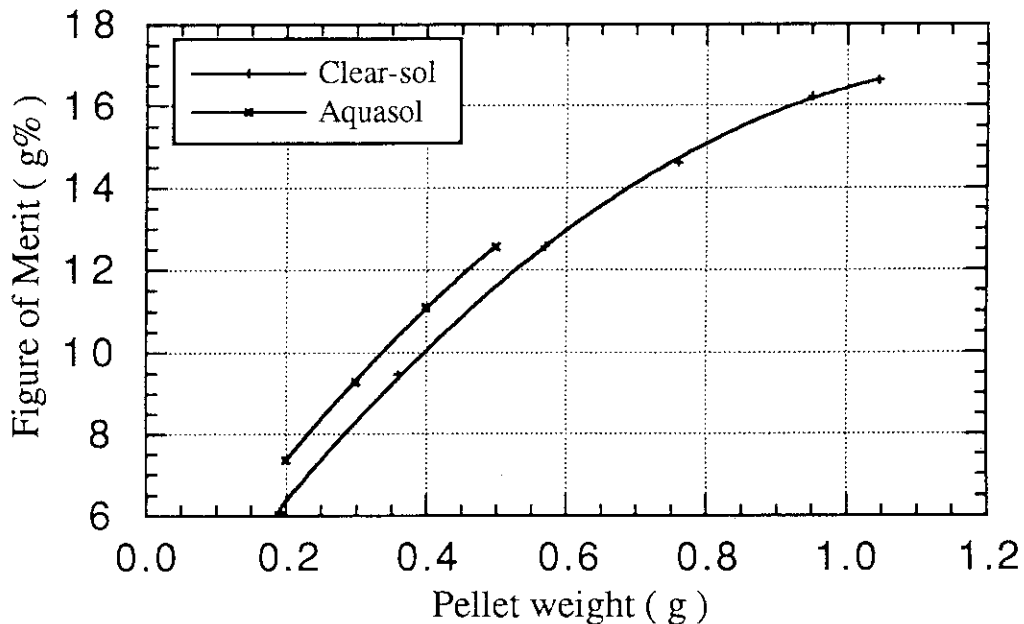


Fig.32 Figure of Merit in clear fluid region versus  $\text{Li}_2\text{O}$  weight.  
 The pellet was dissolved by the acid solvent with the optimum acid volume ratio and incorporated in 10 ml Clear-sol or Aquasol-II cocktails.

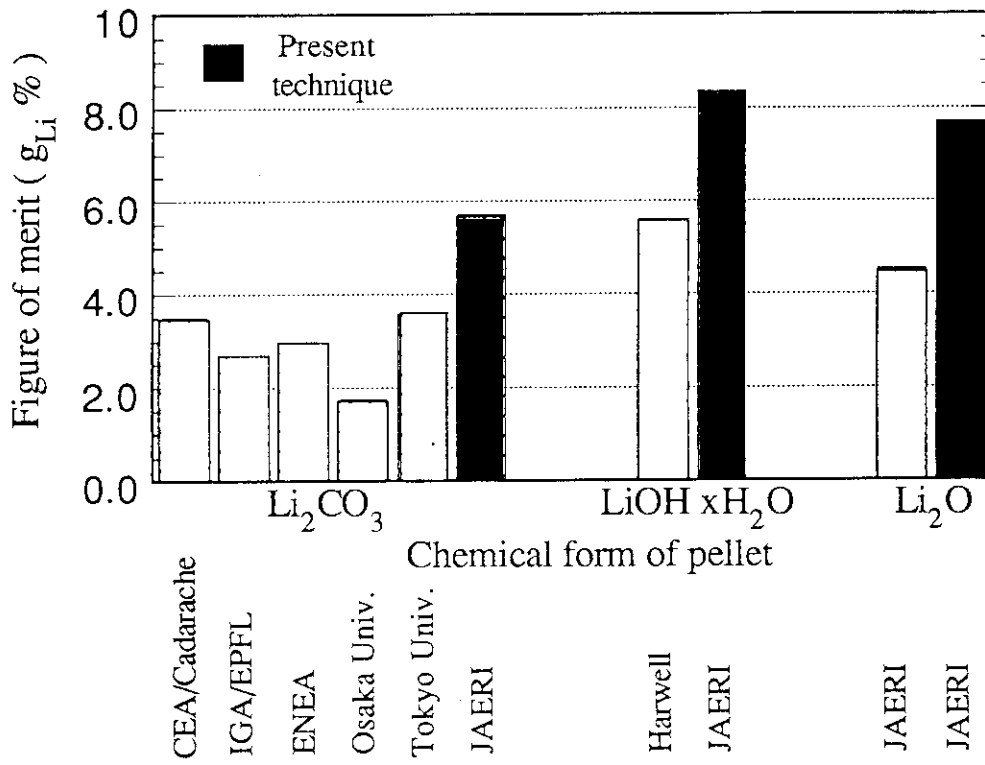


Fig. 33 Comparison of Figure of Merit for the measuring techniques of tritium.