# Fukushima Prefecture Initiative Project (FIP) concerning Study of Simple and Rapid Analysis Methods for Radionuclides

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#### FIP7: Study of Simple and Rapid Analysis Methods for Radionuclides

## ABSTRACT

In order to investigate the impact of the accident at the TEPCO's Fukushima Dai-ichi Nuclear Power Plant on the environment, a new analytical method, which has not been implemented in the current monitoring project, was introduced in Fukushima Prefecture, and the Research Department started acquiring technology to establish analytical techniques and evaluating the accuracy of the new analysis.

In this report, we present the status of analytical methods for the analysis of lowconcentration tritium using an electrolytic enrichment unit, the analysis of organically bound tritium, and the measurement of strontium-90 (Sr-90) using ICP-MS.

## **1. OBJECTIVES**

As a prefecture with nuclear power plants, Fukushima Prefecture has long history of monitoring on radioactive materials in the environment. In particular, following the accident at the TEPCO's Fukushima Dai-ichi Nuclear Power Plant in March 2011, radioactive materials were dispersed into the environment, and in accordance with the Emergency Monitoring Plan, etc., the analysis system for radioactive materials has been strengthened, focusing on highly urgent radioactive Cs, etc., and the analysis results have been made public.

Now, more than 10 years have passed since the accident, and while radiation levels and radioactive material concentrations in the prefecture are decreasing due to decontamination and other factors, a large amount of water containing tritium, which is technically difficult to remove, is stored in tanks on the premises of TEPCO's Fukushima Dai-ichi Nuclear Power Plant [1,2], and it is necessary to continue to investigate whether or not there is any impact on the environment [1,2]. Although the amount of Sr-90 released into the environment is said to be small compared to that of radioactive Cs [3,4], it is an important nuclide in the assessment of internal exposure because of its tendency to remain in the human body, mainly in bones.

However, detailed analysis of tritium and Sr-90, which are pure beta-ray emitting nuclides, is extremely time-consuming and complicated, and there are fewer examples of analysis than for radioactive Cs, so that simplification and speed up of analysis method is needed. On the other hand, the concentrations of these nuclides in the environment are very low, except for some areas in the vicinity of the Fukushima Dai-ichi Nuclear Power Plant, and detailed analysis of these nuclides requires more advanced techniques and time-consuming analysis.

Therefore, in order to enable more rapid and detailed investigation of the status of radioactive materials in the environment while maintaining a monitoring system that contributes to the safety and security of residents, this project, under the advice of the IAEA, will study the following analytical methods that are expected to be necessary in the future: the analysis method of low-concentration tritium using an electrolytic enrichment unit, analysis of organically bound tritium (OBT) and rapid and simple analysis method of Sr-90 using ICP-MS.

#### 2. TRITIUM ANALYSIS IMPLIMENTATION

## 2.1. Analysis of low-concentration tritium using tritium enrichment unit

## 2.1.1. Installation of tritium enrichment unit

It was reported that the tritium concentration in Fukushima Prefecture's environmental water, especially in seawater along the coast, increased immediately after the accident. However, the tritium concentration in environmental water has been decreasing over time and is currently at a level that is difficult to detect with the existing analysis methods used for monitoring by Fukushima Prefecture [5,6]. In order to improve prefecture's tritium analytical facility, it was decided to install a tritium enrichment unit in the Fukushima Prefectural Centre for Environmental Creation. Note that the system would particularly be useful for analysis of very low tritium concentration expected in seawater.

The prefecture aims to establish a system to produce tritium data with high sample throughput. The commercially available system permits only one sample processed one batch so that it is not ideal unit for the prefecture. Thus, it was decided to install the Tritium Enrichment Unit (nTEU) developed by the Isotope Hydrology Laboratory (IHL) of the IAEA with the technical supports from the IHL [7,8]. The principle of tritium enrichment by the nTEU is based on the alkaline electrolytic concentration method using metal electrodes. The nTEU is capable of processing up to 2000 cc of water samples that is reduced to 20 cc of water as electrolysis proceeds, achieving the tritium enrichment factor of about 100 is achieved. This pushes the analytical detection limit of tritium down by a factor of 100, thus is very effective compared with tritium enrichment with the electrolyte membrane system [9]. The unit can process 10 samples in one batch of processing which contribute to increase sample processing time as a whole. Following this decision, the prefecture purchased all necessary parts to build the unit in FY2017. Two experts from the IHL made their visits to assemble and tests the nTEU in the prefecture's facility (Picture 1). In addition, the prefecture personnel received thorough training in operating the equipment at the IAEA Isotope Hydrology Laboratory. The system became operational in 2017 at the Fukushima Prefectural Centre for Environmental Creation (Picture 2). Figure 1 presents an overview of the equipment and its specifications.



Picture 1. Two IAEA staff building the nTEU in the Fukushima Prefecture's laboratory.



Picture 2. nTEU being operated by a prefecture's personnel in the lab.

	Cathode Anode				
Overvie	w of the TEU				
Principle of enrichment	Water electrolysis using metal electrode (Cathode : Mild steel, Anode : Stainless steel)				
Number of samples/operation	10 samples in maximum				
Initial sample volume (in maximum)	2 liters /cell (Automatically refilled from 2L glass bottles)				
Final sample volume	around 10 - 20 mL(Variable)				
Enrichment speed	500 mL $\rightarrow$ 10 mL takes about 7days				
Tritium enrichment factor(2L) (reference value)	>100 (detection limits< $0.05TU = 0.006 \text{ Bg/L}$ )				
Size/Weight	W1,300×D575×H1,910 mm/ 300 kg				



# 2.1.2. Examination of measurement vials

After processing water samples with the nTEU, the water samples are mixed with scintillation cocktails, then subjected for the counting by liquid scintillation counters. The standard size of water sample vials for the liquid scintillation counters installed at the prefecture's laboratory is 100 cc. However, the nTEU yields 10 to 20 cc of enriched water at the end of processing. Thus, adaptation of the analytical procedure to small size vials (20 cc) was needed, while achieving the same level of low background counts (leading to accordingly low detection limit) as 100 cc Teflon vials. The prefecture tested two different vials listed below;

- Hitachi 20 ml low potassium glass vials a genuine part available from the prefecture's liquid scintillation counter (LSC-LB7).
- Plastic low-diffusivity polyethylene vials from PerkinElmer a standard vials used in the IHL for its low background count rate.

These two different vials are tested for their analytical backgrounds and detection limits. First, a series of standard samples with different quenching levels were prepared by making mixtures of the tritium standard solution  $(5.009 \times 10^2 \text{ Bq/g}, 10 \text{ mL})$  purchased from the Japan Radioisotope Association and a liquid scintillator Ultima Gold LLT (PerkinElmer). Then, a quenching correction curve (efficiency curve) was produced for each vial using these test samples. Finally, the LSC- Quenching correction curves (efficiency curves) were generated for each type of vial using the function built-in the prefecture's LSC

system (LSC-LB7). The validity of the obtained efficiency curves was examined by analyzing tritium concentrations of standard solutions of different concentration levels by adapting the efficiency curves produced as described above.

To verify the backgrounds and detection limits of two types of vials, non-tritiated water (provided by Japan Chemical Analysis Center) purified by distillation was mixed with Ultima Gold LLT at a ratio of 1:1, and measurements were made using LSC-LB7 for 500 minutes. The results of the measurement of non-tritiated water using each vial and the detection limits for that measurement are shown in Table 1. The low-diffusion polyethylene vials showed lower background count rates and lower detection limits than the glass vials. The detection limits for each vial are shown in Table 1. Based on these results, it was decided to use plastic vials for the analysis of actual samples. The use of small-volume (20 mL) vials also has the advantage of reducing the effects of chemical quenching after sample preparation, and shortening the time required for the analysis by shortening the time required for the sample to sit before measurement.

	Low-potassium glass vial	Low-diffusion polyethylene vial	Teflon Vial
	(Hitachi)	(PerkinElmer)	(Hitachi)
Vial volume (mL)	20	20	100
BG count rate (cpm) <sup>a</sup>	13.01±0.161	1.071±0.0463	2.236±0.0669
Counting efficiency (%)	23.75	23.28	27.64
Detection limit (Bq/L) <sup>b</sup>	4.87	1.47	0.353

Table 1. Comparison of background values among different vials

a) Mean  $\pm$  standard deviation of three 500-minute measurements, b) Value calculated from BG count rate and counting efficiency

## 2.1.3. Validation of analytical protocols with standard solutions with known tritium contents

In order to obtain parameters needed for tritium analysis including the electrolysis enrichment process, tritium standard solutions were analyzed. The tritium standard solution was diluted from a solution purchased from the Japan Radioisotope Association and treated as unknown samples which were subjected for a decay counting followed by the electrolytical enrichment process.

For the electrolytic enrichment by the nTEU, a constant current of 3.0 A was applied for the first one hour of operation, then the current was increased to 6.5 A for about 5 days. Then the applied current was reduced to 3.0 A for about 15 hours before the end of the operation. A processing time was adjusted in order to make a total integrated current to be 700 Ah. Through this process, amount of water sample was reduced from 250 mL to 13 mL. The processed water was then neutralized, distilled, mixed with 10 mL of sample water and 10 mL of Ultima Gold LLT, and allowed to stand for at least 4 hours in the measurement device before being subjected to tritium concentration measurement by the Liquid Scintillation counter. The results of this analysis are summarized in Table 2. The tritium-spike method was used to calculate the sample enrichment factors and associated parameters. The calculated enrichment ratio was applied to the cell in which the standard sample was analyzed to calculate the tritium concentration of the sample before enrichment. Details of the analysis results are shown in Table 3. The detection limit was also determined to be 0.108 Bq/L.

Table2. Calculation of tririum enrichment factors						
	Cell Number					
	1	10	Average			
Initial Sample Volume(Vi)(mL)	251.00	250.59				
Final Volume after enrichment( <i>Vf</i> )(mL)	13.65	12.97				
Volume Reduction(Vi/Vf)=N	18.39	19.32				
Tritium Concentration After Enrichment( <i>Tf</i> )(Bq/L)	128.3	130.1				
Tritium Concentration Before Enrichment( <i>Ti</i> )(Bq/L)	9.88	9.88				
Tritium Enrichment Factor(Tf/Ti)=Z	12.99	13.17				
Tritium Recovery(Z/N)=R	0.71	0.68	0.69			
Separation factor(β) <sup>a</sup>	8.37	7.72	8.05			
a) $\beta = (\log(Vf/Vi))/((\log(Tf \times Vf) - \log(T)$ Table3. Results of tritium measu	$i \times Vi) = location $	og(1/N)/logF standard soluti	on			
Initial Sample Volume(1	<i>Vi</i> )(mL)	249.	98			
Final Volume after enrichment()	<i>Vf</i> )(mL)	12.0	19			
Volume Reduction(Vi	i/Vf)=N	20.6	8			
Tritium Concentration After Enrichment( <i>Tf</i> )(I	Bq/L) <sup>a,c</sup>	$13.5\pm$	0.69			
Tritium Concentration Before Enrichment( $Ti$ )(Bq/L) <sup>b,c</sup> 0.941 $\pm$ 0.048						
Reference Value(Bq/L) <sup>d</sup> 1.00±0.028						
a) Value analyzed by liquid scintilla b) $Ti = Tf/N/R$	ation counter					
c) Analysis value ± counting error	(1σ)					
d) Reference value ± uncertainty (	k=1)					

2.1.4. Analysis on natural groundwater samples and intercomparison with the IAEA laboratory

As the final stage of the method development in the prefecture's lab, the intercomparison of the tritium analysis on natural groundwater samples were coordinated by the IHL, IAEA. At the Fukushima Prefecture's laboratory, approximately 400 mL of the groundwater sample was distilled under reduced pressure, and 300 mL was subjected to electrolytic enrichment. The electrolytic concentration was operated at a constant current of 2.9 A for about 1 hour as a starting step, then the current was increased to 7.0 A for about 6 days. The current was lowered to 2.9 A for about 15 hours just before the end of the operation. Electrolytic concentration was terminated when the integrated current reached 847 Ah. The enriched sample was neutralized, distilled, mixed with 10 mL of sample water and 10 mL of Ultima Gold LLT, and allowed to stand for at least 4 hours in the measurement device before being subjected to tritium concentration measurement. In this analysis, the tritium recovery R and tritium separation factor  $\beta$  obtained using the tritium-spike method were 0.61 and 6.51, respectively (both values are the average of two Cells). The detection limit obtained from the analysis of the tritium-free water was 0.115 Bq/L. The results of the analysis are shown in Table 4, together with the tritium analysis on the same samples at the Isotope Hydrology Laboratory of the IAEA. As also shown in Figure 4, the results taken by the Fukushima Prefecture and the IAEA showed a generally good agreement. The two samples by the Fukushima laboratory (FK-14 and -33) yielded a slightly lower tritium concentrations than IAEA results. It should be noted that these results still agreed each other if  $2\sigma$  or  $3\sigma$  criteria were applied. To understand reasons for this slight discrepancy would surely contribute to further improve the analytical methodology of the Fukushima laboratory.

Sample ID	Initial Sample Volume(Vi)(mL)	Final Volume after enrichment(Vf)(mL)	Volume Reduction (Vi/Vf)=N	Tritium Concentration After Enrichment( <i>Tf</i> )(Bq/L) <sup>a,c</sup>	Tritium Concentration Before Enrichment( <i>Ti</i> )(Bq/L) <sup>b,c</sup>	IAEA Results (Bq/L)
FK-6	300.40	13.13	22.9	5.02±0.695	0.345±0.038	0.313±0.015
FK-13	300.39	12.48	24.1	5.17±0.745	0.335±0.036	0.332±0.017
FK-14	300.40	12.70	23.7	3.30±0.709	0.217±0.035	0.264±0.015
FK-22	300.48	12.89	23.3	6.90±0.751	0.460±0.037	0.451±0.019
FK-33	300.30	12.84	23.4	7.48±0.762	0.500±0.038	0.608±0.020

Table4. Results of tritium measurements on Prefecture Laboratory and IHL, IAEA

a) Value analyzed by liquid scintillation counter

b) Ti = Tf / N/R

c) Analysis value ± counting error (1 $\sigma$ )



Fig. 4 Comparison of groundwater analysis results between Fukushima and IAEA. A 1:1 line is also shown (a dotted orange line).

## 2.1.5. Introduction of TRIMS, a tritium analysis information management system

As described above, the tritium analytical facility significantly improved their analytical capacity especially for the analysis of low-level tritium from water samples during the course of the FIP7 implementation. The final step of the FIP7 on this part is to establish a data management environment to ensure proper sample handling and data evaluation, as well as sustainable operation of the laboratory in general. For this purpose, the tritium analysis information management system (TRIMS = Tritium Information Management System) developed by the IAEA was adopted to the work environment of the Fukushima laboratory. The software runs on Microsoft's Access database management software and allows users to manage the progress of tritium analysis, including electrolytic enrichment, and calculate the analysis results by registering information related to the analysis in advance. Figures 5 and 6 show an example of the TRIMS frontend. The IAEA experts gave a series of on-line training sessions (13 lectures over 5 months of period) and went through all parameters and data evaluation steps available within the TRIMS. Currently, the tritium analytical system of the Fukushima prefecture and the TRIMS were integrated into a single workflow from sample managements, electrolysis enrichment, decay counting runs, and data reduction and evaluation.

ファイル	TRIMS		e <sup>6</sup> - n													11				
Home P	rojects D	Tistillation El	ectrolysis (	Counting	QAQC	Settings	Utilities	Exi	t A	? bout										
		Lab Analysi	s		QAQC	Settings	Utilities	Exit	A	bout										
» 🔚	TRIMS	Electrolysi	sRuns	ElysRU	N::3002															
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F	Run Pro	pertie								Staff invo	ved:			Re	marks:					
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F	<sup>o</sup> ro cedu	re Detai								Measurem	ent uncer	rtaint		Dat	e and U	ser Star	r		Enrichme	ent Parame
	Cell size (m 300 Pre-set Elec. charge 847   Aliquot vol. (ml 12 Final Elec. charge (At 847   NatOt (g.) 1.5 Final Elec. charge (At 847						Small Scal Large Sca Pipette (m	e (; 0.002 le ( 0.02 l): 0.0087	7		202 221	eated at/ 21/02/02 831	' <b>by: La</b> 20 22	ist modif 021/02/0 11831	F.: 2	0.9	7 ± 0.00			
5	Samples	Details:																		
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2 -	301	250	10041	1192.68	1494.4	1194.35	1	692.55	1994.1	0 1706 95		300.8	13.5		113.53	125.51	20±0.31		847	
3	302	350	10042	1194.24	1495.96	1195.81	1	671.03	1972.6	8 1685.33		300.9	13.4		112.82	125.5	********	Ē	847	
5	303	250	10043	1192.07	1493.78	1193.61	1	689.30	1990.9	7 1703.72		300.9	13.5		112.24	125.06	20±0.35		847	
5	304	1 0 0 0 9	10036	1195.35	1497.07	1196.67	1	677.17	1979.0	7 1692.04		301.1	14.0		113.36	126.49	19.4±0.4		847	
1	305	1 0 0 1 0	10037	1194.28	1496.04	1195.65	1	665.51	1967.4	0 1679.61		301.1	13.2		112.82	125.3	*******		847	
¥ C	306	1 001 1	10038	1192.45	1494.2	1193.8	1	673.21	1975.1	1 1687.50		301.1	13.4		112.27	124.97	122222222		847	
	307	1 001 2	1 0 0 3 9	1193.91	1495.65	1195.17	1	689.36	1991.3	4 1703.83		301.2	13.6		112.9	125.79	19.9±1.6		847	
	308	1 001 3	10040	1193.28	1495.16	1194.86	1	680.02	1981.8	2 1694.52		301.0	13.6		112.64	125.48	19.9±2.7		847	
	309	350	10049	1191.56	1493.29	1192.3	1	672.70	1975.1	9  1687.09		301.7	13.5		112.02	124.71	20.1±4.7		847	
	310	250	10050	1191.28	1493.04	1192.51		681.70	1983.7	3 1696.13		301.3	13.6		112.62	125.35	20±8		847	

Figure 5. TRIMS Electrolytic enrichment management function. This function is fully compatible with the nTEU installed in the Fukushima laboratory.



Figure 6. TRIMS QA (quality assurance and QC (quality control) functions. This function of the TRIMS allows users to monitor a long-term stability and consistency of the analytical system.

## 2.1.6. Detection limits versus total processing/analysis time

Analysis of tritium using an electrolytic enrichment has the advantage of measuring tritium at lower concentrations than Fukushima Prefecture's conventional methods. The enrichment factor depends primarily on the ratio of the initial water volume before electrolysis to the final enriched water volume, therefore higher enrichment factor (thus is the lower detection limit) is possible if the larger amount of water is used for the electrolysis. The major drawback is that it would take more processing time, so that it is important to find out the best balance between the total processing/analysis time versus time efficiency of the lab operation.

A compilation of detection limits and total processing times are provided in Figure

7 for four cases.

- (1) No enrichment and counting with 100 mL vial
- (2) No enrichment and counting with 20 mL vial
- (3) 250 mL initial volume and counting with 20 mL vial
- (4) 1000 mL initial volume and counting with 20 mL vial

Settling time before decay counting was set to 7 days for 100 mL vials and 1 day for 20 mL vial. This directly results in a shorter total analysis time for 20 mL vials without enrichment, but of course the detection limit needs to be compromised. For a direct counting method, 100mL is the largest vial size and detection limit of 0.35 Bq/L is possible. For the analysis with electrolysis, the the lowest detection limit of about 0.04 Bq/L is achieved but requires a total of more than 35 days are needed. Each analysis was performed with 10 samples, one analytical instrument each, and one person in charge.

In case of seawater samples with assumed tritium content of about 0.05 Bq/L [10], it was found that an initial sample volume of 1000 mL is desirable. Then, with electrolytic enrichment with 7.0 A, the total analysis time was about 35 days (about 5 days for pretreatment, 20 days for concentration and post-treatment, and 10 days for measurement).



Figure 7. Total analysis time for different analysis conditions and breakdown of required time for each processing step. Detection limits determined for each procedure are also shown (numbers with Bq/L unit).

## 2.1.7. Summary and future issues

As described above, the Fukushima prefecture laboratory established its own tritium analysis facility that can be used for low-level tritium analysis for example on seawater samples. The Prefecture personnel become quite knowledgeable in operation of nTEU and their LSCs, and are able to maintain the facility in a manner it is able to produce high quality data as validated by the intercomparison exercise. There seems be a minor issue to address in order to further improve their analytical results, perhaps by regularly repeating such intercomparison analysis with the IAEA laboratory. Operation of the analytical laboratory is only possible by continuous efforts to improve the existing protocols and to test and implement new and better analytical protocol to meet generally evolving and expanding analytical targets. The prefecture and the IAEA have agreed to continue this collaboration efforts for coming years even after the conclusion of the FIP7.

## 2.2. Analysis of organically bound tritium (OBT)

## 2.2.1. Overview of organically bound tritium analysis

Another form of tritium targeted in this project is so called the Organically Bound Tritium (OBT) that is the tritium incorporated into organic matter through photosynthesis in plants, etc., from tritium contained in water in the atmosphere, etc., and then transported between the organisms and the environment through diet, metabolism, etc. Figure 8 shows a schematic diagram of OBT transport. Figure 8 is a schematic diagram showing movements of tritium in environments including tritium incorporated into organic matter as OBT. In order to fully understand distribution and concentration of tritium in environment, it is important to have a capacity to quantify OBTs from various forms of materials. However, the OBT analysis requires tedious and time-consuming sample processing steps, there are only handful of laboratory globally. However, it is particularly important for the Fukushima Prefecture to have own capacity to quantify OBT in order to fully understand the distribution and movement of tritium in the environment, including the evaluation of the impact of the nuclear power plant accident in natural environment.



Figure 8. Examples of pathways resulting in organically bound tritium

## 2.2.2. Analytical tests using samples of known concentration

The Prefecture set up equipment required for sample processing required for OBT analysis, including a freeze drying and a tube furnace to combust samples under controlled temperature and oxygen pressure. Overall procedure was examined and refined with an IAEA expert who is the leading scientist in the field of OBT analysis and visited the Fukushima three times during the FIP7 implementation. The expert made valuable suggestions for operation and improvement of analytical protocol of the Fukushima prefecture laboratory (Figure 9). Then He provided samples with known OBT concentration as test samples. The test sample (green leaves) was processed following suggestions from him, and the combustion water were subjected for a direct decay counting. As shown in Table 5, Fukushima Prefecture's lab is able to actually recover sufficient combustion water for decay counting, and succeeded in the analysis with a reasonably small uncertainty. The results agreed with the result of external laboratory within a factor of two, which is in fact satisfactory given that there is certain level of inhomogeneity in OBT contents in provided samples and variability found in analysis in several different labs on the same samples.



Figure 9. Analysis flow of OBT

Table 5. Result of analysis by decay counting in comparison to result of external lab.

Fukushima Lab	External Lab
(This work)(Bq/L)	(Bq/L)
$23.7 \pm 1.04$	$14\pm 2$

# 2.2.3. Summary and future issues

As clearly pointed out by international expert during his visit to the Fukushima Laboratory, the OBT analysis requires significant amount of time, labor and manpower. Also, OBT analysis is a relatively new technique which is being developed and tested actively among international laboratories. In this respect, the prefectures initial OBT analysis on test samples are very encouraging. It would be important to continue this effort with active communication with other laboratory to establish a robust and sustainable workflow including a QA and QC strategies.

## **3. STRONTIUM-90 ANALYSIS IMPLIMENTATION**

## 3.1. Overview of measurement methods

In addition to the tritium analysis, development of analytical capacity for Strontium-90 is another important pillar of the FIP7. Among the nuclides released in nuclear power plant accidents, Sr-90 is a pure beta nuclide (a nuclide that emits only beta rays) and is more difficult to analyze than cesium and other radionuclides. The measurement method normally used in monitoring is very sensitive and has excellent detection limits, but the operation is complicated and takes about 4-6 weeks [11].

Since Sr-90 is an important nuclide for exposure assessment, rapid analysis, measurement, and provision of information are required, especially in emergency. The prefecture obtained an NexION 350S inductively coupled plasma mass spectrometer (ICP-MS, in Picture 3) (PerkinElmer, Inc., Shelton, CT, USA) with ultrapure  $O_2$  (>99.9999%) as a reaction gas in a collision-reaction cell. This system was designed by a group of scientists/engineers in Japan to facilitate the data production of Sr-90 in response to the Fukushima accident, and specifically designed to analyze environmental Sr-90 within a few days [12]. A leading scientist in the group is Prof. Takagai at Fukushima University.



Picture 3. NexION 350S inductively coupled plasma mass spectrometer installed in the Fukushima Prefecture's laboratory

Following the procedure developed and validated by Prof. Takagai's laboratory, Fukushima Prefecture's laboratory carried out own measurements by using the reference materials containing Sr-90. Figure 10 shows actual Sr-88 and Sr-90 signals detected by the Fukushima's ICP-MS from the reference material, demonstrating that the methodology has been adopted in a satisfactory manner. These signals are automatically converted into the radioactivity by using a house-made software to verify the validity of the analysis.



Figure 10. Example of Sr measurement by the ICP-MS (Left: Stable Sr (Sr-88), Right: Radioactive Sr (Sr-90))

## 3.2. Preparation of calibration curves

In order to obtain concentrations of Strontium isotopes, calibration curves should be created. A series of Sr-90 solutions with different concentrations was prepared using Sr-90 standard solution (4.061 Bq/g, 50.3 g) purchased from the Japan Radioisotope Association, and each solution was analyzed for Strontium isotopes using the methodology briefly described above.

The calibration curve determined for stable isotope of Sr (Sr-88) and radioactive Sr (Sr-90) both showed a good signal-to-amount linearity (Figure 10). Some research showed that it is possible to use the calibration curve determined by Sr-88 can be applicable to calculate Sr-90 concentrations [12]. However, as in Figure 11, the slope of calibration curve by Sr-88 is about 30 % larger than that by Sr-90, that would result in systematic underestimation of Sr-90 if calibration curve by Sr-88 were to be applied. Advantage of Sr-90 for preparation of calibration curve is that the mass spectrometer is calibrated against the same isotope as the analyte, leading a better quantification. However, on the other hand, if the calibration by non-radioactive Strontium isotope is possible, the laboratory operation becomes less complicated because it is possible to reduce the use of radioactive solutions in the laboratory.



Figure 11. Calibration curves created by running a series of standard samples with the ICP-MS.

#### 3.3. Analytical tests using environmental samples

In order to verify overall analytical procedure for environmental samples, a set of test analyses were made for Sr-90 in drinking water and that mixed with known amount of Sr-90. It is expected that Sr-90 is not present in drinking water and the analytical results confirmed that. Then, a Sr-90 solution was prepared and measured as unknown water samples. Calibration curves produced with a set of Sr-90 solutions are used to calculate Sr-90 concentrations in those test samples. The results are shown in Table 6.

sample	Added concentration (Bq/L)	Measurement result (Bq/L)	Recovery rate (%)
Drinking water	0	ND	-
Drinking water + Sr-90 solution	292	254	87

Table 6	. Results	of additive	recovery	tests
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## 3.4. Detection limits and analysis time

Analysis time needed to run the drinking water sample was approximately 20 minutes par sample. Detection limit for Sr-90 was also evaluated to be 0.9 Bq/L.

If 2 L of water with a Sr-90 concentration of 0.9 Bq/L is ingested per day, the internal exposure dose for one year is 0.02 mSv, which is well below the additional exposure dose limit of 1 mSv/y. Therefore, this method is applicable to emergency Sr-90 monitoring.

## 3.5. Summary and future issues

The Fukushima prefecture made a significant progress in establishing the analytical facility to analyze Sr-90 with the ICP-MS. The discrepancy between slopes of calibration curves by Sr-88 and Sr-90 might need to further explored, as in an emergency situation, the concentration range that need to be quantified might be much higher and also variable, so it would be useful to have an option to use Sr-88 for calibration standard. Also, it is planned to expand the range of environmental samples that can be analyzed by the developed facility (such as soil, airborne dust filters) so that the Prefecture will become ready for swiftly providing information about Sr-90 distribution and movement in a local environment in case of nuclear emergency.

#### 4. CONCLUDING REMARKS

The prefecture achieved three major goals set at the beginning of the project in a satisfactory manner – these are to establish analysis workflows for (1) Low level tritium in water, (2) Organically Bound Tritium in various forms of organic samples, and (3) Sr-90 in environmental samples. These accomplishments were made possible through comprehensive and continuous technical and scientific supports from Isotope Hydrology Section/Laboratory of the IAEA, on top of remarkable efforts made by the Prefecture's personnel who actually spend a lot of time in the laboratory. Fukushima prefecture is now capable of making their own evaluation of Tritium and Sr-90 independently by using their own laboratory and its staff member.

The established analytical method is expected to be used for detailed analysis of environmental samples in Fukushima prefecture for use in the field of environmental dynamics, etc., and as a monitoring method in emergency situations. Finally, the Fukushima Prefecture and the Isotope Hydrology Section/laboratory of the IAEA agreed on continuing this corporation to further refine or expand the analytical capacities of the prefecture.

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Appendix
Timeline of Activities Related to the IAEA Cooperation Project (FIP7)

Date	Location	Activities
29-30 June 2016	Fukushima	Pre-meeting to discuss about Practical
23-27 October 2016	Vienna	Laboratory tour and discussion on PA
25 October 2016	-	PA signed and project(FIP7) started (initially two years till 25 October 2018
17-21 April 2017	Fukushima	Visit by IAEA experts Tritium Enrichment Unit(TEU) assembled
5-18 June 2017	Vienna	Visit by Prefecture personnel Training in operation of the TEU
3-7 July 2017	Fukushima	Visit by IAEA experts Finalize installation of the TEU and conditioning runs started
15-18 May 2018	Fukushima	Visit by IAEA and external experts Technical mission for organically-bound- tritium(OBT) analysis method and strontium-90(Sr-90) analysis method using ICP-MS
1-5 October 2018	Fukushima	Technical mission for OBT analysis method by IAEA and external expert
7-13 October 2018	Vienna	Visit by Prefecture personnel Mission for electrolytic enrichment method and observation of groundwater sampling method
22 October 2018	-	Project extended for two more years
17-18 December 2018	Fukushima	Mission for electrolytic enrichment method, OBT analysis method and Sr-90 analysis method using ICP-MS Technical guidance and advice from domestic and international experts
3-5 July 2019	Fukushima	Mission for electrolytic enrichment method and OBT analysis method Technical guidance and advice from domestic and international experts
21 December 2020	-	Project extended for three more months – to catch up delay by the COVID situation
17 November 2020	Online(Vienna-	Online training by IAEA experts for
-10 March 2021	Fukushima)	installation and use of TRIMS software
17 March 2021	Online(Vienna- Fukushima)	FIP7 Final Meeting
31 March 2021	-	Completion of the FIP7