Development of analytical methods for radioactive waste samples from TEPCO Fukushima Daiichi Nuclear Power Station site at JAEA Okuma Analysis and Research Center

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Abstract

JAEA is currently constructing the Okuma Analysis and Research Center near the TEPCO's Fukushima Daiichi Nuclear Power Station (1F) site according to the Japanese Government's "Mid-and-Long-Term Roadmap". The Okuma Analysis and Research Center (Okuma Center) analyzes radioactive samples from the 1F site. Laboratory-1 is for radioactive analysis of low and medium level radioactive rubbles and secondary wastes.

Radiometric analysis is applied to measure the content of radio nuclides in the samples. The laboratory-1 starts operation with 200 samples per year at the beginning, and the number of samples will increase with time. Due to the large number of samples to be analyzed, the Okuma Center will face shortage of analytical engineers.

JAEA has studied application of the triple quadrupole ICP-MS, ICP-QQQ-MS, for determination of long half-life nuclides which does not need pre-treatment. For short half-life nuclide determination, radiometric analysis has advantage in terms of sensitivity compared to ICP-QQQ-MS, and JAEA have developed automated sample preparation system to minimize complicated analytical process.

Combination of ICP-QQQ-MS and the automated sample preparation system can be expected to promote the analytical operations efficient, leading to obtain precise analytical data and decrease in radiation exposure.

1. Introduction

The Tohoku Earthquake and the tsunami that followed occurred in March 2011. The surge from the tsunami caused a loss of cooling system in TEPCO's Fukushima Daiichi Nuclear Power Station (1F), units 1-4 reactors. The loss of cooling system allowed the fuel in unit 1-3 reactors at least partially meltdown and caused hydrogen explosions [1]. As the results of the explosions, a large amount of radioactive materials was released into the environment and contaminated a vast area containing the 1F site. Decommissioning of 1F site is in progress according to the Japanese Government's "Mid-and-Long-Term Roadmap" (Roadmap). Radiometric analysis of fuel debris and radioactive wastes such as contaminated rubble and secondary wastes from water processing is needed for the decommissioning. The Roadmap assigned the construction of a hot laboratory and analysis to the Japan Atomic Energy Agency (JAEA). The hot laboratory, "Okuma Analysis and Research Center", will be constructed near the 1F site [2].

The "Okuma Analysis and Research Center" near the 1F site, which provides analytical data to characterize the radioactive wastes for decommissioning of the 1F. The Okuma Center campus consists of three buildings; administrative building, Laboratory-1 and Laboratory-2. Laboratory-1 is to obtain analytical data of radioactive nuclide contents in rubbles and

secondary wastes from liquid waste treatment facility.

Radioactive waste samples from the 1F site are planned to be analyzed by mainly conventional radiometric analysis at the Laboratory-1. Gamma spectrometry of HPGe detector is used to identify gamma emitters. Beta emitters with negligible or no gamma-ray emission are planned to be determined by beta activity, which is measured by a liquid scintillation counter or a low background gas flow counter. These instruments require chemical separation before the measurement. Therefore, each nuclide needs complicated pre-treatment process, purification followed by roughly separation process.

For long half-life nuclides, coupled plasma-mass spectrometry, ICP-MS, has an advantage of sensitivity over radiometric analysis. And ICP-MS could eliminate the need for isolation of radio nuclides.

For short half-life nuclides, such as Sr-90 and Ni-63, conventional radiometric analysis should be used, which requires complicated pre-treatment process typically including dissolution, filtration and extraction. If this time-consuming process could be automized and standardized, efficiency of pre-treatment process could be improved. JAEA studied to optimize the automatization and/or standardization process for the short half-life nuclides.

This paper describes development of analytical methods, ICP-MS for long half-life nuclides and automated/standardized analytical system for short half-life nuclides, to be applied in Laboratory-1 of Okuma Analysis and Research Center.

2. Analytical methods

2.1 Conventional Analytical Methods

Okuma Analysis and Research Center will start operation analyzing 200 samples, collected in 1F site, each year with 38 nuclides at the beginning. The number of samples is planned to be increased more than 1,000 samples per year. Figure1 shows schematic analytical process for samples from the 1F site. The first step after pulverization is extraction of target radio nuclide: H-3, C-14 and I-129, lower boiling point elements, are evaporated from the pulverized samples and recovered with cold trap or gas washing. Analytical samples for Cl, Se and Tc are put into solution by alkaline fusion. The rest of other 32 nuclides are dissolved by acid. After the samples are brought into solution, separation or purification should be done, each nuclide is determined with mainly radiometric analysis.

Decay of these 38 nuclides to be measured are listed in Table 1. Analytical instruments are planned to employ radiometric analysis, namely liquid scintillation counter, low background gas flow counter, alpha spectrometer and gamma spectrometer. All these instruments based on radiometric analysis are very reliable, which have been used many years.

Gamma spectrometry of HPGe detector is used measuring gamma rays to analyze the gamma emitters after just simple pre-treatment. Beta emitters with very low, or no gamma-ray emission, are planned to be measured its activities by beta counting methods, such as a liquid scintillation counter and a low background gas flow counter. It requires chemical isolation of element before the measurement, because beta counter has poor energy resolution. When alpha decay nuclides emit close energy of alpha particles, chemical purification is also required, even if alpha spectrometry has some energy resolution. Electron capture nuclides would be measured low energy X-rays (e.g. Low energy Ge detector). Purification is necessary to avoid increasing background signals by Compton scatter of gamma rays. From the results, nuclides, except of gamma measurement nuclides, should be purified before counting its radio activities.
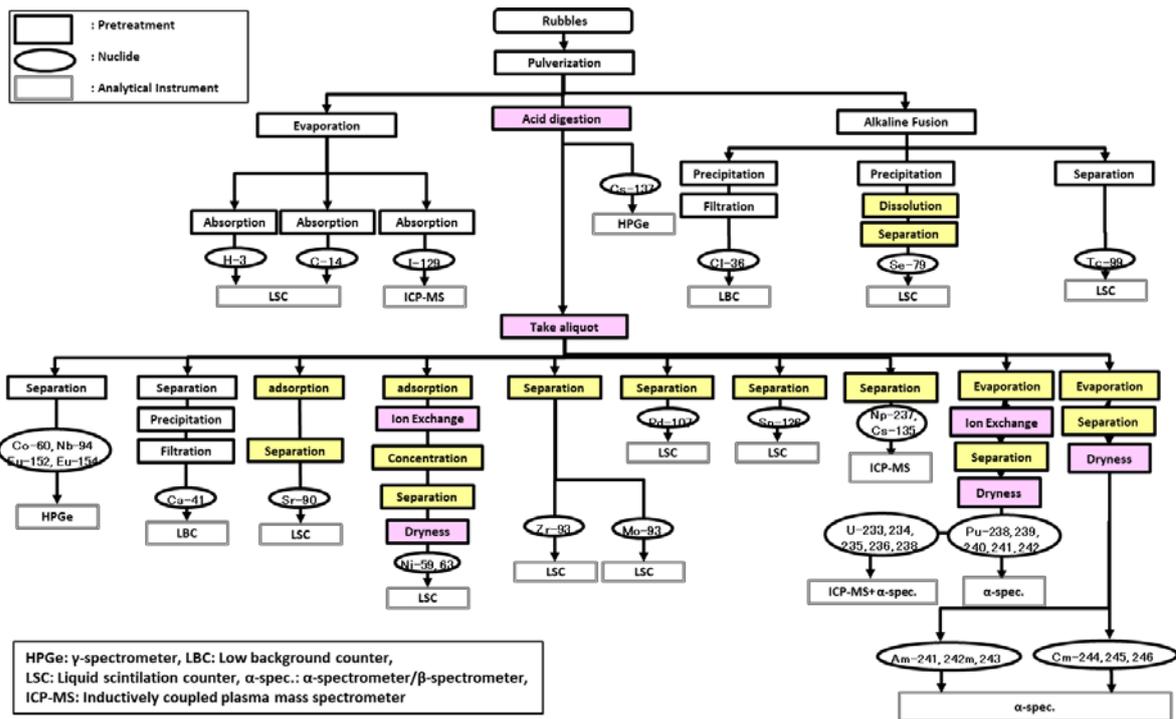
Figure 1 Possible scheme using conventional analytical methods for the 38 nuclides

Table 1 Decay of Nuclides

Type of decay	Analytical instrument (candidate)	Nuclide (Half-life in year, 5.7e3 reads 5.7×10^3.; Energy in MeV)
Beta	Liquid scintillation counter or Low background gas flow counter	H-3(12.3; 0.019), C-14(5.7e3; 0.16), Cl-36(3.0e5; 0.71), Ni-63(100; 0.067), **Se-79(3.0e5; 0.15)**, Sr-90(29; 0.55), **Zr-93(1.5e5; 0.061), Tc-99(2.1e5, 0.29), Pd-107(6.5e6; 0.033), Sn-126(2.3e5; 0.25), 129-I(1.57e7; 0.154), Cs-135(2.3e5; 0.27),** Sm151(90; 0.077), Pu-241(14; 0.021)
	Gamma Spectrometer	Co-60(5.3; 1.2, 1.3), **Nb-94(2.0e4; 0.71,0.87), Sn-126(2.3e5; 0.088),** Cs-137(30; 0.66), Eu-152(14; 0.344), Eu-154(8.6; 0.12), Am-241(4.3e2; 0.060),
Alpha	Alpha spectrometer	**U-233(1.6e5; 4.8), U-234(2.5e5; 4.8), U-235(7.0e8; 4.4), U-236(2.3e7; 4.5), U-238(4.5e9; 4.2), Np-237(2.1e6; 4.8),** Pu-238(88; 5.5), **Pu(239(2.4e4; 5.2), Pu-240(6.6e3; 5.2), Pu-242(3.8e5; 4.9),** Am-241(4.3e2; 5.5)**,Am-243(7.4e3; 5.3),** Cm-244(18; 5.8)**, Cm-245(8.4e3; 5.4, Cm-246(4.8e3; 5.4)**
Electron Capture	Low energy γ-ray/X-ray spectrometer	**Ca-41(1.0e5), Ni-59(1.0e5), Mo-93(4.0e3)**

2.2 Analysis for Long Half-Life Nuclides by ICP-QQQ-MS

Inductively Coupled Plasma Mass Spectrometry(ICP-MS) is one of the powerful analytical instrument with high sensitivity. Ohtsuka compared detection limit of radiation counting method with ICP-QMS [3,4]. ICP-QMS has an advantage for determine nuclide concentration in the samples of long half-life, approximately more than 1,000years, listed with underline in table 1.

As long as using ICP-QMS of single quadrupole mass spectrometer, isobaric interference could not be ignored. table 2 listed nuclides to be measured and its estimated interfering ions. Because Zr, Mo and Nb are straight atomic number, Zr-93 is the one of the most difficult nuclides to be analyzed by mass spectorometer. When Zr-93(half-life 1.5×10^5Y) is measured by ICP-MS, Nb-93(stable) and Mo-93(half-life 4.0×10^3Y) will interfere. Due to analyze Zr-93, we selected triple quadrupole mass ICP-MS (QQQ-ICP-MS: Agilent 8900). Two quadrupole mass separators (QMS) are tandemly arranged, and octapole-based collision reaction cell is set between them, as shown in figure 2. Sample solution was atomized and introduced into plasma. Elements in the solutions are heated and ionized. Ions are led to the first QMS, that is used as a mass filter to pass through only ions of mass number 93, such as [Zr-93], [Nb-93], [Mo-93], [Zr-92H] and [Mo-92 H]. Then these ions are adjusted with reaction gas to be different mass number. The second QMS separates generated ions and collected by electron multiplier detector.

We studied possibility of Zr separation from Nb and Mo with QQQ-ICP-MS using reaction gas. Instrumental conditions were listed Table 3 and elemental standards were used natural elements. Figure 3 shows the mass spectra of m/Z= 90 to 132. Upper mass spectrum is measurement results of Zr, Nb and Mo without adding reaction gas. There are several peaks of Zr, Nd and Mo of m/Z= 90 to 100. Lower mass spectrum is the results of using O_2 gas as reaction gas. Zr peaks were found as a ZrO ion, and Mo, Nb peaks are found NbO_2 and MoO_2 ions. This result showed the Zr separation from Nb and Mo is possible by QQQ-ICP-MS using O_2 gas.

From the results, QQQ-ICP-MS can make possible to measure several nuclides, simultaneously. Therefore, separation process can be simplified so as not to separate each nuclides and purification is unnecessary.

Table 2. Nuclides to be measured and its interfering ions.

nuclides	interfering ion
Nb-94	$[^{94}Zr]^+$, $[^{93}Zr^1H]^+$
Zr-93	$[^{93}Mo]^+$, $[^{92}Zr^1H]^+$, $[^{93}Nb]^+$
Mo-93	$[^{93}Zr]^+$, $[^{92}Zr^1H]^+$, $[^{93}Nb]^+$
Tc-99	no interfering ions
Pd-107	$[^{91}Zr^{16}O]^+$, $[^{91}Zr^{16}O^1H]^+$
Sn-126	no interfering ions

Table 3. Analytical conditions for ICP-QQQ-MS

RF power: 1,500W
Carrier gas (Ar): 0.7 L/min
Signal integration time: 1.0 sec
Reaction gas (O_2) :0.3mL/min

Q1 : Quadrupole1
Q2 : Quadrupole2
ORS : Octopole Reaction Cell system, collision/reaction cell
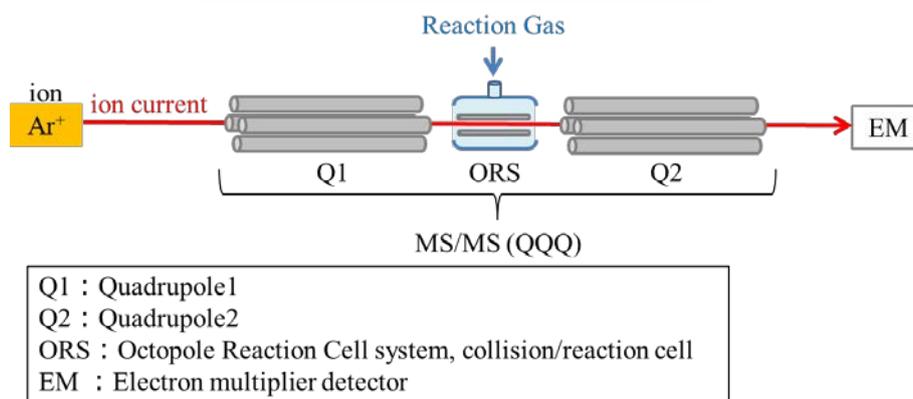EM : Electron multiplier detector

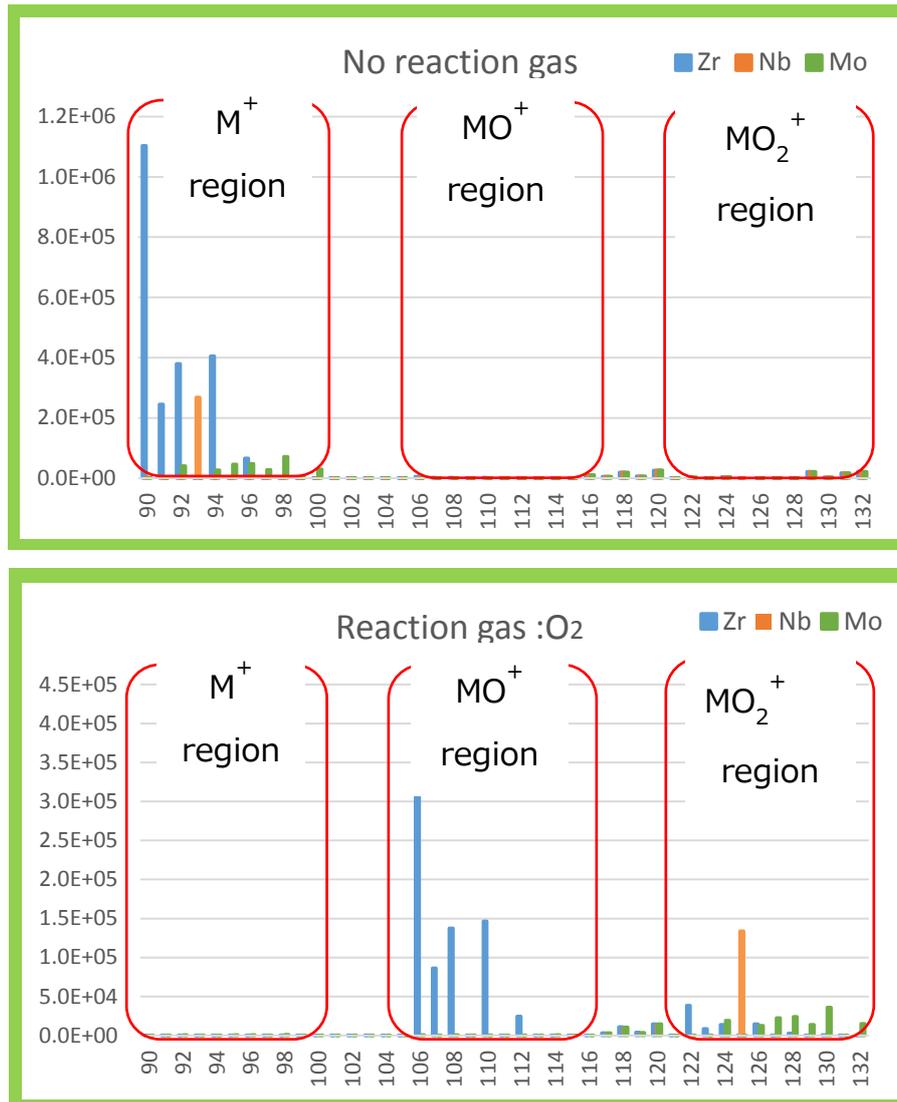Figure 2.   Schematic diagram of ICP-QQQ-MS

Figure 3.   Mass spectra of ICP-QQQ-MS

2.3 Analysis for Short Half-Life Nuclides by automated sample preparation system

Since, ICP-MS has not enough sensitivity for the measurement of short half-life nuclides, radiometric method should be applied to determination. Beta measurement nuclides Ni-63(half-life 100Y) and Sr-90(half-life 29Y) must be separated and purified with a long and complicated separation/purification process before the radiometric measurement. We planned automated preparation system to deal with precise and safety measurement, even if increasing number of analytical samples.

Sample preparation automation has been developed using robotic system [5]. The robot moves just the same process as human's movement based on the analytical manuals. Other automate analysis system is designed assembled in one unit, which is focused on one separation scheme such as for Sr purification. Recently, micro tip analysis is studied to be measuring automatically. These systems achieved fully automated, what man should do is just set samples. These systems are suit for routine sample preparation of similar samples, and must be preparation process should be fixed. However, at Okuma analysis research center, analysis process will be adjusted to the sample condition after the operation, because, sampling plan should be decided the decommissioning processing steps. Automated pre-treatment system should be flexible design to respond change of analytical process.

Analytical process is made up of seven units listed in table 4. Ni-63 preparation process found to be consisted of these 7units operation. We selected suitable instruments for each analytical unit and unified the container. Ion exchange and/or solid extraction instrument for inorganic sample preparation could not find any commercial instrument with acid resistance. The instrument should be prepared, because the process is the most time-consuming and important, which requires well trained person as well. We designed and produced automated solid extraction instruments experimentally, based on conventional solid extraction system for organic analysis as shown in figure 4.

The instrument is build acid resistance materials and have local ventilation system for acid vapor. The instrument can control the flow rate of the solutions, using the container lid to cover the column. Flow control system is important to achieve precise recovery and to estimate the extraction time as well.

Table 4. Analytical fundamental process for preparation

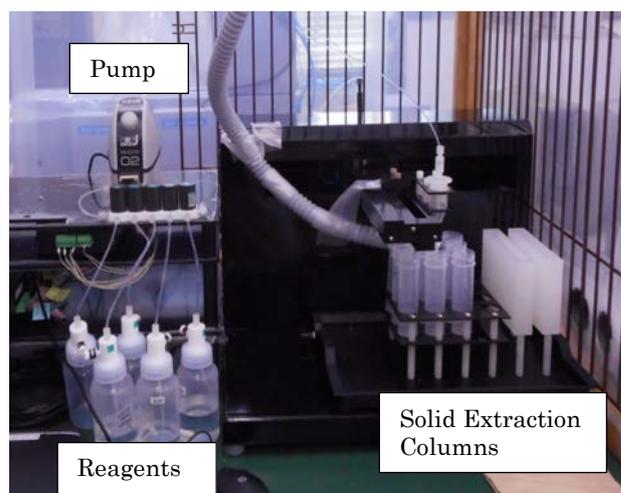| No.	Analytical preparation Unit
①	Dissolution
②	Taking Aliquot and Dispensation
③	Reagents addition
④	Filtration
⑤	Heating, Evaporation
⑥	Volume adjustment
⑦	Ion exchange, solid extraction

Figure 4. Solid phase extraction system

2.4 Proposed Analytical process

For long half-life nuclides, ICP- QQQ-MS has an advantage of sensitivity over radioactivity analysis. We studied this method, as an alternative radiation analysis for long half-life nuclides.

For short half-life nuclides, we studied optimized system of combined each rationalized step to be applied analytical sample preparation process for short half-life nuclides, focused on separation/purification step.

We proposed simplified separation process, combined with ICP-QQQ-MS and automated sample preparation system, as shown in figure 5. Application of ICP-QQQ-MS can make possible to reduce the process from 20 to 12. And each process can be used automated sample preparation system.
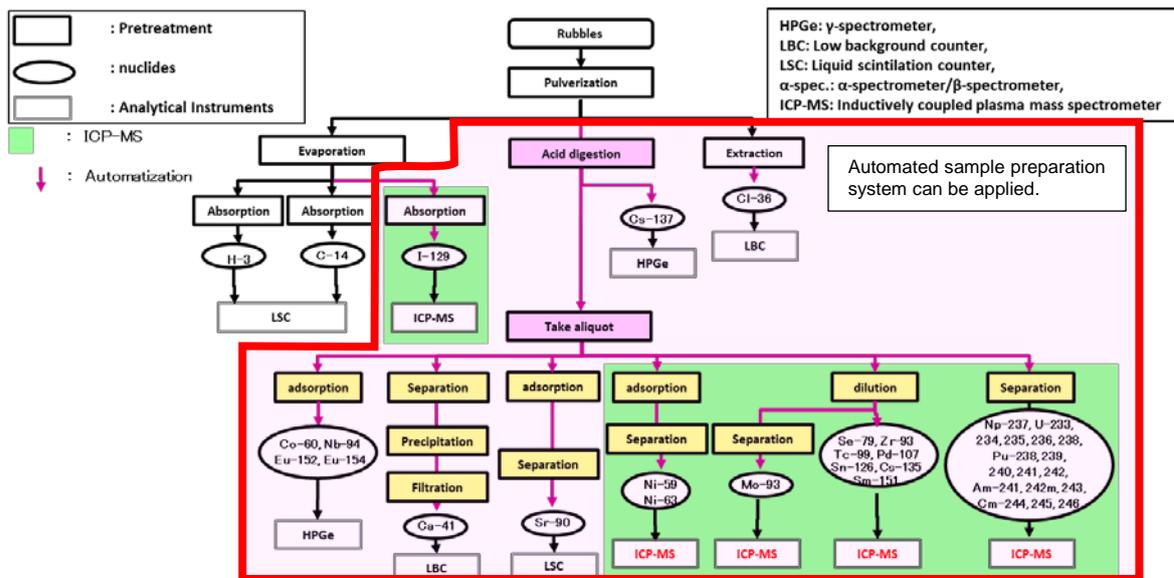
Figure 5. Simplified separation process with introduction of ICP-QQQ-MS and automated sample preparation system.

3. Summary

ICP-QQQ-MS can measure several nuclides in a same time and it reduce the purification process for long half-life nuclide. Short half-life nuclides must be measured by radiometric method after separation and purification from the solutions, because, detection limit of radiometric analysis for short half-life nuclides is lower than that of ICP- QQQ-MS.

Automated sample preparation system is applied to pre-treatment process of short half-life nuclides. All analytical pre-treatment process for nuclides build in fundamental treatment units in combination.

4. Conclusion

- Separation condition of Zr, from Mo and Nb, in the ICP-QQQ-MS was found without chemical purification, using O_2 as a reaction gas. It could measure several nuclides at one time. Pre-treatment process could be simplified and separation time could be shortened.
- Automated system can be applied to purification and/or separation process for nuclides analysis. That could make possible to obtain precise analysis to avoid human error.
- Combination of ICP-QQQ-MS and automated sample preparation system make possible to achieve obtaining precise data and decreasing in radiation exposure.

Acknowledgement

References

[1] Tokyo Electric Power Company Holding web page.

http://www.tepco.co.jp/nu/fukushima-np/outline/2_1-j.html
accessed on June 9, 2017

[2] Inter-Ministerial Council for Contaminated Water and Decommissioning Issues, "Mid-and-Long-Term Roadmap towards the Decommissioning of TEPCO's Fukushima Daiichi Nuclear Power Station", June 12, 2015.

[3] Y.Ohtsuka,"Present Status and Prospects of Ultralow Level Radioactivity Measurement," Radioisotopes, 55, 651 (2006) in Japanese.

[4] T.Ohno and Y.Muramatsu,"Determination of radioactive cesium isotope ratios by triple quadrupole ICP-MS and its application to rainwater following the Fukushima Daiichi Nuclear Power Plant Accident," J. Anal. At. Spectrrom, 29, 347 (2014)

[5] Surugaya, N. et al. "Automated gravimetric sample pretreatment using an industrial robot for the high-precision determination of plutonium by isotope dilution mass spectrometry" Anal. Sci., vol. 24, 739 (2008)