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- Technical Support for the Joint IAEA/Japan On-site Analytical Laboratory at the Rokkasho Reprocessing Plant -

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Confirmation of the availability of an analytical technique, Pu(VI) spectrophotometry for HALW －Technical Support for the Joint IAEA/Japan On-site Analytical Laboratory at the Rokkasho Reprocessing Plant－ (Technical Document)

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Abstract

The Agency requested the Tokai Reprocessing Plant (TRP) to confirm the applicability of three kinds of analytical procedure for Pu(VI) spectrophotometry in On-Site Analytical Laboratory (OSL) at Rokkasho, in order to obtain accurate plutonium(Pu) concentration in High Active Liquid Waste (HALW). Three analytical procedures, ①Calibration method, ②Nd internal standard method and ③Reduction method, were tested.

The measurement sample was prepared by adding the known amount of plutonium in the actual HALW after removing original Pu by solid extraction. We measured the Pu concentration in the sample by three methods and calculated the accuracy and precision. The results of each method are summarized as follows :

① Calibration method

Plutonium concentration calculated by the calibration method agreed with that by adjusted concentration.

② Nd internal standard method

Accurate results were obtained by this method. The error of pretreatment, especially dilution, has not influenced on the Pu measurements.

③ Reduction method

The measured Pu concentrations were higher than those by adjusted.

From the comparison with these results, the calibration method is the most simple and rapid in the three methods. Analysis time was within 1 hour including sample preparation. The detection limit, with the calibration method, was 1.3mgPu/L in the actual HALW measurements.

Process Control Analysis Section, Tokai Reprocessing Center, JNC

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Pu(VI)吸光光度法を用いた高放射性廃液中の微量プルトニウム分析法の適用性評価

－六ヶ所再処理工場保障措置分析所への技術支援－
(技術報告)

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要　旨

IAEAが六ヶ所再処理工場保障措置分析所（On-site Analytical Laboratory）において高放射性廃液（以下、HALWという）中の微量プルトニウム（以下、Puという）濃度分析法として適用を検討しているPu(VI) 吸光光度法について、東海再処理工場のHALWを用いた比較検討試験を実施した。本検討ではPu(VI)吸光光度法におけるPu(VI)吸光度定量方法として、①検量線法、②Nd内標準法、③還元法を検討した。

検討用試料は東海再処理工場にて発生したHALWを採取し、固相抽出操作によってPuを完全に除去した後、既知量のPuを添加することによって調製した。この溶液の吸光スペクトルを測定し、3種類の定量方法を用いた測定結果について正確さ及び精度を評価した。各定量方法の試験結果等について以下に示す。

① 検量線法

測定に必要な試料は1バッチあたり1試料のみでよく、前処理操作は簡便である。調製値と測定値は良好に一致した。

② Nd内標準法

調製値に対して検量線法よりも正確な測定値が得られた。本法では測定に必要な試料として、1バッチあたり2試料（内標準物質であるNdを添加した試料と添加していない試料）を必要とするが、前処理操作に起因するPu濃度の定量への影響は小さい。

③ 還元法

測定値は調製値と比較して全体的に高い結果となった。これは、HALW溶液中の共存元素によるベースラインの変動がPu(VI)吸光度の定量に影響を与えているためと思われる。

3種類の定量方法について比較検討した結果、検量線法が迅速かつ簡便な方法であり、六ヶ所再処理工場保障措置分析所に対して適用性の高い定量方法であることが認められた。検量線法による測定時間は前処理操作を含めて1バッチあたり約1時間であり、HALW試料に対する検出下限値は1.3mgPu/Lであった。

東海事業所　再処理センター　施設管理部　分析第1課

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1. Introduction

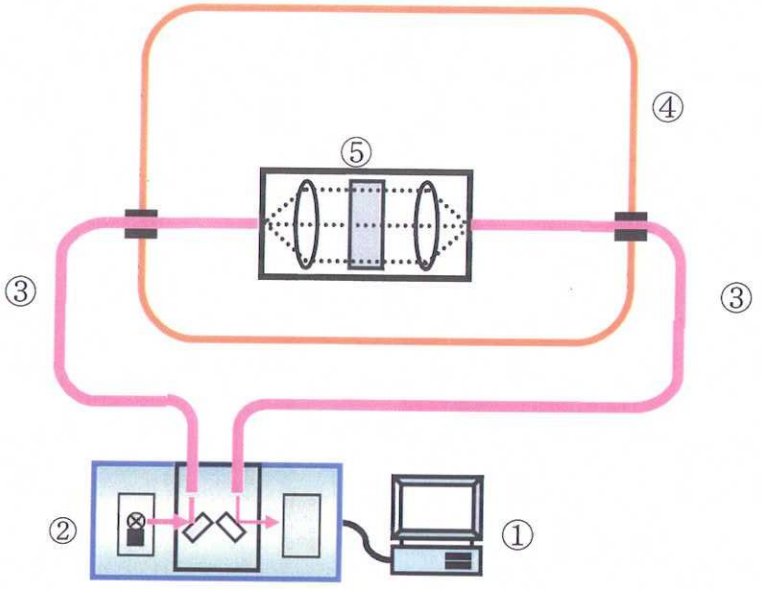
Small amount of plutonium (Pu) should be determined in the High Active Liquid Wastes(HALW), in order to achieve the IAEA safeguards criteria. Tokai Reprocessing Plant has developed measurement technique for trace quantity of Pu in HALW, under the JASPAS, JC-13, using laser induced photoacoustic spectrometry (PAS) and high performance spectrophotometry (HPSP), whose detection limits were obtained less than 0.1mgPu/L /1/. This detection limit was requested from the agency for the safeguards of large scale reprocessing plant. These techniques needed very sensitive instruments and required well-trained operator. The Agency requested TRP to study the applicability of conventional spectrophotometer for Pu determination in TRP under the JASPAS, JC-14 followed by JC-13. The Agency also requested TRP to confirm if this technique could be used for Pu analysis in On Site Laboratory (OSL) in Rokkasho Reprocessing Plant (RRP).

We studied the applicability of conventional spectrometer with optical fiber for which connect with measurement cell to determine Pu concentration in HALW at RRP as a simple and rapid method for OSL. The measurement sample was prepared by adding the known amount of plutonium in the actual HALW after removing original plutonium with solid extraction method. Then, the concentration of Pu was measured and evaluated by three calculation methods, calibration method, Nd internal standard method and reduction method. The most simple and rapid procedure was selected, which can achieve the Agency's requirements. This study was carried out as a part of Japan Support Program for the Agency's Safeguards analysis (JASPAS JU-01-01).

2. Experimental

2.1 Apparatus

The conventional spectrophotometer was applied to this work. The schematic diagram of spectrophotometry system is shown in **Fig.1**. It consists of a conventional spectrophotometer, two optical fibers and a liquid flow type of measurement cell, which was installed in the hot cell.



① PC ② Spectrophotometer ③ Optical fiber ④ Hot cell ⑤Measurement cell

Fig.1 Schematic diagram of spectrometer and analytical cell.

2.1.1 Spectrophotometer

Specifications and measurement conditions for spectrophotometer, Shimadzu UV-2400PC, are listed in **Table 1** and **Table 2** respcetively.

Table 1 Specifications of spectrophotometer

Item	Specifications
Wavelength accuracy	±0.3nm
Photometric accuracy	±0.002Abs.(0～0.5Abs.)
	±0.004Abs.(0.5～1.0Abs.)
Detector	R928 photomultiplier
Light source	Tungsten iodide lamp

Table 2 Measurement conditions

Item	Measurement conditions
Wavelength range	400 to 850nm
Slit width※	2.0nm
Cell length	2.0cm
Wavelength scan speed	20nm/min.

※Slit width : In order to determine the molar extinction coefficient precisely, slit width should be less than 5% of Pu(VI) peak of FWHM, /2/ which is estimated to be less than 5nm. It is impossible to determine it with the 2.0 nm of slit width. We will use "extinction coefficient" without "molar extinction coefficient" in this experiment. The "extinction coefficient" is expressed as an absorbance of 1M at 2cm optical pass length under the measurement conditions. We determined the extinction coefficient with measuring standard solutions with the same analytical conditions as the samples.

2.1.2 Measurement cell

Fig.2 shows the measurement cell and **Fig.3** is the view of it, which is set in the hot cell. Dimensions are given in millimeters. The body of measurement cell was made from stainless steel and flow cell(quartz) was set inside of it. The flow cell length, light path, was 2cm and required volume for replacement of the solution is approximately 15mL.

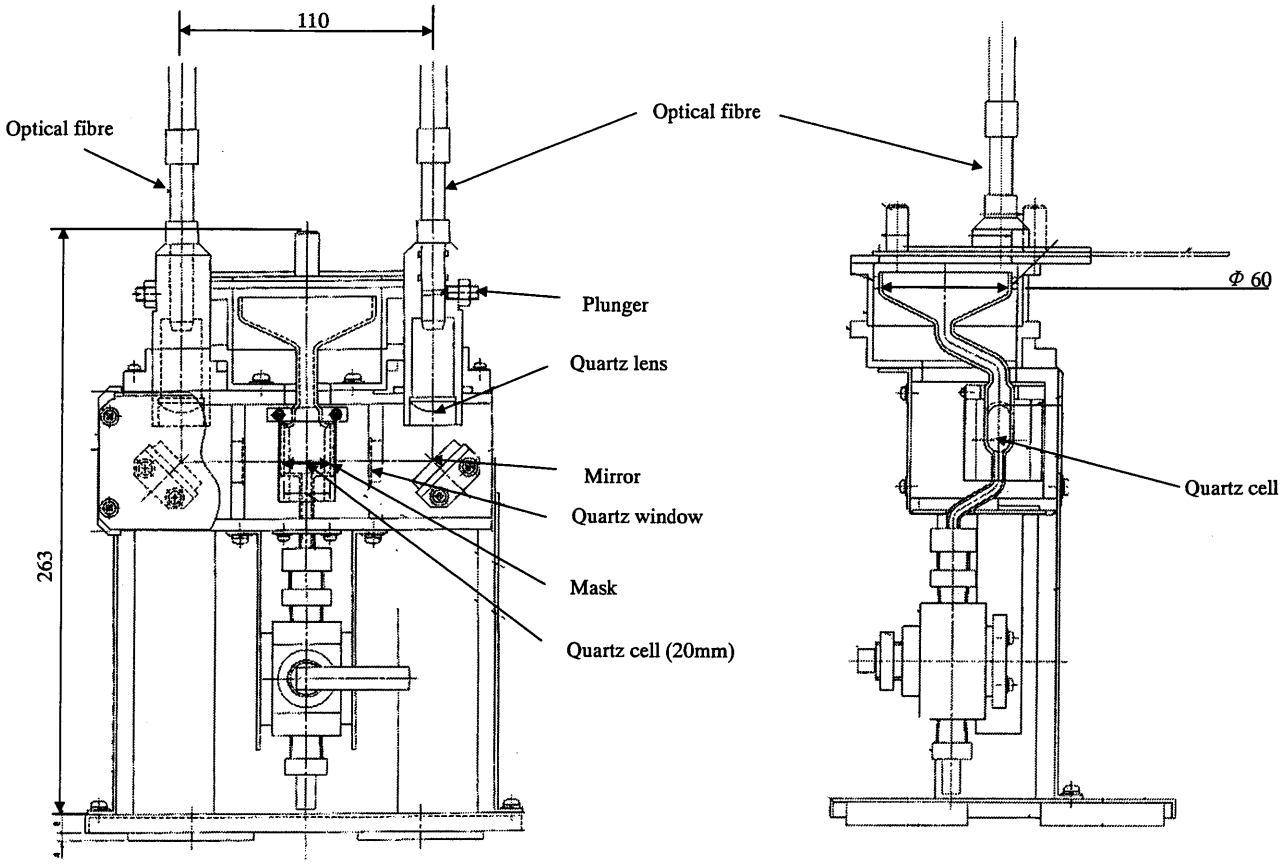


Fig.2 The measurement cell.

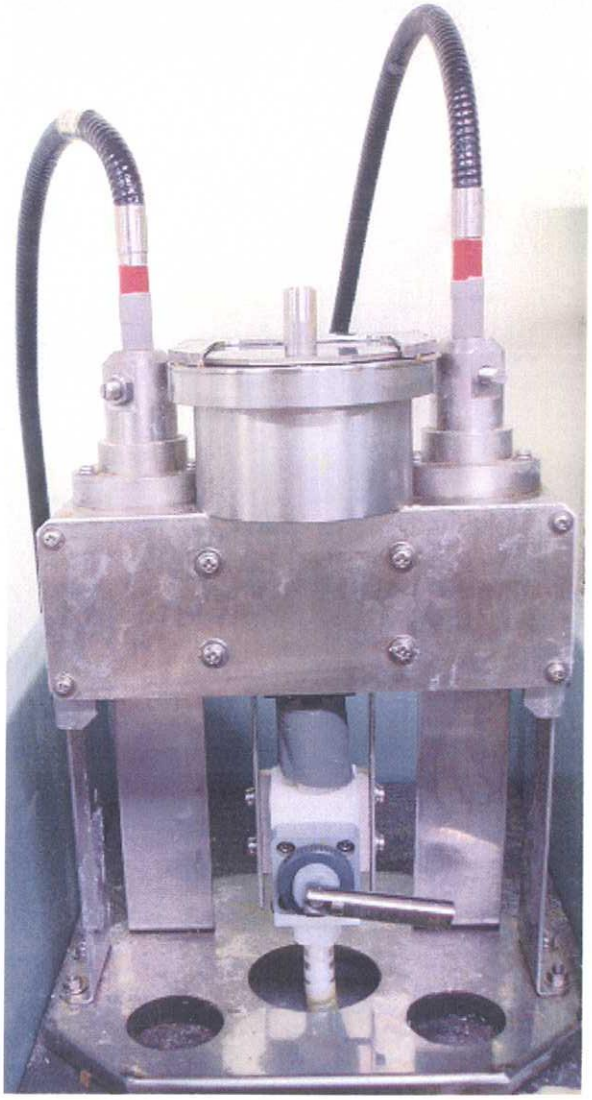


Fig.3 View of the measurement cell.

2.1.3 Optical fiber

The optical fiber was made from quartz, whose length was 7m. Core and cladding diameter of optical fiber were 200μm and 250μm, respectively.

2.2 Reagents and standard solutions

2.2.1 Reagents

All of reagents used of the experiments were analytical grade.

① Nitric acid

Analytical reagent grade (1.38g/cm^3, 60%) was used.

② Neodymium solution

Nd_2O_3 (1.2g) were dissolved in 50mL of 3M HNO_3 (20.2gNd/L).

③ Cerium(IV) Solution, 0.49mol/L solution in water.

Cerium(IV) was used as an oxidation reagent to prepare Pu(VI). 270g of ceric ammonium nitrate $[(NH_4)_2Ce(NO_3)_6]$ was dissolved in the 1L of water.

④ Ascorbic acid , 56.8 mM(10%) solution in water.

Ascorbic acid was used as an reduction reagent for Pu(VI).

2.2.2 Standard solutions

① Plutonium(Pu) solution

Concentration of Pu standard solutions were used 27, 54, 81, 135mgPu/L in 3M HNO_3 .

② Americium(Am) solution

Am solution was collected from Pu storage vessel in TRP.

2.3 Influence of chemical conditions

2.3.1 Acidity

It has been reported that Pu (VI) absorbance will change with acid concentration /3/. **Fig. 4** shows the effect of concentration of nitric acid to Pu(VI) absorbance at 830.6nm. The absorbance at 830.6nm is decreasing with increasing acidity. On the other hand, the formation of plutonium polymer has been investigated when the acidity is lower than 1M /4/. Plutonium polymer formation is favored by increasing plutonium concentration and temperature and decreasing acid concentration. The variation of Pu(VI) absorbances were very small when acidity was between 2 and 3 M. Nitric acid concentration of actual HALW is controlled between 2.7 and 3.0M by the plant operation. In this experiment, acidity of the sample was prepared between 2 and 3M, which is nearly the same acid concentration (3M) as the standard solution. Therefore, influence of acidity was negligibly small for Pu(VI) determination.

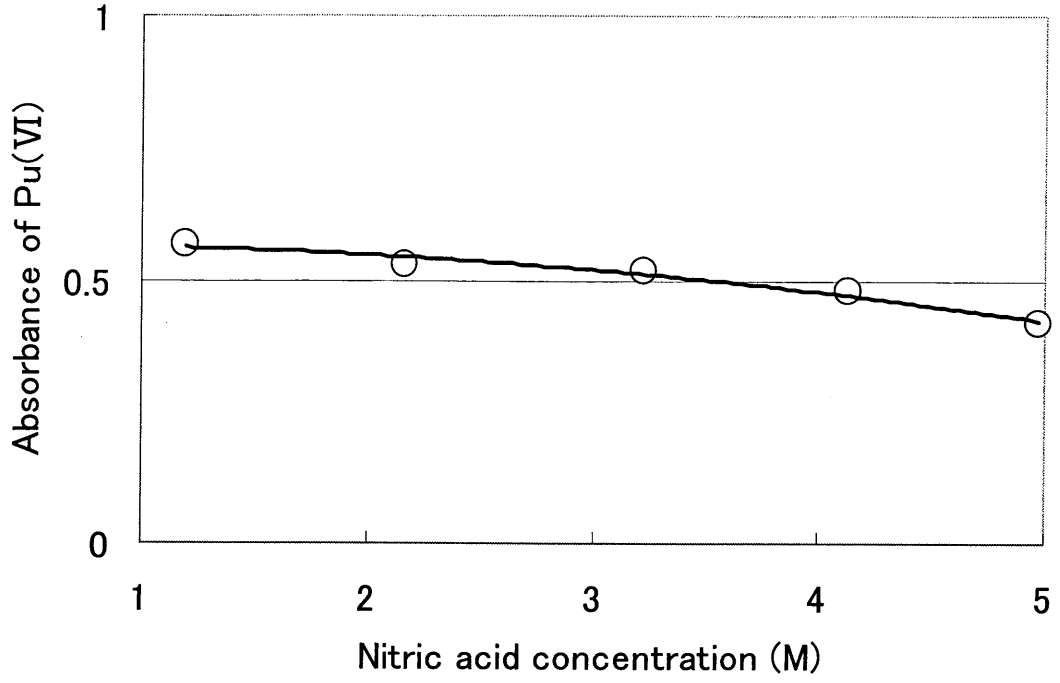


Fig.4 Effect of nitric acid concentration to Pu(VI) absorbance.

2.3.2 Oxidation reagent

H. Muto *et al.* reported the excess amount of Cerium(IV) does not interfere with Pu(VI) measurement /5/,/6/. If Cerium(IV) is more than twice of equimolecular quantities to the Pu molarity in the sample solution, plutonium ion can be converted to Pu(VI) completely /5/.

2.3.3 Hydrofluoric acid (HF)

It is known that fluoride ion makes fluoride complex with Pu, whose solubility is very small in the nitric acid. We used filtration method to remove sludge from HALW. However we have to dissolve it for the practical analysis. When the sludge was dissolved in the HALW sample, the hydrofluoric acid (HF) must be added and heated on a hot plate until near dryness. If the fluoride ion was remained after the evaporation, it may affect Pu(VI) absorbance by forming fluoride complex with Pu. The formation of fluoride complexes is represented by the following equation,

$$Pu^{4+} + HF \Leftrightarrow PuF^{3+} + H^{+}$$

Fig.5 shows the effect of hydrofluoric acid concentration to the Pu(VI) absorption peak. 2mL of 0.01M HF with 8M HNO_3 is added into the sample solution when dissolving sludge in HALW. If all HF was remained in the sample solution, its concentration was 0.0013M. We obtained 29

mgPu/L of Pu(VI) absorbance in 0M and 0.0013M HF solution, which were 0.106 and 0.103, respectively. The difference in absorbance was 0.97(=0.103/0.106). We found that remained HF would be very small, which might not affect Pu(Ⅵ) measurement.

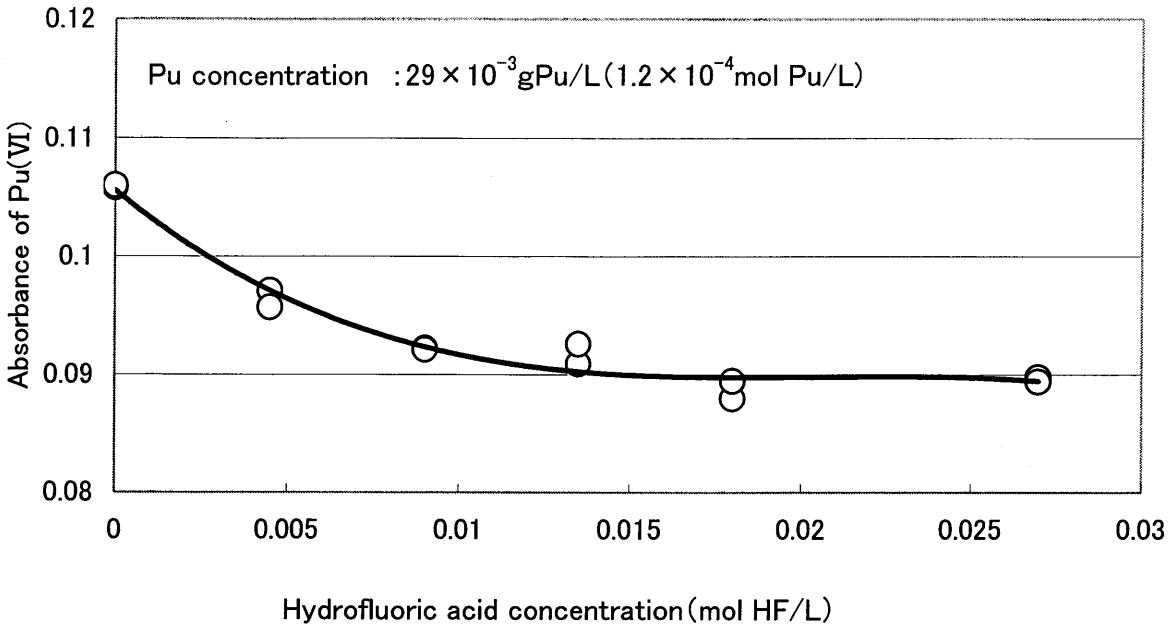


Fig.5 Effect of hydrofluoric acid concentration on the intensity of Pu(Ⅵ) absorption peak.

2.4 Absorption spectrum of HALW

The solution was taken from the HALW concentration evaporator (271E20) at TRP in 02－1 campaign. **Fig.6**－① shows the oxidized absorption spectrum of HALW.

2.4.1 Coexistence elements

Suspended fine particles in HALW, mainly from insoluble residues, would give influences on spectrum such as fluctuations of the baseline due to scattering of the light. **Fig.6**－① shows the spectrum of actual HALW solution after oxidation with Ce(Ⅳ). There are several peaks on the spectrum. Absorbance of baseline increases with shortening in wavelength. Nd (**Fig.6**－②), Am (**Fig.6**－③) and U (**Fig.6**－④) spectra were also shown in the figure 6. We assigned the peaks of the HALW to absorption of these elements.

1) Uranium (U)

U(VI) peak has no influence on Pu(IV) measurement, because U(VI) has no peak near the Pu(VI) peak at 830.6nm.

2) Neodymium (Nd)

Nd(Ⅲ) peak affects Pu measurement increasing the baseline. However the increasing of absorbance by Nd is relatively small compared with that by Am.

3) Americium (Am)

Am(III) peak affects Pu measurement increasing the baseline. When Pu is oxidized to the hexavalent state with Ce(IV), Am(III) could be also oxidized to the Am(VI). The oxidation of the Am(VI) is written as

$$Am^{3+} + 3Ce^{4+} \underset{1.61V}{\overset{-1.69V}{\Leftrightarrow}} Am^{6+} + 3Ce^{3+}$$

and the equilibrium constant using Nernst's equation is expressed as following equation.

$$\varepsilon = -0.08 - \frac{RT}{nF} \times \ln \frac{(Am^{6+}) \times (Ce^{3+})^3}{(Am^{3+}) \times (Ce^{4+})^3}$$

(ε =0 , n=3 , F=9.6×10^{4}C, R=8.31 , T=300 K ,
oxidation –reduction potential =(−1.69)+(1.61)=−0.08V)

We have found the following relationship.

$$\frac{(Am^{6+}) \times (Ce^{3+})^3}{(Am^{3+}) \times (Ce^{4+})^3} = 1 \times 10^{-4}$$

Since a excess amount of Ce(IV) was added sample solution to oxidize Pu, concentration of Ce(IV) should be larger than that of Ce(III). Ce(IV) and Pu concentration in the measurement solution are 980 μ mol and 0.2 μ mol, respectively(2mol of 0.49mol/L, Ce(IV) solution and 2mL of 20mgPu/L were taken for the measurement). Even if 0.4 μ mol of Ce(IV) was consumed for oxidizing Pu(IV) to Pu(VI), almost of Ce(IV) is remained. Ratio of Am(VI) and Am(III) concentration is evaluated 2×10^6. Concentration of Am(VI), therefore, is larger than that of Am(III)※. The value of equilibrium constant leads the absorbance of Am(III) would be less than initial one. From the result of the evaluation, Am does not influence the Pu measurement in HALW after adding Ce(IV) for Pu oxidation, if the equilibrium has been reached.

※If the 50% of Ce^{4+} is reduced to Ce^{3+} before adding sample solution and Pu concentration in the HALW is ten times higher, 200mgPu/L, than that we tested, ratio of Am^{3+} and Am^{6+} concentration (Am^{6+}/Am^{3+}) is calculated 4×10^2. Am, therefore, could not influence the Pu measurement after the equilibrium has been reached even in the conditions.

2.4.2 Suspended particles

We found that fine particles remained in the solution from the results of HALW spectrum evaluation. It is, however, confirmed that the fine particles did not affect Pu (VI) measurement, because large size particles were removed from HALW solution during solid extraction procedure before the spectrophotometric measurement.

The influence of rayleigh scattering which has on the spectrum was considered. We calculated the spectrum of rayleigh scattering caused by fine particles in actual HALW. The calculated baseline is shown in **Fig.6**—⑤.

Rayleigh scattering is represented by the following equations,

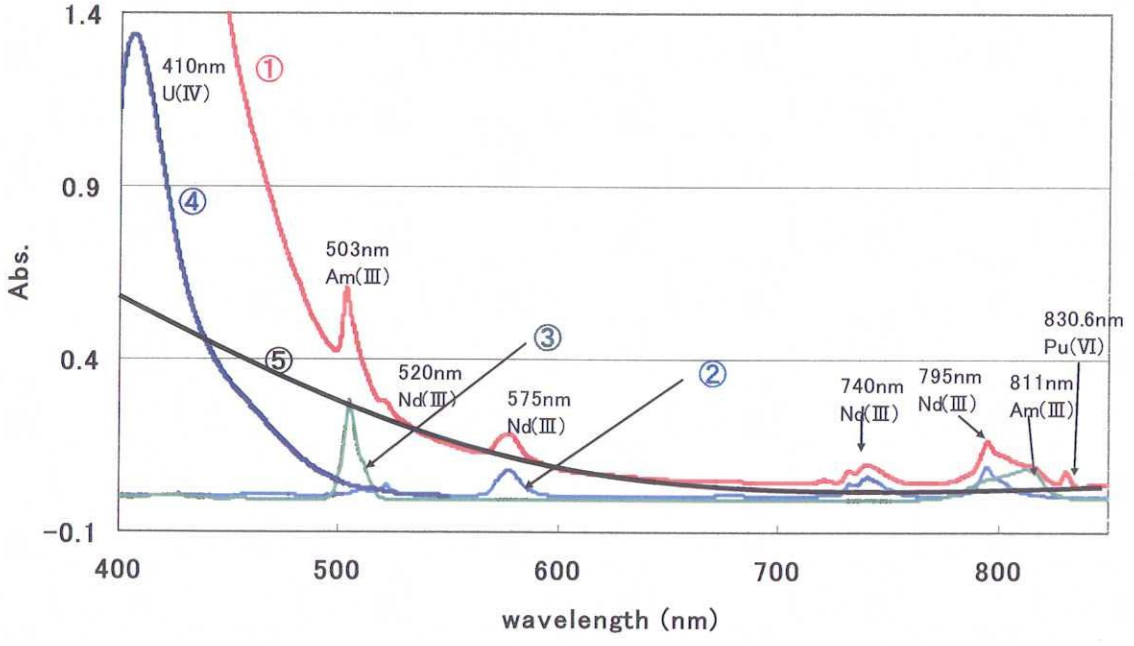
$$\alpha = C/\lambda^4$$

α is the intensity of rayleigh scattering and λ is the wavelength. α is inversely proportional to λ^4.

The absorbance (A) is defined by transmittance (T) and α.

$$A = -\log(T) = -\log(1-\alpha)$$

Absorbance by rayleigh scattering changes, when the wavelength is short. We, therefore, could not find any influences at longer wavelength, at 830.6 nm, for Pu(VI) measurement.



① Oxidized HALW ② Nd solution ③ Am solution ④ U solution
⑤ Rayleigh scattering line

Fig.6 Absorption spectra of HALW, Nd, Am and U solution and rayleigh scattering line.

2.5 Sample preparation and experimental procedures

2.5.1 Preparation of Pu in HALW for the experiment

The known amount of Pu in the HALW solution was necessary for the experiment. Therefore the sample solution was prepared by adding the known amount of Pu standard in the actual HALW after removing original Pu. **Fig.7** shows the preparation procedure for sample solution. We took 5mL of actual HALW. The sample was stirred and introduced into the solid extraction column, packed 2mL of TEVA Spec.Resin. During the extraction, particles were filtrated by the extraction column /7/. **Fig. 8** shows an absorption spectrum of actual HALW solution after Pu removal. Since no significant Pu(Ⅵ) absorption peak was observed, solid extraction was sufficient for removal of plutonium from HALW solution. After the solid extraction, Pu standard solutions were added into HALW. All samples were adjusted to 3M acidity to eliminate the influence of varying absorbance by acid concentration.

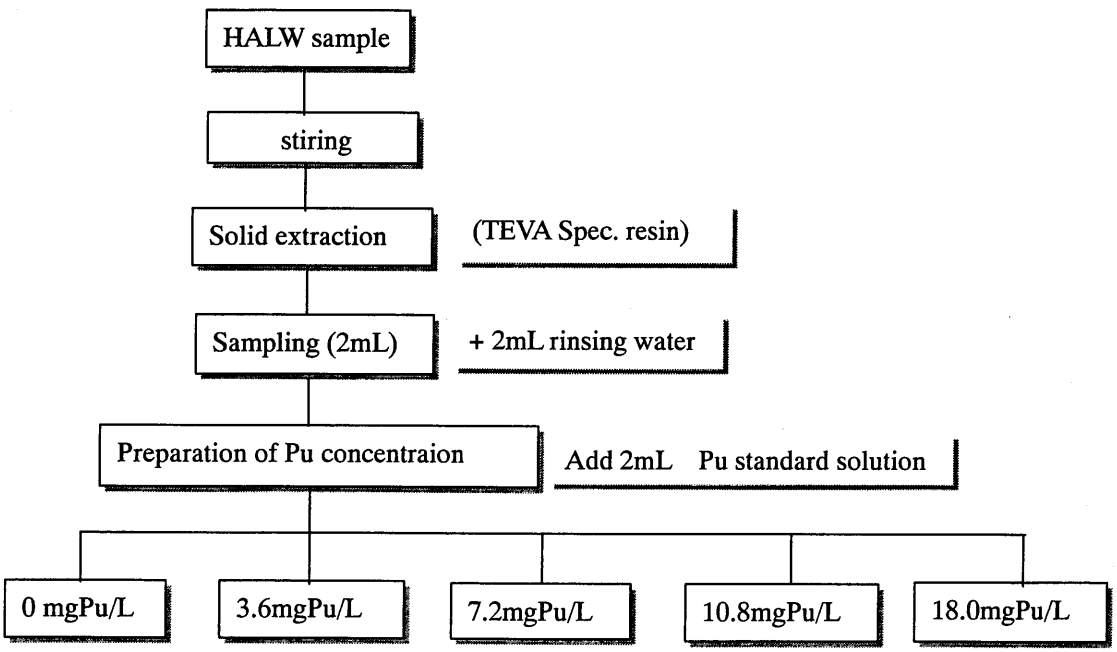


Fig.7 Preparation procedure for sample solution.

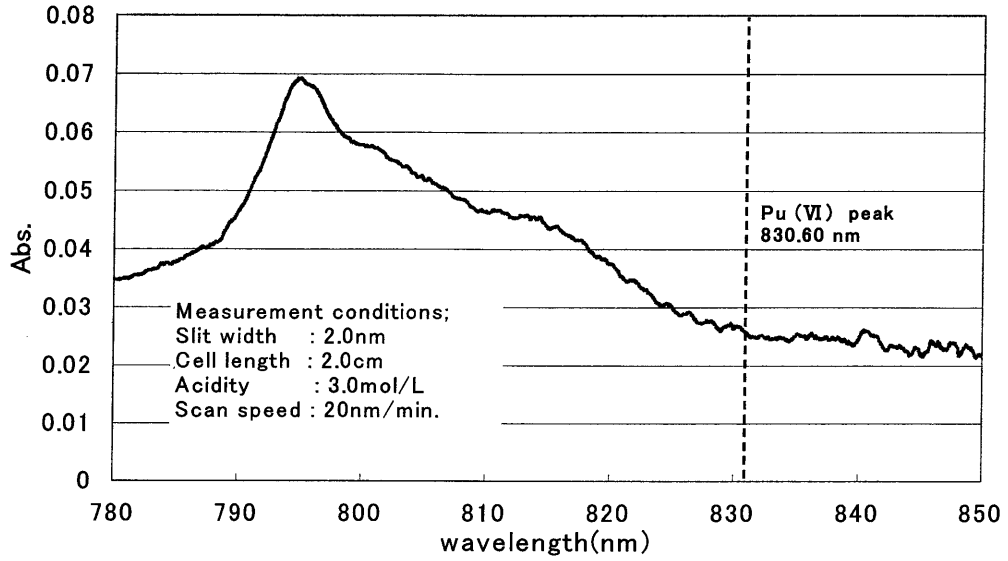


Fig. 8 Absorption spectrum of HALW (after removal treatment of Pu using TEVA-resin).

2.5.2 Experimental procedures

Sample preparation procedures are shown from **Fig.9** to **Fig.11** for three methods.

(1) Calibration method

These samples were oxidized by Ce(Ⅳ) and measured Pu(VI) absorbance.

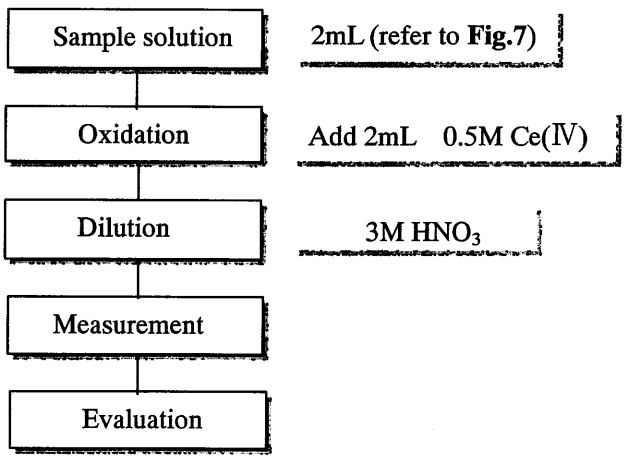


Fig.9 Experimental procedure of calibration method.

(2) Nd internal standard method

Nd internal standard method needs to measure Nd unspiked sample and Nd spiked sample. Pu concentrations were calculated by Nd and Pu peak ratio. (refer to *3.2.2*)

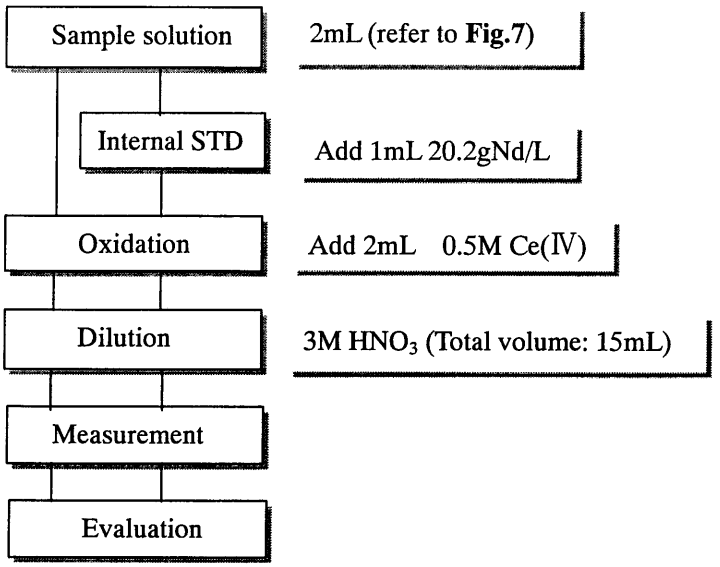


Fig.10 Experimental procedure of Nd internal standard method.

(3) Reduction method

Oxidized and reduced spectra of HALW samples were obtained in order to determine Pu by reduction method. Reductant was added the HALW, then Pu(VI) and Pu(Ⅳ) were reduced to Pu(III). No Pu(VI) absorption peak was found at 830.6nm after adding the reductant.

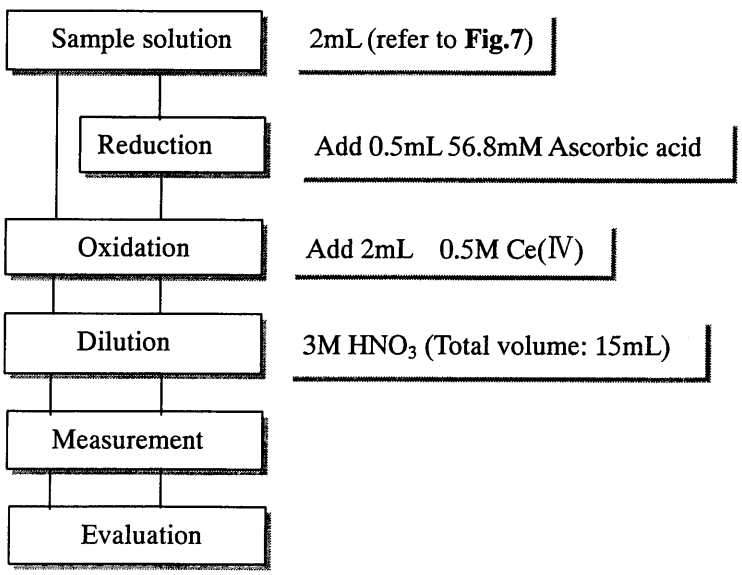


Fig.11 Experimental procedure of reduction method.

3. Calculation of Pu concentration

3.1 Net peak absorption calculation

3.1.1 Pu(VI) absorbance

A typical spectrum of Pu(VI) in HALW was shown in **Fig.12**. The peak wavelength of Pu(VI) was determined 830.6nm with the linear differential method. The baseline was varied every measurement, therefore, net peak absorption was corrected by subtracting estimated baseline from the measured spectrum. The three-point method is the one of the well-known method **/8/**, which can estimate the baseline with interrelation between two wavelengths locating longer and shorter of the peak as shown in **Fig.13**. This method eliminates the effects of background interference and sloping baselines. We selected two wavelengths, 825.85 and 838.35nm, for baseline correction. Equation of the net peak intensity is expressed as follows.

$$A_{Pu} = A_{830.6} - \left\{ \frac{(838.35 - 830.6) \cdot A_{825.85} + (830.6 - 825.85) \cdot A_{838.35}}{(838.35 - 825.85)} \right\} \quad (1)$$

$$= A_{830.6} - B_{830.6}$$

A : Absorbance. Subscript number means wavelength.

$B_{830.6}$: Background intensity at 830.6nm

Three wavelengths, 830.6nm for peak, 825.85 and 838.35nm for reference, were used calculation of the baseline correction.

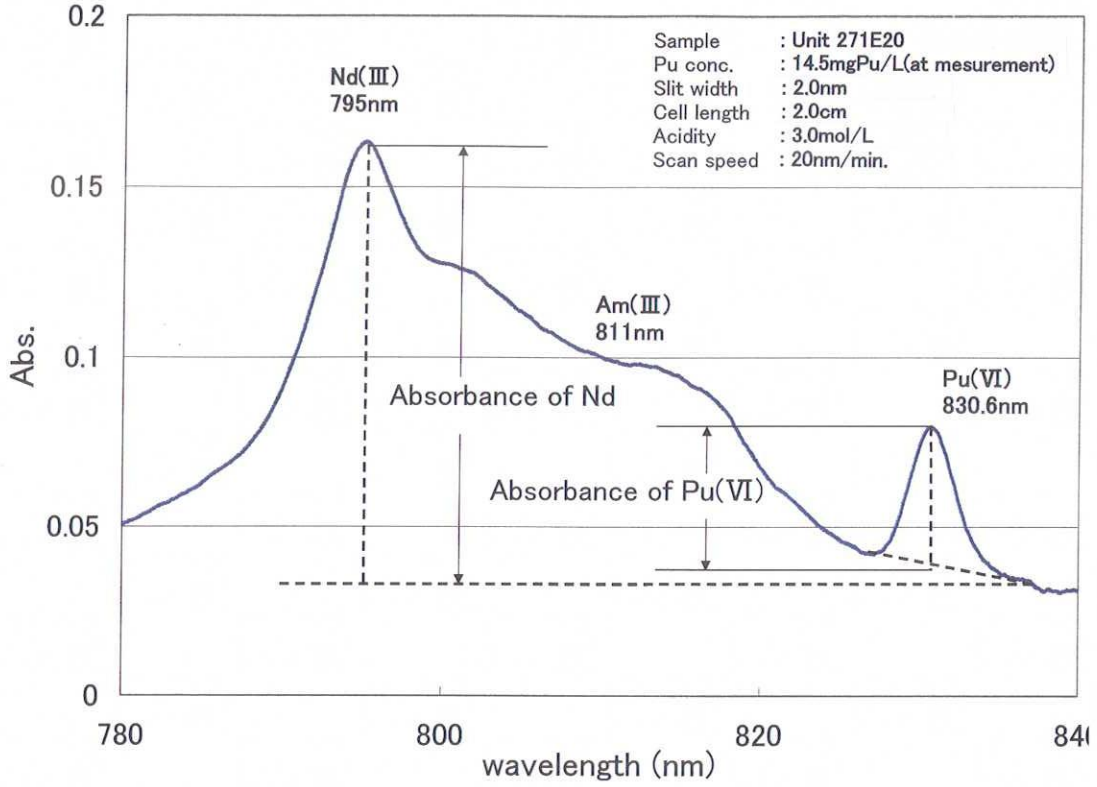


Fig. 12 Absorption spectrum of Pu(Ⅵ) in HALW.

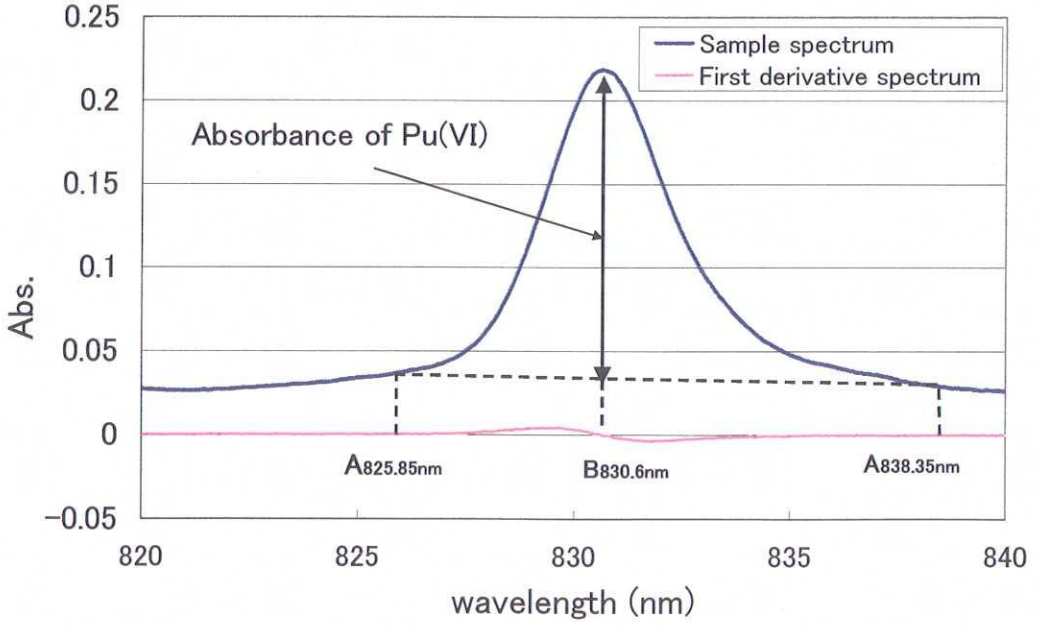


Fig. 13 Three-point correction method (57.6mgPu/L in 3.19M HNO_3).

3.1.2 Nd absorbance

Net absorbance of Nd was calculated on three-point method /8/. However, it could not fit into the estimation of the baseline of Nd peak calculation. It was found that absorbance at shorter wavelength for baseline correction was usually higher than that we estimated by linear relationship. We selected the longer wavelength, 838.35nm, as a background for the baseline correction. Net absorbance of Nd was calculated by subtracting absorbance at 838.35nm from the peak absorbance of Nd at 795nm (**Fig.12**).

3.2 Calculation of Pu concentration

3.2.1 Calibration method

Plutonium concentration in HALW was obtained by calibration curve, using three Pu standard solutions (27, 54, 216 mgPu/L). Absorbance at 830.6nm for Pu(Ⅵ) was calculated on equation (**1**). We calculated the final result from equation (**2**).

$$C_S = C \times V_1 / V \qquad (2)$$

where

C_S Final concentration in the sample, in mgPu/L

C Concentration of the sample in the measurement cell, in mgPu/L

V Volume of the sample, in mL

V_1 Volume of diluted solution, in mL(=15mL)

The calibration curve shows a good linearity with the correlation factor as R^2=0.998.

3.2.2 Nd internal standard method

Plutonium concentration was obtained by the absorbance ratio of Pu(Ⅵ) and Nd(Ⅲ). The extinction coefficient ratio of Pu(Ⅵ) and Nd(Ⅲ) were decided by measuring standard solution.
The plutonium concentration was calculated by equation (**3**).

$$C_{Pu} = \frac{R_1 \cdot R_2}{(R_1 - R_2)} \cdot \frac{AW_{Pu}}{AW_{Nd}} \cdot \frac{\varepsilon_{Nd}}{\varepsilon_{Pu}} \cdot \frac{M_{Nd}}{V} \qquad (3)$$

where

C_{Pu} Concentration of Pu (g/L)

R_1 Absorption Ratio of unspiked sample ($A_{830.6nm}/A_{795nm}$)

R_2	Absorption Ratio of spiked sample ($A_{830.6nm}/A_{795nm}$)
AW	Atomic Weights (239.59※ for Pu, and 144.20 for Nd)
ε	Extinction Coefficient (764.83 for Pu, and 20.29 for Nd)
M_{Nd}	Amount of Nd Spike (0.02023g)
V	Sample Volume (0.015L)

3.2.3 Reduction method

Plutonium concentration is determined by subtracting absorbance of reduced sample from that of oxidized one. **Fig.14** shows typical spectra of oxidized (**Fig.14**−①) and reduced (**Fig.14**−②) HALW solution. Then, absorbance for Pu(Ⅵ) was calculated on following equation **(4)**.

$$A_{real} = A_{ox} - A_{re} \qquad (4)$$

where

A_{real}	Absorbance for Pu(Ⅵ)
A_{ox}	Absorbance of Pu oxidized sample at 830.6nm
A_{re}	Absorbance of Pu reduced sample at 830.6nm

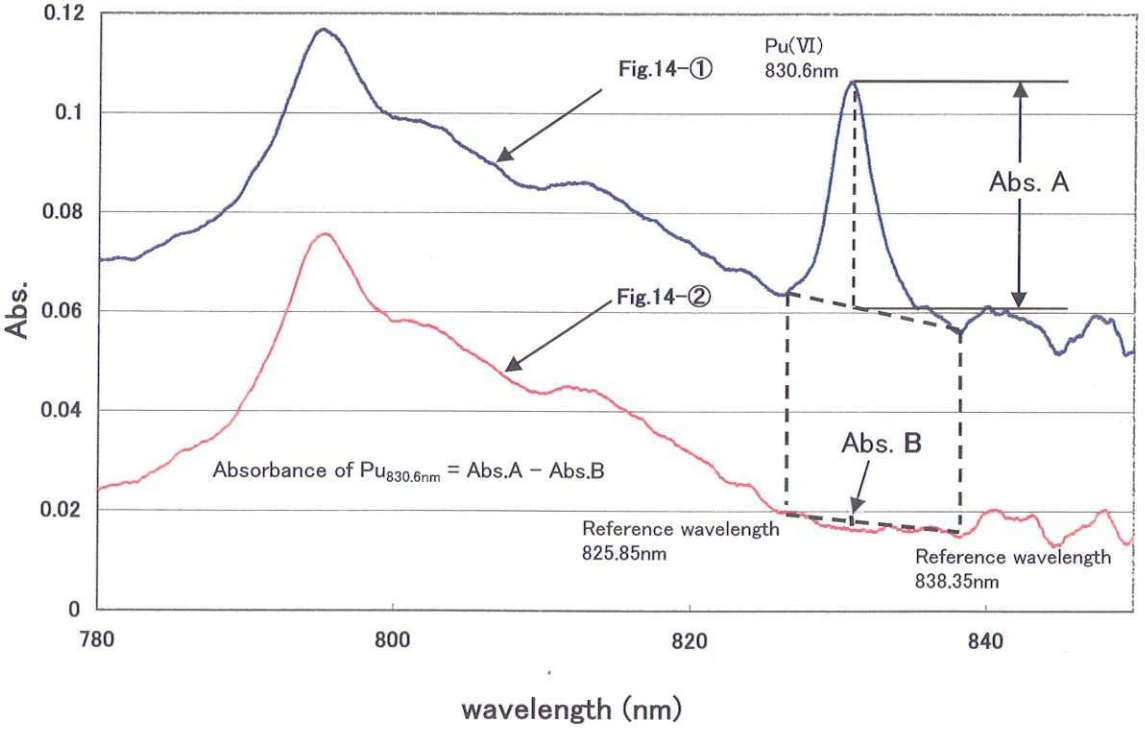


Fig.14 Absorption spectra of oxidized and reduced HALW solution.

※ *Isotopic ratio of Pu in the standard solution*
$^{238}Pu : {}^{239}Pu : {}^{240}Pu : {}^{241}Pu : {}^{242}Pu = 1.41 : 60.1 : 26.7 : 6.57 : 5.17$

4. Results and Discussions

4.1 Results of three analytical methods

Table 3 shows analytical results obtained by three methods. We took two aliquots from the same HALW solution and prepared independently. Each sample was measured 5 times. It was found that the Nd internal standard method gives the most precise results in the three methods.

Table 3 Analytical results for three methods (5 times measurements)

Adjusted value (mgPu/L)	Measured value (mgPu/L)		
	Calibration method	Nd internal standard method	Reduction method
0	0.02±0.24	0.14±0.16	−0.06±0.43
3.6	3.8±0.39	2.7±0.91	4.0±0.55
7.2	6.9±0.28	5.6±0.61	7.5±0.44
10.8	11±0.44	11±0.42	12±0.45
18.0	21±0.57	18±0.42	22±0.72
Correlation factor(R^2)	0.9868	0.9903	0.9913

4.2 Calibration method

We plotted each measurement results calculated by the calibration curve to the adjusted Pu concentrations in **Fig.15**. The results of this method were agreed well with adjusted value 0 to 10.8 mgPu/L. We estimate the difference between the calculated and measured value was 16.7% at the 18.0mgPu/L. Variation of absorbance for Nd peak is shown in **Fig.16.** The error bars correspond to the one standard deviation of the absorbance. Neodymium concentration was the same all the solution, nevertheless the intensity of "18.0mgPu/L sample" was higher than that of other concentration samples. This fact indicates that "18.0mgPu/L of Nd unspiked sample" has preparation error. We can correct the analytical result (21.0±0.57mgPu/L) of the 18.0mgPu/L sample from the Nd absorbance.

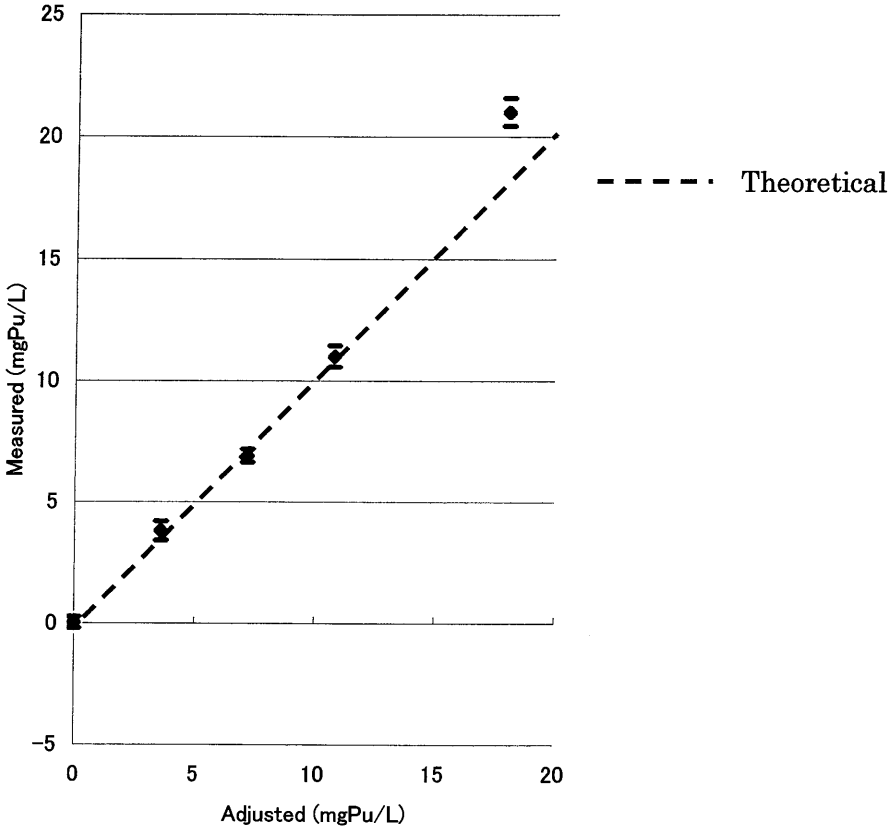


Fig.15 Analytical results of calibration method.

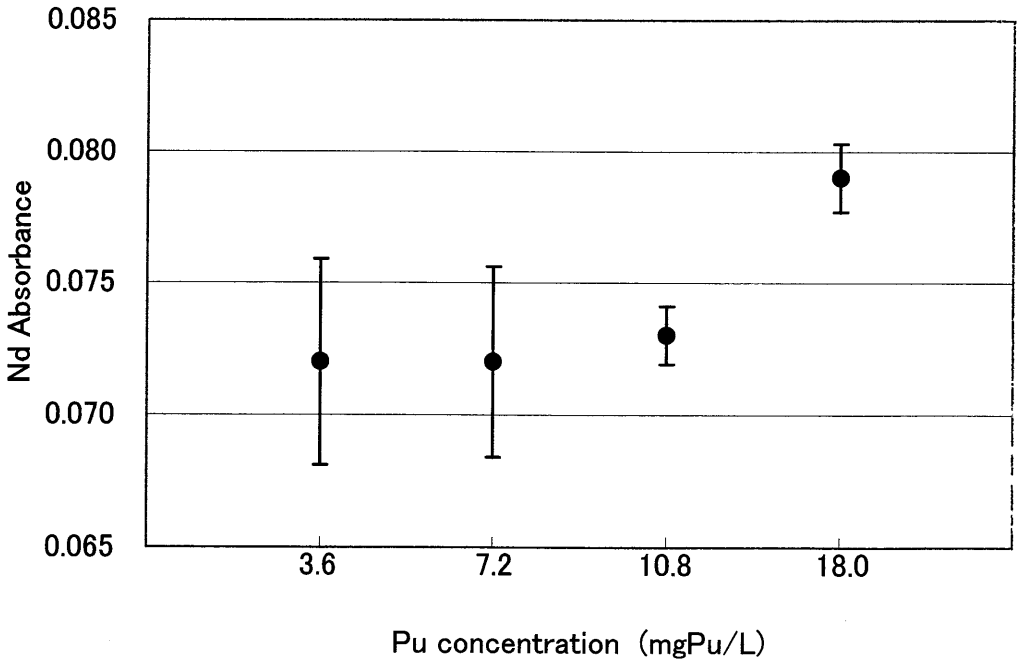


Fig.16 The intensity of Nd absorbance in the sample(Nd unspiked).

4.3 Nd internal standard method

Nd internal standard method gives good agreement of Pu(VI) concentrations between analytical result and adjusted as shown in **Fig.17**.

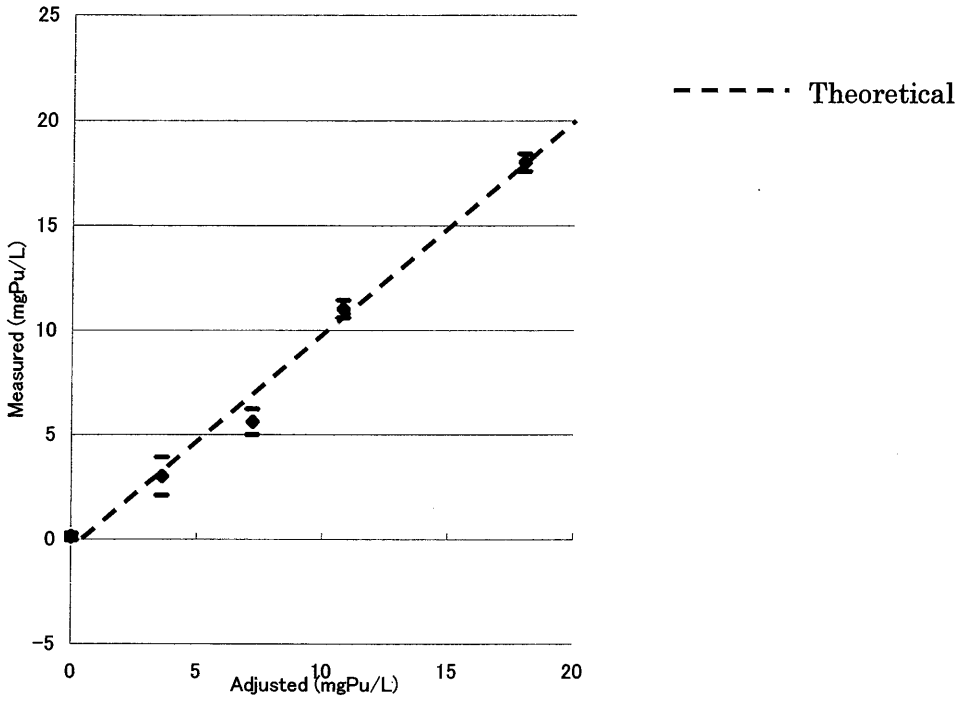


Fig.17 Analytical results of Nd internal standard method.

Because the absorbance ratio of Pu and Nd, Pu/Nd, is not changed by the preparation error, this can be eliminated in the method (Eq.3). It is indicated that the Nd internal standard method is applicable to performing accurate measurements.

4.4 Reduction method

The measurement results with this method were higher than adjusted one as shown in **Fig.18**.

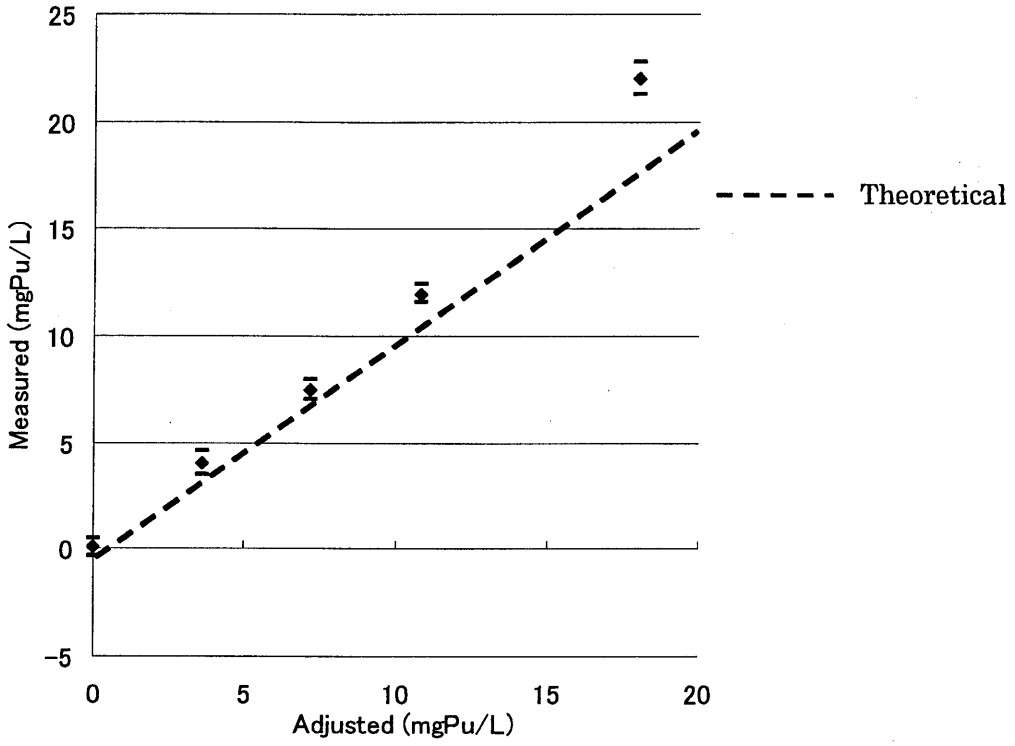


Fig.18 Analytical results of reduction method.

The results of this method were not in accord with those of calculated one. The difference would be due to influence by Am(Ⅲ) peak at 811nm in reduced sample. Because, Am(III) could be oxidized by Ce(VI), however, Am(III) was stabilized when Pu was reduced to Pu(III). Baseline was, therefore, different between oxidized and reduced solution. The data from this test indicated that reduction method can not be used for Pu(VI) determination.

4.5 Blank samples

We measured 3M nitric acid and HALW removed Pu, which was not oxidized. **Table 4** and **Table 5** show the results of the absorbance calculated by the three-point method. The absorbances with standard deviation of 3M of nitric acid and HALW were 0.0003 ± 0.001 and -0.0049 ± 0.0008, respectively. We found that there were significant differences between them. If the baseline absorbance was -0.0049, it must affect Pu measurements in the HALW. There was no differences from the results between adjusted Pu concentrations and obtained ones with the calibration method and Nd internal standard method. Am(III) was not oxidized because oxidation reagents did not add into the sample. Therefore, Am(III) influenced for the baseline measurement.

Table 4 Measurement results of 3.0mol/L nitric acid solution

Sample No.	※Abs.	Average	STDEV.	Average	STDEV.
1	-0.00265	-0.0004	0.0022	0.0003	0.0010
	-0.00035				
	0.00167				
2	-0.00314	0.0006	0.0009		
	-0.00551				
	-0.00494				
3	0.00074	0.0007	0.0002		
	0.00047				
	0.00082				

※Evaluated by three-point method

Table 5 Measurement results of baseline in HALW

Sample No.	※Abs.	Average	STDEV.	Average	STDEV.
1	-0.00453	-0.0048	0.0004	-0.0049	0.0008
	-0.00549				
	-0.00466				
	-0.00461				
2	-0.00314	-0.0045	0.0012		
	-0.00551				
	-0.00494				
3	-0.00573	-0.0053	0.0005		
	-0.00537				
	-0.00467				

※Evaluated by three-point method

4.6 Detection limit

Detection limit was defined as the 3 times of the standard deviation of blank HALW samples. The absorbance of detection limit was 0.0024(=0.0008 × 3). It was converted 1.3mgPu/L, which is fulfills the required value from the agency.

5. Conclusions

Analytical methods to determine the Pu concentration in HALW were studied for OSL measurements. The results using actual HALW were compared with three analytical methods. The conclusions for each method are summarized as follows.

Calibration method

The simple procedure shows that this method is useful for actual HALW measurements for OSL, when the sample preparation has been done accurately.

Nd internal standard method

Nd internal standard method gained good agreement with the adjusted Pu concentration over the all concentration range. This method is the most precise and accurate measurement method.

Reduction method

The results of this method were not in accord with the adjusted values due to the influence of Am(Ⅲ) peak at 811nm of reduced sample. The Reduction method was found to be unsatisfactory for actual use.

6. Reference

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