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Development of Pu analysis in High Active Liquid Waste (JASPAS JC-13)

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Abstract

It has been required from IAEA to determine a small amount of plutonium in the high active liquid waste solutions (HALW) in the tokai reprocessing plant. High performance spectrophotometer (HPSP), which could be obtained lower detection limit than conventional spectrophotometer, is studied to be applied the inspection and verification analysis. The results of applicability test are described in this report.

-Cold Test-

Neodymium, showing an absorption peak near the absorption wavelength of plutonium(VI) , was used as an alternative element to plutonium, in order to review the calculation method of the peak intensity.

-Hot Test-

Plutonium nitrate solution was used for the fundamental test of this method. Since the method is known to be influenced by acidity, suspended sludge and coexistent elements in a sample, each dependency was examined. It was found that measurement results varied about 14% at a nitric acid concentration of 2-4 mol/L. Sludge could be removed by filtration before the measurement. The effect of coexisting elements could be eliminated adjusting the optical balance between reference and sample beam intensity.

In the case of measuring a low concentration plutonium solution, a ratio of the peak intensity to the background intensity (S/B ratio) was not enough to the measured low concentration of Plutonium. Therefore a method should be improved the S/B ratio by analyzing the obtained spectra. Data accumulation method, simple moving average method and Fourier transform analysis was tested. The results showed that a combination of the accumulated average method and the moving average method was the optimum method for the purpose.

Linearity of the calibration curve was found between 0-11 mgPu/L. Synthetic sample solution, which simulated the actual constituents of the HALW with plutonium, showed a good linear relation at 0-11 mgPu/L. The detection limit for plutonium concentration was 0.07 mgPu/L. When the synthetic HALW solution containing plutonium was measured, the detection limit was 0.2 mgPu/L.

Measurement of the actual HALW to which added known amount of plutonium was also indicated a good linear relation. The detection limit was calculated to 0.2 mgPu/L for the actual HALW measurement.

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高放射性廃液中のプルトニウム分析法の開発
(JASPAS JC-13)

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要　旨

東海再処理施設にて発生する高放射性廃液（HALW）中の微量のプルトニウム濃度を測定することはIAEAから求められてきた。通常の吸光光度計よりも低濃度まで測定することができる、高感度吸光度計(HPSP)の査察検認分析への適用性に関する検討を行った。

はじめにコールド試験として、プルトニウムの吸収波長近くに吸収を持つネオジムを用いた試験を実施し、ピーク強度の計算方法について確認し、ピークの吸光度からバックグランドの吸光度を差し引く方法（三波長法）を用いることが可能であることを確認した。

次にプルトニウム溶液を用いて、硝酸濃度、スラッジ濃度、共存イオンの影響について確認した。硝酸濃度についてはHALWの変動範囲の2～4mol/Lの範囲では約14%値が変化することが確認できた。また、スラッジについては測定前にろ過することによりその影響が除去できることを確認した。共存イオンについては、三波長法により補正することが可能であることが確認できた。

また、実際のHALWを用い、既知量のプルトニウムを添加して調製した試料を用いて検討を行った。極低濃度のプルトニウムを測定する場合には、SN比を向上させる観点から複数回測定を行い、さらに、重み関数を用いた移動平均法を使用することにより、その値を低下させることができた。検出限界値はHALWにおいて0.2 mg/Lであった。

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Contents

1. Introduction

In accordance with safeguards criteria being undertaken, much attention has recently been required on plutonium amount in high active liquid waste from reprocessing plant. Tokai Reprocessing plant has been requested by the IAEA to identify a small amount of plutonium in the high active liquid waste (HALW) temporally stored in the facility.

The study is carried out as a part of the Japan Support Programme for Agency Safeguards (JASPAS) in order to establish analytical technique for verification, which allows immediate and precise analysis of a small amount of plutonium contained in the HALW. Review on the Laser Induced Photo Acoustic Spectrometry (LIPAS) is studied within a framework of the JASPAS since 1993 and its effectiveness as an analytical method in the safeguards is being evaluated. It was found that LIPAS is sensitive and effective to determine low concentration plutonium in HALW. However, stability of LIPAS system, especially laser, is not enough to use as a safeguards and/or accountancy analysis. In this paper, results of High Performance Spectrophotometry (HPSP) study are described.

Typical conventional analytical methods for plutonium measurement in HALW are the Isotope Dilution Mass-Spectrometry (IDMS) and the X-ray Fluorescence (XRF). While the IDMS features high accuracy, it requires complicated pretreatment to obtain analytical results and takes much time. Therefore, it is not considered to be appropriate for the inspection analysis at the facility. The XRF can immediately provide results and shows excellent performance in the high concentration region (1 gPu/L or more). However, it is influenced by the coexistent elements, which are difficult to be compensated. This makes the XRF inappropriate for Pu analyses in HALW. Other existing methods to analyze plutonium concentration in the HALW is α-ray measurement. This method also requires complicated pretreatment such as extraction, and isotopic compositions of plutonium must be known. These prerequisites do not confirm to the needs of the analytical method to be developed in the present study.

In the nitric acid solution, plutonium takes the oxidized forms of Pu(III), Pu(IV) and Pu(VI), among which Pu(VI) is known to have a high sensitive and sharp absorption peak in the visible (near infrared) region[1]. However, a plutonium concentration in the HALW is expected to be lower than the detection limit of this method (approximately 10^{-2} Abs), which makes it difficult to take measurement by the conventional spectrophotometer.

In this study, an instrument that is capable of taking measurements for analyzing plutonium existing in small quantity in the HALW both simply and promptly without being influenced by the coexistent elements. As a result of review and examination, the High Performance Spectrophotometry (HPSP) was selected to satisfy these conditions.

Principle

The HPSP is classified as an absorption analysis method, but signal detection and treatment is different from the standard double beam spectrophotometer (simply called spectrophotometer hereinafter). It directly measures a difference in strength of light (I_R-I_S) between the reference light (I_R) and the sample light (I_S) with strict blank correction, not detecting signals of zero transmission factor and those cutting 100% light. This means transmission of light is relatively decided by comparing with sample and reference. According to this principle, measurements within the absorbance range (0.02~0.0002 Abs, corresponding to 10~0.1 mgPu/L of plutonium), which are usually difficult to be taken, can be measured. This measurement principle has been incorporated into a device developed by JASCO Corporation. However, it has only been applied to the characteristic evaluation of Langmuir Blodgett Films.

In this study, this technique was first applied to a solution system, and the device was modified to be able to measure a high radioactive solution sample. As a high radioactive sample considered is placed in air-tight box which is shielded by the lead (hereafter called an inner box) and handled by remote control equipment such as a manipulator, this system had the sample cell in the inner box and used the optical fiber to deliver incident and transmitted lights.

This paper reports the review on the method that can analyze a plutonium concentration in the HALW by HPSP simply and rapidly.

2. Principle of Measurement

Difference of the principle of measurement by conventional spectrophotometry, the method considered can not measure the absolute value of the transmitted light but measures a very small difference in the intensity of the light by taking a ratio of the transmitted to the reference light intensity.

Fig. 2-1 shows comparison of output signal (shape, form) from the detector. V_R represents the output level from the detector against the reference light intensity R, and Vs the output level from the sample light intensity S. The conventional spectrophotometer measures the 100% transmitted reference, 0% (black) and sample signal intensities alternately, so that it can measure the absolute absorbance, but it is difficult to detect a very small variance of transmitted intensity due to a wide measurement range (0 to 100%). On the other hand, as the HPSP directly measures a difference in transmitted light (V_R-Vs) between the reference light and the sample one, it can detect even a small difference.

Fig. 2-2 shows the block diagram of the system. The light passing the measurement sample and the reference sample is alternately detected via a sector mirror by the Si detector installed in the integrating sphere. This figure illustrates that the output signal from the detector ④ is amplified by the amplifier ⑥, and then divided into D.C. elements temporally invariant and A.C. elements containing various frequencies by the signal element separator ⑧. The ratio of the D.C. elements $(V_R+V_S)/2$ that is amplified by the D.C. amplifier ⑦ to the A.C. elements (V_R-V_S) amplified by the A.C. amplifier ⑨ is calculated by the divider ⑪.

When the incident light is designated as I_0, the transmitted light I, the device constant k, and the material concentration c, the Lambert-Beer Law, which is the principle for measuring the concentration, is expressed as:

$$I = I_0 e^{-kc}$$

In the system considered, I_S and I_R correspond to the incident light I_0 and the

transmitted light I, respectively. Fig. 2-2 shows $I_R \propto V_R$ and $I_S \propto V_S$ so that calculation of the ratio (A.C. element $(I_R - I_S)$ to D.C. element $(I_R - I_S)/2$) by the divider ⑨ is:

$$\frac{\frac{I_R - I_S}{I_R + I_S}}{2} = 2 \times \frac{1 - e^{-kc}}{1 + e^{-kc}}$$

$$= 2 \times \frac{e^{\frac{1}{2}kc} - e^{-\frac{1}{2}kc}}{e^{\frac{1}{2}kc} + e^{-\frac{1}{2}kc}}$$

$$= 2 \tanh\left(\frac{1}{2}kc\right) \qquad (2.1)$$

When $kc \ll 1$, that is, a sample hardly absorbs the light,

$$\cong kc$$

Thus,

$$const \cdot \frac{I_R - I_S}{I_R + I_S} \cong kc \qquad (2.2)$$

This means a result of the ratio calculation of $(I_R - I_S)$ and $(I_R + I_S)$ corresponds to the absorbance, which is proportional to the material concentration, and therefore qualitative analysis can be performed.

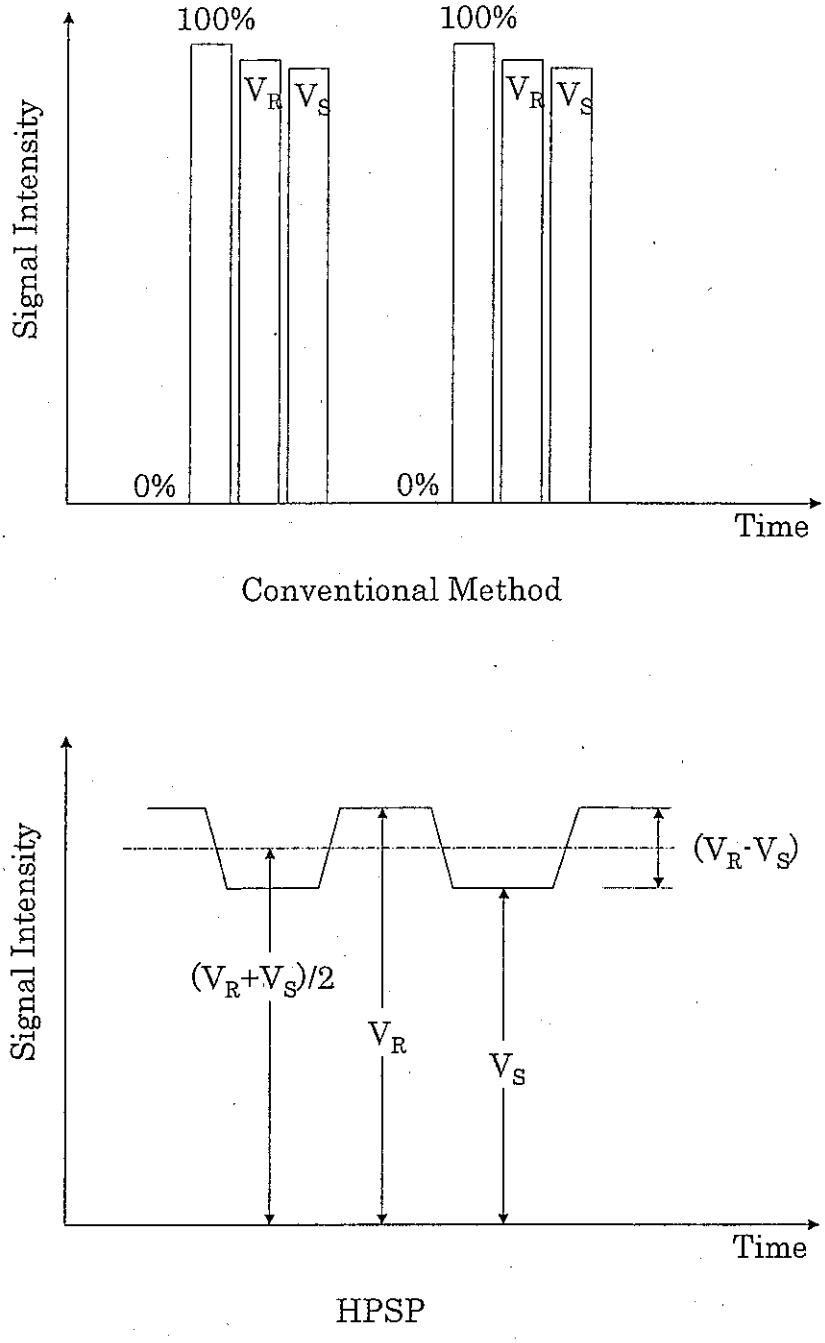
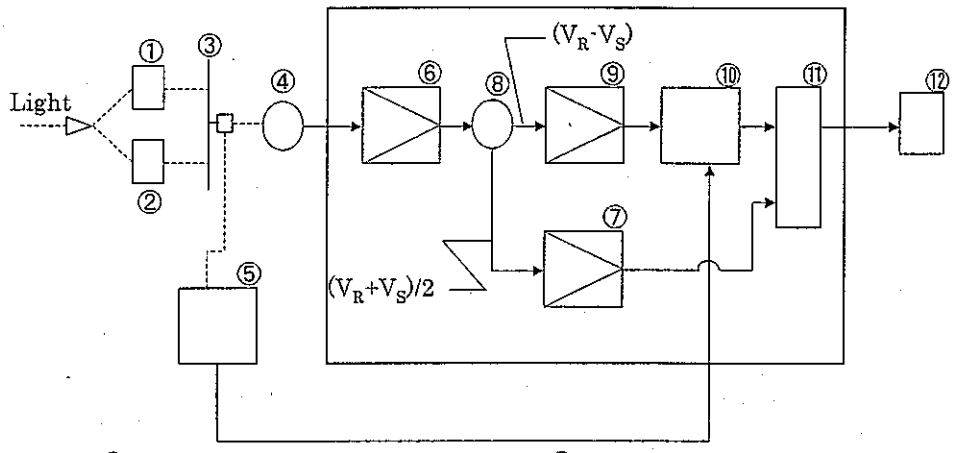


Fig. 2-1 Comparison of Output Waveform from Detector



① Measurement Cell
② Reference Cell
③ Sector Mirror
④ Integrating Sphere Detector
⑤ Synchronizing Signal Generating Circuit
⑥ Amplifier
⑦ D.C. Amplifier
⑧ Signal Element Separator
⑨ A.C. Amplifier
⑩ Synchronous Commutator
⑪ Divider
⑫ Recorder

Fig. 2-2 Block Diagram of HPSP Electric Processing Circuit

3. HPSP system

3.1 General

Fig. 3-1 and 3-2 show the appearance of the system and the configuration of the system, respectively. This system mainly consists of a optical measurement part, a signal processing unit and a control unit.

As seen in Fig. 3-2, the light source consists of a halogen lamp ①, which emits light ranging from the near infrared region to the visible radiation, and the light source converging system ②. Light travels through the higher order light cut filter ③, converging on the incident slit ④ of the monochrometer ⑥.

Monochromatic light separated by monochrometer installed in the spectroscope converges on a part of the two-branch fiber ⑧ through a lens. Light converged on the one-branch fiber ⑪ is led to the flow type sample cell ⑩ which is placed in the inner box. Fig. 3-3 and 3-4 show the appearance and the cross section of the flow type sample cell, respectively.

Light passing through the sample cell is led to the detector ⑯ via fiber. On the other hand, light transmitting the 1 m-long bundle fiber ⑨ passes through the balance adjustment filter ⑫ which is installed to retain a difference from luminous energy of the sample light within 1%.

After passing through the balance adjustment filter, light passes through the reference cell ⑬ and then the ND filter ⑭ for fine adjustment of luminous energy before reaching the detector ⑯.

Two types of ND filters with transmissivity of 0-10% and 0-100% are used in this measurement in order to correct a variation in the baseline caused by the effects of a sample mixed with multiple elements, that shows absorption over the whole wavelength.

The sample light and the reference light are alternately led to the integrating

sphere (40 mmϕ) ⑯ by sector mirror ⑮. The entered light repeats diffuse reflection on the inner wall of the integrating sphere, and is measured by detector through the window provided on the inner surface of the integrating sphere.

To ensure stable measurement on the surface receiving light, the detector uses a Si photocell that features higher spectroscopic sensitivity than photomultiplier in the wavelength range to be measured (near infrared region). The light detected by Si photocell is signal-processed by electric processing circuit and collected to the personal computer (PC) via interface. Data processing including wavelength movement of the monochrometer, signal input from the detector and spectral representations is performed by the computer.

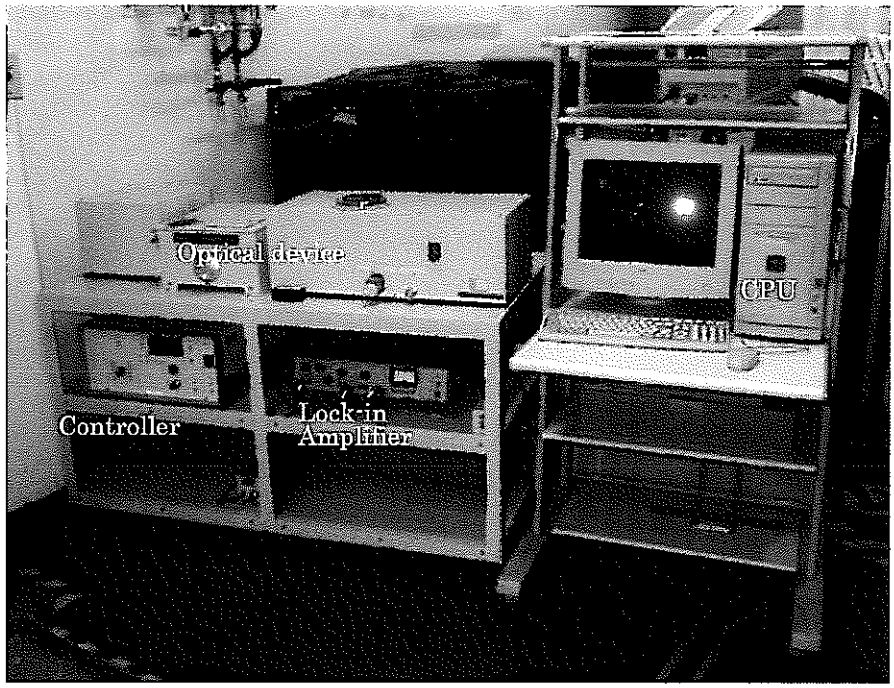
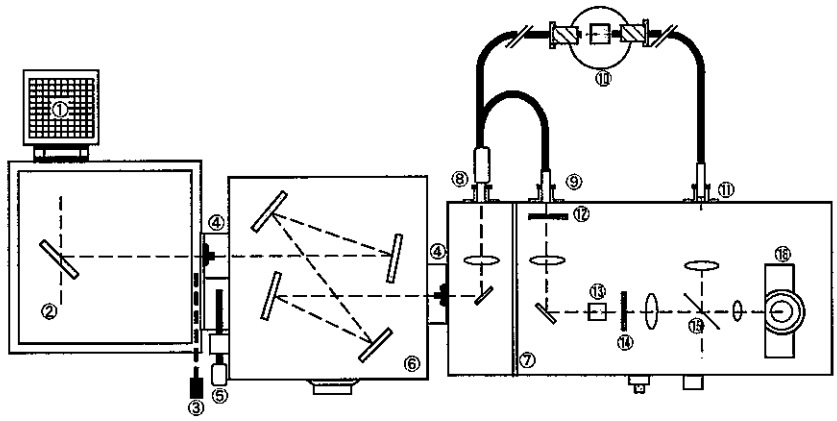


Fig. 3-1 High Performance Spectrophotometer



① Light Source(Halogen150W)
② Light Source Converging System
③ High Order Light Cut Filter
④ Slit
⑤ Wedge
⑥ Monochrometer
⑦ Double-beam Optical System
⑧ Two-branch Fiber
⑨ Fiber for Reference Light
⑩ Sample Cell
⑪ Fiber for Sample Light
⑫ Balance Adjustment Filter
⑬ Reference Cell
⑭ ND Filter
⑮ Sector Mirror
⑯ Integrating Sphere/Detector (Si Photocell)

Fig. 3-2 Outline of the Main Body of High Performance Spectrophotometer

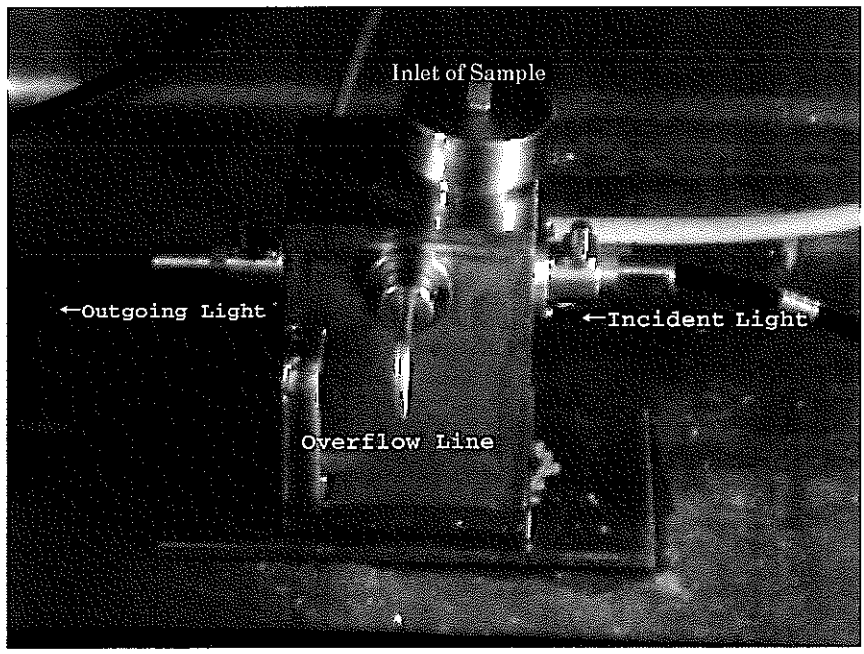


Fig. 3-3 Flow-type Sample Cell

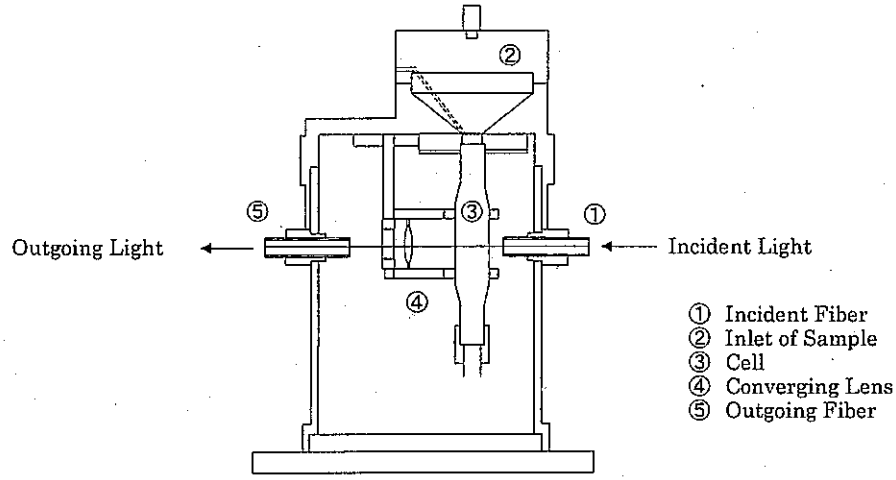


Fig. 3-4 Outline of Flow-type Sample Cell

3.2 Specifications of Each Part

Specifications of this system are shown in Table 3-1.

Table 3-1 Specifications of High Performance Spectrophotometer

Item	Specifications
Range of Wavelength Measured	750 nm~860 nm (range of 800~860 nm is guaranteed)
Type of Measurement	Double-beam, lock-in type
Measured Item	Transmission measurement
Scope of Measurement	Corresponding to 2×10^{-2} ~ 4×10^{-4} Abs
Light Source	Halogen lamp
Monochrometer	Focal length: 25 cm Diffraction grating: 600/1000 nm, 1 μm blaze Wavelength resolution: 0.2 nm (half band width)
Optical Fiber, 2-brached Fiber	Made of Quartz with an inner diameter of 3 mmϕ
Sample Cell	Flow type quartz glass Optical path length: 10 mm
Integrating Sphere	Inner diameter 40 mmϕ
Detector	Si photocell of electronic cooling type Light receiving area: 25 mm^2
A.C. Amplifier	Analog type lock-in
Data Processing	Absorptivitiy (%)

3.3 Improvements over the General Purpose Equipment (Used for Measurement of Langmuir Blodgett Films)

① To apply to measurement of High Active liquid Waste solution (remote control), an optical fiber made of quartz was used as the transmitting of the light to and from optical sample cell. In addition, a difference in light intensity between the reference light and the sample one can be corrected by using similar an optical fiber for the reference light.

② Use of a high power halogen lamp (150 W) covers a loss of the light intensity

incurred by the optical fiber.

③ In order to ensure stable measurement on the light receiving surface, a Si photocell detector, that shows a high spectroscopic sensitivity in the range of the wavelength, was applied (near infrared region) is used.

④ In consideration of handling nitric acid samples for the reference, the reference cell holder was made air-tight to protect the optical components in the main body from corrosion.

⑤ The variable-type ND filter which was free from dependency on the wavelength and that can easily adjust the light intensity was selected so that more strict adjustment can be attained.

3.4 Operational Procedures of HPSP System

Operational (measurement) procedures of the HPSP system are given below:

① Calibration of HPSP System

Turn on power, and calibrate* the main system. Calibration procedures are described in Attachment 2.

* Calibration should be conducted during the start-up operations after the long term shutdown (2 to 3 months).

② Selection of Measurement Conditions

Input the conditions such as measurement sensitivity, the range of wavelength to be measured and the sweep rate to the PC. When the measurement sensitivity is changed, a value of [SENSITIVITY] of the lock-in amplifier should be also changed.

③ Measurement of Base Spectrum

Fill the reference and sample cells with a solution that can be blank. For example, if a plutonium nitric solution is to be measured, prepare a nitric acid solution with the same concentration as the sample. If HALW is to be measured, use the synthetic HALW solution. Set the measurement mode of the PC to [Reference], and start measurement.

When the base spectrum was measured within the sensitivity that was inputted in the above (2), proceed to step (4). If not, go back to step (2) and input the measurement sensitivity again. Input a larger value this time than the previous value inputted.

④ Measurement of Spectrum

Leave the solution in the reference cell, which was set in 3-4. ③, while a sample to be measured should be placed in the sample cell. Select the measurement mode of the PC [Sample], choose the spectrum file to be used for a reference, and then start measurement.

⑤ Analysis of Results

Peak intensity of the spectrum obtained should be calculated by various analytical methods (the three-point method, the data accumulation method, the simple moving average method, and Fourier analysis, if necessary).

⑥ Concentration Calculation

Calculate a concentration of the material from the predetermined analytical curve.

3.5 Balance Adjustment of Base Spectrum by Optical Control

Based on the principle, the system measures a difference of light intensity between the reference and the sample. Therefore, the balance between the signal intensity of these lights should be maintained. An example of balance adjustment is shown in Fig. 3-5.

As shown in the figure, when the light intensity of the sample considerably reduces, the absorption peak deviates from the full scale. Decreasing the reference light intensity by optical control will lower the whole baseline (or vice versa depending on the cases) to allow proper measurement. The light intensity can be adjusted by the use of the coarse and fine optical filters.

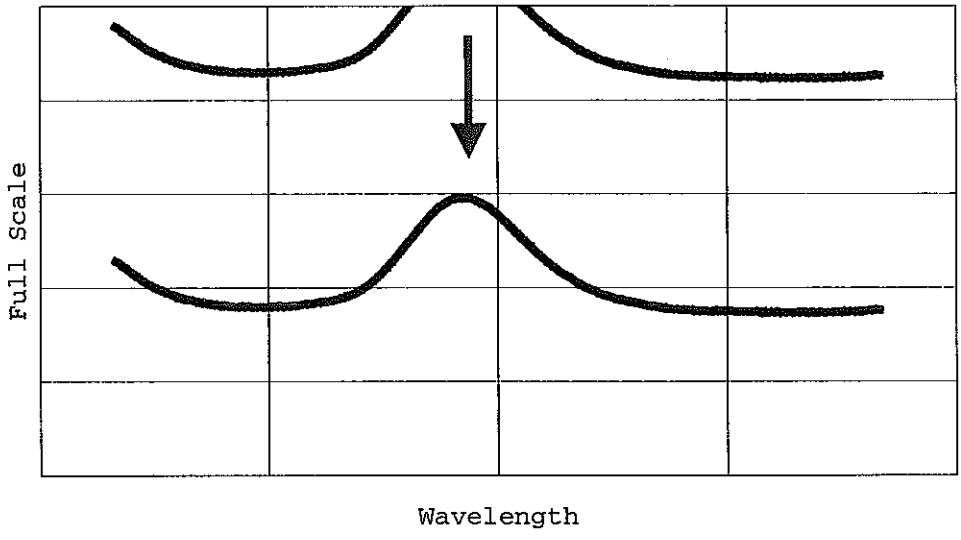


Fig. 3-5 Example of Balance Adjustment by Optical Control

4. Reagents and Samples for Measurement

① Neodymium Solution

In the cold test, a neodymium solution was used as an alternative to plutonium. Neodymium shows a sharp absorption peak near the absorption wavelength of plutonium(VI) , with the absorption factor of about 1/25 of plutonium.

The neodymium solution was prepared by the neodymium nitrate, which is dissolved in the nitric acid of 1 mol/L. The test solution was prepared diluting mother solution of 25 g/L, to desired concentrations with 1 mol/L nitric acid solution.

For the standard solution in determining an analytical calibration curve, the commercially available standard solution for atomic absorption spectrometry (1000 mg/L) was used.

② Cerium(IV) Solution

Cerium(IV) was used as an oxidant to prepare the plutonium to be hexavalent[2]. By dissolving di-anmonium cerium nitrate into the 2.2 mol/L nitric acid solution, the 0.05 mol/L cerium(IV) solution was prepared. Addition of Cerium(IV) was determined to be 2 ml (0.1 mmol/L) to the sample of 8 ml. This quantity added can completely oxidize contained plutonium in the HALW to hexavalent.

③ Plutonium nitrate Solution

The source plutonium solution (5.018 mgPu/g) was made by qualified standard plutonium metal (CRM-126) after adjusted by gravimetric method. Plutonium taken from the mother solution was diluted with the 2.2 mol/L nitric acid to obtain the solution of 279.4 mgPu/L. This was further diluted with nitric acid of the same concentration, and then solutions of each plutonium concentration were prepared for measurement.

The plutonium standard solution used in the HALW measurement was made from the mother solution that had been already standardized and prepared to attain desired concentrations.

④ Synthetic HALW Plutonium Solution

The solution prepared by simulating the HALW at the Tokai Vitrification Facility (TVF) was mixed with the source plutonium solution to prepare the synthetic HALW solution containing plutonium. The constituents of the synthetic HALW are shown in Table 4-1.

Table 4-1 Constituents of Synthetic HALW

Element	Concentration [10^{-2} mol/L]	Element	Concentration [10^{-2} mol/L]
Na	100	R,E	25.8(g-oxide/l)
P	1.63	Zr	0.87
Fe	17.4	Mo	0.94
Cr	2.5	Co	0.84
Ni	3.91	Ag	0.05
Rb	0.48	Cd	0.056
Cs	2.14	Sn	0.039
Sr	1.14	Se	0.08
Ba	1.53	Te	0.37

⑤ HALW Sample

The HALW generated at the Tokai Reprocessing plant includes sludge, fission products and crud. As these coexistent materials may give influences on spectrum measurement of plutonium(VI) such as fluctuations of the baseline due to irregular reflection or absorption of range of the wide wavelength. They should be removed or corrected. Effects of sludge could be removed by filtering. The effect of the fission products, crud and others would be eliminated through adjusting of optical balance.

It was confirmed that the HALW measured in this study did not contain sludge, therefore filtering was not necessary. It is, however, often found sludge in the HALW.

5. Results and Discussion

5.1 System Performance Test Using Neodymium Solution

5.1.1 Spectrum Measurement of Neodymium

Neodymium spectrum was obtained on its concentration of 10-250mg/L. The results were shown in Fig. 5-1.

Each spectrum in the figure demonstrates the concentration dependency between the neodymium concentration and the HPSP intensity.

These spectra were obtained by continuous measurement; however, the baselines were not stable, so that it would be inappropriate to use reading of the peak top as the measured value without being corrected. As fluctuation in the baseline is due to the principle of this method considered, it cannot be corrected by hardware. Thus an approach from the software was examined in 5-1-2.

It should be noted that the unit of the HPSP intensity was given in a arbitrary unit of "HPSP Intensity [-]". HPSP system measures a difference between the reference light and the sample one. The value does not correspond to the absolute absorbance.

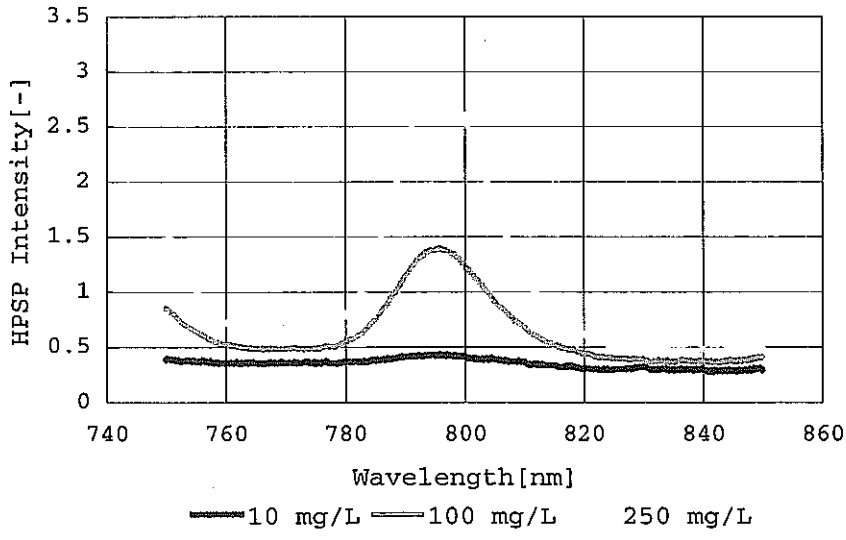


Fig. 5-1 Spectrum of Neodymium(III) [5% Full Scale]

5.1.2 Review of Baseline Correction Method

According to the principle mentioned in Section 3, this method considered does not measure the zero reference point (black in terms of the standard spectrophotometer) so that correction of the zero point or the baseline would be required. Previous review identified that the baseline considerably varied due to the effects of the coexistent elements. Accordingly, application of the three-point method (Fig. 5-2) to the HPSP spectrum was examined to calculate the peak intensity (HPSP Intensity) after correcting the baseline.

Wavelength (three points) to calculate the peak intensity was evaluated from the spectrum shown in Fig. 5-2. Neodymium showed absorption at 795 nm. The baseline correction wavelengths were determined to be 770nm and 840 nm. The calculation method of the peak intensity with using three-point (770, 795 and 840 nm) is shown in Equation (5.1):

$$A_{Nd} = A_{795} - \left\{ \frac{(840-795)\cdot A_{770} + (795-770)\cdot A_{840}}{(840-770)} \right\} \qquad (5.1)$$

$$= A_{795} - B_{795} \qquad (5.2)$$

A_{770}, A_{795}, A_{840}: signal intensity at each wavelength (770 nm, 795 nm and 840 nm)

B_{795}: background signal intensity at 795 nm

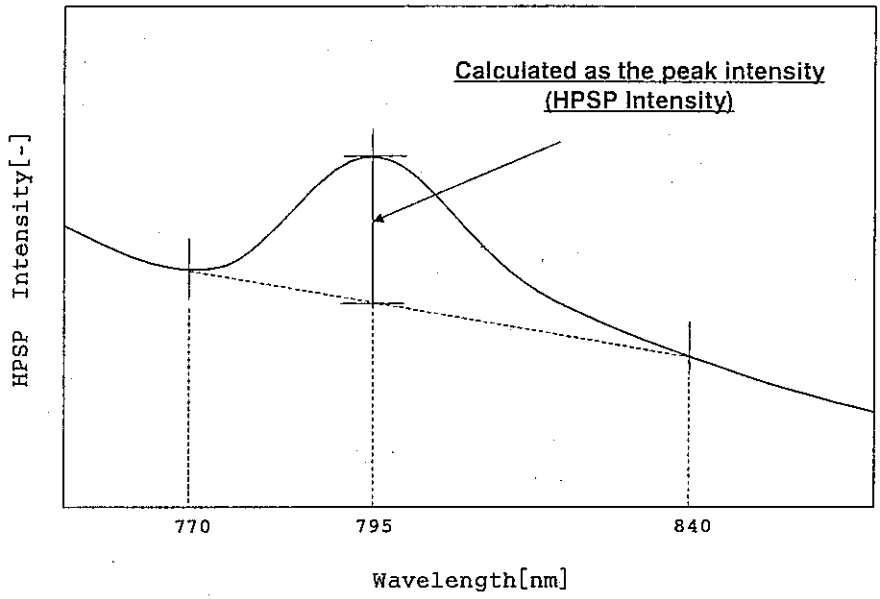


Fig. 5-2 Concept of Three-Point Method for Nd Measurement

5.1.3 Review of Full Scale

Based on the three-point method described in 5-1-2, changes in measurement results and conditions due to different full scales (see Attachment 1 for detailed information) were examined. Measurements were conducted at each sensitivity on the neodymium solutions that were prepared within the range of 0~250 mg/L. The results were compared and reviewed for each examination item. Conditions of measurement are as follows:

Full scale : 1, 2 and 5%

Samples measured : blank, neodymium standard solutions (10, 50, 100, 200 and 250 mg/L)

Number of measurements: five for each sample (ten for Blank)

Calculation of the detection limits was subject to the definition of the IUPAC (recommendation of 1976) (see Attachment 3). Fig. 5-3 shows the analytical curves depending on different full scales, and Table 5-1 lists the results of measurement.

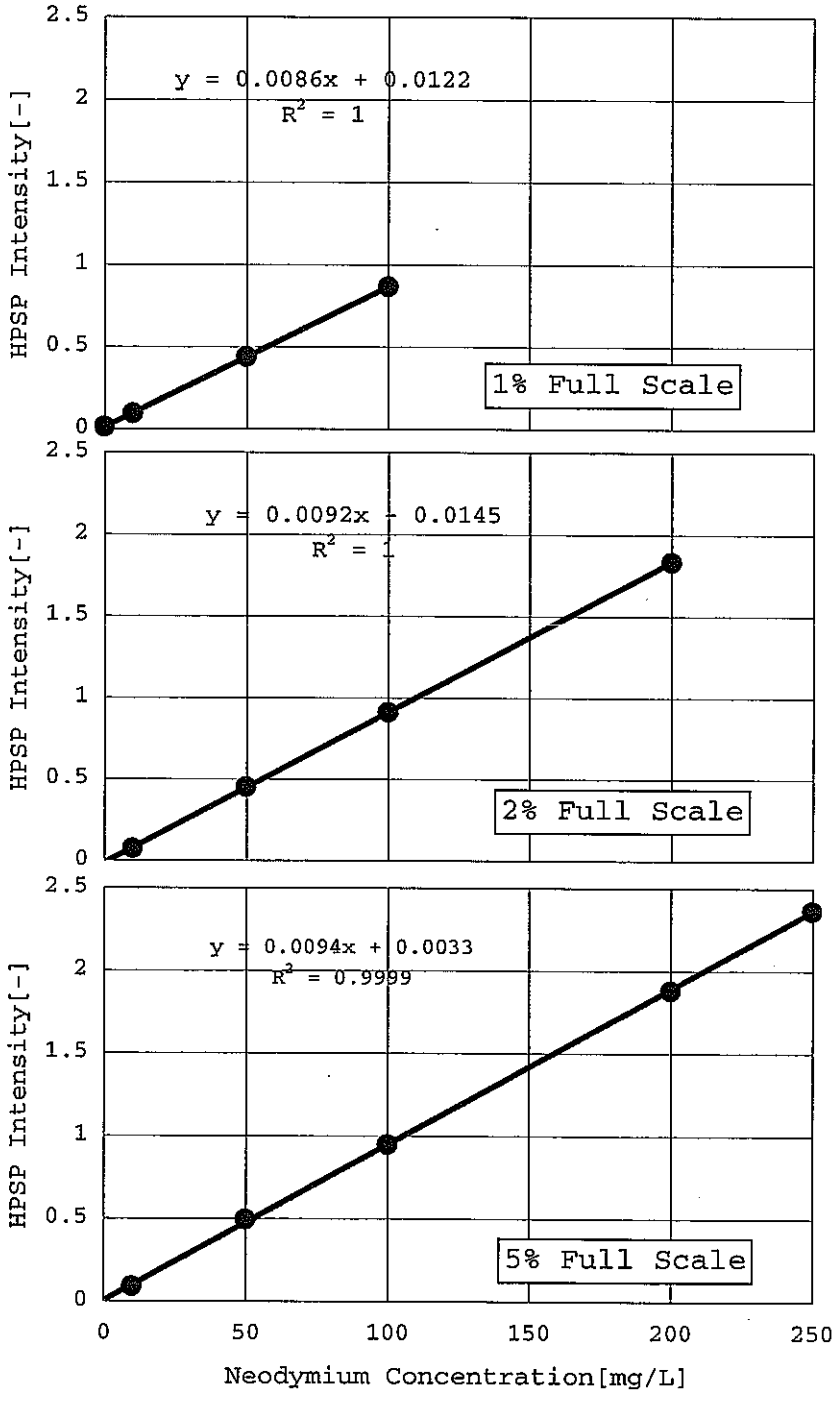


Fig. 5-3 Relation between Neodymium Concentration and Intensity at Each Sensitivity

Table 5-1 Measurement Sensitivity and Detection Limit at Each Scale

Full Scale	5%	2%	1%
Measurement Sensitivity	Low ◄——► High		
Range of Measured Nd Concentrations [mg/L]	0-250	0-200	0-100
Range of Measured Wavelength [nm]	850-750	850-750	820-780
Upper/Lower Points correction for baseline[nm]	840/770	840/770	820/780
Standard Deviation (Blank)	0.03	0.03	0.04
Sensitivity of Calibration Curve (dy/dx)	0.0414	0.0405	0.0394
Detection Limit [mgPu/L]	2.20	2.22	3.27

These results showed a good relation with the signal intensity and the concentration ranges corresponding to the all full scales measured. Upper limit of Pu concentration is 100 mg/L.

In the base measurement spectrum explained in the procedures (3) in 3-4, nitric acid was used as a reference. As the base spectrum of nitric acid has a gradient, both ends of the wavelength to be measured are deviated at 1% full scale. Therefore, measurement was limited to the wavelength from 780 nm to 825 nm. (Refer to Fig. 5-4.)

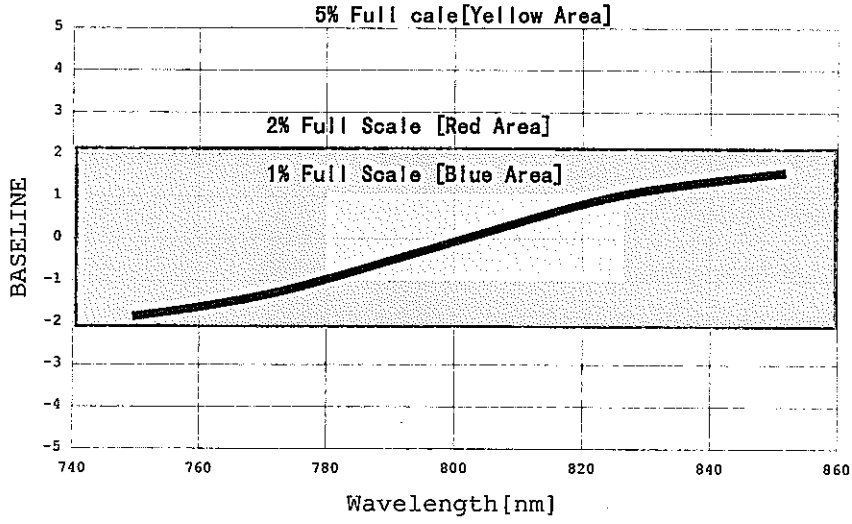


Fig. 5-4 Measurable Wavelength Ranges by Full Scale

The detection limit at 5% full scale measurement was found to be 2.5 mgNd/L, approx. 0.1 mgPu/L when converted into the plutonium concentration.

5.2 Measurement of Plutonium Solution

5.2.1 Measurement of Plutonium Nitrate Solution

5.2.1.a HPSP Spectrum

Plutonium(VI) contained samples, prepared in 4.3③, was measured based on procedures given in 3-4 ①~⑥. The three-point method was applied to calculation of the peak intensity of plutonium(VI) . The peak top was assumed 830.6 nm and the baseline correction 840.6 nm and 820.6 nm. The peak intensity (HPSP Intensity) at that time was obtained from the equation (5.3).

$$A_{Pu} = A_{830.6} - \left\{ \frac{(840.6-830.6)\cdot A_{770} + (830.6-820.6)\cdot A_{840}}{(840.6-820.6)} \right\} \qquad (5.3)$$

$$= A_{830.6} - B_{830.6} \qquad (5.4)$$

$A_{830.6}$, $A_{820.6}$, $A_{840.6}$	:	signal intensity at each wavelength (830.6nm, 820.6nm and 840.6 nm)
$B_{830.6}$	:	background signal intensity at 830.6 nm
Samples measured	:	blank, 1.11, 2.78, 5.56 and 11.1 mgPu/L
Acid concentration	:	2.2 mol/L
Number of measurement	:	ten times each
Measurement sensitivity	:	10% full scale
Range of wavelength measured	:	800~860 nm (0.2 nm/Step)

An example of spectrum obtained by measurement is shown in Fig. 5-5.

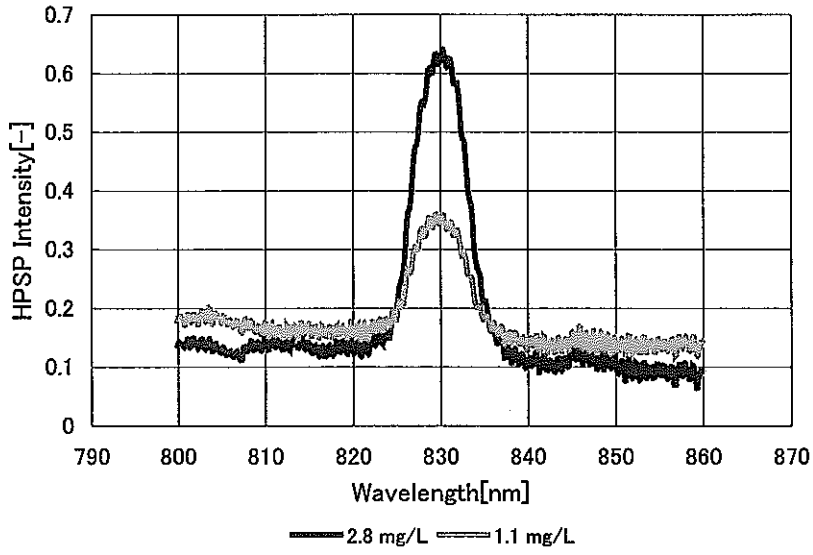


Fig. 5-5 Spectrum of Plutonium(VI) [Full scale: 10%, Nitric Acid: 2.2 mol/L]

5.2.1.b Effects of Nitric Acid Concentration

The absorption coefficient varies depending on the wavelength of light and a solvent (in this case acid concentrations). Influence of the nitric acid concentrations to

the peak intensity were studied. Samples with the known concentration of plutonium(4.5 mgPu/L) were prepared by the nitric acid. Those concentrations are 2.0~4.0 mol/L. Measurement Conditions were as follows:

Samples measured	:	4.5 mgPu/L
Acid concentration	:	2.0, 2.6, 3.3 and 4.0 mol/L
Number of measurement	:	ten times each
Measurement sensitivity	:	10% full scale
Range of wavelength measured	:	800~860 nm (0.2 nm/Step)

Results of measurement are shown in Fig. 5-6.

According to the figure5-6, it was found that the peak intensity of plutonium(VI) decreased with an increase in nitric acid concentrations. Approximately 14% difference was found between 2 mol/L and 4 mol/L of acid concentration. Thus based on the analytical curve prepared under the conditions of the acid concentration of 3 mol/L, the error range would be about 0.1~0.2 mgPu/L equivalent, when plutonium concentration is 4.5 mgPu/L.

It is known that plutonium(VI) takes forms of nitric acid ions, $PuO_2NO_3^+$, $PuO_2(NO_3)_2$ and $PuO_2(NO_3)_3^-$ in the nitric acid solution. The existence form of plutonium(VI) depends on the nitric acid concentration in the solution. When the nitric acid concentration increases, plutonium in the solution coordinates more NO_3^- ions.

$$PuO_2^{2+} + NO_3^- \Leftrightarrow PuO_2NO_3^+ \quad (5.5)$$

$$PuO_2NO_3^+ + NO_3^- \Leftrightarrow PuO_2(NO_3)_2 \quad (5.6)$$

$$PuO_2(NO_3)_2 + NO_3^- \Leftrightarrow PuO_2(NO_3)_3^- \quad (5.7)$$

Plutonium(VI) exists as $PuO_2NO_3$and $PuO_2(NO_3)_2$ ions when the acid concentration is 4 mol/L or less. If acidity is more than 4 mol/L, $PuO_2(NO_3)^-$ is formed,

and $PuO_2(NO_3)_3^-$ becomes dominant at 10 mol/L. $PuO_2NO_3^+$ and $PuO_2(NO_3)_2$ show absorption at 830 nm, and $PuO_2(NO_3)_3^-$ at 812 nm. As the ratio of the existence form of plutonium(VI) changes with the nitric acid concentration higher, absorption at 830 nm is considered to be lower.

It is predicted from the past operating results that the nitric acid concentration in the HALW (271E10, 20) will be around 3.0±0.3 mol/L. When the concentration changed by ±0.3 mol/L, the variation corresponded with 4.5 mgPu/L±0.07 mgPu/L. The uncertainty obtained from the iterated measurement in the 3 mol/L nitric acid was 4.5 mgPu/L±0.04 mg/L. The combined uncertainty that contributes to a variation of nitric acid concentrations can be obtained by the following equation:

$$u(HNO_3)/C_{Pu} = \sqrt{(0.07/4.5)^2 + (0.04/4.5)^2} = 0.018 \qquad (5.8)$$

$$u(HNO_3) = C_{Pu} \times 0.018 = 4.5 \times 0.018 = 0.08$$

Thus the uncertainty can be expressed as: 4.5 mgPu/L±0.08 mgPu/L

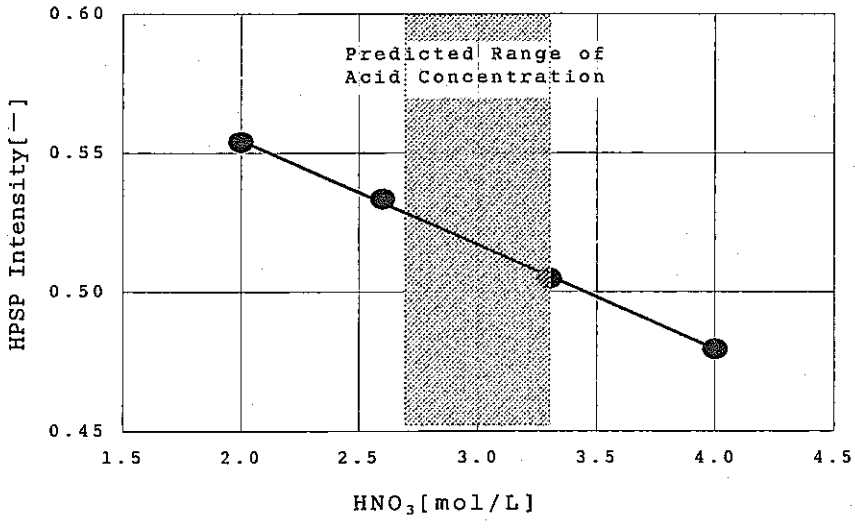


Fig. 5-6 Relation between Acid Concentration and Peak Intensity
[Plutonium Concentration: 4.5 mgPu/L, Full Scale: 10%]

5.2.2 Measurement of Plutonium in Synthetic HALW

The actual HALW includes cruds, fission products (FP) and sludge. In order to examine the effects of these coexistent materials and elements on the plutonium(VI) spectrum, Plutonium in the synthetic HALW solution were measured. Measurement Conditions were as follows:

Samples	:	blank (synthetic HALW), 1.11, 2.78, 5.56 and11.1 mgPu/L (in synthetic HALW)
Acid concentration	:	2.2 mol/L
Number of measurement	:	ten times
Measurement sensitivity	:	10% full scale
Range of wavelength measured	:	810~860 nm (0.2 nm/Step)
Reference	:	synthetic HALW

The reference solution, which is necessary for the optical balance adjustment between reference and sample, is important to HPSP measurement system. The synthetic HALW was s selected as a reference to ensure elimination of the effects of the coexistent materials. The balance adjustment of the base spectrum under the above conditions could be performed within the range of 10% full scale. Fig. 5-7 shows an example of the spectrum using synthetic HALW as a reference.

Similar to the results of measurement in 5-2-1, the measured spectrum indicated that noise components with regular cycles overlapped on the spectrum. (The noise with regular cycles is called as "systematic noise", hereafter.)

The actual HALW samples may have different concentrations of the coexistent elements for every batch. It is impossible to prepare suitable synthetic HLAW for each measurement. Accordingly, nitric acid was determined to be used as the reference so that the balance may be adjusted flexibly. A method to adjust the optical balance by the optical filter was examined.

The advantage of using the nitric acid solution as the reference lies in a

relatively flat spectrum of the nitric acid within the range of the wavelength measured, which allows the balance adjustment of various samples only by the optical filter control.

Taking into account of these considerations, modification was made to the conventional system by installing the Circular Linear-Wedge Neutral Density Filter (ND filter) that could control the transmissivity with a range of 0-100% to control the light energy of the reference. This allowed balance adjustment to be accommodated with the samples having the baseline of large absorption or those showing great fluctuations in the baseline. The system was designed as a two-stage adjustment structure first ND filter that could control the transmissivity of 0-100%(coarse) and second one could control 0-10%(fine). The synthetic HALW samples with plutonium were measured by the modified instrument.

Measurement Conditions were as follows:

Samples measured	:	blank (synthetic HALW), 1.0, 2.5, 5.0 and 10.0 mgPu/L (in synthetic HALW)
Acid concentration	:	2.2 mol/L
Number of measurement	:	ten times each
Measurement sensitivity	:	10% full scale
Range of wavelength measured	:	810~860 nm (0.2 nm/Step)
Reference	:	3.0 mol/L nitric acid

Fig. 5-8 shows the spectrum of the optically adjusted balance with using nitric acid as the reference.

According to Fig. 5-8, the obtained spectrum took a form of the plutonium absorption peak overlapping on the convex shape baseline. The peak intensity was calculated by three-point method at the same wavelength positions as the case of the plutonium nitrate solution and calculates plutonium concentration by calibration curve (Fig. 5-9). It was found that a correlation coefficient was not good compared with the

measurement result of the plutonium nitrate solution.

Since there was a possibility that the base line correction by three-point method was inappropriate to the spectrum, linear differential was performed on the synthetic HLAW spectrum and the wavelength for the base line was determined. Fig. 5-10 and 5-11 show the results for the spectrum of 1 and 2.5 mgPu/L, respectively.

The linear differential curve of the 2.5 mgPu/L spectrum clearly indicates its peak, while the 1 mgPu/L spectrum shows a very small peak, but does not clearly present the position (wavelength) for baseline. When looking into the linear differential curve of the 2.5 mgPu/L in detail, it is considered most adequate to determine the peak wavelength at 830 nm, taking the lower peak point at 823 nm and the upper peak point at 837 nm. Results of the peak intensity calculation by using the three-point method with these wavelengths selected were:

$$A_{Pu} = A_{830} - \left\{ \frac{(837-830)\cdot A_{823} + (830-823)\cdot A_{837}}{(837-823)} \right\} \qquad (5.9)$$

$$= A_{830} - B_{830} \qquad (5.10)$$

A_{830}, A_{823}, A_{837} : signal intensity at each wavelength (830nm, 823nm and 837 nm)

B_{830} : background signal intensity at 830 nm

The peak intensity calculated from the above equation was used for obtaining the calibration curve. The correlation coefficient was R^2= 0.9946, which showed better correlation. For measuring samples, whose baseline will fluctuate or peak will deviate from the set value, it is necessary to determine the three wavelengths at the peak and upper and lower points.

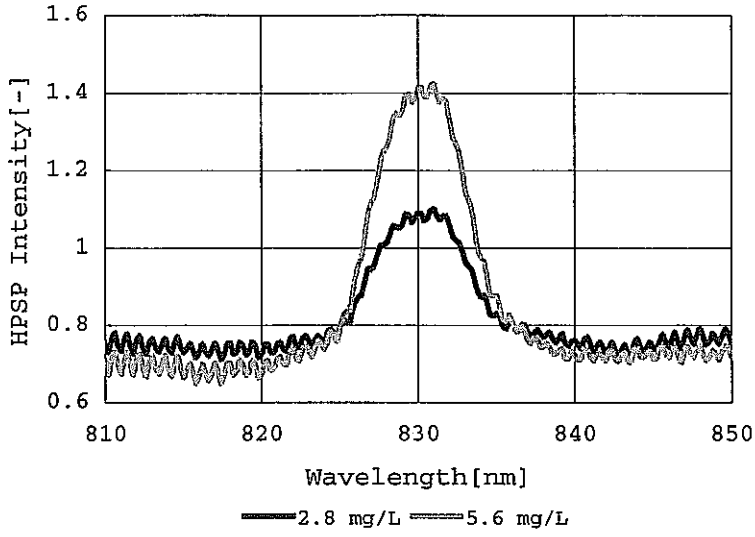


Fig. 5-7 Plutonium(VI) Spectrum in Synthetic HALW
[Full Scale: 10%, Reference: Synthetic HALW]

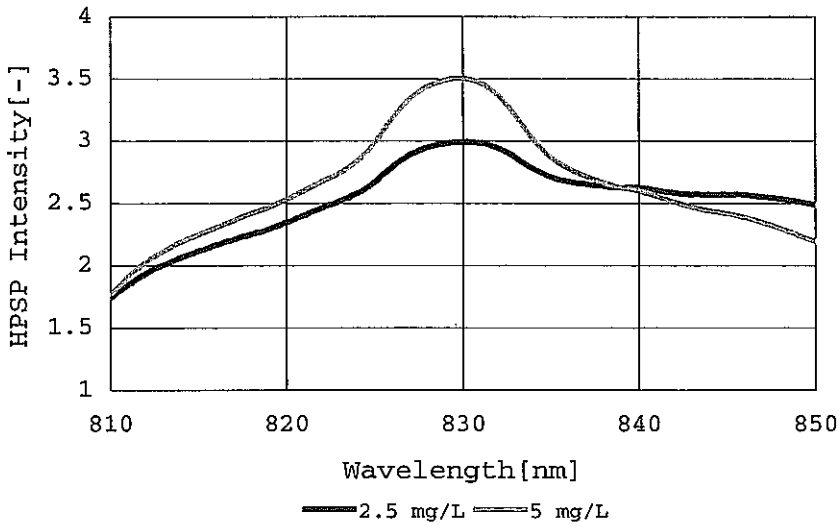


Fig. 5-8 Plutonium(VI) Spectrum in Synthetic HALW
[Full Scale: 10%, Reference: 3M-HNO_3]

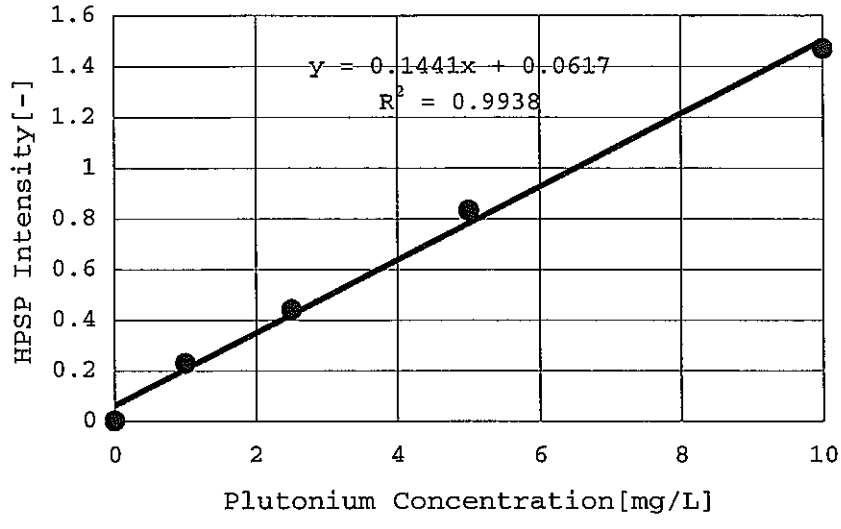


Fig. 5-9 Calibration curve of Plutonium(VI) in Synthetic HALW
[Full Scale: 10%, Reference: 3M-HNO_3]

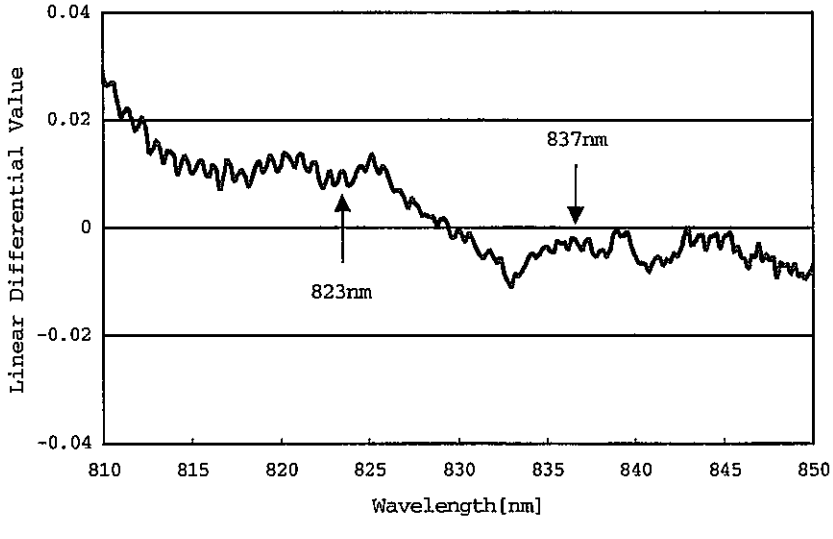


Fig. 5-10 Linear Differential Curve [1 mgPu/L]

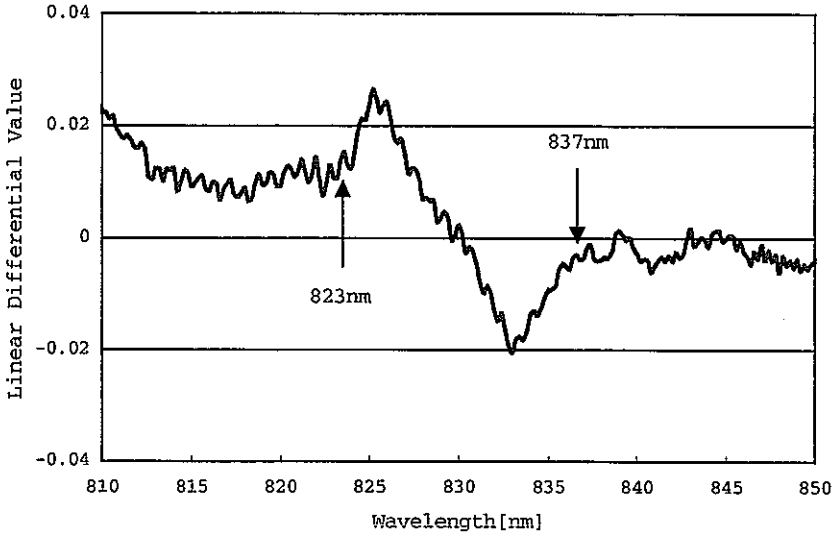


Fig. 5-11 Linear Differential Curve [2.5 mgPu/L]

5.3 Improvement of Spectrum S/N Ratio by Data Analysis

The figure shows that a relation between the plutonium concentration and intensity were existed; however, systematic noise components were observed on the spectrum in every wavelength. HPSP system was designed to be high sensitivity, which cannot be measured by the conventional spectrophotometry, therefore it is indispensable to remove such cyclic noise components in order to improve the S/N ratio. Motors and other parts of the instrument that may transmit cyclic signals were checked, but noises during measurement could not be eliminated. Therefore, a method to remove them by data processing after the measurement was studied.

Systematic noise components overlap on the measured spectrum of plutonium in the synthetic HALW. This leads to an unfavorable S/N ratio when a sample is a very low concentration on the order of mg/L. As this noise did not changed by time, it was not derived from convection or accumulation in the sample, but specific to the system. It could not be removed during measurement and thus an attempt was made to eliminate it by the spectrum data analysis. Calculation methods chosen were the

Data accumulation method, simple moving average method and Fourier transform analysis.

Fig. 5-12~5-20 show the spectrum after calculation. Fig. 5-21 and 5-22 indicate the relation between the HPSP intensity and the concentration after calculation. Tables 5-2 and 5-3 list the detection limits evaluated by a combination of each calculation method. (As for Fourier transform analysis, the analytical method with using the actual data is described in Attachment 4.)

5.3.1.a Data Accumulation Method

The data accumulation method is to repeat the measurement for a number of times, and then averages absorbance for all scanning. This method does not require differences of frequency characteristics between signals and noises, showing high ability to detect signals. However, it is only applied to repeatable measurement. When the measurement was done N times, the S/N ratio will theoretically increase by $\sqrt{N}$ times.

Ten times accumulation was found to be enough for this method. The method is popular in the field of the spectrum analysis and does not require complicated operations. As for the measurement results random noise was decreased, however, systematic noise was not decreased.

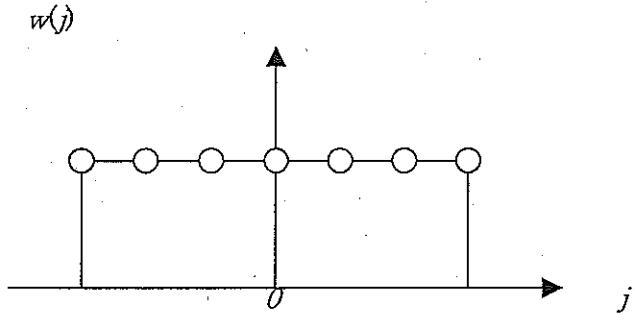
5.3.1.b Simple Moving Average Method

The simple moving average method smoothes the obtained wave form by applying the rectangular weight function. Assuming the input signal as n numbers of discrete values $x(i)$ (here, i= -m, ···, -1, 0, 1, ···, m), "weight function," $w(i)$, (here, i= -m, ···, -1, 0, 1, ···, m) that consists of N(= 2m+1) numbers of discrete points was used to calculate a smoothed value $y(i)$:

$$y(i) = \frac{1}{W}\sum_{j=-m}^{m} w(j)\cdot x(i+j) \qquad i = \mathrm{m+1,m+2,\cdots\cdots,n-m} \qquad (5.11)$$

$$W = \sum_{j=-m}^{m} w(j)$$

The "weighting function" of the simple moving average can be expressed in the typical diagram shown below:



When the discrete point is assumed to be 5, the equation becomes:

$$X_m = \frac{x_{m-2} + x_{m-1} + x_m + x_{m+1} + x_{m+2}}{5} \qquad (5.12)$$

The simple moving average method allows calculation by simple operations. It showed good results in noise removal (decrease). Compared with the data accumulation method, a decrease in the noise components was clearly observed in the all concentration ranges. This method also significantly improved precision in the low concentration ranges. Furthermore, distinct improvements of precision were confirmed in other concentration ranges. It was found that this is one of the effective methods to analyze the HPSP spectrum.

5.3.1.c Fourier Transform Analysis

In general, the Fourier transform refers to fluctuations of the spectrum on the time axis interpreted into the frequency axis in cyclic terms. With assuming the real $f(x)$ and the imaginary $F(u)$,

$$f(x) \supset F(u) \quad \text{or} \quad F(u) = FT[f(x)] \qquad (5.13)$$

The Fourier transform used here is the fast Fourier transform (FFT) which improves the processing capability of the discrete Fourier transform, a digital processing method.

Definition of the discrete Fourier transform is briefly explained below.

The discrete Fourier transform (DFT) to the data sequence of N numbers [*X(m)= X(0), X(1), X(2), ··· X(N-1)*] is defined as follows:

$$Y(k) = \frac{1}{N}\sum_{m=0}^{N-1} X(m)\cdot e^{-i2\pi km/N} \qquad k=0,1,2,\cdots\cdots,N\text{-}1 \tag{5.14}$$

Here,

$$W = e^{-i2\pi/N} \tag{5.15}$$

W denotes the phase factor, and is expressed as

$$W = e^{-i2\pi/N} = \cos\frac{2\pi}{N} - i\sin\frac{2\pi}{N} \tag{5.16}$$

Moreover, the following abbreviations are used:

$$X(m) \supset Y(k) \text{ or } Y(k) = FT[X(m)]$$

Equations (5.14) and (5.16) lead to

$$Y(k) = \frac{1}{N}\sum_{m=0}^{N-1} X(m)\left(\cos\frac{2\pi km}{N} - i\sin\frac{2\pi km}{N}\right) k=0,1,2,\cdots\cdots,N\text{-}1 \tag{5.17}$$
$$= A(k) - iB(k)$$

$$A(k) = \frac{1}{N}\sum_{m=0}^{N-1} X(m)\cdot\cos\frac{2\pi km}{N} \tag{5.18}$$

$$B(k) = \frac{1}{N}\sum_{m=0}^{N-1} X(m)\cdot\sin\frac{2\pi km}{N} \tag{5.19}$$

According to equation (5.17), the result of DFT consists of the data sequence including real part and imaginary part.

Calculating X(m) from Y(k) inversely is possible by inverse discrete Fourier transform:

$$Y(k) \xrightarrow{\text{Fourier Transform}} X(m) \xrightarrow{\text{Inverse Fourier Transform}} Y(k)$$

The fast Fourier transform developed by Cooley and Turkey in 1965 is a calculation method that succeeded in considerably shortened calculation time. If the number of data, N, is the second power, the data is divided into two, each of which is calculated with using the data divided into two, and finally reduced to the data number 2. Calculation time is reduced considerably using the previous results and calculating regressively, compared with the conventional calculation method ($N \times N$).

The Fourier transform has the following characteristics.

Calculation by the Fourier transform could reduce the noise components of the HPSP spectrum, resulting in improvement of the S/N ratio. The good relation between the concentration and the peak intensity after calculation was found. It would be noted that the Fourier transform was an excellent method to separate the signal components from the noise components. However, it currently requires many manual operations. Thus this method should be developed into a program in order to apply to the routine use.

According to Fig. 5-12~5-20, a combination of the data accumulation method and the simple moving average method is effective to the spectrum of every concentration of the pure plutonium solutions and the synthetic HALW with plutonium samples.

Detection limits of the three analytical methods were calculated following the IUPAC recommendation in 1976. As for the number of measurements of blanks to

calculate detection limit, the IUPAC recommends 20 times, but we adopted nine in this measurement.

Fig. 5-21 and 5-22 show a good relation between plutonium concentration and the intensity after calculation. The detection limit of a combination of the data accumulation method and the simple moving average method came at 0.074 mgPu/L (corresponding to approx. 1.5×10^{-4} abs), which achieved the best result in all the methods applied. This value is about two orders of magnitude lower than that of conventional spectrophotometry. In addition, a combination of the data accumulation method and the Fourier analysis provided the detection limit approximately 30% lower than that obtained by data accumulation method.

Compared with Pu measurement results in the pure Pu solutions, Pu measurement in the synthetic HALW was not obtained accurate and sensitive results, due to effects of the coexistent elements, and its detection limit was 0.2 mgPu/L.

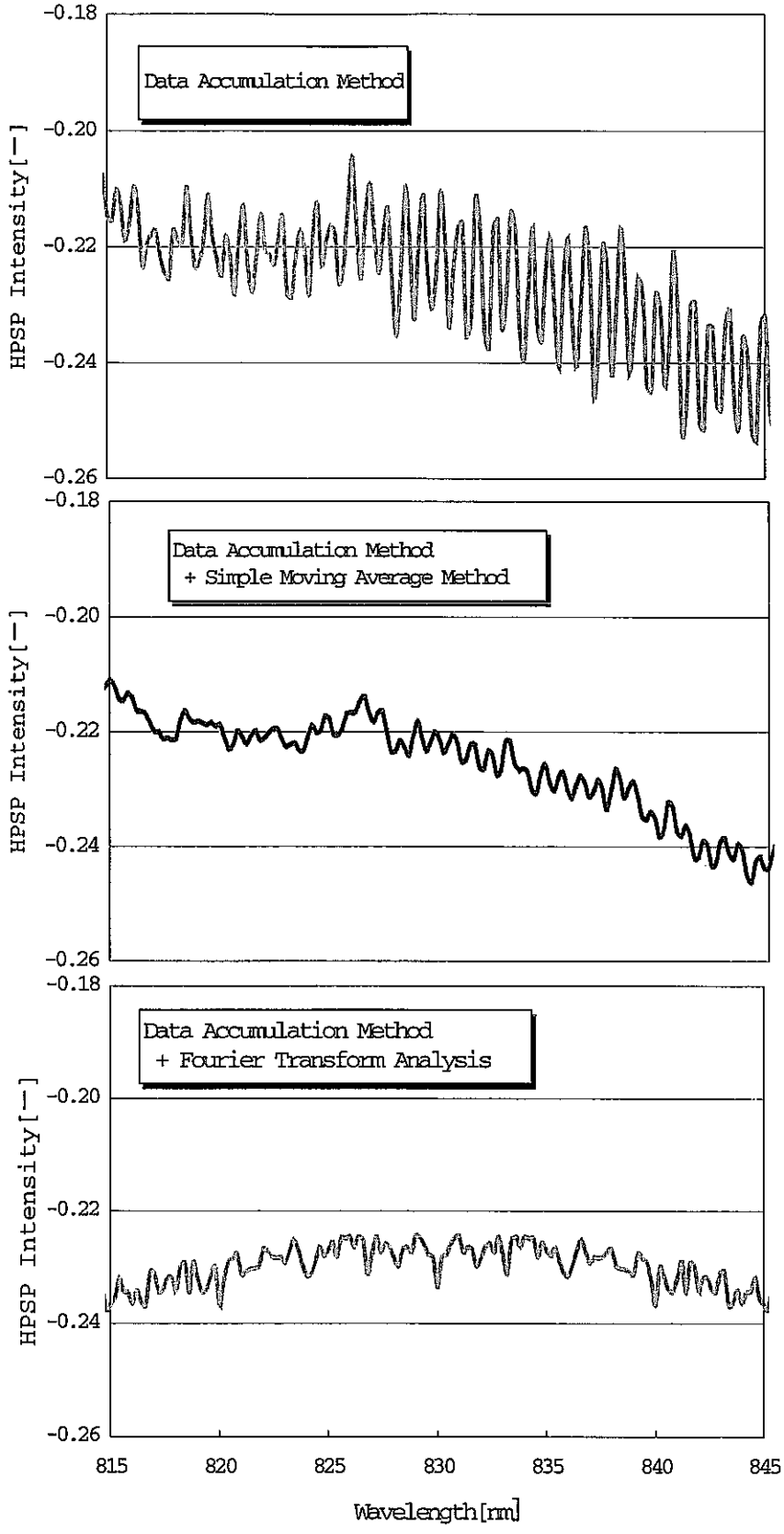


Fig. 5-12 Results of Spectrum Analysis [Nitric Acid Solution]

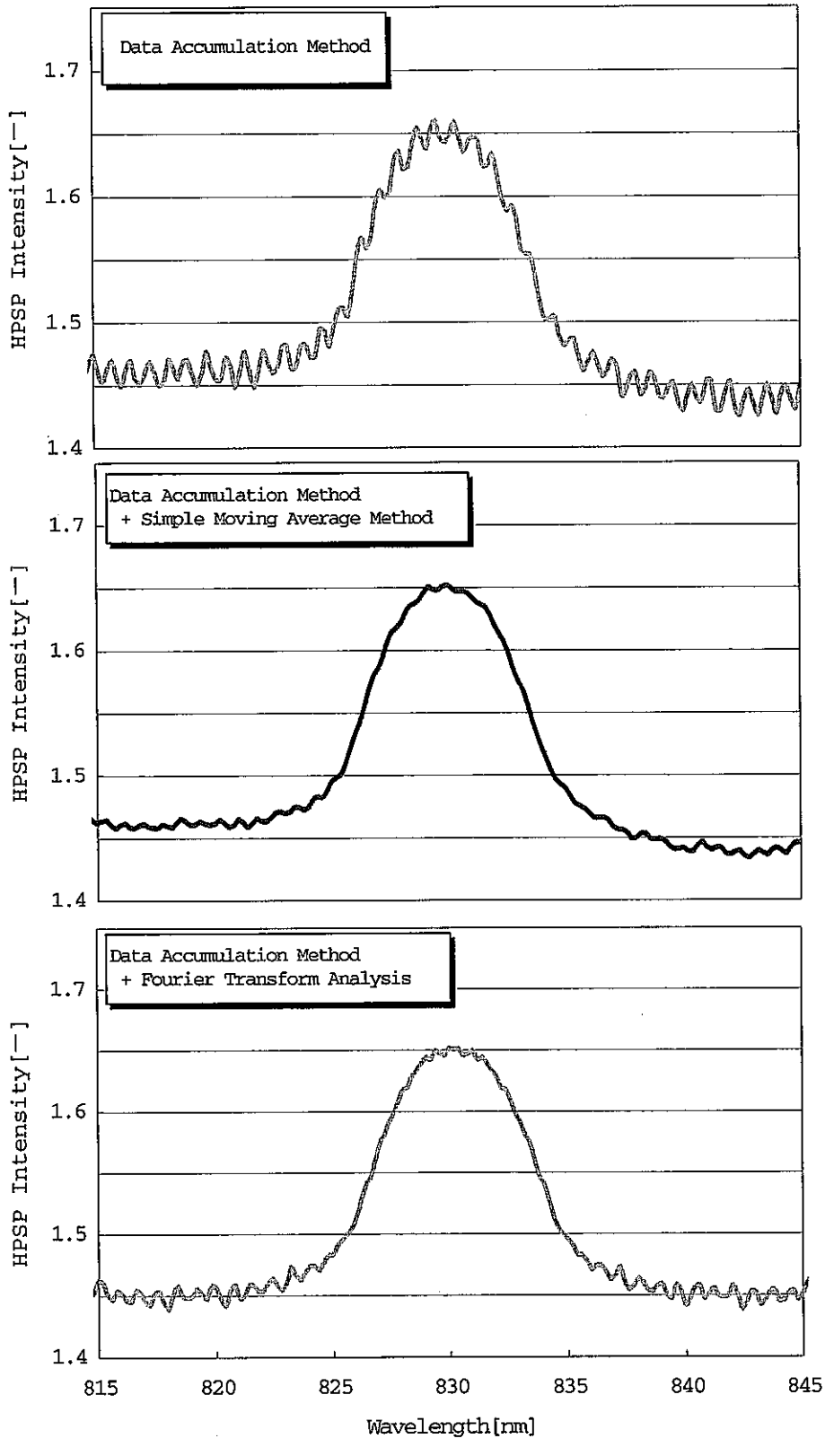


Fig. 5-13 Results of Spectrum Analysis [1.11 mgPu/L in Nitric Acid]

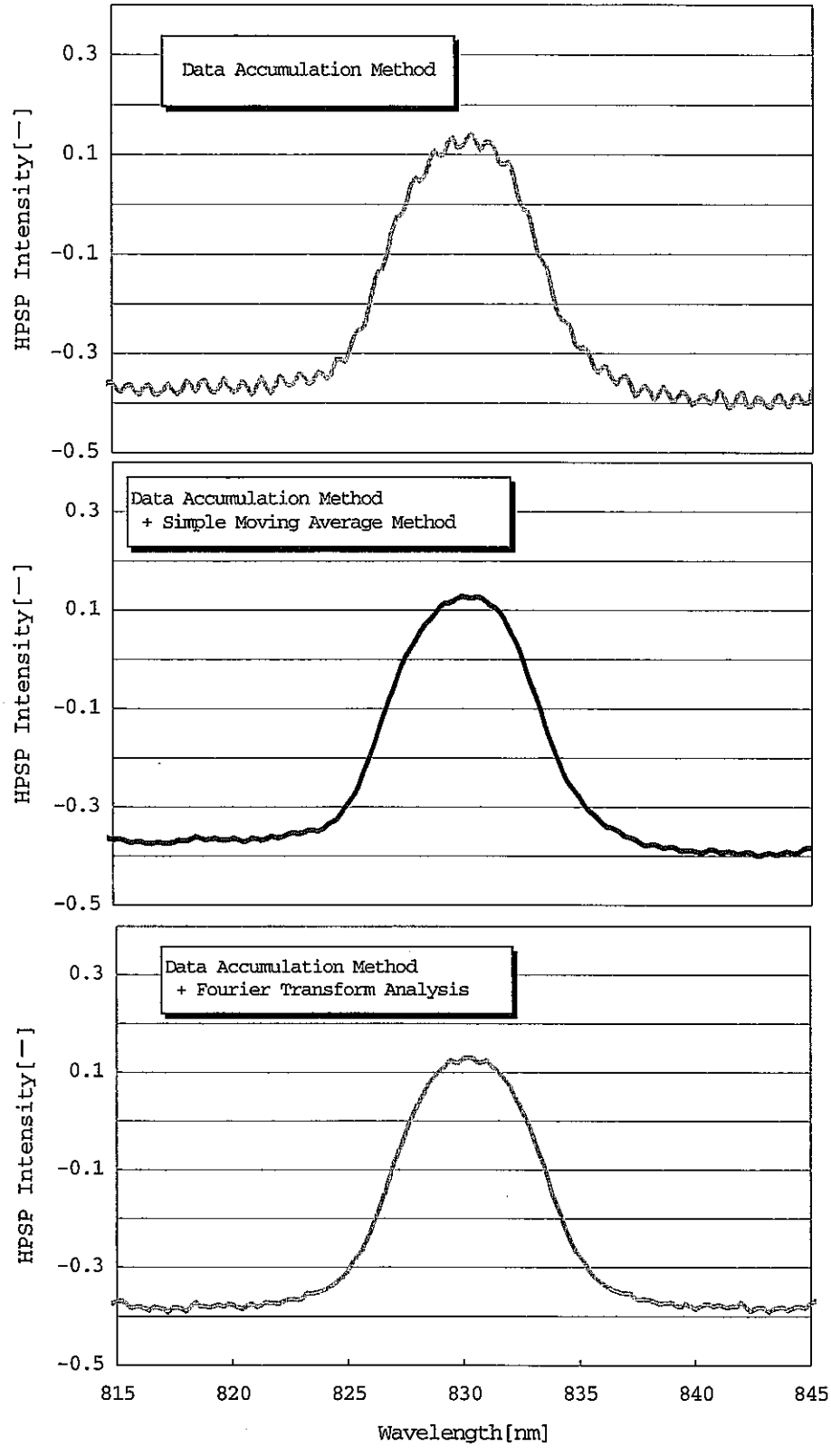


Fig. 5-14 Results of Spectrum Analysis [2.78 mgPu/L in Nitric Acid]

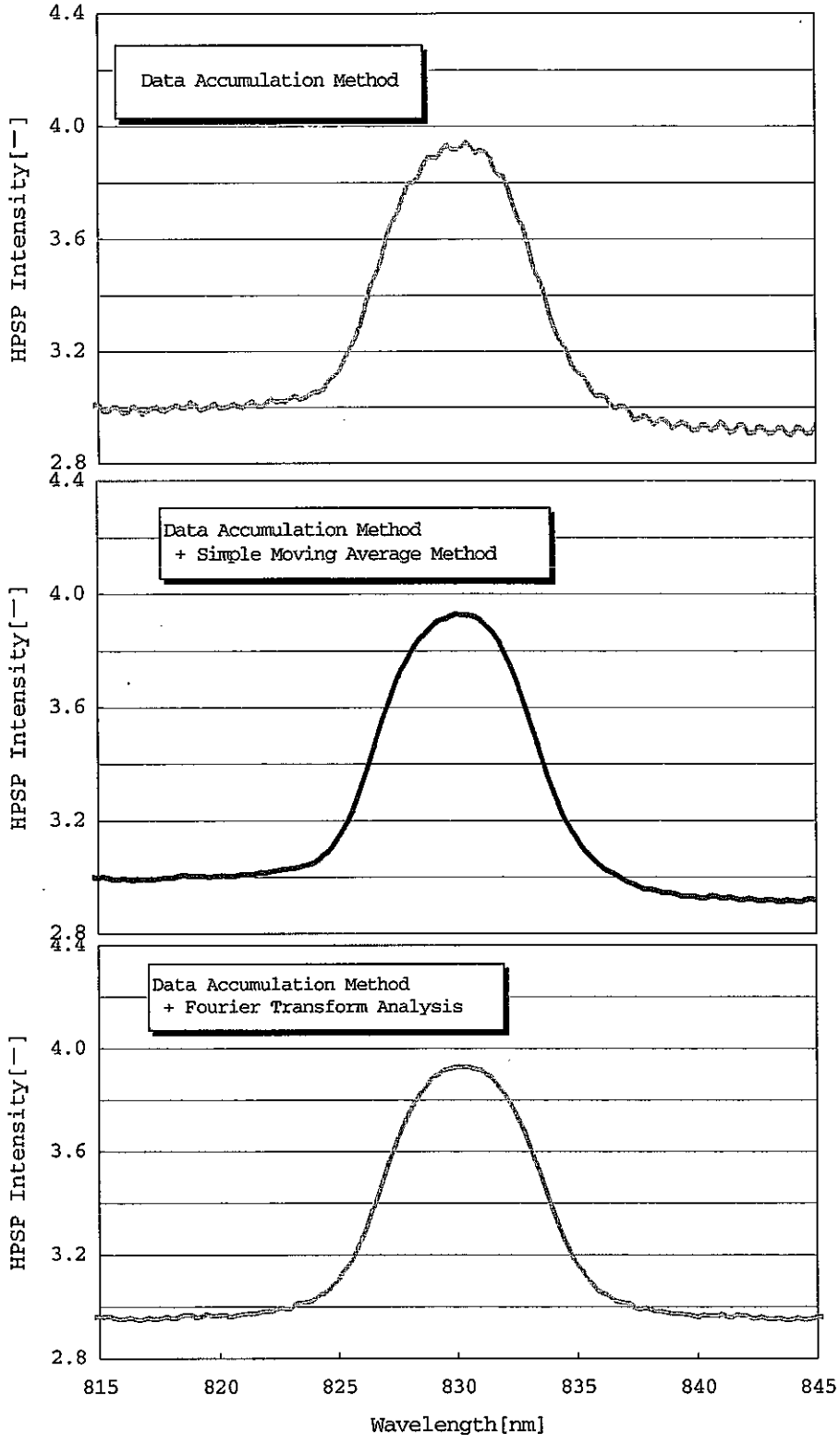


Fig. 5-15 Results of Spectrum Analysis [5.56 mgPu/L in Nitric Acid]

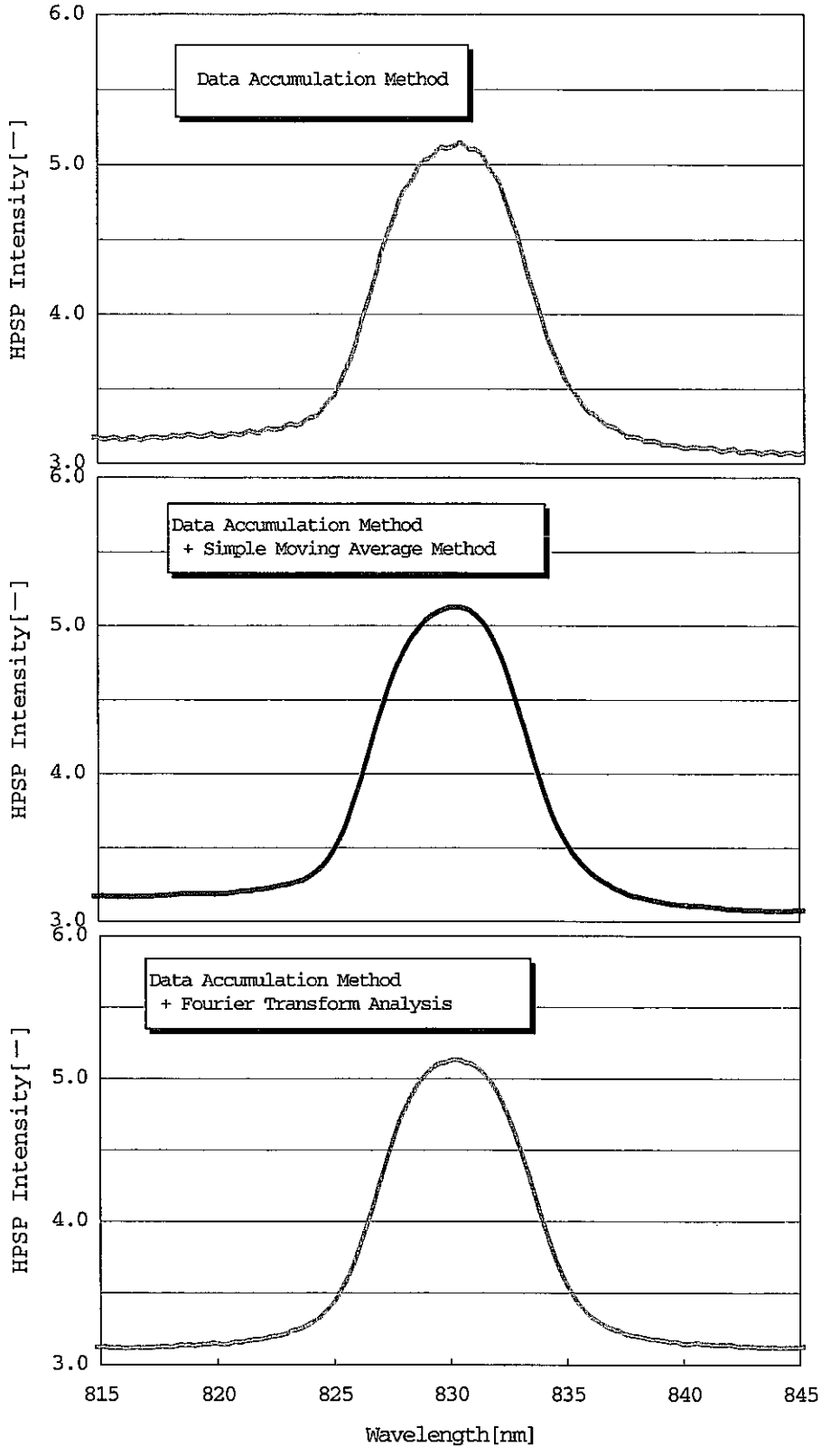


Fig. 5-16 Results of Spectrum Analysis [11.1 mgPu/L in Nitric Acid]

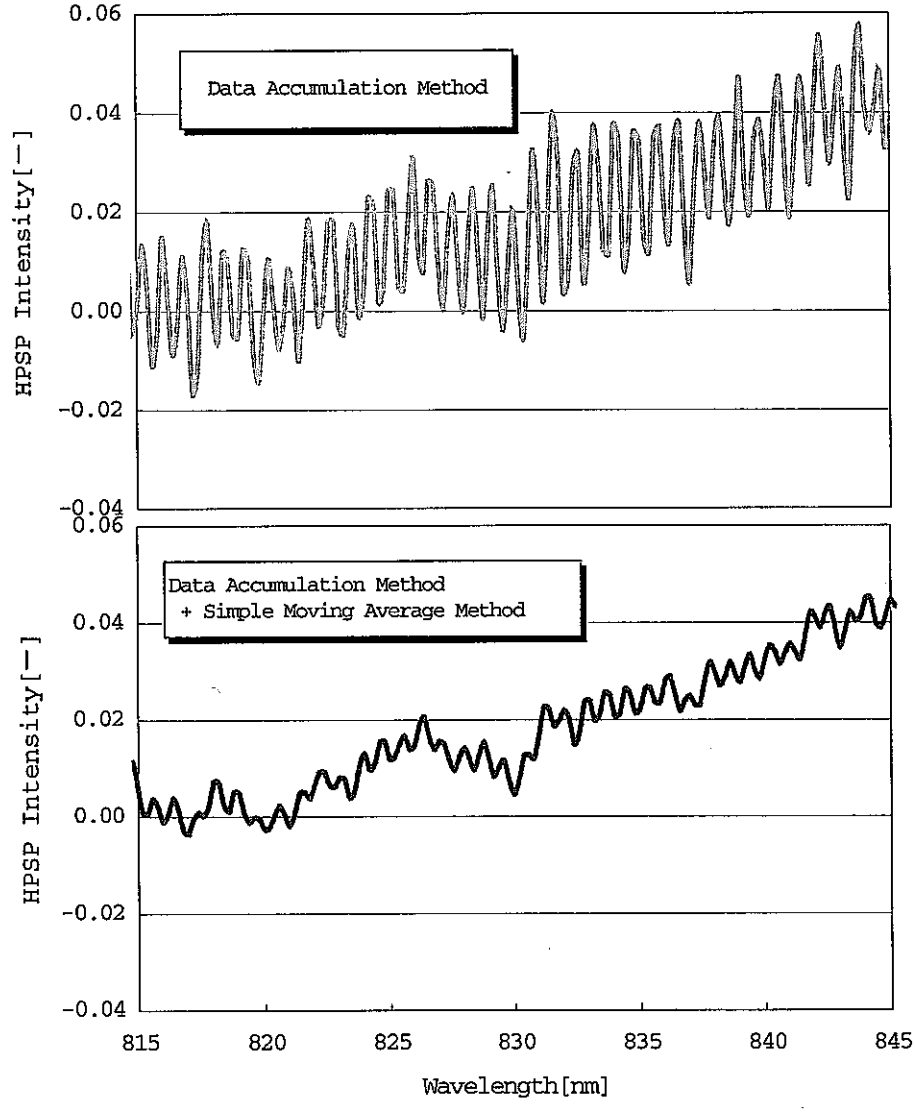


Fig. 5-17 Results of Spectrum Analysis [Synthetic HALW solution]

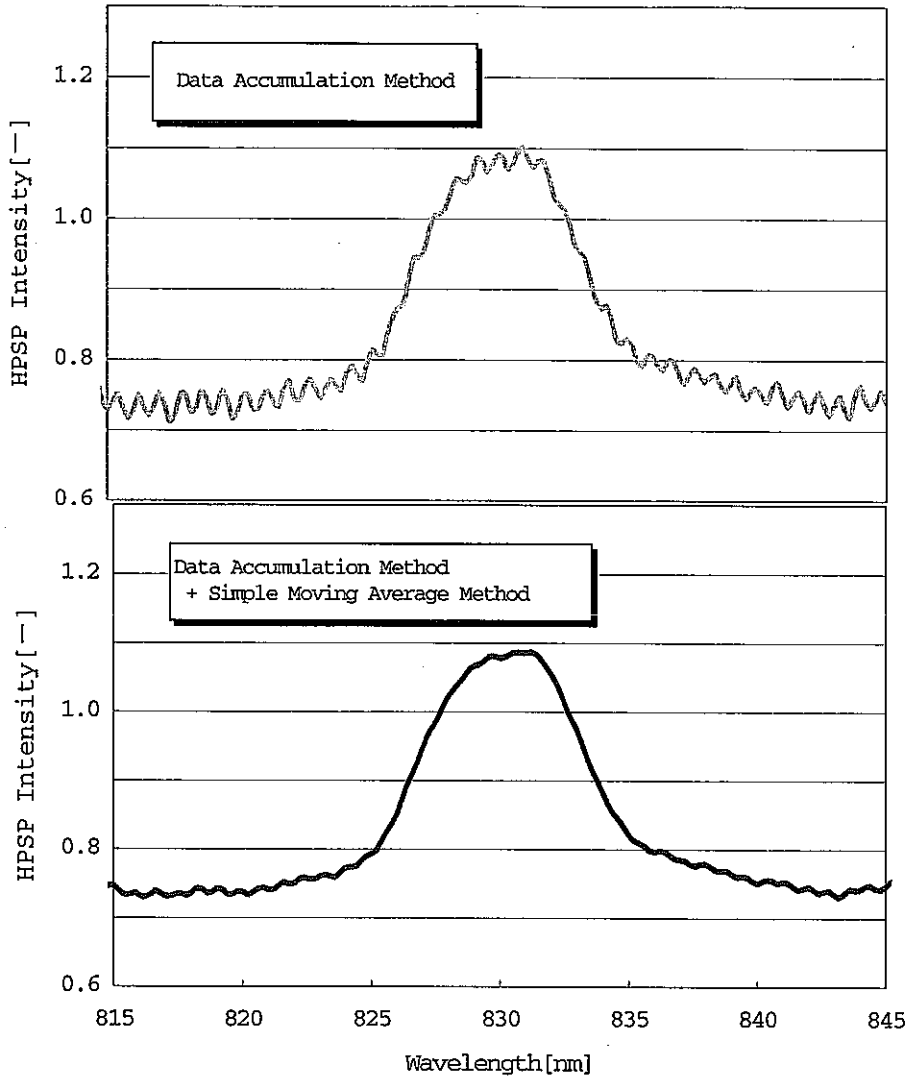


Fig. 5-18 Results of Spectrum Analysis [2.78 mgPu/L in Synthetic HALW]

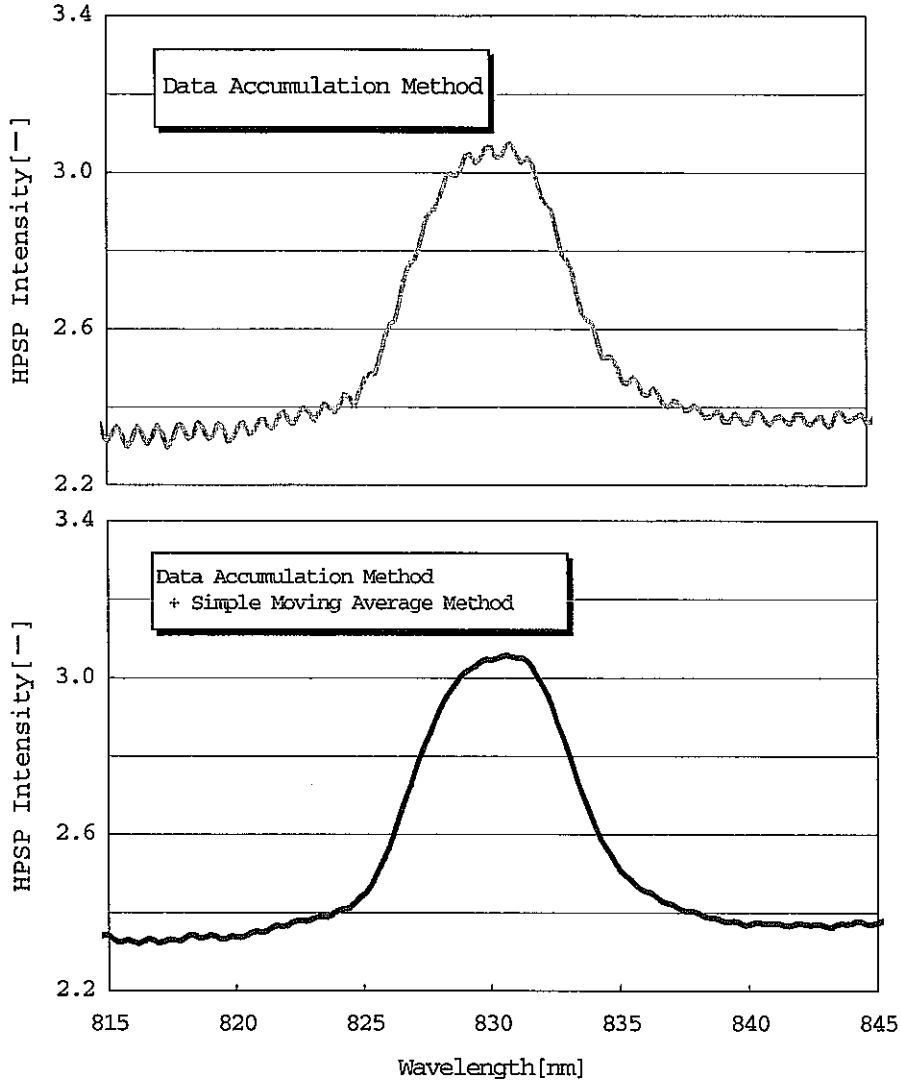


Fig. 5-19 Results of Spectrum Analysis [5.56 mgPu/L in Synthetic HALW]

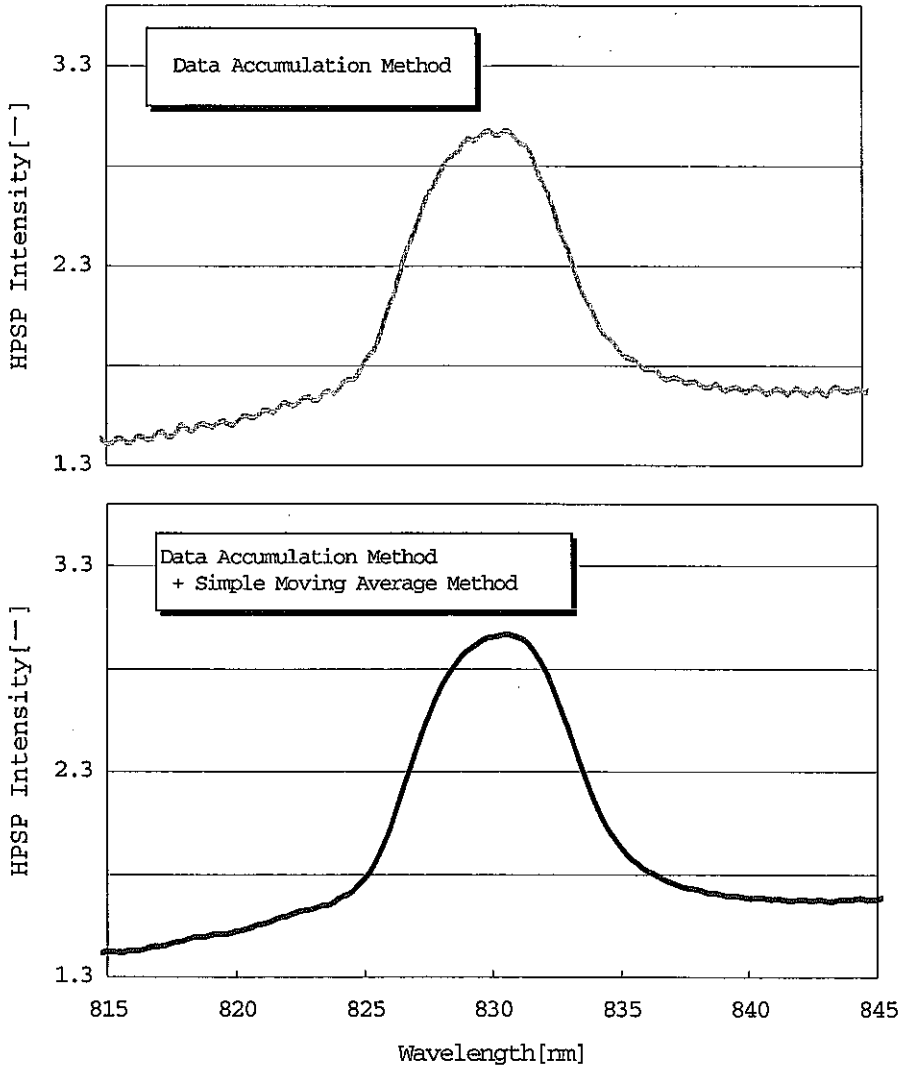


Fig. 5-20 Results of Spectrum Analysis [11.1 mgPu/L in Synthetic HALW]

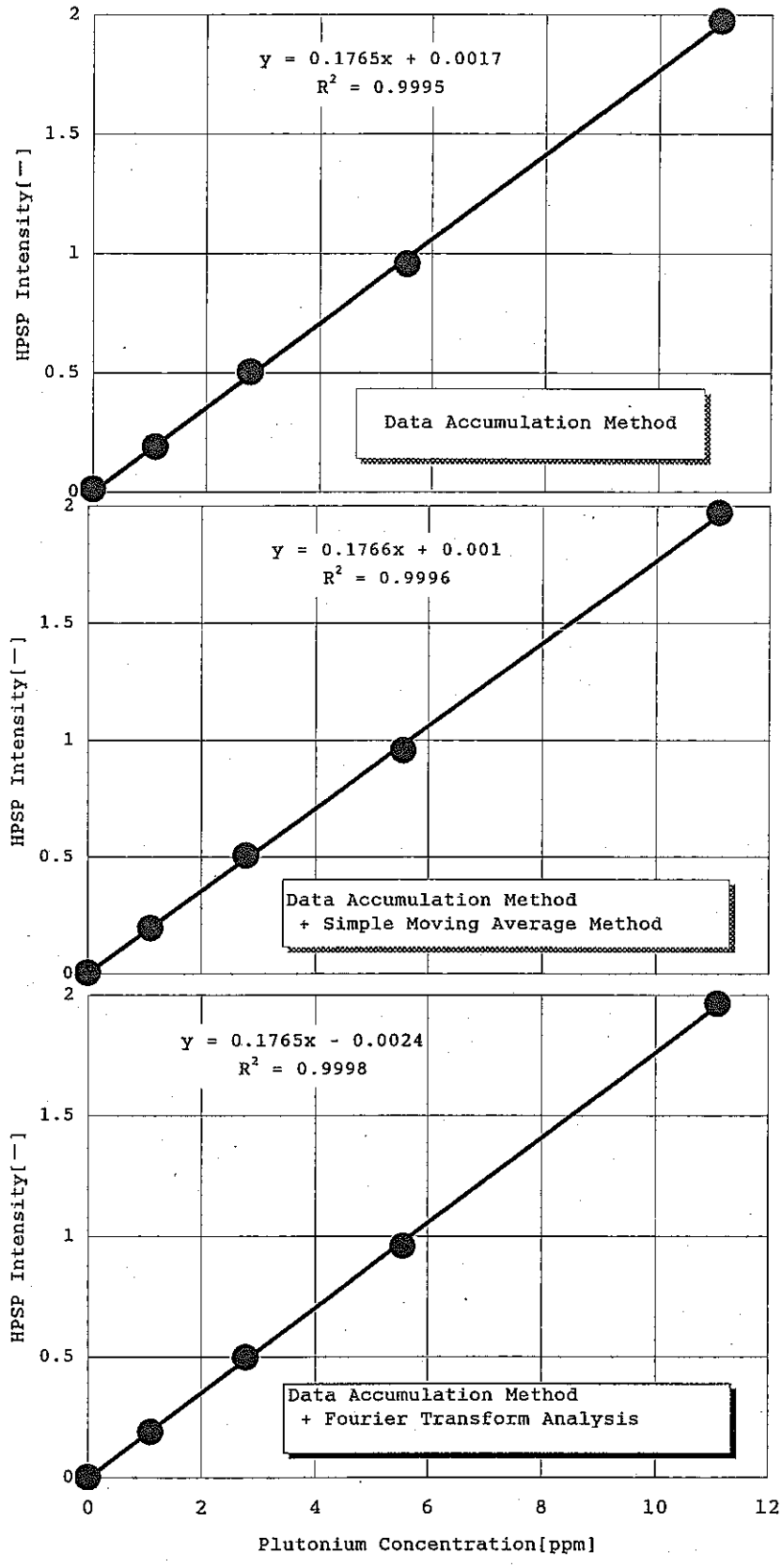


Fig. 5-21 Relation between Plutonium Concentration and HPSP Intensity [Nitric Acid]

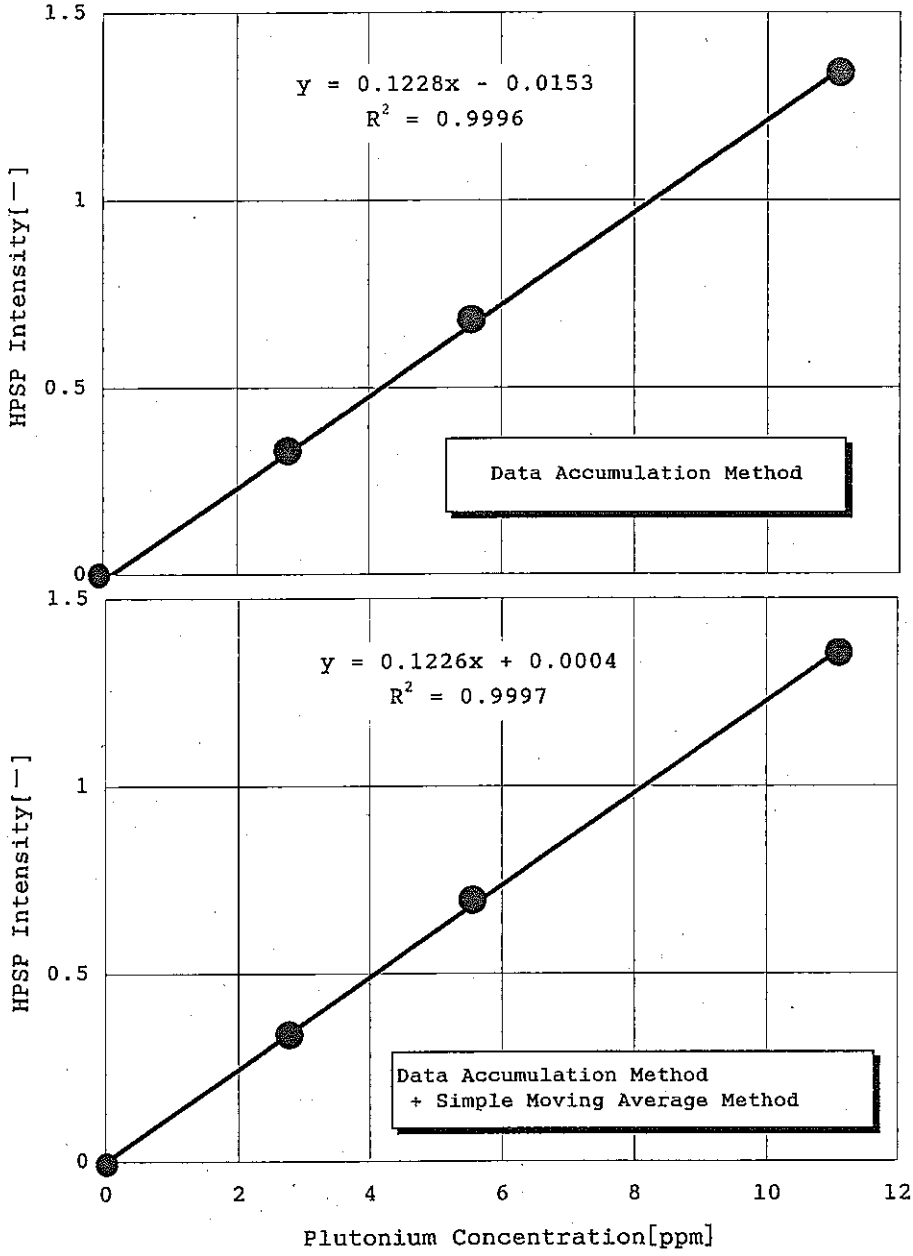


Fig. 5-22 Relation between Plutonium Concentration and HPSP Intensity [Synthetic HALW]

Table 5-2 Detection Limit and Lower Limit of Determination of Plutonium in Nitric Acid Solution

	DAM	DAM+SMAM	DAM+FTA
Standard Deviation (s)	1.03E-02	4.35E-03	7.24E-03
3*s	3.09E-02	1.30E-02	2.20E-02
10*s	1.03E-01	4.35E-02	7.24E-02
Sensitivity (S)	1.76E-01	1.77E-01	1.77E-01
Detection Limit	0.175mgPu/L	0.074mgPu/L	0.123mgPu/L
Lower Limit of Determination	0.584mgPu/L	0.246mgPu/L	0.410mgPu/L

DAM: Data Accumulation Method

SMAM: Simple Moving Average Method

FTA: Fourier Transform Analysis

Table 5-3 Detection Limit and Lower Limit of Determination of Plutonium in Synthetic HALW

	DAM	DAM+SMAM
Standard Deviation (s)	1.33E-02	7.50E-03
3*s	3.99E-02	2.24E-02
10*s	1.33E-01	7.50E-02
Sensitivity (S)	1.23E-01	1.23E-01
Detection Limit	0.325mgPu/L	0.183mgPu/L
Lower Limit of Determination	1.083mgPu/L	0.609mgPu/L

DAM: Data Accumulation Method

SMAM: Simple Moving Average Method

6. Application to the Actual HALW solution

6.1 Measurement Scheme

Plutonium concentration in the HALW at the Tokai Reprocessing Plant would exceed the dynamic range of this system, the samples were diluted before measurement. Fig. 6-1 shows the measurement procedures.

Distributing injectors were used for HALW solution and standard solution taking, and auto burets for adjusting the volume.

The aliquot of HALW, 1 mL, was taken from the sample vial. As the standard addition, 0.5 or 1 mL plutonium standard solution was added. The calibration curve method was prepared and measured with assuming the same as the 0 mL standard addition. Cerium (IV) of 2 mL (0.1×10^{-3} mol) was added as an oxidant. After the volume was adjusted to 10 mL by 3.0 mol/L nitric acid, the sample was introduced into the flow type of sample cell for the measurement.

Component Condition for measurement were:

Measurement sample	:	HALW (272V14)
Measurement sensitivity	:	10% full scale
Sensitivity of lock-in amplifier	:	220 mV
Number of measurements	:	five times
Spectrum calculation	:	data accumulation method + simple moving average method
Range of wavelength measured	:	800~860 nm (0.2 nm/Step)

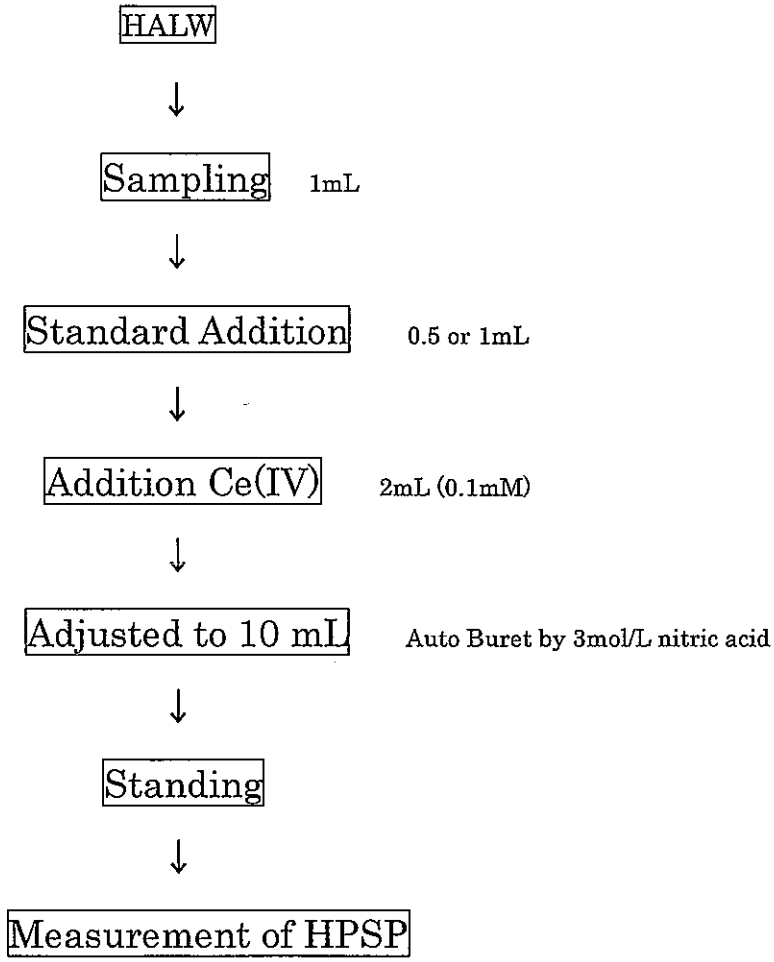


Fig. 6-1 Flow sheet for HALW Measurement

6.2 Baseline Correction

In 5-2 correction of the baseline was examined for measurement of plutonium in the synthetic HALW. However, the baseline of the actual HALW sample can not be estimated due to different concentrations of coexistent elements, especially neodymium in this case. Thus the three-point method should be used determining for Pu concentration.

In this study, the three wavelength, for Pu peak wavelength and base line correction wavelength were determined from the linear differential curve which plotted the linear differentials of the spectrum obtained in order to calculate the HPSP

intensity from the spectrum.

Plutonium Standard Sample

Fig. 6-2 indicates the spectrum of plutonium standard sample and its differential spuctrum.

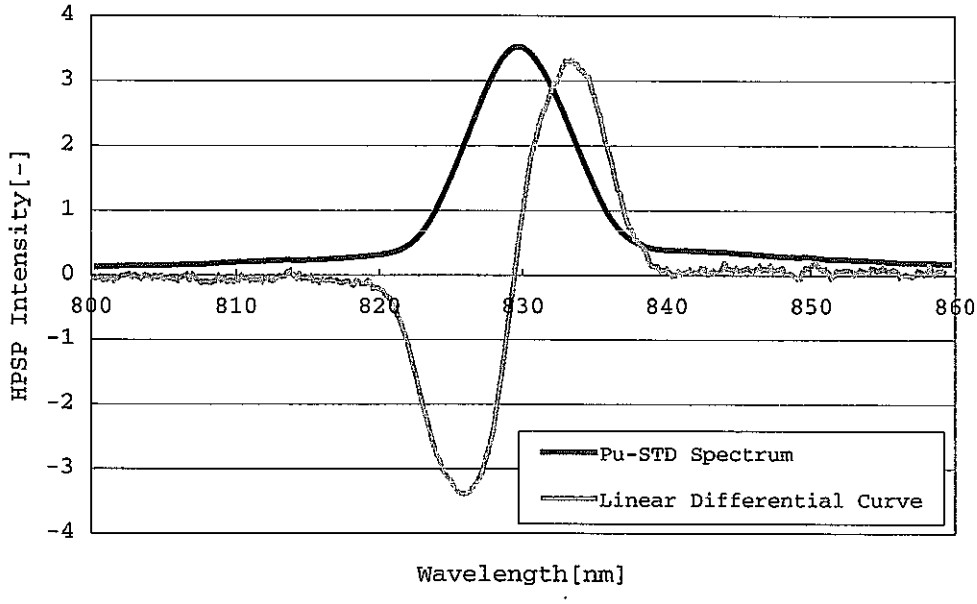


Fig. 6-2 Spectrum and Differential Spectrum of Plutonium Standard

According to Fig. 6-2, the peak top was determined to be the wavelength at which the linear differential value reached or passed zero, and 829.8 nm found to be satisfied this condition. Two points before and after the peak top were assumed to be the wavelength at which the linear differential values approached zero as close as possible and a variation of the value remained constant. In this case, 819.8 nm and 839 nm were selected. The equation of the HPSP intensity calculation with using the three-point method determined by the linear differential curve is shown below:

$$A_{Pu} = A_{829.8} - \left\{ \frac{(839.8 - 829.8) \cdot A_{819.8} + (829.8 - 819.8) \cdot A_{839.8}}{(839.8 - 819.8)} \right\} \quad (6.1)$$

$$= A_{829.8} - B_{829.8} \quad (6.2)$$

$A_{829.8}$, $A_{819.8}$, $A_{839.8}$: signal intensity at each wavelength (829.8 nm, 819.8 nm and 839.8 nm)

$B_{829.8}$: background signal intensity at 829.8 nm

HALW

Fig. 6-3 shows the HALW spectrum and its linear differential curve.

According to Fig. 6-3, the peak top was determined to be the wavelength at which the linear differential value reached or passed zero, and 829 nm satisfied this condition. As for the two points before and after the peak top, the point which passed zero was selected for the shorter wavelength, and the point which approached zero as close as possible with a variation in values before and after the point remaining constant was determined for the longer wavelength. In this case, 823 nm and 840 nm were selected. The equation of the HPSP intensity calculation with using the three-point method determined by the linear differential curve is shown below:

$$A_{Pu} = A_{829} - \left\{ \frac{(840 - 829) \cdot A_{823} + (829 - 823) \cdot A_{837}}{(840 - 823)} \right\} \quad (6.3)$$

$$= A_{829} - B_{829} \quad (6.4)$$

A_{829}, A_{823}, A_{840} : signal intensity at each wavelength (829 nm, 823 nm and 840 nm)

B_{829} : background signal intensity at 829 nm

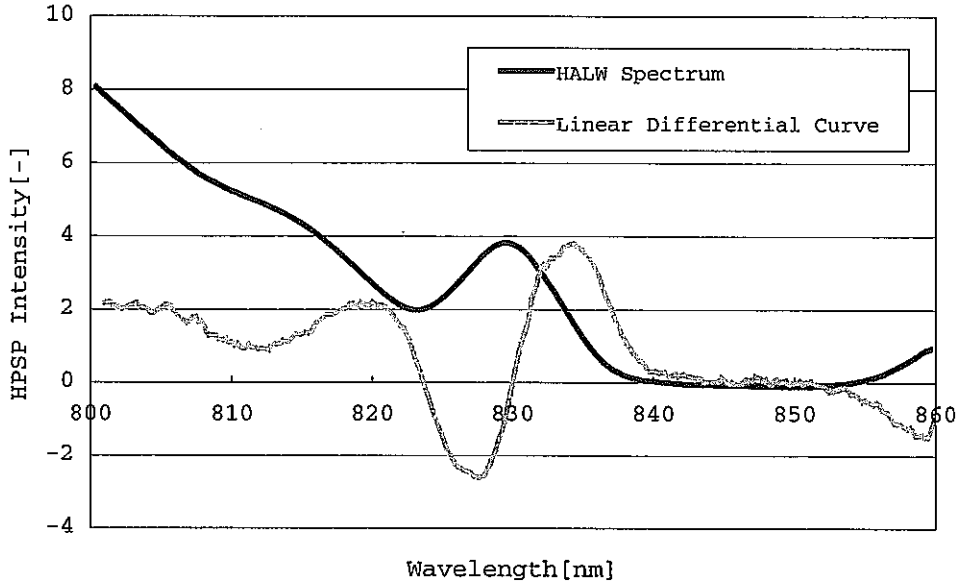


Fig. 6-3 Spectrum and Linear Differential Curve of HALW

6.3 Determination by Calibration Curve Method

Based on the principle of measurement of this system, it is impossible to measure absolute values of elements, and thus an amount of plutonium in the HALW was determined by the analytical curve method. The analytical curve used in this section was developed by referring to the results obtained through preparation and measurement of the plutonium standard solution in a desired range of 0~20 mgPu/L.

Fig. 6-4 and 6-5 show the analytical curve and the HALW spectrum, respectively.

Within a range of 0~20 mgPu/L, the analytical curve indicated a good linearity with the correlation factor (R^2) of 0.9999. The measured blank provided a minus value, but this did not interfere measurement in particular.

Table 6-1 lists the results of the intensity calculated by the three-point method described in 6-2. Though differences were seen between two measurements (30% difference), the plutonium concentration in the HALW, which was obtained from the analytical curve that used the averaged measurements, was 14 mgPu/L. With the dilution magnification multiplied, the plutonium concentration in the undiluted HALW

was calculated to be 115 mgPu/L.

Fig. 6-5 indicates that the entire spectrum has a gradient. This is caused by a large amount of neodymium that coexisted in the HALW.

Table 6-1 Pu Measurements in HALW

Sample No.	1	2
823	1.27	1.98
829	2.63	3.78
840	-0.12	0.03
Intensity	1.93	2.60
Pu conc. (mg/L)	12.3	16.5
Average (mg/L)	14.4	

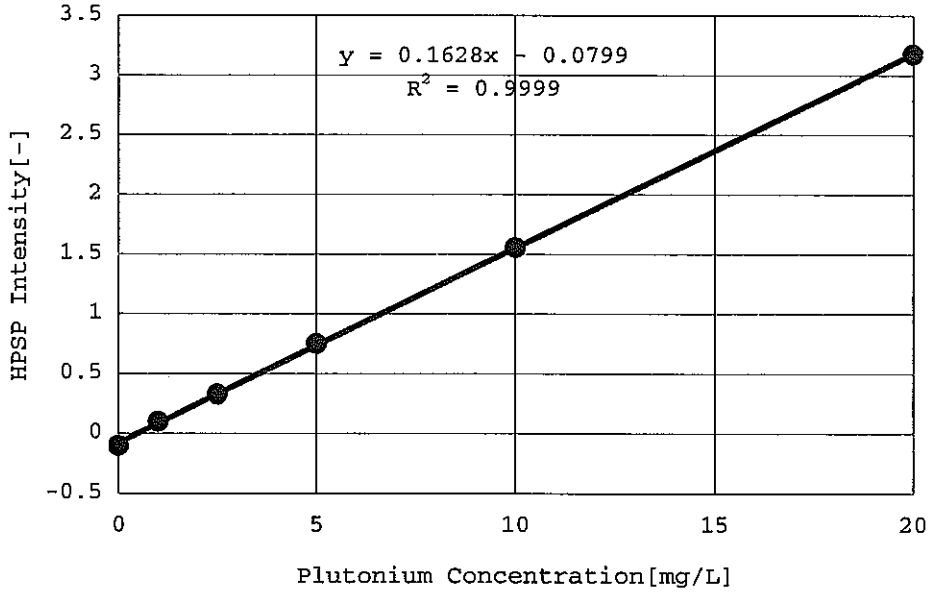


Fig. 6-4 Calibration Curve of Plutonium(VI) in Nitric Acid Solution

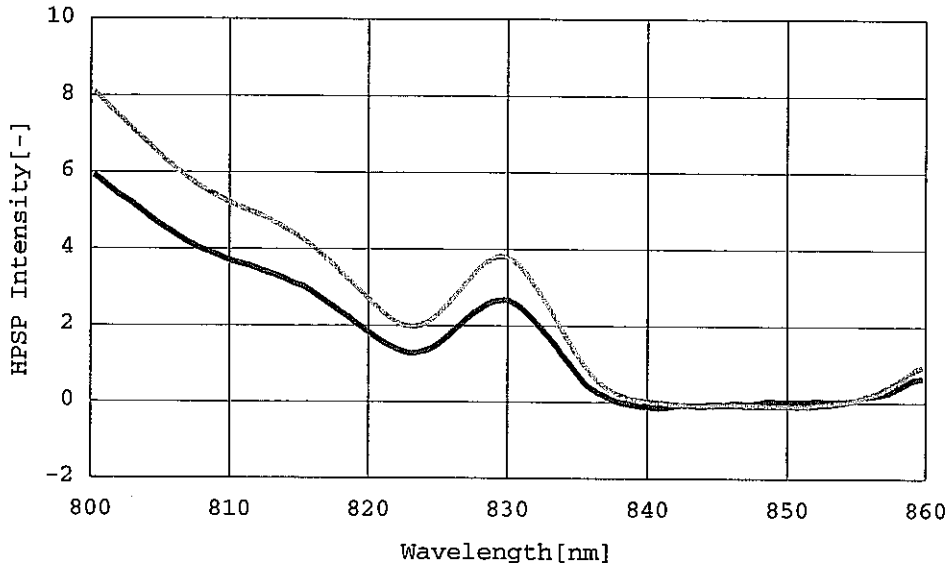


Fig. 6-5 Plutonium(IV) Spectra in HALW

6.4 Determination by Standard Addition Method

To compare with the calibration curve method described in 6-3, the plutonium standard solution was added to the HALW solution.

Each spectrum after calculation is given in Fig. 6-6. The results of measurement and their plotted graph are shown in Table 6-2 and Fig. 6-7, respectively.

Fig. 6-6 shows that absorption of plutonium(VI) increases in proportion to plutonium standard solution added. The plutonium concentration was 11.5 mgPu/L, obtained from the Fig. 6-7. The plutonium concentration in the undiluted HALW was calculated to be 92 mgPu/L.

Table 6-2 Results of Measurement of HALW by Standard Addition Method

Standard addition	0		0.5mL (6.25mg/L)		1.0mL (12.5mg/L)	
Sample No.	1	2	1	2	1	2
823nm	1.27	1.98	2.09	2.46	2.82	2.65
829nm	2.63	3.78	4.84	5.34	6.64	6.48
840nm	-0.12	0.03	-0.16	0.05	0.37	0.28
Intensity	1.93	2.60	3.68	3.88	4.83	4.81
Average	2.26		3.78		4.82	

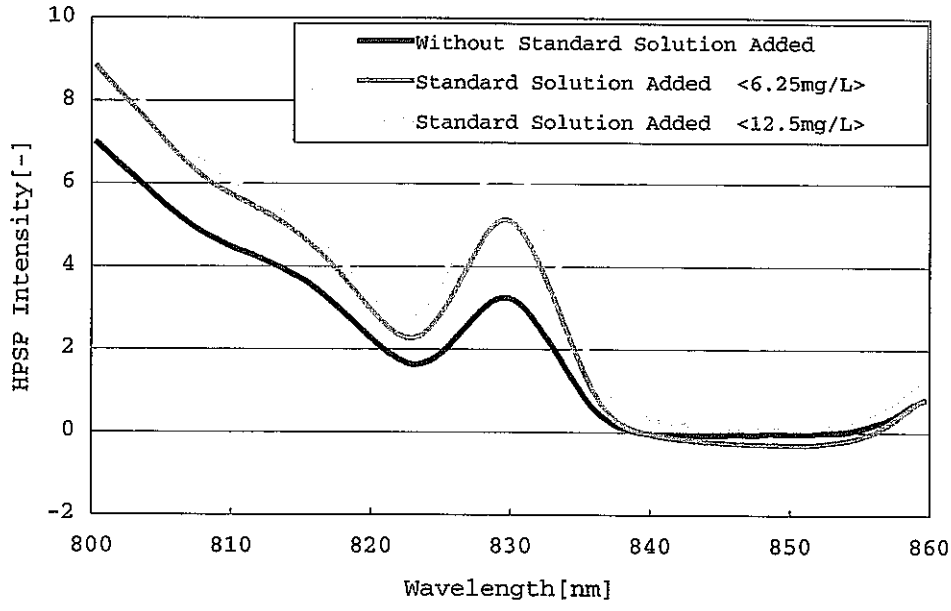


Fig. 6-6 Spectra in Standard Addition Method

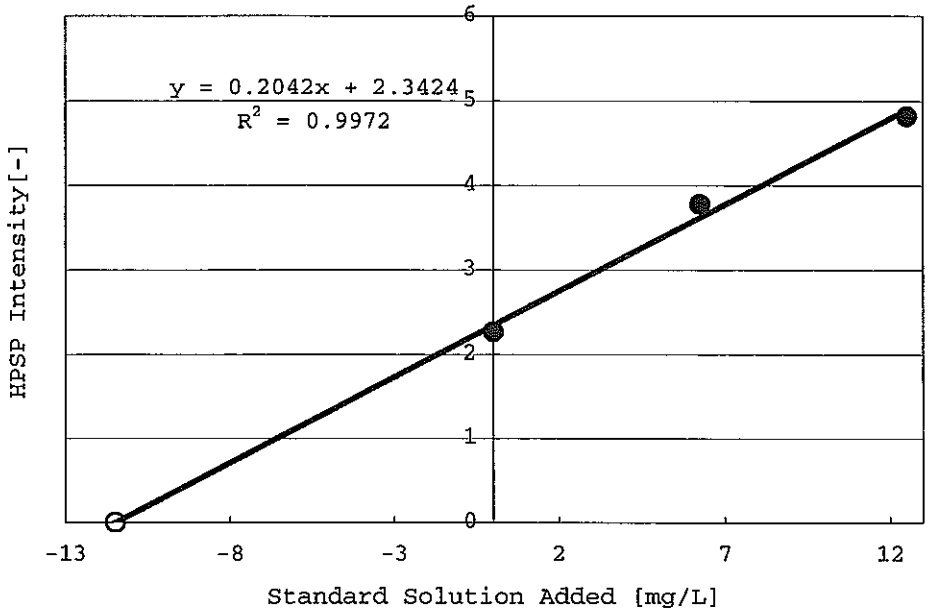


Fig. 6-7 Determination of Plutonium in HALW by Standard Addition Method

7. Demonstration to IAEA

Demonstration of the HPSP to the IAEA was held at the analytical laboratory in the Tokai Reprocessing Center on May 12, 2000 to compare the spectra with those of the conventional spectrophotometer (SP). The results are reported below:

Contents

Samples shown in Table 7-1 were prepared. Spectra were measured by HPSP and SP to compare and review the results. Fig. 7-1 shows preparation of each sample.

Table 7-1 Samples for Demonstration to IAEA

	1.3 mgPu/L	6.6 mgPu/L
Nitric Acid Solution	○	△
Synthetic HALW Solution	○	△
HALW (Pu removed)	○	△

* Pu concentrations listed are the final ones after preparation.

○ for HPSP measurement

△ for SP measurement

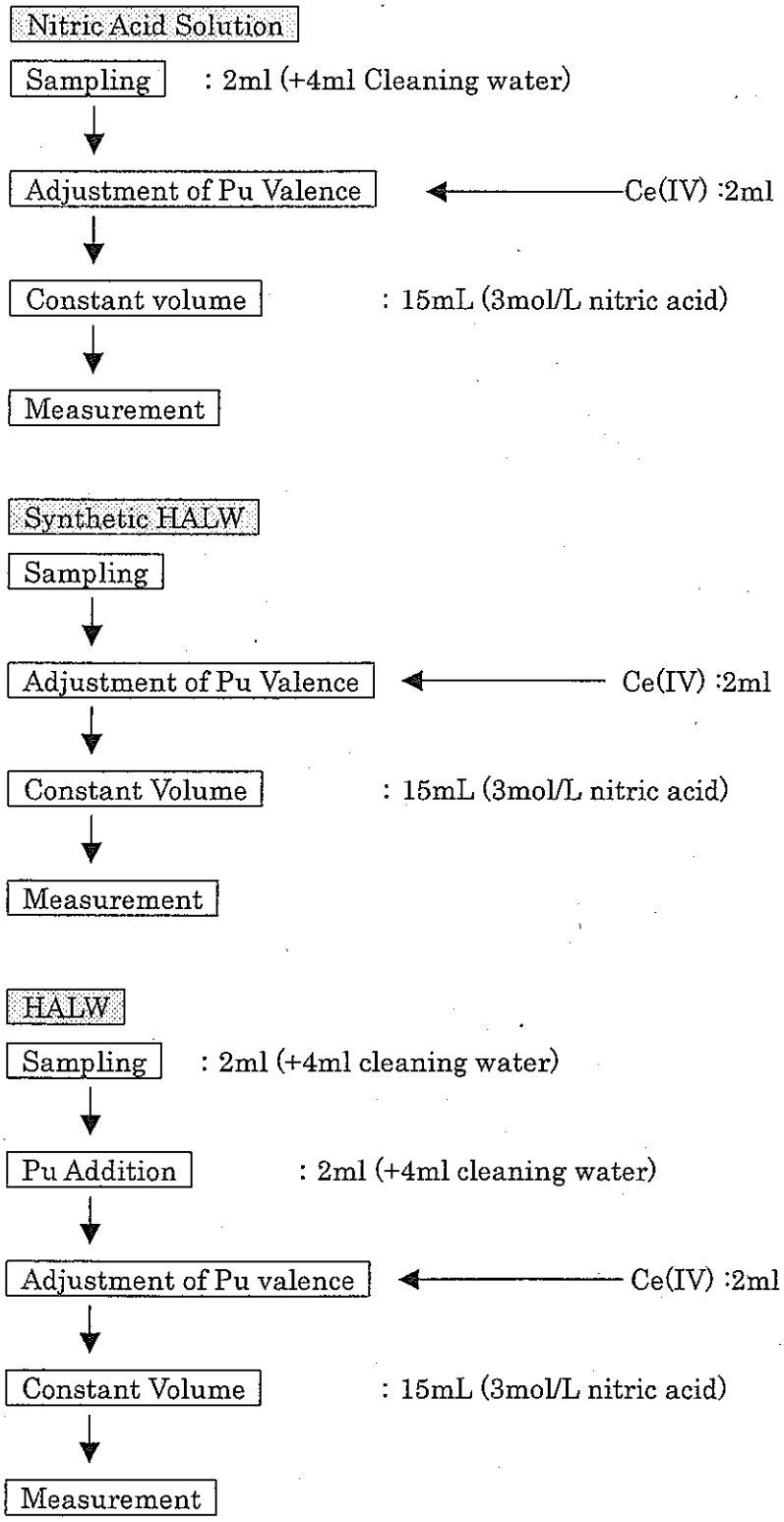


Fig. 7-1 Scheme of Sample Preparation

Results

Fig. 7-2 and 7-3 show the results of HPSP measurement and those of SP measurement, respectively.

The HPSP measured the three types of samples (nitric acid solution, synthetic HALW solution and HALW) to which a low concentration plutonium (1.3 mgPu/L) was added. The SP measured the samples of the same conditions as those of the HPSP, but could not detect the significant peak of plutonium(VI) . Thus three types of samples (nitric acid solution, synthetic HALW solution and HALW) to which plutonium with a concentration of 6.6 mgPu/L was added were subject to measurement.

In the HPSP measurement, significant peaks could be identified in the nitric acid solution and the synthetic HALW solution, while effects of neodymium, the coexistent element, prevented detection of a significant peak in the HALW. This revealed that detection of plutonium with 1 mgPu/L or below in the HALW would be difficult.

In the SP measurement, samples of a concentration by about five times (6.6 mgPu/L) greater than the HPSP measurement were used, and significant peaks could be obtained. These results confirmed that the SP could be applied to the HALW samples prepared up to a concentration of approximately 5 mgPu/L.

According to the above results of measurement, it would be appropriate to use the HPSP for measurement of a low concentrated plutonium and the SP for a high concentrated plutonium.

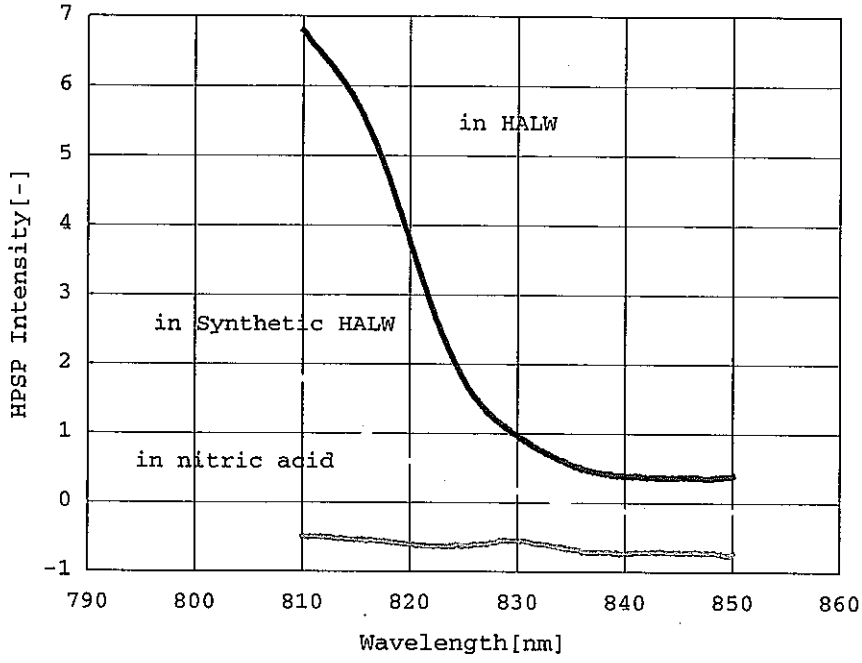


Fig. 7-2 Pu(VI) Spectra obtained by HPSP (1.3 mgPu/L)

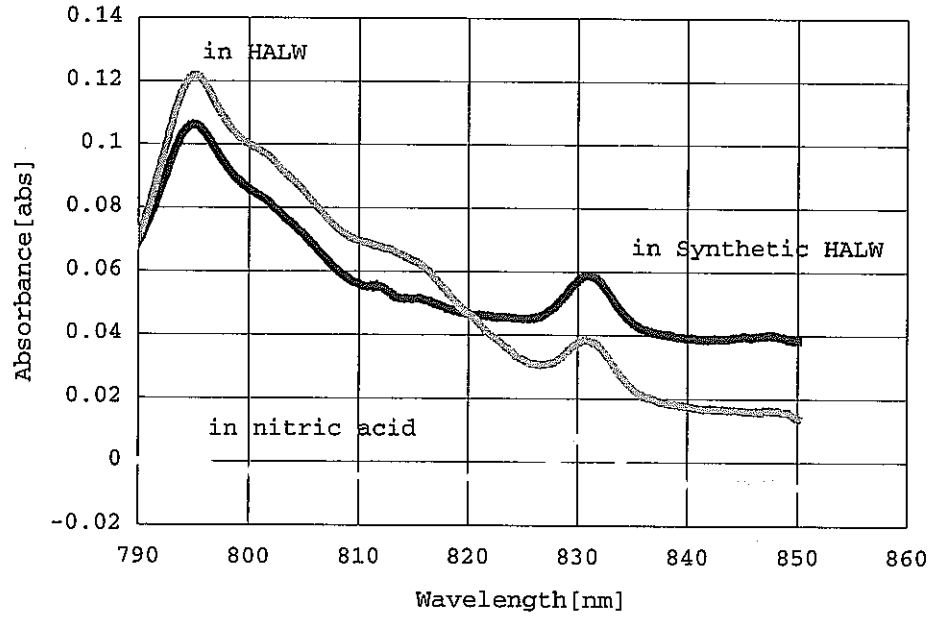


Fig. 7-3 Pu(VI) Spectra obtained by conventional spectrophotometer (6.7 mgPu/L)

8. Conclusions

The following findings were obtained in this study:

- This system was applicable to measurement on sample solutions.
- Remote operation and measurement could be performed by the system consisted with an optical fiber for transmission of the incident and transmitted lights.
- Measurement with higher sensitivity by utilizing the characteristics of the lock-in amplifier was possible.
- The sensitivity did not give significant effects on the detection limit.
- The detection limit was calculated to be 0.07 mgPu/L for the pure plutonium solution and 0.2 mgPu/L for the synthetic HALW.
- In measuring an unknown sample, it is recommended that the form and coexistent materials be previously identified, and that the full scale could be adjusted to 5~10%.
- A combination of the data accumulation method and the moving average method was effective in smoothing the spectrum which showed the relatively degraded S/N ratio due to noises generated during measurement.
- The neodymium spectrum contained as the coexistent element gives effects on the HALW measurement, but use of the three-point method eliminated potential problems occurred in the peak intensity calculation.
- Use of nitric acid as the reference allowed the optical balance to be adjusted only by the optical control.
- Effects of acid concentrations on measurement were negligible as the acid concentration of the actual HALW solution.
- The system is considered applicable, as plutonium samples with very low concentrations in a higher accuracy.

9. Reference

1 O.J.Wick "PLUTONIUM HANDBOOK A Guide to the Technology VOLUME" CHAP13, THE AMERIKAN NUCLEAR SOCIETY LA GRANDE PARK, ILLINOIS 1980

2 MacDonald A.H.Kerr, D.J.Sauage, "Operational experience with the ceric oxidation ferrous reduction and dichromate titration method for plutonium in fast reactor fuel reprocessing", IAEA-SM-206/66 (1983)

Attachment 1 Sensitivity of Measurement

Sensitivity of measurement for the HPSP system refers to a value of full scale allocated to the data which was inputted to the alternate current amplifier (⑨ in Fig. 2-2, hereafter called lock-in amplifier) during measurement of the signal intensity. The full scale expresses a scale of longitudinal range used in measurement. Based on the assumed concentration of the element to be measured, the signal intensity (voltage) taken into the lock-in amplifier is controlled and then the full scale is allocated so that the intensity/V may be as low as possible.

In measuring a sample with larger absorption (higher concentration), the larger (lower sensitive) full scale should be established.

Controlling the full scale helps obtain the data with the same resolution with regardless of the degree of absorption. This contributes to measurement with high sensitivity even on a sample showing very low absorption, attaining measurement of the absorbance range that the conventional spectrophotometry normally cannot detect.

Attachment 2 Calibration Setting of High Performance Spectrophotometry (HPSP)

1. Start-up the system.

   Power on the system, and set the controller as follows:

   HALOGEN: ON

   DETECTOR: MODE/MANUAL Si

   METER SELECT: DC AMP

   MONOCHRO: MODE/FREE

   FILTER: ·····

2. Set the wavelength of monochrometer to [400 nm].
3. Close the shutter of the light source converging system. (PULL)

   Control [DC AMP ZERO ADJ] so that the digital panel meter of the controller may display [0V].
4. Open the shutter.
5. Turn the sample light shutter of the double beam optical system to [CLOSE].
6. Tune the ND filter counter to [00.00].
7. Control the slit provided at the incident/outgoing inlet of the monochrometer so that the digital panel meter may indicate [0.25] (slit width is about 1~2 mm as a yardstick).
8. Turn the METER SELECT switch to LOCK-IN.
9. Control SENSITIVITY of the lock-in amplifier so that the digital panel meter may indicate [5V] (slit width is about 112 mV as a yardstick). Input the value of sensitivity shown into the PC. Tune the PHASE at the same time.
10. Open the sample light shutter.
11. Set the wavelength of monochrometer to [550 nm].

Attachment 3 Calculation of Detection Limit

According to the IUPAC definition (Recommendation in 1976), the following correlation is obtained with assuming a concentration of the material for determination, c, and the peak intensity, x:

$$x = g(c)$$

Within a range of the analytical curve showing a linear form, the sensitivity, S, is assumed to be a ratio of x to a change of c, and expressed as:

$$S = \frac{dx}{dc}$$

When a minimum detectable value of the object material is assumed to be C_L, its value is determined by the minimum value of x_L of x that is detected with a sufficient certainty:

$$x_L = \bar{x}_b + 3s_b$$

Here, $\bar{x}_b$ refers to the average of the blank value x_b, and s_b is the standard deviation of x_b. If the sensitivity S takes a linear form within the concentrations to be measured, the detection limit C_L can be obtained by:

$$C_L = \frac{x_L - \bar{x}_b}{S}$$

Attachment 4 Fourier Analysis with Using Actual Data

1. Obtain the HPSP data.

Wavelength[nm]	Data
855.8	-0.39101
855.6	-0.38943
855.4	-0.40647
855.2	-0.403
855.0	-0.38596
.	.
.	.
.	.
.	.
805.6	-0.36418
805.4	-0.35661
805.2	-0.35219
805.0	-0.36103
804.8	-0.3585

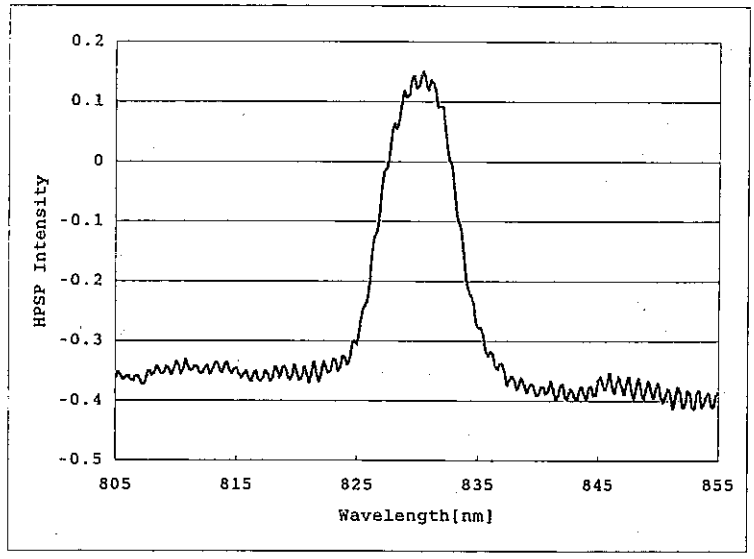


Fig. Plutonium(VI) Spectrum by HPSP

2. Determine the data number *N*, centering on the peak of spectrum.

$N = 2^n$ * In this case 256 points

3. Perform the fast Fourier transform.

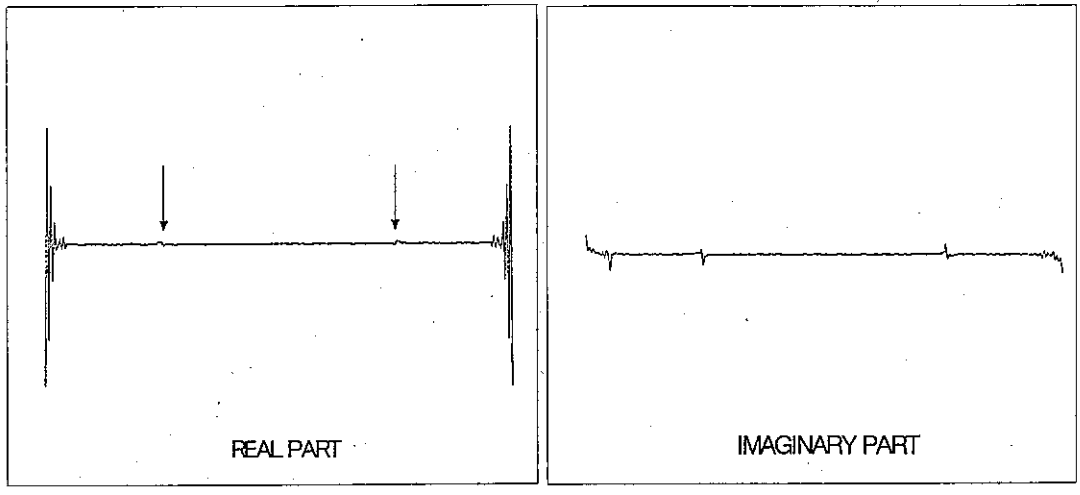
* Execute through the analysis tool command of Microsoft's Excel.

It is outputted in a form of $Y(k) = A(k) - iB(k)$.

Fast Fourier Transform (FFT)
-76.1339890933333
-17.5614585497584+2.22992219906144i
14.2485935263582+0.584212704745982i
-11.761284305286+0.9052344588615 34i
7.10954204274748+0.281819691058089i
.
.
.
.

```
-4.5171153208858-0.713791910290836i
7.10954204274748-0.281819691058119i
-11.761284305286-0.905234458861467i
14.2485935263582-0.584212704746052i
-17.5614585497584-2.22992219906134i
```

4. Plot the results by separating the real part ($A(k)$) from the imaginary part ($B(k)$).



If the figure pattern is symmetric to the origin, such as Lorentzian curve, the DFT appears only in the real part, while in the pattern asymmetric to the origin the DFT appears in both the real and imaginary part. In this study, the data that were nearly symmetric to the origin were sampled, so that the DFT rarely appears in the imaginary part, though not impossible. Therefore, noise components are considered to be included in the imaginary part.

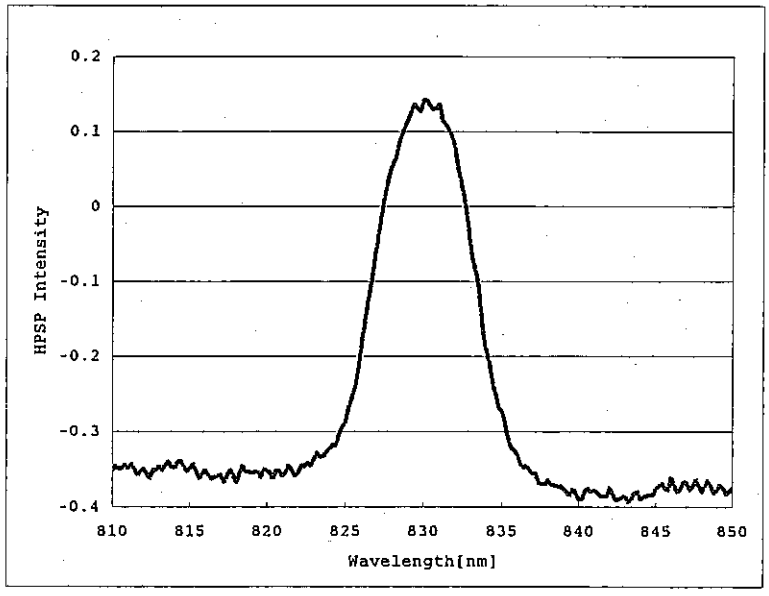
In addition, portions pointed by arrow appear irregularly, and thus they are likely the noise components.

5. Based on the above results, remove the noise components.

Fast Fourier Transform (FFT)		Removal of Noise Components
-76.1339890933333		-76.1339890933333
-17.5614585497584+2.22992219906144i		-17.5614585497584+2.229922199061440i
14.2485935263582+0.584212704745982i	→	14.2485935263582+0i
-11.761284305286+0.9052344588615 34i		-11.761284305286+0.9052344588615 34i
7.10954204274748+0.281819691058089i		7.10954204274748+0i
.		.
.	→	.
.		.
.		.
.		.
-4.5171153208858-0.713791910290836i		-4.5171153208858-0.713791910290836i
7.10954204274748-0.281819691058119i	→	7.10954204274748-0i
-11.761284305286-0.9052344588614 67i		-11.761284305286-0.9052344588614 67i
14.2485935263582-0.584212704746052i	→	14.2485935263582-0i
-17.5614585497584-2.22992219906134i		-17.5614585497584-2.22992219906134i

6. Plot the data after the inverse Fourier transform.

Fig.



Plutonium(VI) Spectrum by HPSP after Noise Components Removed by FFT

At last, the inverse Fourier transform was performed to return the spectrum to the original form. It was impossible to remove the noises completely. As these tasks will take much time if these procedures are followed sequentially, it is necessary to prepare macro or others beforehand.