Short Communication

Quantitative analysis of neodymium, uranium, and palladium in nitric acid solution by reflection absorption spectrophotometry

Toshiyuki Fujii,[1*] Souichirou Egusa,[1,2] Akihiro Uehara,[1] Hajimu Yamana,[1] and Yasuji Morita[3]

[1] Division of Nuclear Engineering Science, Research Reactor Institute, Kyoto University, 2-1010, Asashiro Nishi, Kumatori, Sennan, Osaka, 590-0494, Japan

[2] Graduate School of Engineering, Kyoto University, Kyoto daigaku-Katsura, Nishikyo-ku, Kyoto 615-8530, Japan

[3] Nuclear Science and Engineering Directorate, Japan Atomic Energy Agency, Tokai-mura, Ibaraki-ken 319-1195, Japan

*Author to whom correspondence should be addressed

tosiyuki@rri.kyoto-u.ac.jp

TEL: +81-72-451-2469, FAX: +81-72-451-2634

E-mail: tosiyuki@rri.kyoto-u.ac.jp

Abstract

Quantitative analysis of Nd, U, or Pd in 3 mol dm^{-3} (M) HNO_3 was performed by reflection absorption spectrophotometry at ultraviolet-visible-near-infrared (UV/Vis/NIR) region. A sample chamber with optics for reflection measurement was designed and attached to a UV/Vis/NIR spectrophotometer by optical fibers. The reflection absorbance showed linear relations with concentrations of Nd, U, and Pd at the absorbance region less than 0.1. The quantitative analysis was found to be possible for 3 M HNO_3 solutions containing [Nd] ~ 0.2 M, [U] ~ 0.04 M, or [Pd] ~ 0.01 M.

Keywords

Absorption spectrophotometry; Reflectance; Neodymium; Uranium; Palladium; Nitric acid.

Introduction

Ultraviolet-visible-near-infrared (UV/Vis/NIR) absorption spectrophotometry is useful for quantitative analysis of complexes in solutions. For the purpose of process control in the nuclear fuel cycle, applicability of the absorption spectrophotometry is investigated [1,2]. The transmission absorption spectrophotometry with optical cells is commonly used for quantitative analysis. The method is highly precise, but basically off-line. The liquid sample is placed in an optical cell and its transmittance is measured. Flow cell is designed for online and in-line measurements of liquid stream. The liquid sample runs through an optical cell and the transmittance of the cell is measured. If the transmission system is installed to the nuclear fuel cycle, the system should equip the optical windows which contact with the radioactive solutions. Fragility of the optical windows may be problematic for avoiding a leak of the solution from the system. Without the optical windows, the transmittance of sample solution may be measured if a part of optics is directly immersed in the sample. An optical probe called "immersion probe", which consists of optical fibers and stainless steel (or hastelloy, titanium, quartz, and so on), is designed for this purpose. Direct contact of the solution with optical material is undesirable from the viewpoint of corrosion. If one considers high temperature systems like pyroprocessing or vitrification, the material damage becomes significant.

The reflection absorption spectrophotometry is known as a high-sensitive analytical method for chemical species adsorbed onto metallic surface [3]. The reflection technique is generally used in the infrared region [3]. A utilization of this technique at UV/Vis region has been reported for Langmuir monolayer [4]. A chemical species adsorbed onto the interface between dodecane and sulfuric acid has been analyzed by UV/Vis reflection absorption spectrophotometry [5]. An advantage of the reflection technique may be that the optics can be arranged above the solution surface and do not contact with the sample solution. Optical windows are not required for the container of the sample solution. It may be utilizable for online monitoring of liquid samples treated in the nuclear fuel cycle. We report the applicability of UV/Vis reflection absorption spectrophotometry for nitric acid solutions containing Nd, U, or Pd, in which Nd and Pd are major fission product (FP) elements of rare earth elements and platinum group elements, respectively.

Experimental

All chemicals were reagent grade. $Nd(NO_3)_3 \cdot 6H_2O$ was dissolved in HNO_3 to prepare various concentrations of Nd(III) in 3 mol dm^{-3} (M) HNO_3. Similarly, $UO_2(NO_3)_2 \cdot 6H_2O$ was dissolved in 3 M HNO_3. Pd metal was dissolved in boiling 13.3 M HNO_3 [6], and then the solution was diluted with H_2O to prepare Pd sample of 3 M HNO_3.

The absorption spectrum was measured by using a UV/Vis/NIR spectrophotometer (JASCO, V-7200) at room temperature. A cubic sample chamber of ~200 mm on a side was designed for reflection absorption measurement, whose plane view is shown in Fig. 1 schematically. The chamber was connected with the spectrophotometer by optical fibers. An aluminum mirror was set at the focal point. The incident angle of analytical light was designed to be 5°. The deuterium and tungsten light sources were switched at 350 nm. The reflection intensity was measured in the wavelength range of 200-1000 nm at 1 nm intervals of 0.2 sec integration time each. The band widths were 1 nm (200-800 nm) and 5 nm (800-1000 nm). The detectors, secondary electron multiplier (SEM) for UV/Vis region and PbS semiconductors for NIR region, were switched at 800 nm. The obtained data was used as the blank spectrum. Then, the aluminum mirror was replaced by the sample solution in a quartz cell, and the reflectance was measured. A metal free HNO_3 solution with the same acidity was also analyzed as reference. The transmission absorption spectrum was also measured for comparison.

Results and discussion

Neodymium possesses characteristic absorption bands in UV/Vis/NIR region [7]. The reflection intensity (R) of water and 3 M HNO_3 solution with or without Nd(III) was measured (Fig. 2a). A low signal-to-noise (S/N) ratio at around 800 nm is due to switching of detectors. The reflectance of water was measured to be ~0.08% relative to that of the aluminum mirror. The reflectance of the aluminum mirror is commonly certified to be ~90%. The refractive indexes of water and quartz are 1.33 and 1.46 (Vis region, room temperature) [8]. From the Fresnel equations with the refractive indexes, for the system with 5° incident and reflection angles, 93% of analytical lights transmit the quartz cell and 0.2% of the transmitted lights should be reflected at the water surface. The R value of 0.08% means that ~40% of the reflected lights are successfully collected at the inlet of optical fibers directed to the detector. The absorption band at 960 nm is attributable to the vibrations of H_2O. This is assigned to the combination transition $2\nu_1 + \nu_3$, where ν_1 is the symmetric O-H stretch and ν_3 the asymmetric O-H stretch modes [9]. The absorption in UV region for 3 M HNO_3 solution is due to the electron transition of NO_3^- [10,11].

The transmission absorbance (A) is defined by the Lambert-Beer low, $A = -\log (I/I_0)$, where I_0 and I are the intensity of incident light and transmitted light, respectively. Similar to A, the reflection absorbance (A_R) is defined as,

$$A_R = -\log (R/R_0) \qquad (1)$$

where R_0 is the reflection intensity measured for solvent (3 M HNO_3) in quartz cell, and R is that containing solutes. The absorption spectra of Nd obtained are shown in Fig. 2b, in which the transmission absorption spectrum reproduces the spectra reported for nitrate systems [12-16]. The reflection absorption spectrum is similar to the transmission absorption spectrum but the absorbance A_R was found to be smaller than A. The A_R values in Fig 2b are shown in Fig 2c as a function of A. At the absorbance region from 0 to 0.1, A_R is identical with A, while A_R is less sensitive at $A > 0.1$. This is due to the detection limit of our analytical apparatus. The analytical light intensity is depreciated by connecting the sample chamber with optical fibers, and under this condition, the reflected light intensity of $R < 0.08\%$ is analyzed. For several absorption bands positioned by arrows shown in Fig. 2b, the dependence of A_R on Nd concentration was investigated. The result of A_R *vs* [Nd] is shown in Fig. 2d. It is clear that, in the region $A_R \leq 0.1$, A_R is proportional to [Nd]. Quantitative analysis of ~0.2 M Nd in 3 M HNO_3 is possible by employing the calibration lines for absorption bands at 460 nm and 679 nm, whose coefficient of determination is better than 0.997. For quantitative analysis of HNO_3 solutions with lower Nd concentration, A_R of strong absorption bands like 578 nm should be useful.

The A and A_R values were measured for U in 3 M HNO_3. The absorption spectra obtained are shown in Fig. 3a. The transmission absorption spectrum perfectly reproduced the pioneering work [17]. Uranium dissolved in HNO_3 is U(VI) and forms uranyl ion, UO_2^{2+}. The electronic structure of UO_2^{2+} has been studied in detail [18,19]. The absorption bands possesses peaks via the stretching vibration of O=U=O. The reflection absorption spectrum is similar to the transmission absorption spectrum. The A_R values are shown as a function of U concentration (Fig. 3b). Linear correlation is found in the region of $A_R < 0.1$. Quantitative analysis of ~0.04 M U in 3 M HNO_3 is possible by employing the calibration lines for absorption bands at 370 nm and 468 nm, whose coefficient of determination is better than 0.994. The curve of A_R for absorption bands at 415 nm can be used as an alternative of the calibration lines.

Palladium is known as one of the noble metal fission product elements in reprocessing of spent nuclear fuels. Its complexation characteristics in solvent extraction processes [20,21] are hence of interest. In our previous study, the complexation of Pd^{2+} with NO_3^- was studied in detail by transmission absorption spectrophotometry [6]. The A and A_R values of Pd in 3 M HNO_3 obtained in the present study are shown in Fig. 4a. The transmission absorption spectrum reproduced the reported spectra [6,22,23]. The reflection absorption spectrum is similar to the transmission absorption spectrum. The A_R values are shown as a function of Pd concentration (Fig. 4b). Again, the linear correlation can be obtained in the region of $A_R < 0.1$. Quantitative analysis of ~0.01 M Pd in 3 M HNO_3 is possible by employing the calibration line resulted from absorption intensities at the shoulder of absorption bands. In diluted [Pd] region, peak maximum can be used to prepare the calibration line.

Increasing the intensity of light source and the sensitivity of detectors improves the current system of reflection absorption spectrophotometry. Besides that, measurement of the surface of sample solution without using quartz cell should increase the reflectance light intensity. From the Fresnel equations, if we do not use the quartz cell, ~2% of the transmitted lights are reflected at the solution surface. This means that the reflectance light intensity increases ~10 times more than that with the quartz cell.

The nonflatness of liquid surface due to the surface tension and vibrations (microvibrations) under the experimental circumstance is problematic. The former shifts the focal point and the latter depresses the S/N ratio. Installing autofocus device, vibration-free system, and multiple detector may be required.

Conclusions

The UV/Vis/NIR reflection absorption technique for nitric acid solutions was developed. Quantitative analysis of Nd, U, and Pd was possible for 3 M HNO_3 solution containing ~0.2 M Nd, ~0.04 M U, or ~ 0.01 M Pd. By using A_R of stronger/weaker absorption bands, possible concentration range for quantitative analysis can be expanded. This technique may be applicable for analyzing radioactive solutions in nuclear fuel cycle.

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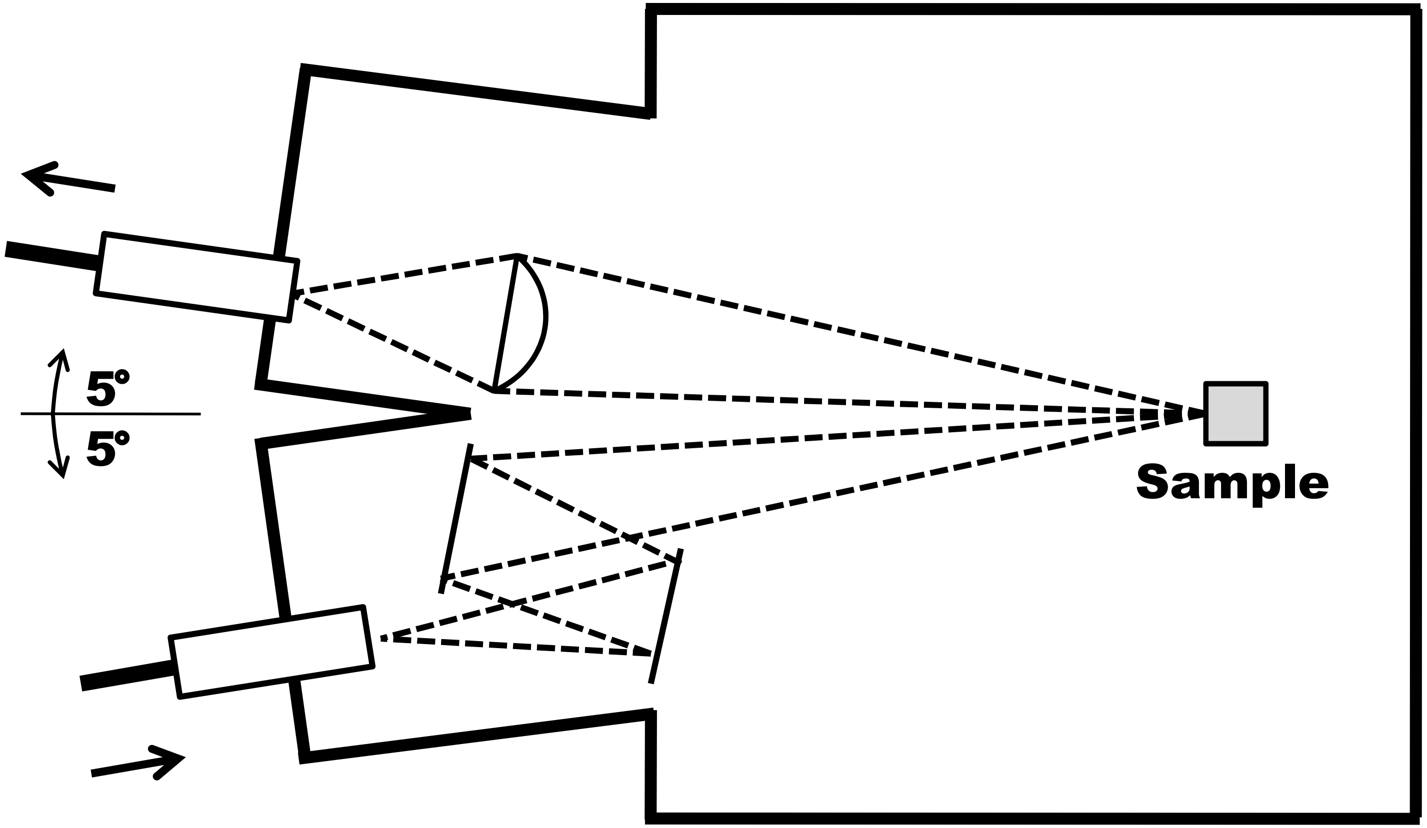
Figure captions

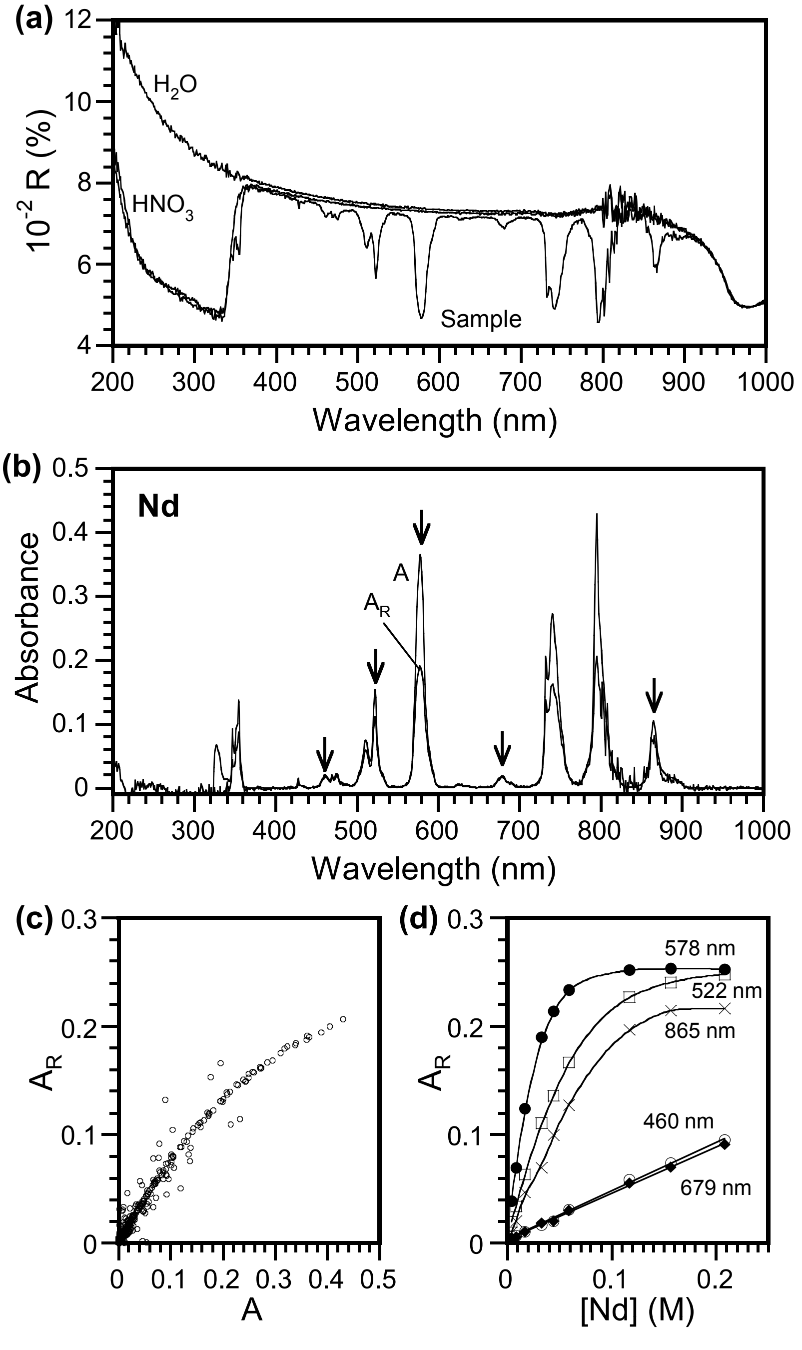
Fig. 1 Optical alignment of sample chamber for reflection absorption measurement.

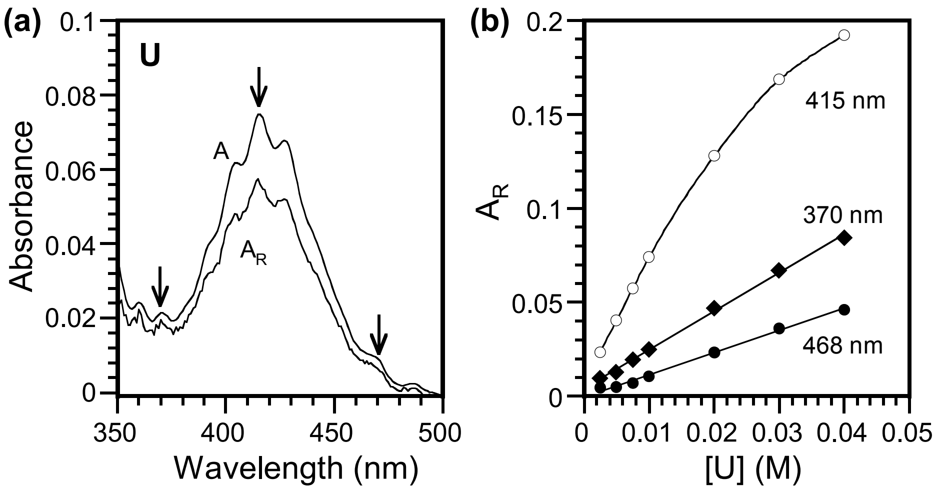
Fig. 2 Reflection absorption spectra of Nd(III) in 3 M HNO_3. **a** Reflectance of H_2O, 3 M HNO_3, and 0.04 M Nd(III) in 3 M HNO_3. **b** Transmission absorbance A and reflection absorbance A_R for 0.04 M Nd(III) in 3 M HNO_3. Absorbances at wavelengths positioned by arrows were used in Fig. 2d. **c** A_R *vs* A **d** Dependence of A_R on Nd(III) concentration.

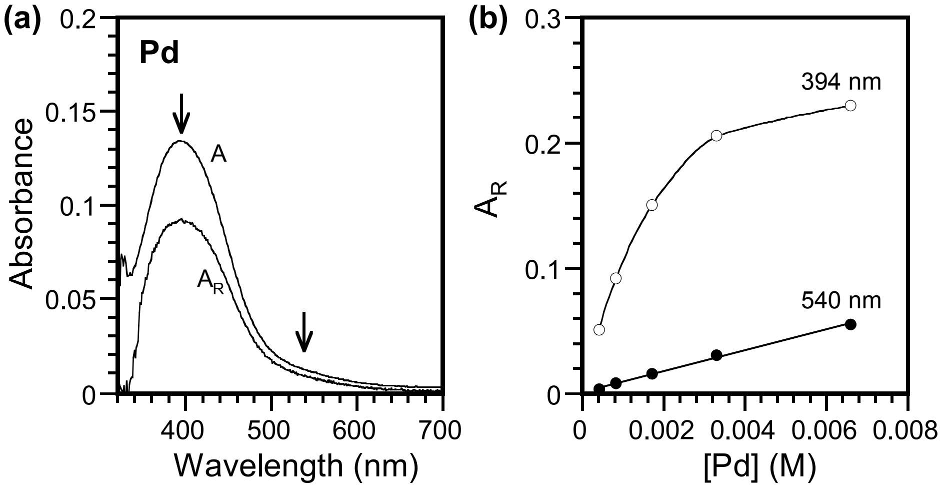
Fig. 3 Reflection absorption spectra of U(VI) in 3 M HNO_3. **a** Transmission absorbance A and reflection absorbance A_R for 0.0075 M U(VI) in 3 M HNO_3. Absorbances at wavelengths positioned by arrows were used in Fig. 3b. **b** Dependence of A_R on U(VI) concentration.

Fig. 4 Reflection absorption spectra of Pd(II) in 3 M HNO_3. **a** Transmission absorbance A and reflection absorbance A_R for 0.001 M Pd(II) in 3 M HNO_3. Absorbances at wavelengths positioned by arrows were used in Fig. 4b. **b** Dependence of A_R on Pd(II) concentration.


5°
5°
Sample


(a)
12
10
8
6
4
10^{-2} R (%)
H_2O
HNO_3
Sample
200 300 400 500 600 700 800 900 1000
Wavelength (nm)
(b)
0.5
0.4
0.3
0.2
0.1
0
Absorbance
Nd
A
A_R
200 300 400 500 600 700 800 900 1000
Wavelength (nm)
(c)
0.3
0.2
0.1
0
A_R
0 0.1 0.2 0.3 0.4 0.5
A
(d)
0.3
0.2
0.1
0
A_R
578 nm
522 nm
865 nm
460 nm
679 nm
0 0.1 0.2
[Nd] (M)


(a)
U
A
A$_R$
Absorbance
0
0.02
0.04
0.06
0.08
0.1
350
400
450
500
Wavelength (nm)
(b)
A$_R$
0
0.05
0.1
0.15
0.2
415 nm
370 nm
468 nm
0
0.01
0.02
0.03
0.04
0.05
[U] (M)


(a)
Pd
Absorbance
0.2
0.15
0.1
0.05
0
A
A_R
400
500
600
700
Wavelength (nm)
(b)
0.3
0.2
0.1
0
A_R
394 nm
540 nm
0
0.002
0.004
0.006
0.008
[Pd] (M)