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1   Short Communication

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3   Quantitative analysis of neodymium, uranium, and palladium in nitric acid solution by

4   reflection absorption spectrophotometry

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22

23 **Abstract**

24 Quantitative analysis of Nd, U, or Pd in 3 mol dm^{-3} (M) HNO_3 was performed by

25 reflection absorption spectrophotometry at ultraviolet-visible-near-infrared

26 (UV/Vis/NIR) region. A sample chamber with optics for reflection measurement was

27 designed and attached to a UV/Vis/NIR spectrophotometer by optical fibers. The

28 reflection absorbance showed linear relations with concentrations of Nd, U, and Pd at

29 the absorbance region less than 0.1. The quantitative analysis was found to be possible

30 for 3 M HNO_3 solutions containing [Nd] ~ 0.2 M, [U] ~ 0.04 M, or [Pd] ~ 0.01 M.

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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

61 reflection technique may be that the optics can be arranged above the solution surface

62 and do not contact with the sample solution. Optical windows are not required for the

63 container of the sample solution. It may be utilizable for online monitoring of liquid

64 samples treated in the nuclear fuel cycle. We report the applicability of UV/Vis

65 reflection absorption spectrophotometry for nitric acid solutions containing Nd, U, or Pd,

66 in which Nd and Pd are major fission product (FP) elements of rare earth elements and

67 platinum group elements, respectively.

68

69 **Experimental**

70 All chemicals were reagent grade. $Nd(NO_3)_3 \cdot 6H_2O$ was dissolved in HNO_3 to prepare

71 various concentrations of Nd(III) in 3 mol dm^{-3} (M) HNO_3. Similarly, $UO_2(NO_3)_2 \cdot 6H_2O$

72 was dissolved in 3 M HNO_3. Pd metal was dissolved in boiling 13.3 M HNO_3 [6], and

73 then the solution was diluted with H_2O to prepare Pd sample of 3 M HNO_3.

74 The absorption spectrum was measured by using a UV/Vis/NIR

75 spectrophotometer (JASCO, V-7200) at room temperature. A cubic sample chamber of

76 ~200 mm on a side was designed for reflection absorption measurement, whose plane

77 view is shown in Fig. 1 schematically. The chamber was connected with the

78 spectrophotometer by optical fibers. An aluminum mirror was set at the focal point. The

79 incident angle of analytical light was designed to be 5°. The deuterium and tungsten

80 light sources were switched at 350 nm. The reflection intensity was measured in the

81 wavelength range of 200-1000 nm at 1 nm intervals of 0.2 sec integration time each.

82 The band widths were 1 nm (200-800 nm) and 5 nm (800-1000 nm). The detectors,

83 secondary electron multiplier (SEM) for UV/Vis region and PbS semiconductors for

84 NIR region, were switched at 800 nm. The obtained data was used as the blank

85 spectrum. Then, the aluminum mirror was replaced by the sample solution in a quartz

86 cell, and the reflectance was measured. A metal free HNO_3 solution with the same

87 acidity was also analyzed as reference. The transmission absorption spectrum was also

88 measured for comparison.

89

90 **Results and discussion**

91 Neodymium possesses characteristic absorption bands in UV/Vis/NIR region [7]. The

92 reflection intensity (R) of water and 3 M HNO_3 solution with or without Nd(III) was

93 measured (Fig. 2a). A low signal-to-noise (S/N) ratio at around 800 nm is due to

94 switching of detectors. The reflectance of water was measured to be ~0.08% relative to

95 that of the aluminum mirror. The reflectance of the aluminum mirror is commonly

96 certified to be ~90%. The refractive indexes of water and quartz are 1.33 and 1.46 (Vis

97 region, room temperature) [8]. From the Fresnel equations with the refractive indexes,

98 for the system with 5° incident and reflection angles, 93% of analytical lights transmit

99 the quartz cell and 0.2% of the transmitted lights should be reflected at the water surface.

100 The R value of 0.08% means that ~40% of the reflected lights are successfully collected

101 at the inlet of optical fibers directed to the detector. The absorption band at 960 nm is

102 attributable to the vibrations of H_2O. This is assigned to the combination transition $2\nu_1$

103 $+ \nu_3$, where ν_1 is the symmetric O-H stretch and ν_3 the asymmetric O-H stretch modes

104 [9]. The absorption in UV region for 3 M HNO_3 solution is due to the electron transition

105 of NO_3^- [10,11].

106   The transmission absorbance (A) is defined by the Lambert-Beer low, $A = -\log$

107 (I/I_0), where I_0 and I are the intensity of incident light and transmitted light, respectively.

108 Similar to A, the reflection absorbance (A_R) is defined as,

5

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

110

111   where R_0 is the reflection intensity measured for solvent (3 M HNO_3) in quartz cell, and

112   R is that containing solutes. The absorption spectra of Nd obtained are shown in Fig. 2b,

113   in which the transmission absorption spectrum reproduces the spectra reported for

114   nitrate systems [12-16]. The reflection absorption spectrum is similar to the

115   transmission absorption spectrum but the absorbance A_R was found to be smaller than A.

116   The A_R values in Fig 2b are shown in Fig 2c as a function of A. At the absorbance

117   region from 0 to 0.1, A_R is identical with A, while A_R is less sensitive at $A > 0.1$. This is

118   due to the detection limit of our analytical apparatus. The analytical light intensity is

119   depreciated by connecting the sample chamber with optical fibers, and under this

120   condition, the reflected light intensity of $R < 0.08\%$ is analyzed. For several absorption

121   bands positioned by arrows shown in Fig. 2b, the dependence of A_R on Nd

122   concentration was investigated. The result of A_R vs [Nd] is shown in Fig. 2d. It is clear

123   that, in the region $A_R \leq 0.1$, A_R is proportional to [Nd]. Quantitative analysis of ~0.2 M

124   Nd in 3 M HNO_3 is possible by employing the calibration lines for absorption bands at

125   460 nm and 679 nm, whose coefficient of determination is better than 0.997. For

126   quantitative analysis of HNO_3 solutions with lower Nd concentration, A_R of strong

127   absorption bands like 578 nm should be useful.

128   The A and A_R values were measured for U in 3 M HNO_3. The absorption

129   spectra obtained are shown in Fig. 3a. The transmission absorption spectrum perfectly

130   reproduced the pioneering work [17]. Uranium dissolved in HNO_3 is U(VI) and forms

131   uranyl ion, UO_2^{2+}. The electronic structure of UO_2^{2+} has been studied in detail [18,19].

132   The absorption bands possesses peaks via the stretching vibration of O=U=O. The

6

133 reflection absorption spectrum is similar to the transmission absorption spectrum. The

134 A_R values are shown as a function of U concentration (Fig. 3b). Linear correlation is

135 found in the region of $A_R < 0.1$. Quantitative analysis of ~0.04 M U in 3 M HNO_3 is

136 possible by employing the calibration lines for absorption bands at 370 nm and 468 nm,

137 whose coefficient of determination is better than 0.994. The curve of A_R for absorption

138 bands at 415 nm can be used as an alternative of the calibration lines.

139   Palladium is known as one of the noble metal fission product elements in

140 reprocessing of spent nuclear fuels. Its complexation characteristics in solvent

141 extraction processes [20,21] are hence of interest. In our previous study, the

142 complexation of Pd^{2+} with NO_3^- was studied in detail by transmission absorption

143 spectrophotometry [6]. The A and A_R values of Pd in 3 M HNO_3 obtained in the present

144 study are shown in Fig. 4a. The transmission absorption spectrum reproduced the

145 reported spectra [6,22,23]. The reflection absorption spectrum is similar to the

146 transmission absorption spectrum. The A_R values are shown as a function of Pd

147 concentration (Fig. 4b). Again, the linear correlation can be obtained in the region of A_R

148 < 0.1. Quantitative analysis of ~0.01 M Pd in 3 M HNO_3 is possible by employing the

149 calibration line resulted from absorption intensities at the shoulder of absorption bands.

150 In diluted [Pd] region, peak maximum can be used to prepare the calibration line.

151   Increasing the intensity of light source and the sensitivity of detectors improves

152 the current system of reflection absorption spectrophotometry. Besides that,

153 measurement of the surface of sample solution without using quartz cell should increase

154 the reflectance light intensity. From the Fresnel equations, if we do not use the quartz

155 cell, ~2% of the transmitted lights are reflected at the solution surface. This means that

156 the reflectance light intensity increases ~10 times more than that with the quartz cell.

157   The nonflatness of liquid surface due to the surface tension and vibrations

158   (microvibrations) under the experimental circumstance is problematic. The former shifts

159   the focal point and the latter depresses the S/N ratio. Installing autofocus device,

160   vibration-free system, and multiple detector may be required.

161

162   **Conclusions**

163   The UV/Vis/NIR reflection absorption technique for nitric acid solutions was developed.

164   Quantitative analysis of Nd, U, and Pd was possible for 3 M HNO_3 solution containing

165   ~0.2 M Nd, ~0.04 M U, or ~ 0.01 M Pd. By using A_R of stronger/weaker absorption

166   bands, possible concentration range for quantitative analysis can be expanded. This

167   technique may be applicable for analyzing radioactive solutions in nuclear fuel cycle.

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206

Figure captions

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

209 **Fig. 2** Reflection absorption spectra of Nd(III) in 3 M HNO_3. **a** Reflectance of H_2O, 3

210 M HNO_3, and 0.04 M Nd(III) in 3 M HNO_3. **b** Transmission absorbance A and

211 reflection absorbance A_R for 0.04 M Nd(III) in 3 M HNO_3. Absorbances at wavelengths

212 positioned by arrows were used in Fig. 2d. **c** A_R *vs* A **d** Dependence of A_R on Nd(III)

213 concentration.

214 **Fig. 3** Reflection absorption spectra of U(VI) in 3 M HNO_3. **a** Transmission absorbance

215 A and reflection absorbance A_R for 0.0075 M U(VI) in 3 M HNO_3. Absorbances at

216 wavelengths positioned by arrows were used in Fig. 3b. **b** Dependence of A_R on U(VI)

217 concentration.

218 **Fig. 4** Reflection absorption spectra of Pd(II) in 3 M HNO_3. **a** Transmission absorbance

219 A and reflection absorbance A_R for 0.001 M Pd(II) in 3 M HNO_3. Absorbances at

220 wavelengths positioned by arrows were used in Fig. 4b. **b** Dependence of A_R on Pd(II)

221 concentration.

222

5°
5°

Sample

(a)

U

A

A_R

Absorbance

350 400 450 500

Wavelength (nm)

(b)

A_R

415 nm

370 nm

468 nm

0 0.01 0.02 0.03 0.04 0.05

[U] (M)

(a)

Pd

A

A_R

(b)

394 nm

540 nm