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ARTICLE

Development of a Non-Contact Chemical Analysis Method for Process Management in Reprocessing Plants

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In the process of chemical analysis in reprocessing plants, the simplification of complicated operations for the manipulator is required. To make the process of chemical analysis easier, a non-contact method for chemical analysis in reprocessing plants was developed utilizing Raman spectroscopy. Raman spectroscopy is a type of non-contact and non-destructive chemical analysis method that can be applied to quantification analysis. In this study, uranyl nitrate in nitric acid solution and tributyl phosphate (TBP) in dodecane solvent sealed in a plastic container were examined as target samples. In the measurement, an equipment to align the optical axis was developed to improve simplicity of the method. Statistical analysis called partial least squares (PLS) regression was applied to quantitative analysis to improve the analysis accuracy. By utilizing PLS, 1 g L^{-1} uranyl nitrate and 1 vol% TBP could be detected. It was confirmed that this method can be applied to both inorganic and organic materials. By using this method, it is possible to analyze high-dose samples in containers without opening those containers. This method allows us to simplify the analysis process for operators significantly and reduce the amount of radioactive waste liquid.

KEYWORDS: reprocessing plant, simplified operation, Raman, no-pretreatment, uranyl, chemometrics

I. Introduction

In reprocessing plants, to ensure the reprocessing process is performed properly, high-dose analytical samples such as uranium (U) and Plutonium (Pu) are analyzed by chemical methods, e.g., high performance liquid chromatography (HPLC), in an analytical box. High-dose samples are sealed in plastic sample containers and carried to the analytical box.[1,2] Then the chemical analysis is carried out remotely by manipulators in the analytical box, which is shielded by lead glass. Because the chemical analysis includes many complicated processes for the manipulator, such as opening the sample container, the addition of reagents, dilution and filtration, and because of the remote operation, it takes a lot of time and requires skilled operators to perform. Moreover, due to the various pretreatment steps, relatively large amounts of radioactive waste liquid is one of the problems in the current method.

Raman spectroscopy is a type of non-contact and non-destructive chemical analysis method. In Raman analysis, excitation light is exposed to a target and this scattering light is detected. Among this scattering light, Stokes and anti-Stokes scattering includes information of molecular vibration energy. The relationship between the intensity and the energy of the scattering light is obtained as a Raman spectrum. By utilizing peak intensity, peak area, and peak shift in the Raman spectrum, qualitative, quantitative, and chemical bonding state analysis can be performed.[3] The light source for Raman spectroscopy is a laser, so when the container is light transmissive, non-contact analysis from outside of containers can be performed by this method.[4,5]

In this study, to reduce the time required for the operation, and to construct a method by which the analysis can be performed with the manipulator without requiring skilled operators, a non-contact analysis method that enables quantification of chemical species without opening the sample containers was developed. Utilizing Raman spectroscopy, samples were analyzed from outside of the sample container without pretreatment. To improve the simplicity of this method, analysis equipment was developed for optical axis alignment. In the future, the system is envisioned that could automatically conduct measurements of concentration just by installing containers within the equipment. To achieve this, analytical conditions have been selected that enable spectral analysis to be performed automatically and without subjectivity.

Uranyl nitrate in nitric acid and tributyl phosphate (TBP) in organic solvent were selected as target samples because they are often used in reprocessing plants. A white plastic container made mainly of polyethylene and some additives was used as a sample container in this study because sample containers made of plastic are often used in reprocessing plants. In previous reports,[6-9] chemometrics were often used for quantitative analysis by Raman spectroscopy to improve the analysis accuracy. Among statistical analyses, partial least squares (PLS) regression is less sensitive to noise and outliers that are not related to the response variable, because this method utilizes the information of the response variable in addition to the explanatory variable to build the quantitative models. Therefore, PLS analysis was selected to be applied to the quantification.

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II. Experimental

1. Material

All chemicals were used without further purification: TBP (Tributyl Phosphate, TCI, >99.0%), dodecane (Fujifilm, 99.0+%), HNO_3 (Kanto Chemical), The U test solution was prepared by dissolving uranium dioxide powder in HNO_3 solution. The concentration of U was confirmed by ICP-AES (5110 VDV, Agilent).

2. Instruments

The Raman measurement system is presented in **Fig. 1**. The portable-type Raman spectrometer (HyperFlux PRO Plus, Tornado) was coupled with the Raman probe via optical fiber cables. The excitation wavelength of 785 nm was chosen to suppress fluorescence derived from the sample container. The experiment in this study was performed in the laboratory to verify the detectability of the target material (U, TBP) from outside of the sample container by a portable-type Raman spectrometer. The sample container was made of polyethylene with some additives and the color was white. The transmittance of this container at 785 nm is 20%.

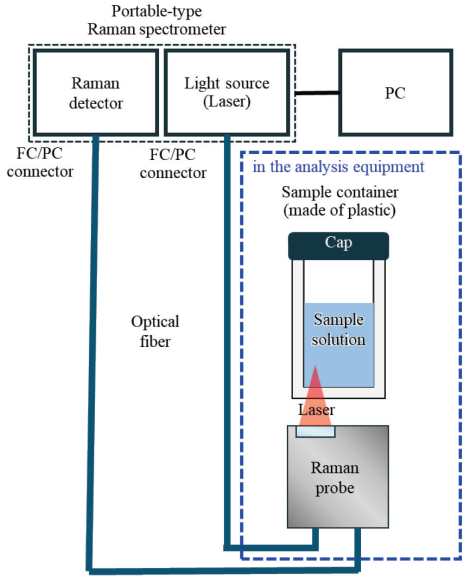

Fig. 1 Measurement system of Raman spectroscopy in this study

In this experiment, the equipment for optical axis alignment has been developed to make operation by manipulators easier. Its appearance and description are shown in **Fig. 2**. This equipment was designed to align the optical axis just by placing the sample container in the equipment. The equipment consists of the lid of the case of the plastic container, the case for the plastic container, the case for the Raman probe and the handle for the manipulators. The arrangement of the cases of the plastic container and the Raman probe is designed so that the focus of the laser emitted from the Raman probe is aligned with the sample solution contained in the plastic container. The lid functions to shield the laser emitted from the Raman probe. Therefore, Raman measurement can be performed just by placing the sample container in the opening shown in Fig. 2. Furthermore, the handle is attached for easy grasping of the equipment by manipulators. The introduction of this jig will greatly simplify the analysis operation by the manipulator.

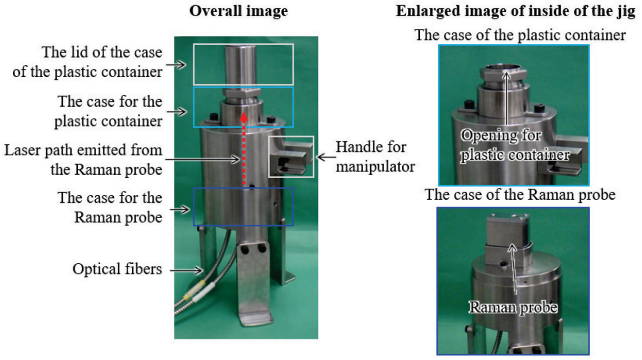

Fig. 2 The analysis equipment for adjusting optical axis

3. Statistical Analysis

Quantification analysis was performed by PLS utilizing software (panorama, labCognition). Before applying PLS analysis, baseline correction of the Raman spectrum was performed. The overview is shown in **Fig. 3**. In this experiment, the plastic container was used to match the conditions with the actual environment. Generally, the plastic container affects the spectrum due to its fluorescence background, as shown by the green area in Fig. 3. To remove this fluorescence background, correction by the baseline correction method was performed. In the case of the plastic containers, airPLS[10] was applied as the baseline correction method because the fluorescence background could be automatically calculated and removed, thus it's suitable for operations that do not require skilled operators.

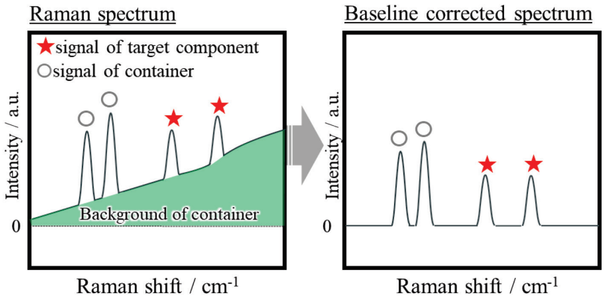

Fig. 3 Overview of baseline correction process of the spectrum

III. Results and Discussion

The Raman spectrum and calibration curve of uranyl nitrate in nitric acid is presented in **Fig. 4**(a). The peak of the uranyl ion (UO_2^{2+}) is known to appear at approximately 860-880 cm^{-1}.[8, 11-13] In a Raman spectrum of 1.0 to 200 [g L^{-1}] of U concentration, the peak of UO_2^{2+} appears around 870 cm^{-1} from 1.0 [g L^{-1}], and the peak of NO_3^- appears around 1048 cm^{-1}.[8,11,13] In this experiment, the objective was to calculate the U concentration from the peak level of the uranyl ion, so it was considered to be acceptable that all of the peak of NO_3^- wasn't included in the graph of Fig. 4. The calibration curves in Fig. 4(b), (c) were obtained by PLS. In Fig. 4(c), the error bars are very small relative to the measured values, making them difficult to see. The values obtained by PLS were indicated as Raman factor. Because to create a single calibration curve over the entire range would result in poor quantification precision on the lower concentration side, the calibration curve was divided into two ranges: (b) 10 [g L^{-1}] or more U and (c) 10 [g L^{-1}] or less U. The coefficient of determination (R^2) was over 0.99, indicating a good correlation. From this result, it was confirmed that U could be detected and quantified from outside of the sample container by the portable-type Raman spectrometer. On the other hand, it was observed that the calibration curve on the lower concentration side showed relatively high scattering. This is due to the weaker signal derived from the samples in lower concentrations, which are more susceptible to the influence of background interference from the plastic container's fluorescence. As like UO_2^{2+}, PuO_2^{2+} has Raman peak around 833 cm^{-1}, so it could be detected, too.[13-16]

For TBP in organic solvent, the Raman spectrum and calibration curve are shown in **Fig. 5**(a), (b). The peaks of P-O and C-O are assigned at 773, 815, 833 cm^{-1}. P-O-C is assigned at 910 cm^{-1}, and PO_3 appears at 722 cm^{-1}.[16,17] These peaks are derived from TBP, so could be applied to the determination of TBP. The calibration curves are shown in Fig. 5(c), (d), which were calculated by PLS. In Fig. 5(c), the error bars are very small relative to the measured values, making them difficult to observe. The coefficient of determination was over 0.99, indicating a good correlation, too. It was also confirmed that TBP in a plastic container

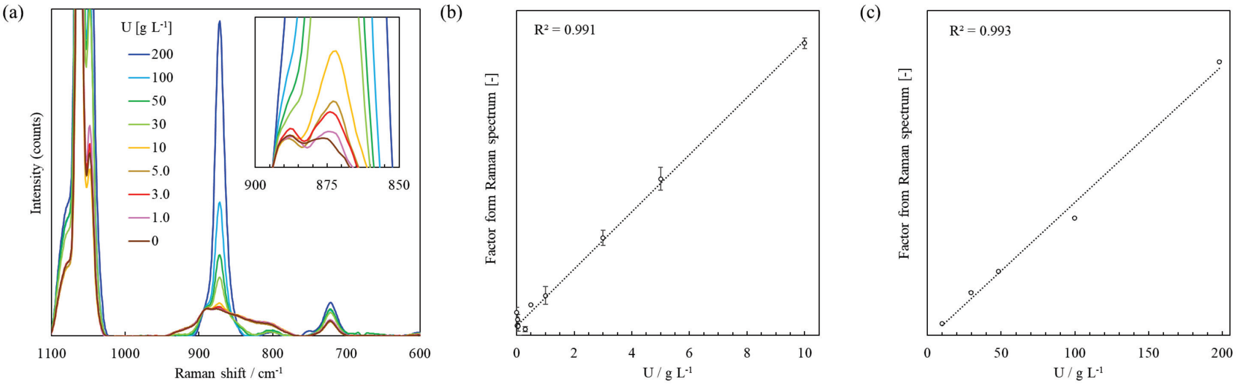

Fig. 5 (a) Raman spectrum of uranyl nitrate in 3 mol L^{-1} nitric acid solution in the plastic container, (b) Calibration curve in the range of 10 g L^{-1} or more U, (c) Calibration curve in the range of 10 g L^{-1} or less U

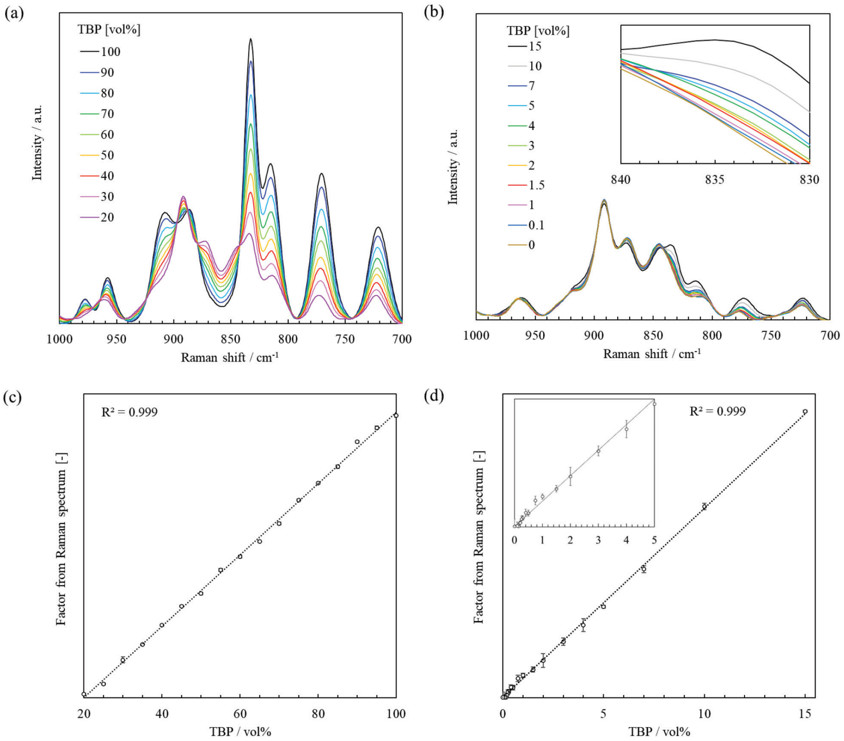

Fig. 4 Raman spectrum of TBP in dodecane solvent in the plastic container, (a) over all view, (b) close-up view of 15 vol% or less TBP. (c) Calibration curve in the range of 20 vol% or more TBP, (d) Calibration curve in the range of 15 vol% or less TBP

could be determined by a portable-type Raman spectrometer. On the other hand, as is the case in the quantification of U, there is relatively high scattering at lower concentrations.

To improve accuracy in the lower concentration range, changing the container has been proposed. While this may increase the effort required for transferring samples, it could be viable for applications that necessitate higher precision analysis. The scattering in the calibration curves largely depends on the background interference from the plastic container. Therefore, the possibility of changing the container to a glass one which has lower background interference and is more transmissive was considered. The result of TBP in a glass container is shown in **Fig. 6**. In this figure, the error bars are very small relative to the measured values, making them difficult to see. The relative standard deviation in the range of 1.0% to 10 vol% is found to be higher when using the plastic container, ranging from 0.3% to 18%, while it is lower when using the glass container, ranging from 0.3% to 7%, indicating that using a glass container improves accuracy. Furthermore, there is another advantage of using a glass container that it could be measured in a shorter time. It's because the transmittance of this container at 785 nm is 90%, which is much higher than that of the plastic container, which is 20%. It usually takes several minutes to obtain a spectrum in the plastic container, but it could be measured in less than one minute in the glass container.

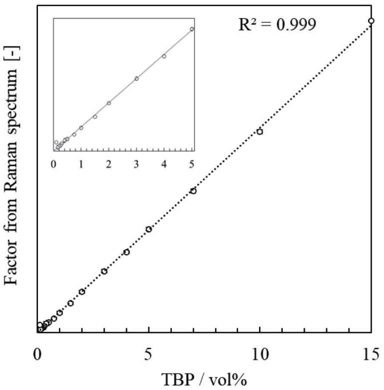

Fig. 6 Calibration curve in the range of 15 vol% or less TBP in the glass container.

IV. Conclusion

In this study, non-contact analysis method that enables quantification of chemical species without opening the sample containers was developed utilizing Raman spectroscopy. It was confirmed this method could analyze U (VI) in nitric acid and TBP in dodecane in a sample container made of plastics. Moreover, to aim the measurement system by which the analysis can be performed automatically in the future, the equipment for optical alignment and the auto baseline correction method was applied.

The benefits of applying this method are shown in **Table 1**. This method has many advantages, such as no-pretreatment, shorter analysis time, lower difficulty, reduction of waste liquid. Therefore, this method has the potential to be applied to various forms of non-destructive measurement.

Table 1 Benefits of developed method

Items	Current method (e.g., HPLC)	This study
Pretreatment	･Opening the container ･Addition of reagents ･Dilution etc.	Not necessary
Time required for analysis	About 1 hour (including pretreatment)	≦10 minutes
Difficulty of operation	High (It needs skilled operators)	Low
Waste liquid	Increased by pretreatment	Not increased during analysis

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