Radioactive Carbon Isotope Monitoring System Based on Cavity Ring-down Laser Spectroscopy for Decommissioning Process of Nuclear Facilities*

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Abstract
In decommissioning process of nuclear facilities, large amount of radioactive isotopes are discharged as waste. Radioactive carbon isotope (\(^{14}\)C) is one of the key nuclides to determine the upper limit of concentration in the waste disposal. In particular, \(^{14}\)C on the graphite reactor decommissioning should be separated from stable carbon isotopes (\(^{12}\)C and \(^{13}\)C) and monitored for the public health and safety. We propose an isotope analysis system based on cavity ring-down laser spectroscopy (CRDS) to monitor the carbon isotopes (\(^{12}\)C, \(^{13}\)C and \(^{14}\)C) in the isotope separation process for the graphite reactor decommissioning. This system is compact and suitable for a continuous monitoring, because the concentration of molecules including the carbon isotope is derived from its photo absorbance with ultra high sensitive laser absorption spectroscopy. Here are presented the necessary conditions of CRDS system for \(^{14}\)C isotope analysis through the preliminary experimental results of \(^{13}\)C isotope analysis with a prototype system.

Key words: \(^{14}\)C, Radioactive Waste, Isotope Analysis, Laser Spectroscopy, Decommissioning

1. Introduction
In the nuclear plants, \(^{14}\)C is generated by a thermal neutron interaction with N, O and C in coolants, moderators, fuels and constructional materials \(^{(1)}\). In decommissioning graphite reactor particularly, reduction of discharging \(^{14}\)C is important. Thus, \(^{14}\)C separation methods are being developed for the decontamination and decommissioning of nuclear reactor. One of the promising methods is \(^{14}\)C separation by using vibrational excited CO plasma chemical reactions \(^{(2)}\). Through the process, gaseous CO\(_2\) and polymer deposit are enriched in \(^{13}\)C. The final product obtained in the process is gaseous CO\(_2\) because the polymer deposit reacts with O\(_2\) to form CO\(_2\). Assuming that initial abundance ratios of \(^{14}\)C/\(^{12}\)C and \(^{13}\)C/\(^{12}\)C in CO\(_2\) are \(6\times10^{-7}\) and \(1\times10^{-2}\), their abundance ratios after the process of 4 stages are estimated at \(3\times10^{-8}\) and \(2\times10^{-3}\), respectively. The concentration of \(^{14}\)C in the CO\(_2\) gas is lower than 3 Bq/cm\(^3\) (30 ppbv). Thus, to monitor the final product on the process, a carbon isotope (\(^{12}\)C, \(^{13}\)C and \(^{14}\)C) analysis with several percentages of a precision is required.

Conventional mass spectrometer, such as quadrupole mass spectrometer, has been applied to carbon isotope analysis. However, extensive sample preparation processes are
required to avoid an isobaric interference. For $^{14}$C measurement, an accelerator mass spectrometer and a liquid scintillator counting are used generally. However they are not suitable for a continuous monitoring of $^{14}$C, because accelerator mass spectrometer is huge with room-size systems and liquid scintillator discharges large amount of organic waste. Hence, it is necessary to develop a compact and continuous monitoring system for the carbon ($^{12}$C, $^{13}$C and $^{14}$C) isotope analysis.

For gaseous sample, an isotope analysis based on laser absorption spectroscopy (LAS) is a simple method without a complex sample preparation. However, LAS is not suitable for the gas monitoring in the isotope separation process, because a lower detectable concentration, or specifically highly sensitivity, is required.

Cavity ring-down laser spectroscopy (CRDS) is known for a high sensitive LAS using ultra long light path in a high-finesse optical cavity called “ring-down” cavity (3). The carbon isotope analysis based on CRDS is expected to be a simpler and more compact system with higher sensitivity than these conventional methods noted above.

We propose an isotope analysis system based on CRDS to monitor the carbon isotopes ($^{12}$C, $^{13}$C and $^{14}$C) in the isotope separation process for the graphite reactor decommissioning. With the aim of accomplishing the carbon isotope analysis based on CRDS, we have demonstrated a basic performance of a prototype system for $^{13}$C (4).

Here are presented the necessary conditions of CRDS system for $^{14}$C isotope analysis through preliminary experimental results of $^{13}$C isotope analysis with the prototype system.

2. Principle of Measurement

2.1 Principle of CRDS

CRDS is based on a measurement of a temporal intensity decay of laser light stored in the ring-down cavity. The temporal evolution of the laser intensity transmitted through the ring-down cavity $I(t)$ decays exponentially as a function of time $t$.

$$I(t) = I_0 (1 - R)^2 \exp \left\{ - \frac{1}{\tau_0} \exp \left\{ - ct \sum_j \sigma_j N_j \right\} \right\}$$

$$= I_0 (1 - R)^2 \exp \left\{ - \beta_0 \left[ t - \left( \sum_j \sigma_j N_j \right) \beta_0 \right] \right\}$$

where $R$ is the reflectivity of the cavity mirror, $\tau_0 = L_0 / (c(1 - R))$ is the time constant of ring-down decay without the intracavity absorbing species, $L_0$ is the cavity length, $c$ is the velocity of light, $\sigma_j$ is the absorption cross section of the intracavity absorbing species $j$ and $N_j$ is the concentration of the intracavity absorbing species $j$. $\beta_0 = 1 / \tau_0$ is called the background ring-down rate without the intracavity absorbing species, the ring-down rate with the intracavity absorbing species is defined as

$$\beta = \beta_0 + c \sum_j \sigma_j N_j \beta_0 .$$

Therefore, the photo absorbance $\sum \sigma N$ can be derived from $\beta$. CRDS is highly sensitive, because the effective absorption path; $c \times \tau_0$ is extremely long, which reaches to several kilometers.

2.2 System Overview

For the isotopic analysis, a narrowband tunable laser is required to distinguish any inappreciable photo-absorption spectrum lines that depend on the isotopomers. Thus, we have adopted CRDS with a cw diode laser (CW-CRDS) (4).
Figure 1 shows a schematic diagram of the carbon isotope analysis system based on CW-CRDS. A CW laser beam is injected into the ring-down cavity, and then the laser intensity transmitted through the ring-down cavity is measured by a photo detector.

Provided that one of the simplest versions of CW-CRDS, which is called rapidly swept cavity ring-down spectroscopy with cw laser (RS-CW-CRDS)\(^{(5)}\), is applied to the system, a rapid sweep of the cavity length allows a cavity mode to switch between on resonance and off resonance and leads to the ring-down decays. Unless the time scale of the sweep is much shorter than the ring-down time \(\tau\), the ring-down decays cannot be obtained.

Figure 2 shows the conceptual drawing of the signal obtained from the measurement of \(^{14}\)C\(^{16}\)O\(_2\) with RS-CW-CRDS. Here, we take the \(^{14}\)C\(^{16}\)O\(_2\) measurement as an example. The laser photons injected into the sample gas are absorbed by all the molecules that exist along the light path. The absorption spectrum is obtained by a sweep of the laser wavelength over the absorption lines. The ring-down rate for the measuring absorption line of \(^{14}\)C\(^{16}\)O\(_2\) is written as follows:

\[
\beta = \beta_0 + c \sigma_{14,0} N_{14} + c \sum_k \sigma_{14,k} N_{14} + c \sum_j \sigma_j N_j
\]

where \(N_{14}\) is the concentration of \(^{14}\)C\(^{16}\)O\(_2\) molecules, \(\sigma_{14,0}\) is the photo absorption cross section of the measuring line of \(^{14}\)C\(^{16}\)O\(_2\), \(\sigma_{14,k}\) is the photo absorption cross section of other line \(k\) of \(^{14}\)C\(^{16}\)O\(_2\), \(N_j\) is the concentration of other molecule and \(\sigma_j\) is the photo absorption cross section of other molecule \(j\).

When the interference of other lines and other molecules are not dominant, the concentration of \(^{14}\)C\(^{16}\)O\(_2\) (molecule of interest) can be derived from the ring-down rate \((\beta - \beta_0)\) at the measuring line.

\[
N_{14} = \frac{(\beta - \beta_0)}{c \sigma_{14,0}}. \tag{4}
\]

Thus, the concentration of the molecule of interest is derived from \(\beta - \beta_0\) with high quantitiy because its photo absorption cross section is generally well known with high precision. In addition, the isotopic ratio is obtained from the ratio of the concentration of molecules related to the same element, such as \(^{12}\)C\(^{16}\)O\(_2\) and \(^{14}\)C\(^{16}\)O\(_2\).

### 2.3 Precision of Isotope Ratio

On laser spectroscopy, a fluctuation of signals is generally caused by a fluctuation of the measuring system and a statistical fluctuation of signal counts. In CRDS, the statistical fluctuation of signal counts is negligible small because many laser photons interact with a lot of the absorbing molecules and are detected as the signal. Thus, the fluctuation of CRDS signals is caused by a fluctuation of the measuring system, such as a mechanical fluctuation.
and an electrical fluctuation. Consequently, a standard deviation of the ring-down rate is generally used to specify a detectable concentration of CRDS \(^5\).

Here, we define the lower detectable concentration of absorbing molecule \(N_{i\text{ lim}}\) as its standard deviation \(\delta N_i\). In the other words, \(N_{i\text{ lim}}\) means a concentration measured with a precision of 100 \%, or \(S/N = 1\).

Thus, \(N_{i\text{ lim}}\) for \(^i^\text{C}16\text{O}_2\) \((i=13, 14)\) is written as

\[
N_{i\text{ lim}} = \delta N_i = \frac{\delta (\beta - \beta_i)}{\sigma_i c} = \frac{\sqrt{\delta \beta_i^2 + \delta \rho_i^2}}{\sigma_i c},
\]

where \(\sigma_i\) is the photo absorption cross section for \(^i^\text{C}16\text{O}_2\), \(\delta (\beta - \beta_i), \delta \beta_i\) and \(\delta \rho_i\) are the standard deviations of \(\beta - \beta_i, \beta\) and \(\rho_i\), respectively. Provided that \(\delta \beta_i\) is nearly equal to \(\delta \rho_i\), \(N_{i\text{ lim}}\) is given by

\[
N_{i\text{ lim}} = \sqrt{2} \frac{\delta \rho_i}{\sigma_i c}.
\]

Additionally, a detection sensitivity \(\alpha\) which indicates a performance of the system for LAS and CRDS is defined as

\[
\alpha = \sqrt{2} \frac{\delta \rho_i}{c}.
\]

The \(^i^\text{C}1^\text{C}\) isotope ratio: \(\Delta_i\) \((i=13 \text{ or } 14)\) is derived from the concentrations of \(^{12}^\text{C}16\text{O}_2\) \(N_{12}\) and \(^{13}\text{C}16\text{O}_2\) \(N_i\), i.e. ring-down rates. Thus, \(\Delta_i\) is written as

\[
\Delta_i \equiv \frac{N_i}{N_{12}} \approx \frac{(\beta_i - \beta_0) \sigma_i c}{(\beta_{12} - \beta_0) \sigma_{12} c}.
\]

The precision of the isotope ratio \(\delta (\Delta_i)/\Delta_i\) is written as

\[
\frac{\delta (\Delta_i)}{\Delta_i} = \sqrt{\left( \frac{\delta (\beta_i - \beta_0)}{\beta_i - \beta_0} \right)^2 + \left( \frac{\delta (\beta_{12} - \beta_0)}{\beta_{12} - \beta_0} \right)^2},
\]

where \(\delta (Y)\) and \(\delta_Y\) are the standard deviation of \(Y\) \((Y = \Delta_i, \beta_i - \beta_0, \beta_{12} - \beta_0, \beta_i, \beta_{12}, \beta_0)\). Provided that \(\delta \beta_{12}\) and \(\delta \beta_i\) are nearly equal to \(\delta \rho_i\), \(\delta (\Delta_i)/\Delta_i\) is given by

\[
\frac{\delta (\Delta_i)}{\Delta_i} = \sqrt{2} \frac{\delta \rho_i}{(\beta_i - \beta_0) \Omega_i} \left( \frac{1}{(\beta_i - \beta_0)^2} + \frac{1}{(\beta_{12} - \beta_0)^2} \right),
\]

where \(\Omega_i\) is defined as \(\Omega_i \equiv (\beta_i - \beta_0)/(\beta_{12} - \beta_0)\). In the case that the relative uncertainty of the \(^{12}\text{C}16\text{O}_2\) concentration is lower than the relative uncertainty of \(^{13}\text{C}16\text{O}_2\) concentration, namely \(\Omega_i \ll 1\), \(\delta (\Delta_i)/\Delta_i\) is given by
\[
\frac{\delta(\Delta_i)}{\Delta_i} \approx \frac{N_{i,\text{lim}}}{N_i}.
\]  

(11)

Thus, requirements for the gases monitoring in the isotope separation process are described as follows:

(A) The ring-down rates caused by the intracavity molecular absorptions except for the absorption of measuring line are much lower than \( \delta \beta_i \).

(B) The precision of the isotope ratio \( \delta(\Delta_i)/\Delta_i \) is lower than the required value \( a \) of several percentages.

In order to measure the isotope ratio with the precision of \( a \), \( N_{i,\text{lim}} \) should be lower than \( a \times N_i \). According to Eq. (11), for example, the detectable concentration of 2 ppbv for \(^{12}\text{C}^{16}\text{O}_2\) and 100 ppmv for \(^{13}\text{C}^{16}\text{O}_2\) are required to measure the carbon isotope ratio in the isotope separation process gas with the precision of 5%.

We have two ways to achieve the desired low detectable concentration; (a) measurement at the IR-fundamental band that has a strong absorption cross section and (b) measurement with highly sensitive spectroscopy, that is, CRDS.

3. Results and Discussions

3.1 \(^{13}\text{CO}_2\) Measurement

For \(^{12}\text{C}^{16}\text{O}_2\), near-IR overtone or combination absorption bands are typically one to several orders of magnitude weaker than IR fundamental absorption band; however, they are strong enough to be measured with CRDS. In the near-IR spectral region of 1.3 and 1.6 \( \mu \)m InGaAsP/InP diode lasers are developed and used widely for optical communications. Particularly, in the past several years, multiple-quantum-well DFB diode lasers have been developed, with single-mode and near-room temperature operation, high stability, spectral bandwidth of few MHz, and an output power of several mW \(^0\). From these characteristics, DFB diode lasers are very suitable for the measurement of near-IR absorption bands of \(^{13}\text{C}^{16}\text{O}_2\).

Heretofore, we have demonstrated some basic experimental measurements of the overtone absorption lines of carbon dioxide \((^{12}\text{C}^{16}\text{O}_2, ^{13}\text{C}^{16}\text{O}_2)\) by RS-CW-CRDS with a DFB diode lasers at 6200 cm\(^{-1}\) (1.6 \( \mu \)m). The experimental setup is described on our previous work in Ref. (4). The picture in Fig. 3 shows a prototype CRDS system for \(^{13}\text{C}\) isotope analysis.

Fig.3 Prototype CRDS system for \(^{13}\text{C}\) isotope analysis
In the previous work, the large fluctuation of ring-down rate was caused by longitudinal modes of the high-finesse ring-down cavity and led to the low sensitivity of the system. We therefore used a DFB diode laser with a fiber pig tail output (Furukawa Electric, FOL15-DCWB) to obtain the Gaussian spatial profile. Then, we optimized the mode matching of the laser beam to the cavity.

Figure 4 shows the distribution of the ring-down rate for $10^3$ signals at a fixed laser wavelength for nitrogen filling in gas cell. The measured standard deviation of $\beta_0$ was estimated to be 42 s$^{-1}$ for averaging of $10^3$ signals. The value of measured $\delta_{\beta_0}$ was one order of magnitude smaller than that of our previous work [4].

From the standard deviation of the measured ring-down rate, the detectable concentration for $6210.569$ cm$^{-1}$ line of $^{13}$C$^{16}$O$_2$ ($\sigma_{13}=3.5\times10^{-21}$ cm$^2$/molecule for a total pressure of 6 Torr) was determined to be 3 ppmv, which is much less than the required value of 100 ppmv. The $\alpha$ in the prototype system was determined to be $2\times10^{-9}$ cm$^{-1}$.

### 3.2 Requirements for $^{14}$CO$_2$ Measurement

In order to achieve the detectable concentration for $^{14}$C$^{16}$O$_2$ of 2 ppbv, the fundamental absorption line at 2200 cm$^{-1}$ (4.5 µm) should be measured with CRDS. According to the HITRAN database [7], the absorption intensity of the CO$_2$ fundamental line is 6 orders of magnitude larger than that of the overtone line at 6200 cm$^{-1}$. We estimated the requirements for $^{14}$CO$_2$ measurement with CW-CRDS thought calculated absorption spectra of a gaseous sample.

The absorption cross sections of molecules in the gaseous sample was calculated with Voigt line shape function for 2200 cm$^{-1}$ region, a total pressure of 6 Torr and a temperature of 296 K. Although, the photo-absorption line intensities of $^{14}$C$^{16}$O$_2$ were known less well than those of $^{12}$C$^{16}$O$_2$ and/or $^{13}$C$^{16}$O$_2$, M. Wahlen, R.S. Eng and K.W. Nill reported on the spectroscopic characteristics of the $^{14}$C$^{16}$O$_2$ fundamental absorption band [8][9]. Since line intensities for some lines, $\gamma_{\text{air}}$ and $\gamma_{\text{self}}$ are not reported in Refs. (8) and (9), the data of $^{12}$C$^{16}$O$_2$ fundamental lines listed in HITRAN were substituted for these of $^{14}$C$^{16}$O$_2$. For other molecules considered in the paper, we used their spectroscopic characteristics in HITRAN database.

Figure 5 shows the calculated absorption spectra of the molecules of $^{14}$C$^{16}$O$_2$, CO$_2$, CO and H$_2$O in the IR region (2209.1 cm$^{-1}$) for a total pressure of 6 Torr and a temperature of 296 K. The concentrations of $^{14}$C$^{16}$O$_2$, CO$_2$, CO and H$_2$O were 30 ppbv, $1.6\times10^3$, $1.7\times10^3$, and $1.8\times10^3$ respectively.
100 %, 100 % and 100 %, respectively. Table 1 shows the absorption cross sections and ring-down rates of $^{14}$C$^{16}$O$_2$, CO$_2$, CO and H$_2$O at 2209.124 cm$^{-1}$. Here, CO$_2$ stands for $^{12}$C$^{16}$O$^{16}$O, $^{13}$C$^{16}$O$^{16}$O, $^{12}$C$^{16}$O$^{18}$O, $^{12}$C$^{16}$O$^{17}$O, $^{13}$C$^{16}$O$^{18}$O, $^{13}$C$^{16}$O$^{17}$O, $^{12}$C$^{18}$O$^{18}$O and $^{12}$C$^{17}$O$^{18}$O. CO stands for $^{12}$C$^{16}$O, $^{13}$C$^{16}$O, $^{12}$C$^{18}$O, $^{12}$C$^{17}$O, $^{13}$C$^{18}$O and $^{13}$C$^{17}$O. H$_2$O stands for H$_2$$^{16}$O, H$_2$$^{18}$O, H$_2$$^{17}$O, HD$^{16}$O, HD$^{18}$O and HD$^{17}$O. The absorption cross sections of CO$_2$, CO and H$_2$O are multiplied by their natural abundance.

First, the calculated ring-down rate for $^{14}$C$^{16}$O$_2$ at 2209.124 cm$^{-1}$ is $9 \times 10^4$ s$^{-1}$, that is within typical measurable range of CRDS. On the other hand, the contribution from the neighboring absorption lines of $^{14}$C$^{16}$O$_2$ is negligible, because the ratio of the absorption cross section of the 2209 cm$^{-1}$ line to all other lines of $^{14}$C$^{16}$O$_2$ is $10^{-6}$. In addition, we decided that $^{14}$C$^{16}$O$^{18}$O, $^{14}$C$^{16}$O$^{17}$O, $^{14}$C$^{16}$O$^{16}$O, $^{14}$C$^{15}$O$^{18}$O, $^{14}$C$^{15}$O$^{17}$O and $^{13}$C$^{15}$O$^{18}$O have no contribution for the $^{14}$C$^{16}$O$_2$ measurement through the consideration of the abundance of oxygen ($^{16}$O: 99.762%, $^{17}$O: 0.038%, $^{18}$O: 0.200%). It is found that a fluctuation of ring-down rate of CRDS system must be kept smaller than $5 \times 10^3$ s$^{-1}$ to measure $^{14}$C$^{16}$O$_2$ with precision of 5 %. This means $\alpha$ of $2 \times 10^{-7}$ cm$^{-1}$ is required for CRDS system.

Next, we describe the absorption caused by other molecules. There are no absorption lines for N$_2$ and O$_2$ in this region. The contribution from the absorption lines of H$_2$O and CO$_2$ (except $^{14}$C$^{16}$O$_2$) are negligible, because the ratio of the ring-down rate of $^{14}$C$^{16}$O$_2$ to these of H$_2$O and CO$_2$ are lower than $9 \times 10^{-3}$ at 2209.124 cm$^{-1}$. On the other hand, the concentration of CO in the gaseous sample must be kept lower than 1 % to measure $^{14}$C$^{16}$O$_2$ with precision of 5 %, because the ring-down rate of CO (its concentration of 100 %) is factor 5 larger than that of $^{14}$C$^{16}$O$_2$ at 2209.124 cm$^{-1}$.

Here, a single mode PbSSe diode laser and a quantum cascade laser are applicable to a CW laser source for an IR spectral region. In particular, the quantum cascade laser is one of the promising candidates for the laser source at IR spectral region because its performance has been improved recently (6). In addition, an IR photo detector and cavity mirrors that have highest reflectivity at 4.5 µm were easily available.

### Table 1

<table>
<thead>
<tr>
<th>Molecule: i</th>
<th>Photo absorption cross section: $\sigma$</th>
<th>$\Delta \beta (^{14}$C$^{16}$O$_2)/\Delta \beta_i$</th>
</tr>
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<tbody>
<tr>
<td>$^{14}$C$^{16}$O$_2$</td>
<td>$5 \times 10^{-16}$</td>
<td>1</td>
</tr>
<tr>
<td>CO$_2$ (except $^{14}$C$^{16}$O$_2$)</td>
<td>$3 \times 10^{-26}$</td>
<td>$2 \times 10^{-3}$</td>
</tr>
<tr>
<td>CO</td>
<td>$7 \times 10^{-23}$</td>
<td>5</td>
</tr>
<tr>
<td>H$_2$O</td>
<td>$1 \times 10^{-25}$</td>
<td>$9 \times 10^{-3}$</td>
</tr>
</tbody>
</table>

4. Conclusions

We propose an isotope analysis system based on CW-CRDS to monitor the carbon isotopes ($^{12}$C, $^{13}$C and $^{14}$C) in the isotope separation process for the graphite reactor decommissioning.

For $^{13}$C monitoring, the near-IR overtone or combination absorption bands of $^{13}$C$^{16}$O$_2$ was adopted. The $\alpha$ in the prototype system was determined to be $2 \times 10^{-9}$ cm$^{-1}$. The detectable concentration at 6200 cm$^{-1}$ (1.6 µm) line was estimated to be 3 ppmv from the standard deviation of the measured ring-down rate.

For $^{14}$C monitoring, fundamental absorption band of $^{14}$C$^{16}$O$_2$ at 2200 cm$^{-1}$ (4.5 µm) must be adopted. Through the calculation of absorption spectra based on spectroscopic database, the calculated ring-down rate for $^{14}$C$^{16}$O$_2$ (its concentration of 30 ppbv) at 2209.124 cm$^{-1}$ is $9 \times 10^4$ s$^{-1}$, that is within typical measurable range of CRDS. It is found that a fluctuation of ring-down rate of CRDS system must be kept smaller than $5 \times 10^3$ s$^{-1}$ to measure $^{14}$C$^{16}$O$_2$ with precision of 5 %. This means $\alpha$ of $2 \times 10^{-7}$ cm$^{-1}$ is required for CRDS system.
absorption caused by other molecules such as N₂, O₂, H₂O and CO₂ are negligible. On the other hand, the concentration of CO in the gaseous sample must be kept lower than 1 %.

The present method would have a large potential for a continuous monitoring of carbon isotope analysis without a complex sample preparation.

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References