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RESEARCH

Development of isotope-spectroscopic analysis apparatus using glow discharge hollow cathode cell

Daisuke Ishikawa[1] · **Shuichi Hasegawa**[1,2]

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Abstract

The screening analyses on various samples, such as gas, liquid residue, and solid samples, are required for the decommissioning of Tokyo Electric Power Corporation Fukushima Daiichi Nuclear Power Plant. We have developed spectroscopic system incorporating laser absorption spectroscopy and glow discharge optical emission spectroscopy. There are many other kinds of emission spectroscopy existing. Sputtering has been applied to produce neutral atomic vapors and induce emissions from them. Advantages in the use of sputtering are that chemically complex solid samples can be readily vaporized into their atomic species. The rare earth element Tm was utilized as a proxy for fissile elements to assess the system for laser absorption spectroscopy and emission spectroscopy analysis at 130 mA in 300 Pa Ne. As a result, a mixture of the two methods resolved a dynamic range of approximately 10 ppm (w/v) to 1000 ppm (w/v) (Tm number of atoms: 3.6×10^{15} to 3.6×10^{17}). In addition, laser absorption spectroscopy could resolve the hyperfine structure of Tm-169. With the integration of the two methods could extend dynamic ranges of analyses, which was demonstrated experimentally.

1 Introduction

The Tokyo Electric Power Corporation Fukushima Daiichi Nuclear Power accident [1] caused the meltdown of three reactor units. It has been assumed to have produced the most amount of fuel debris ever. Currently, the characteristics, for example elements and amount, of the fuel debris are not well understood. For appropriate decommissioning, information on the debris is immediately required, such as the elemental composition, and spatial mapping, over this large quantity of samples. However, high radiation prohibits access to the samples and, therefore, it is difficult to perform chemical pre-treatment for any analysis. Consequently, it is not appropriate to apply conventional methods. In this regard, it is necessary to develop analytical methods for the sample screening. Although high reproducibility and low detection limits mean methods like inductively coupled plasma—atomic emission spectroscopy (ICP-AES) could be considered as one of the major techniques for the analysis, these require high power supplies to induce the ICP and high cost for keeping operation. On the other hand, we aim to develop the analytical system to be compact, low cost, and rapid for gathering rough information on the samples.

The physical pre-treatment is simple and fast compared to chemical pre-treatment. Other examples producing atomic vapor from solid samples are laser ablation [2] and electron beam [3] vaporization. Here, we have focused on sputtering coupled with glow discharge produced by application of high voltage. For the spectroscopy, the technique is well established, with Paschen [4] having proposed the glow discharge atomic source one century ago. Also in industry, glow discharge optical emission spectroscopy (GD-OES) [5–7] has been applied for the measurement of trace amounts of the elements in metal alloys [8].

With the use of glow discharge, we have been developing an analytical spectroscopic system to produce a neutral atomic vapor from solid samples with mixed elements [9, 10]. The characteristics of this system are that it requires little chemical pre-treatment, it can reduce time and effort spent in sample handling due to the integration of two methods (emission spectroscopy and laser absorption spectroscopy) into one, and it is readily maintainable with the use of vacuum parts commercially available. We employed the f-block element Tm as a proxy for fissile elements. Tm has

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✉ Shuichi Hasegawa
hasegawa@n.t.u-tokyo.ac.jp

[1] Department of Nuclear Engineering and Management, University of Tokyo, 7-3-1 Hongo, Bunkyo-ku, Tokyo 113-8656, Japan

[2] Nuclear Professional School, University of Tokyo, 2-22 Shirane, Shirakata, Tokai, Naka, Ibaraki 319-1188, Japan

absorption lines around 400 nm like the fissile elements, Uranium, Plutonium, and Thorium. Since Tm has only one stable isotope, Tm-169, isotopic interference can be ignored. In addition, Tm-169 has a simple hyperfine structure because of its dipolar spin. The rare earth elements are not readily dissolvable in solution—if the effectiveness of sputtering is shown, it can make pre-treatment easy and reduce the amount of waste solution.

In this paper, we report the assessment of an analytical system of laser absorption spectroscopy and emission spectroscopy on neutral atomic vapor produced by sputtering with glow discharge. This system is targeted for sample screening. The emission spectroscopy clarifies the elemental composition of the samples and the laser absorption spectroscopy is able to detect small quantities of elements and obtain information on the nuclides present. The feasibility of obtaining nuclear information is confirmed with the resolution of the hyperfine structure of Tm by Doppler-free laser absorption spectroscopy. With the integration of the two methods, limitations in one method can be overcome by the application of the other.

2 Experimental setup

For the use of a neutral atomic vapor source with glow discharge, we focused on the structure of the hollow cathode. The density of the electronically excited species produced by electronic collision is expected to be highest in the center [11]. The hollow cathode structure has been utilized as a neutral atomic vapor and light source since its inception 50 years ago [12–14]. Glow discharge hollow cathode cells are commercially available for wavelength calibration [15]. These cells are sealed with glass and it is, therefore, difficult to use these cells for samples other than the factory inserted sample. Consequently, with a sample exchange capability in mind, we have fabricated a neutral atomic source with removable hollow cathode [10]. It consists of a double cathode structure, wherein the inner cathode can be changed for each analysis to avoid memory effect of previous samples. The scales of the cathode are briefly described as follows. The inner cathode is made of Ti and the outer is nichrome. The hollow diameter of the inner cathode is 4.1 mm and outer diameter is 5.1 mm. The length of the cathode along the laser absorption is 27 mm. The inner diameter of the outer cathode (nichrome) is 5.2 mm and the outer diameter is 10 mm. The surface of the plasma is a Ti tube, because it has properties suitable for high temperature and is easily changeable for each analysis due to low cost. The production of neutral atomic vapor was confirmed with a sample placed on the inner cathode. We employed Ne (99.999%, Tokyo Gas Chemical) and Ar (99.9999%, Japan Fine Products) as the buffer gas. For the Tm samples, a foil (99.9%, 0.1 mm thick, Alfa Aesar) was employed as well as standard solution (AccuStandard, 10,000 ppm). The liquid residue was prepared by heat evaporation illumination of an infrared lamp after dropping of the standard solution on the inner cathode. The experimental setup is shown in Fig. 1. The light source was a diode laser (Nichia, NDV4316) in a home-made Littrow type external cavity diode laser (ECDL) system, fabricated for the achievement of narrow bandwidth. Single-mode lasing operation was confirmed by an etalon (Free Spectral Range (FSR): 300 MHz, Finesse: 23). Frequency calibration was made by a wavemeter (High Finesse, WSU-30). The transmission of the laser light through the hollow cathode was observed with a photodetector. To identify the chemical species in the discharge, the emission was observed on a Czerny-Turner spectrometer (Ocean Optics, Flame-S, wavelength resolution: 1.02 nm, observable range:

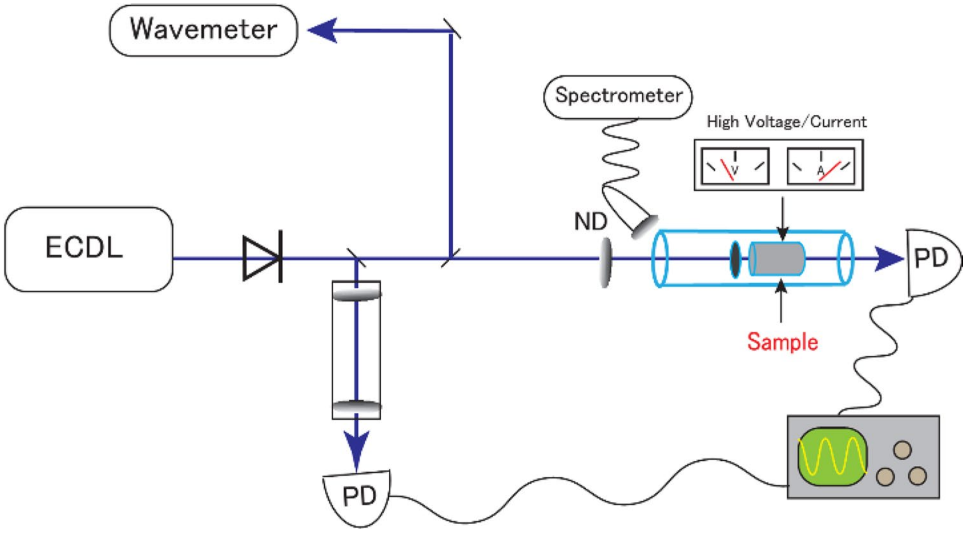

Fig. 1 Experimental setup

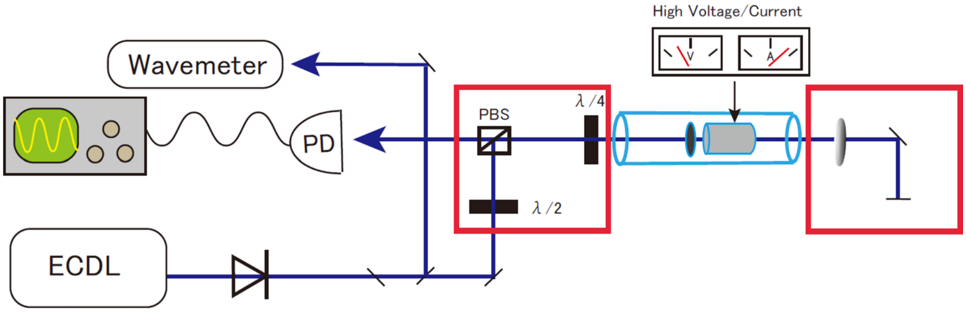

Fig. 2 Doppler-free laser absorption spectroscopy setup. The polarization optics added for saturated absorption spectroscopy are highlighted with red boxes

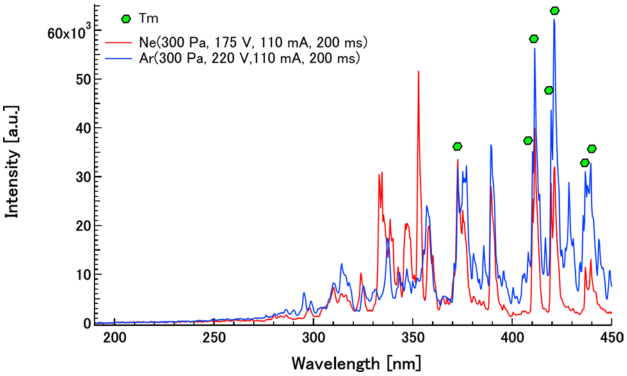

Fig. 3 Emission spectra of Tm foil

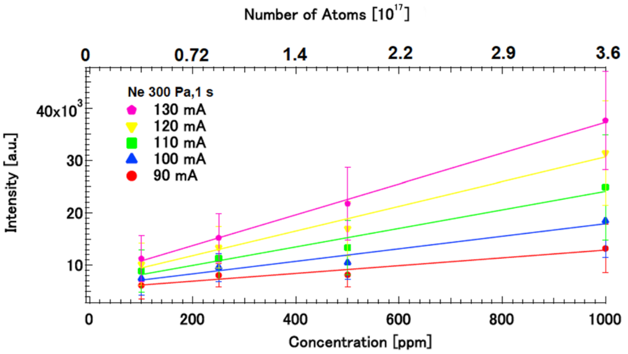

Fig. 4 The calibration curve of the emission signal at the transition 418.76 nm for Tm [$N=10$, error: 1σ (68% Cl)]

190–880 nm, cumulative time: 1 ms—65 s) via fiber insertion with collimator lens.

The experimental setup of the Doppler-free laser absorption spectroscopy is shown in Fig. 2. Here, saturation absorption spectroscopy was applied with the use of polarization [16]. The pump beam induced transition saturation and the probe beam was returned back through the hollow cathode. The large overlap of the pump and probe beams was favorable, and polarization plates were installed [17, 18] wherein the half wavelength polarization plate was utilized to match the polarization of the pump beam for reflection of the polarizing beam splitter. The quarter wavelength polarization plate was employed to change the polarization of the probe beam. Those are highlighted as red boxes in Fig. 2.

3 Results

3.1 (Result 1) Emission spectra analysis

To verify the function of the neutral atomic vapor source, Tm was vaporized from the foil (Fig. 3). Since the rare earth metals form oxides in air, the glow discharge was utilized to accelerate ions for the sputtering to ensure penetration of the oxide surface. Buffer gases of Ne and Ar were used for generating Tm vapors. In the following experiments, Ne was used for buffer gas, because glow discharge with Ne was more stable than with Ar.

To obtain the calibration curve, the transition at 418.76 nm ($4f^{12}(^3F_4)5d_{5/2}\,6s^2$ $J=7/2 \rightarrow 4f^{13}(^2F^{O})4s^2\ ^2F_{7/2}^{O}$ $J=7/2$) [19] was chosen, as there is little to interfere with the Tm peaks at this wavelength. The experimental conditions were as follows: the pressure of Ne was 300 Pa and the current was 90–130 mA. The concentrations of the solutions were 100, 250, 500, 1000 ppm (w/v). A 100 µL drop was placed on the inner cathode and heated to dry into a liquid residue type sample by the infrared lamp. The solid angle of the light source, the collimation lens was 0.013 π str, and the integration time was 1 s. As a result, a calibration curve was produced as shown in Fig. 4 and the Limit of Detection (LOD) was 61 ppm (w/v) (Tm atom: 2.2×10^{16}) at 130 mA. The solid angle can be increased to 1πstr in which case the minimum achievable LOD is expected to be approximately 1 ppm. This is valid considering the LOD of GD-OES is 1–100 ppm (w/w) [20].

3.2 (Result 2) Laser absorption spectroscopy

Based on the result of the production of the neutral atomic vapor shown in Fig. 3, laser absorption spectroscopy was applied. Here, it was focused on the transition of 409.42 nm ($4f^{13}(^2F^{O})\ 6s^2$ $J = 7/2 \rightarrow 4f^{13}(^2F_{7/2}{}^{O})6s6p\ (^1F_1{}^{O})$ $J = 5/2$)

[19]. Since the fissile elements like Th, U, and Pu [19, 21], have large transitions near this wavelength, the fabricated laser source is applicable to such elements. As shown in Fig. 5, the laser absorption spectrum was clearly observed and fitted with a Gaussian function.

The Full Width at Half Maximum (FWHM) of the peak in Fig. 5 was 1.44 GHz and the average temperature of Tm was calculated to be 1630 K. With the use of this temperature, the cross-section of the absorption was calculated as $\sigma = 5.9 \times 10^{-12}$ cm^2 with formula (1) [22].

$$\sigma = \frac{\lambda_0^3}{8\pi}\frac{g_j}{g_i}A_{ji}\sqrt{\frac{M}{2\pi RT}} \tag{1}$$

(λ_0: wavelength of resonance, g_i: degeneracy in low energy state, g_j: degeneracy in high energy state, A_{ji}: Einstein A coefficient, M: atomic weight, R: gas constant, T: absolute temperature)

From the Lambert–Beer Law, the atomic density of Tm was calculated to be 5.9×10^9 cm^{-3} on the condition the vapor was confined only in the 2.6 cm interaction length.

With the use of this transition, the experiment was set to have pressure of Ne: 300 Pa and the current: 130 mA. To prepare the Tm liquid residue, drops of 100 μL of 50, 100, 250, 500, 1000 ppm (w/v) solution were dried by heating. The calibration curve of the laser absorption spectroscopy was made as shown in Fig. 6.

As Fig. 6 shows, the signal was saturated for concentrations more than 500 ppm. As a result, the calibration curve was made, consisting of three points. The LOD was 22 ppm (w/v) (Tm number of atoms: 7.9×10^{15}). The LOD of laser absorption spectroscopy is reported to be 60 ppb (v/v) [23], which is quite better than that of our system. One of the reasons for the difference is the length of interaction. For better LOD, one method is to make the diameter of the laser spot larger and the other is to make the light interaction length longer.

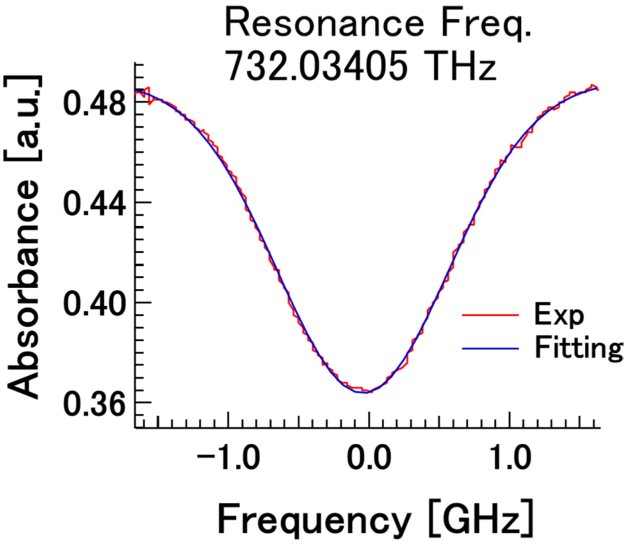

Fig. 5 Laser absorption spectrum of Tm (Ne: 500 Pa, 51 mA, 216 V)

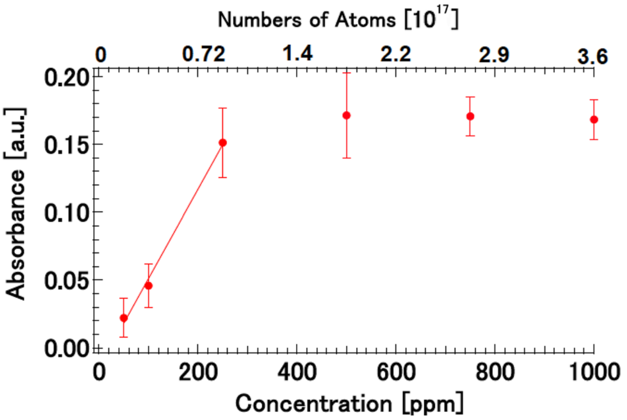

Fig. 6 The calibration curve of laser absorption spectroscopy for Tm [Ne: 300 Pa, current: 130 mA, $N = 10$, error: 1σ (68% CI)]

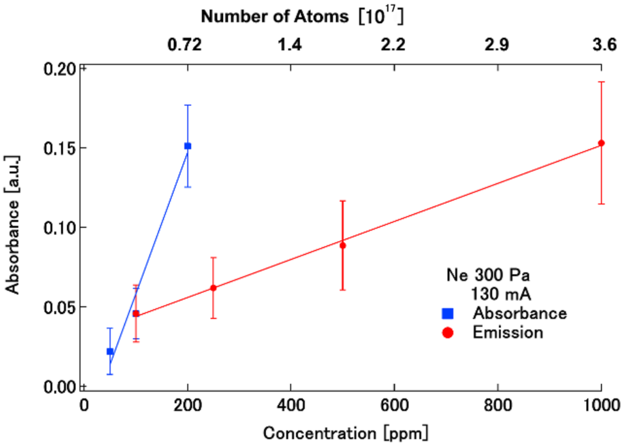

Fig. 7 The calibration curves of emission signal and laser absorption signal (Ne: 300 Pa, current: 130 mA, R^2 for emission: 0.998, R^2 for laser absorption: 0.995)

Figures 4 and 6 show that emission spectroscopy is suitable for larger sample concentrations, while laser absorption spectroscopy is applicable for smaller concentrations of samples. This indicates with the capability of the apparatus to analyze a wide range of sample concentrations. With the calibration of the signal at 100 ppm (w/v), the calibration curves shown in Figs.4 and 6 consolidated into one figure (Fig. 7). Figure 7 shows that the two methods cover approximately the concentration range 50 ppm (w/v) to 1000 ppm (w/v). As a result, the concentration analysis capability limitations of one method can be overcome with the use of another method.

To investigate nuclear properties, the isotope shift is required to be resolvable at sub-GHz frequencies. This is particularly important in order to ascertain the abundance ratio of radioisotopes. Since Tm has only the one isotope, it is suitable to demonstrate spectral resolution of the system. The nucleus has the spin of 1/2 and the hyperfine structure would be expected to be formulated by Eq. (2). The hyperfine structure provides information on nuclear properties, though resolution requires sub-GHz order in the case of Tm. Successful resolution confirms the capability of the apparatus to investigate isotope ratios of the sample constituents.

$$E = \frac{A}{2}\{F(F+1) - J(J+1) - I(I+1)\} \tag{2}$$

(F: total angular momentum quantum number for atom, J: total angular momentum quantum number for electrons, I: nuclear spin)

The hyperfine structure of Tm for the transition at 409.42 nm is shown in Fig. 8 [24].

There are three transitions in the hyperfine structure: (1) $\Delta F = 0$ ($F = 3$, $F' = 3$), (2) $\Delta F = -1$ ($F = 4$, $F' = 3$), and (3) $\Delta F = -1$ ($F = 3$, $F' = 2$). To investigate the resonance frequency of the hyperfine structure, Doppler-free laser absorption spectroscopy was applied. The 480 MHz splitting measured in Fig. 9 is appropriately close to the value of 473 MHz reported in Ref. [25]. Accuracy was ensured with the use of the wavemeter. The observed signal corresponds to the resonance (2) and (3). Although the resonances of two of the three transitions were observed, the leftmost transition was not observed because the frequency of this transition was far from the others and it is very weak [26].

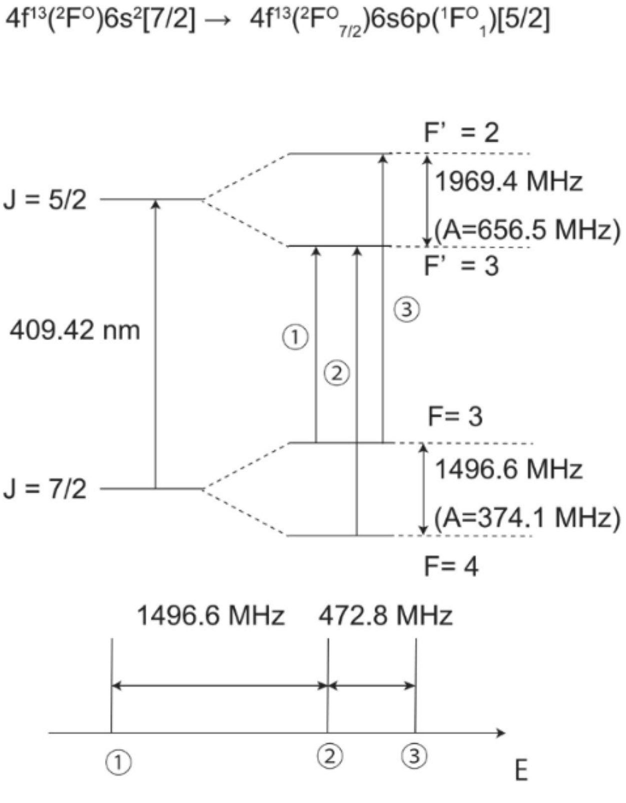

Fig. 8 *T*m hyperfine structure at 409.42 nm

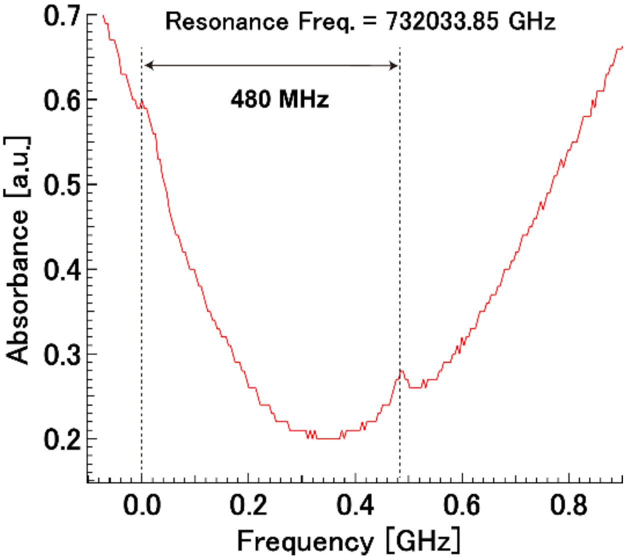

Fig. 9 Saturation absorption spectrum for Tm (Ne: 500 Pa, current: 76 mA)

The energy of the hyperfine structure is given as shown in Formula (2) [24]. Accordingly, the hyperfine A coefficient was assessed to be 660 ± 10 MHz. This result replicated the literature result of 656.5 ± 0.43 MHz [25] and, therefore, the system was able to resolve and obtain hyperfine splitting information. As a result, it is expected to be able to resolve the presence of multiple isotopes and determine their abundance ratios.

4 Conclusion

An assessment of a glow discharge system with a neutral atomic source was made for the application of laser absorption spectroscopy. In addition, the emission of the glow discharge could be utilized for elemental analysis. For sample screening, the integration of laser absorption and emission spectroscopy showed that the dynamic range was approximately 10–1000 ppm (w/v). Emission spectroscopy is confirmed to be able to obtain general information on the sample constituents, and laser absorption spectroscopy is confirmed to be able to investigate low abundance elements in the sample. It was also shown that the laser absorption spectroscopy could resolve hyperfine structure. This indicates the feasibility of obtaining isotope information as part of the sample analysis. For the real sample analysis of Fukushima Daiichi Nuclear Power Plant, remote handling system, e.g., will be required for radiation control. In order to reduce handling radioactivity, smaller quantity is preferable. In the future, we plan to achieve much lower abundance detection with the use of longer interaction light paths.

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Author contributions All authors contributed to the design of the apparatus. Experiments were performed by DI. The first draft of the manuscript was written by DI and all authors edited the manuscript. All authors read and approved the final manuscript.

Data availability statement The datasets are available from the corresponding author on reasonable request.

Declarations

Competing interests The authors declare no competing interests.

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