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Received: September 20, 2022; Revised: October 22, 2022; Accepted: October 24, 2022; Available online: October 31, 2022.

DOI: 10.46770/AS.2022.234

ABSTRACT: Discussing the spatial distribution of nanoparticles (NPs) in fresh plants is significant because dehydration may result in inaccurate sample imaging information. In this study, the spatial distribution of elements in cucumber leaves was achieved using laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS) system equipped with a cryogenic chamber. The cryogenic chamber eliminated the thermal effect of the ablation process, which improved signal stability. Thus, lower relative standard deviations were achieved for NIST 612 and spiked agar gel in a cryogenic chamber compared to those at room temperature. The imaging of Ce in fresh cucumber leaves was conducted under cryogenic conditions. The distribution information of $^{63}$Cu, $^{64}$Zn, $^{31}$P, $^{140}$Ce, and $^{13}$C in cucumber leaves revealed that Ce$^{3+}$ has a higher negative effect than CeO$_2$. To the best of our knowledge, the present study is the first to achieve imaging of Ce in plants in a cryogenic chamber, which has significant implications for assessing NPs of environmental risk at the native state of biological tissues.

INTRODUCTION

Laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS) is a powerful and versatile technique for the elemental analysis of solid materials.\(^1\)\(^-\)\(^2\) Because of its low limit of detection (LOD), high spatial resolution, and high sensitivity, the LA-ICP-MS technique is used to investigate the distribution of elements in biological samples.\(^3\)\(^-\)\(^6\)

LA-ICP-MS has also been widely applied for the analysis of plant materials. Shelden et al. prepared a mapping of soluble ions in plant tissues using LA-ICP-MS to investigate the link between Na" toxicity and root growth responses to salt stress.\(^7\) Based on inherent metallic impurities, Zhang et al. tracked the distribution of graphene and graphene oxide in soybean plants and detected the materials by LA-ICP-MS.\(^8\) The transportation and distribution of La$_2$O$_3$ nanoparticles (NPs) in plant stems and leaves was also explored by LA-ICP-MS and micro X-ray fluorescence ($\mu$-XRF).\(^9\) In summary, the LA-ICP-MS technique is useful for elemental imaging, achieving high sensitivity of elemental distribution in the plants. However, LA-ICP-MS for elemental imaging of fresh plant tissues is still limited.\(^10\) During LA-ICP-MS operation, biological samples with high water content tend to dehydrate because of the continuous flow of carrier gas.\(^11\) This dehydration may change the position of NPs within the plant, resulting in inaccurate sample imaging information. To overcome this problem, Yamaji et al. used a paraffin-embedded method to pretreat the rice node and reported that structure of the node tissue was well maintained after being cryo-sectioned and freeze-dried.\(^12\) However, paraffin embedding possibly led to the loss of metal elements.\(^13\) Thus, a cryogenic chamber was used to imaging biological tissues with LA-ICP-MS.\(^14\) Moreover, the low temperature preserves the original state of the sample to provide actual biological information and greatly simplifies the sample preparation process by preserving moisture. Moreover, the distribution of NPs may not be distorted in this case.

The environmental risk of CeO$_2$ is an increasing concern of
CeO$_2$ NPs, which are extensively utilized metal-based engineered NPs in industrial and commercial products and largely released into the environment. Thus, the exposure of CeO$_2$ in plants has significantly increased. Thus, investigating the distribution of CeO$_2$ NPs in plant tissues is essential for exploring phytotoxicity. Recently, many studies have focused on the transformation and translocation of CeO$_2$ in various plant species at the physiological level, acquiring considerable achievements. A series of useful tools, such as ICP-MS, TEM, and $\mu$-XRF have been used for detecting the content and distribution of Ce in plant tissues. The reports on TEM and $\mu$-XRF showed limitations in sample preparation, and not quantitation. Although ICP-MS was used for detecting Ce with high sensitivity, only the data on the total concentration of Ce was obtained. Herein, we achieved the distribution imaging of Ce in fresh cucumber leaves on a relatively larger scale of approximately 50×70 mm through LA in a cryogenic chamber, thus providing key information on absorption, transformation, and translocation of NPs in fresh plants. Moreover, discussing information on spatial distribution of Ce in fresh leaves of cucumber without complicated sample preparation is favorable. Elements Zn, Cu, and P were essential for plant growth. Hence, Zn, Cu, and P were imaged to evaluate the impact of elemental CeO$_2$/Ce$^{3+}$ on essential plant elements, which is animportant indicator of the potential risk of Ce.

In this study, the distribution of Ce in fresh leaves of cucumber cultivated with CeO$_2$/Ce$^{3+}$ was investigated. Plants were cultivated in the presence of CeO$_2$ NPs and Ce$^{3+}$ under same conditions. A cryogenic chamber was used to provide cryogenic conditions to preserve the original state of the sample. We aimed to evaluate the variations of other elements (Cu, Zn, and P) essential for plant growth and the effect of CeO$_2$/Ce$^{3+}$. The spatially resolved mapping of $^{14}N$Ce, $^{63}Cu$, $^{65}Zn$, and $^{31}P$ on fresh cucumber leaves with cryogenic ablation was obtained. $^{13}C$-labeled internal standard was used for the analysis. The results showed that Ce was predominantly distributed at the edge of the leaves. Furthermore, Cu, Zn, and P were reduced in the cucumber leaves cultivated with CeO$_2$ compared to those cultivated with Ce$^{3+}$. Thus, CeO$_2$ may possibly have more negative effect on plants than Ce$^{3+}$.

**EXPERIMENTAL**

**Reagents and materials.** A glass reference material (SRM NIST 612) was provided by the National Institute of Standards and Technology. Ce(NO$_3$)$_3$·6H$_2$O was purchased from Tianjin Damao Chemical Reagent Factory (China). CeO$_2$ NPs (20-50 nm, 99.5% metal basis) was obtained from Aladdin (China). Ultrapure water (18.2 MΩ cm) from Milli-Q water purification system (Millipore, USA) was used in the experiments. Hoagland nutrient solution was purchased from Scientific Phygene (China). Cucumber seeds were purchased from the Shou He Agriculture (China). The size, shape, and structure of CeO$_2$ NPs were assessed by scanning electron microscopy (SEM, Hitachi, Japan) with an SU8010 field-emission electron microscope at a voltage of 5.0 kV. The hydrodynamic diameter and zeta potential of CeO$_2$ NPs in a medium (CeO$_2$ NPs dissolved in deionized water or nutrient solution) were measured using a Nano Zetasizer system (Nanosizer ZS90, USA).

**Plant growth.** Cucumber seeds were sterilized with 5% NaClO for 10 min and then germinated in the dark for 3 days. Subsequently, the germinant cucumber seeds were placed in a 50-mL centrifuge tube with cotton as the substrate. The plants were allowed to grow in a greenhouse with light at 25 °C for 16 h and then in the dark at 16 °C for 8 h. Finally, Hoagland nutrient solution (4 mL) was added to the tube, and the germinant cucumber seeds were allowed to grow in the tube for 10 days, following which the substrate was removed. The cucumber plants were divided into three groups and parallely grown under two conditions for 9 days: (1) Hoagland solution (1/4 strength) containing 200 mg/L of CeO$_2$ NPs and (2) Hoagland solution (1/4 strength) containing 200 mg/L of Ce(NO$_3$)$_3$·6H$_2$O.

**Agarose standard preparation.** The agarose standard was prepared according to a previous study. The standard solution was diluted to 100, 200, 500, 1000, and 2000 μg/L with deionized water. Agar powder (0.1 g) was added to the diluted standard solution (5 mL), which was placed in a container. Agarose was homogeneously dissolved by heating the mixture on a heating platform and shaking. The heated mixture was then quickly poured into a mould. After becoming semisolid gelatin, the mixture was placed in an air oven at 60 °C for 1.5 h. Six agarose standards within a range of 0-100 μg g$^{-1}$ were used for Cu, Zn, and Ce. The elemental concentration of the spiked agar gel was 0, 5, 10, 25, 50, and 100 μg/g of Cu, Zn, and Ce. The center of the agarose membrane was cut and placed on a microscope slide for ablation. $^{13}C$ was used as an internal standard.

**Operating Parameter of LA-ICP-MS.** A quadrupole-based ICP-MS instrument (PerkinElmer NexION 2000, PerkinElmer, USA) was used in the present study. An NWR Image 266-nm LA system (Elemental Scientific Lasers, Bozeman, MT) was coupled with the ICP-MS instrument (PerkinElmer, USA) for testing. A low-dispersion cell was equipped in the standard TwoVol2 chamber of the LA system. Ablation experiments were conducted using the cryogenic chamber described in a previous study. The nebulizer gas introduced the aerosol from the LA into ICP to achieve the ionization of the elements. LA-ICPMS was optimized daily using the SRM NIST 612 glass for high sensitivity and stability; the $^{238}U/^{232}Th$ signal ratio was also measured (close to 1). The operating parameters of LA-ICP-MS are shown in Table 1.

**Imaging of Ce in cucumber leaves in a cryogenic chamber.** The refrigerant tank and power supply for the Peltier elements were set
was approximately 0.5×0.5 cm fixed on a glass slide using a double-sided tape. The imaging area was approximately 0.5×0.5 cm². The slide was rapidly placed in a cryogenic chamber, which was then tightly inserted into the LA system. The ablation mode of scanning line per line was adopted, and no gap was left between the lines.

RESULTS AND DISCUSSION

Ablation effect on NIST 612, and spiked agar gel under cryogenic conditions. The images of the ablated traces of NIST 612, spiked agar gel, and leaf under cryogenic conditions and at room temperature (approximate 20−25 °C) are shown in Fig. 1. Smoother ablated traces without inhomogeneous particulates were achieved in NIST 612 in a cryogenic chamber (Fig. 1A). The traces of agar ablation in the cryogenic chamber were clear compared to those at room temperature (Fig. 1B); ablation at room temperature produced significant quantities of impurities at the edge of the agar traces. Moreover, the widths of the ablated leaf traces at room temperature increased due to the thermal effect of the ablation process (Fig. 1C). In contrast, the leaf traces in the cryogenic chamber were not deformed due to the elimination of the thermal effect. Thus, ablation in a cryogenic chamber allows more standard ablated traces and reduces thermal effect.

As a standard material, the NIST 612 glass was used to optimize the performance of LA-ICP-MS. The ablation signals of 140Ce, 115In, 238U, 59Co, and 232Th in NIST 612 were acquired. The signals of ablation lines were achieved in a cryogenic chamber and at room temperature. The average signal intensities of a single ablation line were calculated. The RSD was obtained from the average signal intensities of five ablation lines at NIST 612. The results in Table 2 indicate that the RSDs for 140Ce, 115In, 238U, 59Co, and 232Th were in the range of 6.83−8.19% at room temperature and 3.0−4.07% under cryogenic condition, indicating that precision was improved in a cryogenic chamber. Notably, the signal intensities of 140Ce, 115In, 238U, 59Co, and 232Th were reduced in the cryogenic chamber. This reduction in signal intensities was observed because ablation at room temperature produced heavy thermal effect, which partially melted NIST at a high temperature. The aerosol from the melted NIST enhanced the signal. Moreover, this aerosol possibly produced inhomogeneous particulates, which increased the RSD. In contrast, the thermal effect was eliminated.

Table 1. Parameters of LA-ICP-MS

<table>
<thead>
<tr>
<th>LA System</th>
<th>PerkinElmer NexION2000D</th>
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<tbody>
<tr>
<td>RF power</td>
<td>1500 W</td>
</tr>
<tr>
<td>Plasma-gas flow (Ar, L min⁻¹)</td>
<td>15</td>
</tr>
<tr>
<td>Auxiliary-gas flow (Ar, L min⁻¹)</td>
<td>1.2</td>
</tr>
<tr>
<td>Nebulizer gas flow (Ar, L min⁻¹)</td>
<td>1.25</td>
</tr>
<tr>
<td>Monitored isotopes</td>
<td>¹³C, ⁶⁰Cu, ⁶⁰Zn, ¹⁴⁰Ce, ¹¹⁵In, ²³⁸U, ⁵⁹Co, ²³²Th</td>
</tr>
<tr>
<td>Internal standard</td>
<td>¹³C</td>
</tr>
<tr>
<td>Dwell time</td>
<td>50 ms</td>
</tr>
<tr>
<td>Laser energy</td>
<td>5 J/cm² for plant; 10 J/cm² for NIST</td>
</tr>
<tr>
<td>Total duration of one quadrupole cycle</td>
<td>250 ms</td>
</tr>
</tbody>
</table>

| Laser | Diode Pumped Solid State (DPSS)@ 266 nm |
| Mode of ablation | Single line scan |
| Wavelength | 266 nm |
| Sweeps | 1 |
| Scan speed | 125 μm s⁻¹ for plant; 5 μm s⁻¹ for leaf |
| Laser spot | NIST |
| Ablation-cell gas (He) | 700 ml/min |
| Repetition rate | 100 Hz |

Table 2. Relative standard deviations (RSDs) for average values of five ablation lines in the NIST 612 glass and the spiked agar gel

<table>
<thead>
<tr>
<th>The NIST 612 glass</th>
<th>The spiked agar gel</th>
</tr>
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<tbody>
<tr>
<td>²⁰Ce at 20°C</td>
<td>6.83%</td>
</tr>
<tr>
<td>²³¹In at 20°C</td>
<td>7.13%</td>
</tr>
<tr>
<td>²³⁸U at 20°C</td>
<td>8.09%</td>
</tr>
<tr>
<td>⁵⁹Co at 20°C</td>
<td>6.94%</td>
</tr>
<tr>
<td>²³²Th at 20°C</td>
<td>8.19%</td>
</tr>
<tr>
<td>⁶⁰Zn/⁶⁰Co at 20°C</td>
<td>3.83%</td>
</tr>
<tr>
<td>⁴⁴Ca/⁴⁴Co at 20°C</td>
<td>3.07%</td>
</tr>
<tr>
<td>¹⁴⁰Ce/¹⁴⁰Ce at 20°C</td>
<td>3.02%</td>
</tr>
</tbody>
</table>

The ablation signals of ¹⁴⁰Ce, ¹¹⁵In, ²³⁸U, ⁵⁹Co, and ²³²Th were reduced in the cryogenic chamber. This reduction in signal intensities was observed because ablation at room temperature produced heavy thermal effect, which partially melted NIST at a high temperature. The aerosol from the melted NIST enhanced the signal. Moreover, this aerosol possibly produced inhomogeneous particulates, which increased the RSD. In contrast, the thermal effect was eliminated.

Fig. 1 Images of the ablated traces of NIST 612 (A), spiked agar gel (B), and leaf (C) in a cryogenic chamber and at room temperature.
in the cryogenic chamber. Although the signals of $^{140}$Ce, $^{115}$In, $^{238}$U, $^{59}$Co, and $^{232}$Th were reduced without the aerosol from melted NIST, the sensitivity was improved. Additionally, the RSD decreased because the aerosol from the melted NIST was eliminated.

Agarose gel was used as a matrix to match the plant for LA-ICP-MS imaging. In the spiked agar gel, the signals of $^{63}$Cu, $^{66}$Zn, and $^{140}$Ce were acquired. $^{13}$C was used as an internal standard to eliminate deviations because of its considerable concentration and relatively homogeneous distribution in plants. The results of plant imaging with $^{13}$C as an internal standard were corrected to obtain the accurate results. The RSD of spiked agar gel that the calculated method was consistent with NIST 612 was acquired. The RSD of $^{66}$Zn/$^{13}$C, $^{63}$Cu/$^{13}$C, and $^{140}$Ce/$^{13}$C was 3.02%-3.83% at room temperature and 1.82%-2.90% under cryogenic conditions (Table 2). The lower RSDs of the spiked agar gel were consistent with those of the NIST ablated under cryogenic conditions. These results indicate that LA under cryogenic conditions has good reproducibility and promotes the stabilization of the signal. Fig. 2 shows the spatially resolved mapping of $^{63}$Cu/$^{13}$C (B, F), $^{66}$Zn/$^{13}$C (C, G), and the intensity of $^{13}$C (D, H). The upper row of the figures describes the mapping of leaf ablation at room temperature, while the lower row presents the mapping of leaf ablation in a cryogenic chamber. The mapping results confirmed that improved imaging and more homogeneous $^{13}$C internal standard distribution were achieved.

The 266-nm laser generates a considerable thermal effect, which adversely affects the ablated traces and experimental results.
Thus, the cryogenic chamber eliminated the thermal effect of the ablation process to improve signal stability, thus achieving good imaging.

**Distribution of Ce in cucumber tissues with cryogenic ablation.**

The native structures of biological tissues and their original elemental distributions should be maintained during the bio-imaging process with laser ablation ICP-MS. However, the elemental imaging in fresh plant tissue was limited due to the dehydration of high water content during the ablation caused by the continuous flow of the He or Ar carrier gas. In addition, the procedure for fixing tissues in formalin solution or paraffin embedding to the dissolution of metals from the biological samples by formalin solution or paraffin embedding. In this work, we used a cryogenic chamber to maintain the native state of the biological sample. The distribution of Ce in plant leaves after exposure to CeO$_2$/Ce$^{3+}$ was evaluated by LA-ICP-MS with a cryogenic chamber.

The SEM images of CeO$_2$ NPs in Fig. 3 show uniform particle size distribution, with diameters of approximately 20-50 nm. The hydrodynamic size of CeO$_2$ NPs in 1/4 strength Hoagland nutrient solution was measured to be 377 ± 49 nm, with a zeta-potential of -9.4 ± 1.3 mV. The results indicate that the CeO$_2$ NPs were not mono-dispersed in the 1/4 strength Hoagland solution and exhibited agglomeration.

Cucumber plants were incubated with (1) 200 mg/L CeO$_2$ NPs + 1/4 strength Hoagland nutrient solution and (2) 200 mg/L Ce$^{3+}$, + 1/4 strength Hoagland nutrient solution. The elemental concentration illustrated in Fig. 4A was 25 μg/g, with uniformity in the relative intensities of $^{63}$Cu/$^{13}$C, $^{66}$Zn/$^{13}$C, and $^{140}$Ce/$^{13}$C. The RSDs of the relative intensities of $^{63}$Cu/$^{13}$C, $^{66}$Zn/$^{13}$C, and $^{140}$Ce/$^{13}$C were 8.4%, 9.2%, and 7.9%, respectively. Figures 4B, C, and D show the standard curves of $^{63}$Cu/$^{13}$C, $^{66}$Zn/$^{13}$C, and $^{140}$Ce/$^{13}$C of the spiked agar gel under cryogenic conditions, with relative coefficients above 0.99. The distribution of $^{63}$Cu, $^{66}$Zn, and $^{140}$Ce in cucumber leaves with $^{13}$C internal standard after cultivation in the presence of CeO$_2$ NPs or Ce$^{3+}$ is illustrated in Fig. 5. The results show that Cu and Zn were mainly distributed in the veins and edges of the cucumber leaves, while Ce was mainly distributed on the edges of the leaves. Remarkably, the concentration of Ce in cucumber leaves cultivated with Ce$^{3+}$ was higher than that cultivated with CeO$_2$ NPs. This can be explained by the transportation of metal ions through the channels in the roots of the plants and the direct entry of CeNPs into the plants through the channels without transformation. In the present study, the larger CeO$_2$ NPs were unable to enter the plant roots directly. Thus, we proposed the assumption that the larger CeO$_2$ NP first degraded in the plant root cells to generate smaller CeO$_2$ NPs and Ce$^{3+}$ ions, which were then absorbed by the plant root cells. Consequently, the plant leaves incubated with Ce$^{3+}$ absorb more Ce with respect to CeO$_2$ at the same incubation time, which is consistent with the results of a previous study. Conversely, the agglomeration of CeO$_2$ NPs in the Hoagland solution increased the hydrodynamic size of CeO$_2$, which further restricted the uptake of CeO$_2$ NPs by the root cells of cucumbers.

Figure 5 further revealed that Cu and Zn in cucumber leaves after incubation with Ce$^{3+}$ were significantly reduced compared to...
Fig. 6 Imaging of $^{31}\text{P}$ (A, C) with $^{13}\text{C}$ as an internal standard and the intensity of $^{13}\text{C}$ (B, D) in cucumber leaves (A) and (B) cultivated with CeO$_2$ NPs (C) and (D) cultivated with Ce$^{3+}$. Scan bar: 50 μm.

those incubated with CeO$_2$ NPs. A previous study reported that CeO$_2$ had no effect on the dry weight of the plants$^{25}$ or the content of trace elements in plants.$^{26}$ However, the presence of Ce$^{3+}$ could reduce growth-related elements in plants.$^{27,28}$ This is because Ce$^{3+}$ occupied more ion channels, which caused the reduction for transporting other elements. These assumptions are well demonstrated by the spatially resolved mapping profile of $^{31}\text{P}$ with $^{13}\text{C}$ as the internal standard in Fig. 6. An intensive signal in cucumber leaves was observed for $^{31}\text{P}$ when cucumber plants were incubated with CeO$_2$ NPs, while no $^{31}\text{P}$ signal was observed in the imaging of cucumber leaves when the plant was cultivated with Ce$^{3+}$. These results indicate that Ce$^{3+}$ has higher negative effect than CeO$_2$, which is also consistent with the results of a previous study.$^{29}$ A uniform internal standard intensity should be obtained in imaging of LA-ICP-MS. Figures 6B and D revealed that the uniform internal standard intensity of $^{13}\text{C}$ was acquired with cryogenic chamber, which improved the imaging quality of fresh biological samples and illustrated the advantages of imaging in a cryogenic chamber.

CONCLUSION

In summary, we achieved spatial distribution of $^{140}\text{Ce}$, $^{63}\text{Cu}$, $^{66}\text{Zn}$, $^{31}\text{P}$, and $^{13}\text{C}$ in cucumber leaves by LA-ICP-MS. Using a cryogenic chamber, the evaporation of water in the fresh cucumber leaves was suppressed, thus maintaining the native state of biological tissues. Lower signal fluctuations of NIST 612 and spiked agar gel were observed, indicating that the cryogenic conditions improved the results. Overall, CeO$_2$/Ce$^{3+}$ had important physiological responses in cucumber leaves, resulting in different contents of Zn, Cu, and P. Additionally, Cu, Zn, and P were found to have been reduced in cucumber leaves cultivated with Ce$^{3+}$ compared to those cultivated with CeO$_2$, and that 200 mg/L of Ce$^{3+}$ had a more negative effect on plants than 200 mg/L of CeO$_2$. As a new approach to assessing the environmental risk of NPs, imaging by cryogenic chamber can provide more accurate biological information on fresh plants. Thus, LA-ICP-MS with cryogenic chamber can be applied to study crucial biological mechanisms related to fresh plants.

AUTHOR INFORMATION

Mingli Chen is currently a professor in the Department of Chemistry, Northeastern University (China). She received her Ph.D. degree in Analytical Chemistry (2010) from Northeastern University, China. In 2011–2012, she worked as a visiting scholar in Prof. Purnendu K. Dasgupta group at University of Texas at Arlington, USA. She has been working as member of editorial board for Atomic Spectroscopy. Her current research interest focuses on sample pretreatment techniques and spectroscopy analysis.

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Notes
The authors declare no competing financial interest.
ACKNOWLEDGMENTS

The authors are grateful for the financial support of the National Natural Science Foundation of China (21727811 and 2227040283) and the Fundamental Research Funds for the Central Universities (N2105017). Special thanks are due to the instrumental analysis from the Analytical and Testing Center, Northeastern University.

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