

# Analysis of Leachate Copper from Sediment at a Small Abandoned Mine Site by Handy-type Liquid Electrode Plasma Atomic Emission Spectrometer

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(Received on August 25, 2021; accepted on October 6, 2021)

Sediment, soil and drainage water were collected at an abandoned copper mine, and the leachate copper prepared with 1M HCl were qualitatively analyzed by a handy elemental analyzer based on liquid electrode plasma atomic emission spectrometry (LEP-AES). Quantitative values obtained by the handy analyzer with standard addition or conventional calibration method combining with self-internal standard method, and ones by flame atomic absorption spectrometer were compared. The analytical condition for LEP-AES, the accuracy and the precision were discussed. The elongation of interval of pulsed applied voltage enhanced intensities of emission line, but background rising for copper emission line overlapping tail of broad OH band prevent expected improvement of the limit of detection. Copper species in sediment exist as divalent basic copper sulfate confirmed by XANES/EXAFS spectra recorded by a laboratory type spectrometer.

KEY WORDS: handy atomic emission spectrometer; abandoned copper mine; acid leachate; liquid electrode plasma; laboratory XAFS spectrometer; basic copper sulfate.

## 1. Introduction

Atomic emission spectrometry using micro-plasma have been intensively investigated in terms of miniaturization of a spectrometer, low power consumption, reduction of carrier gas requirement, and so forth.<sup>1–8)</sup> Takamura and his research group confirmed discharge phenomena in a microchannel filled with electrolyte solution by application of high voltage, and developed liquid electrode-plasma atomic emission spectroscopy (LEP-AES) which could record atomic emission spectra by simply applying pulsed DC high voltage without any carrier gas.<sup>4,9)</sup> As for properties of the novel LEP-AES, it has been reported that intensity of emission lines would increase with the applied voltage<sup>10–12)</sup> and the application time,<sup>11,13)</sup> acid and/or electrolyte concentration in sample solution<sup>10,14)</sup> and so on. The excitation temperature of LEP was determined to be 6 200 K.<sup>15)</sup> The detection limit varies by several orders of magnitude depending on the element.<sup>16)</sup> A handy elemental analyzer based on LEP-AES has been commercialized recently, and has been applied for quantitative analysis of silver nanoparticles,<sup>17)</sup> lead in leachate from soil samples,<sup>13,18)</sup> and so forth. We have confirmed

precision of LEP-AES for quantitative analysis of aqueous solution sample could improve through the use of H $\alpha$  Balmer line (656 nm) as an internal standard, and applied this self-internal standard method to quantitative elemental analysis of leaching solution from soils in the mountain district of Shikoku, Japan.<sup>19)</sup>

Mine drainage and/or low-grade ore have been sometimes left without particular processing after closure especially in small-scale mines, and then elution of mineral elements and the environmental impacts have been a subject of interest.<sup>20–24)</sup> In order to investigate behavior of heavy metals around abandoned mine site, development of facile on-site analytical method have become increasingly important. Permissible limit of many kinds of heavy metals in uniform effluent standard is regulated in Japan by Ministry of Environment, and that of copper is 3 mg·L<sup>-1</sup>.<sup>25)</sup> In the present study, we collected sediment and soil samples at a small abandoned copper mine site, and carried out quantitative analysis of copper species in the leachate solution using a handy elemental analyzer based on LEP-AES. Effects of the measuring conditions on sensitivity and accuracy were discussed. To investigate copper species in the sediment and soil samples, Cu K-edge XANES/EXAFS characterization were also performed using a laboratory-type spectrometer.

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## 2. Experimental

Sediment samples were collected at the bottom of mine drainage on abandoned Mochibe copper mine, Kamiyama-cho, Tokushima, western Japan (Fig. 1: 34°01'25"N, 134°22'29"E). The drainage water (pH: 6.6, EC: 0.76 mS·cm<sup>-1</sup>) and the soil beside the drainage were also collected. The drainage joins a small tributary (pH: 4.8, EC: 0.31 mS·cm<sup>-1</sup>) of Akui River (Yoshino River system) and flows downstream. The sediment and soil samples were dried at 383 K for 5 h. The 1 g of the dried sediments were soaked with 25 mL of 1 M HCl (2.5 mL for the soil sample), shaken for 1 min, left for 10 min, and shaken again for 1 min. The supernatant was centrifugalized with a hand-operated centrifuge (Hettich), and then filtered with a syringe filters (SRP25, 0.45 μm; Minisart) to obtain the leachate sample. The 10M HCl was added to drain water to adjust the HCl concentration to 1M. A copper standard solution (Cu 1000. Wako), hydrochloric acid (35%. Nacalai, GR) and Milli-Q water were used for sample preparation.

The atomic emission spectra induced by liquid electrode plasma (LEP) were recorded with a handy elemental analyzer MH-5000 (Micro Emission Ltd., Japan).<sup>16,18</sup> The 40 μl of each sample solution was put into a disposal microchip (LepiCuve-02. Micro Emission) made of resin, and 3 ms pulsed 600 V DC was applied for 10 cycles at 5 ms intervals. Number of the iteration was 10 for each disposal chip. Five sets of the measurements were carried out using one new disposable vessel for each sample, and the average emission intensity of each set was used for the quantitative analysis. The standard addition method was applied for quantitative analysis of Cu, where the emission line at 324.8 nm was used. The emission line intensity was normalized with an emission line at 656.3 nm from excited atomic hydrogen to improve the precision.<sup>19</sup> The Cu concentration of the leachate solution and the mine drainage was also determined by the flame atomic absorption spectrometry (FAAS) using a Z-5010 polarized Zeeman atomic absorption spectrometer (Hitachi, Japan). The leachate solution was diluted with Milli-Q water (1: 100) for FAAS.

The X-ray emission and absorption spectra were recorded with a laboratory-type spectrometer Looper (Rigaku)<sup>26</sup> in air. A curved Ge(440) and Ge(220) monochromator crystal

was used for Cu K-edge XANES and EXAFS experiments, respectively. For X-ray fluorescence (XRF) experiments, Mo Kα<sub>1</sub> line (17.5 keV) monochromatized with a Ge(440) monochromator crystal and a Si-PIN detector X-123 (Amptek) were utilized for the excitation source and the X-ray spectrometer, respectively. The open-type X-ray source equipped with LaB<sub>6</sub> cathode and Mo target was operated at 18 kV and 50 mA for XAFS, and 25 kV and 10 mA for XRF experiments. Data reduction for EXAFS analysis was performed with a REX2000 program.<sup>27</sup> For XANES, removal of background and the normalization procedure were carried out using IGOR Pro program.<sup>28</sup>

## 3. Results and Discussion

### 3.1. X-ray Chemical Analysis

Figure 2 shows X-ray fluorescence spectra of sediment and soil samples. Intense Cu Kα line was observed from sediment samples along with Mn, Fe and Zn K-lines. Weak Cu Kα line was detected from soil sample. The copper content in each dried sample was briefly analyzed with X-ray absorption spectra recorded in transmission mode using the mass absorption coefficient<sup>29</sup> at 9 000 eV. The same procedure was used to determine contents of Fe, Mn and Zn. The estimated content of the four elements is listed in Fig. 2.

Figure 3 shows Cu K-edge XANES spectra of sediment and soil samples, and reference compounds. The first

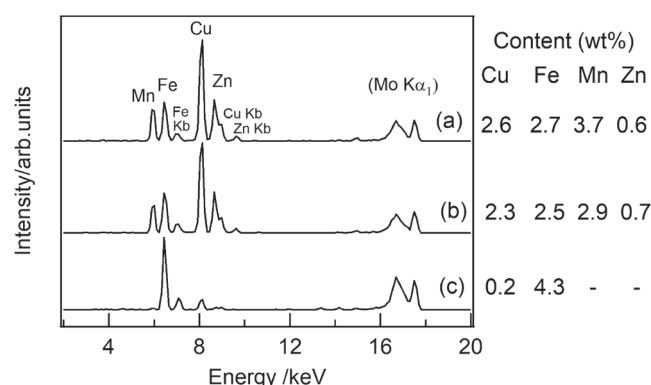


Fig. 2. XRF spectra of (a) sediment-A, (b) -B and (c) soil samples, and the metal content.

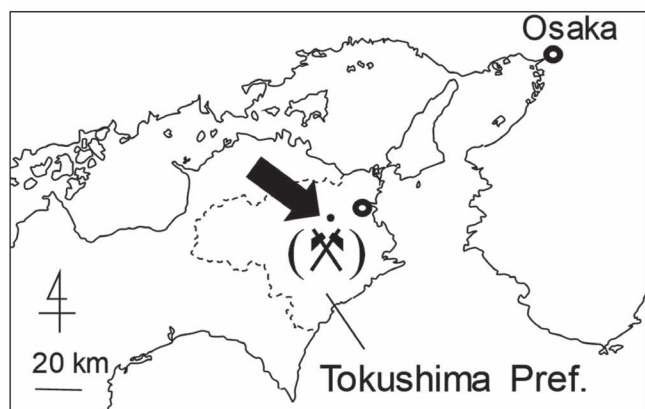
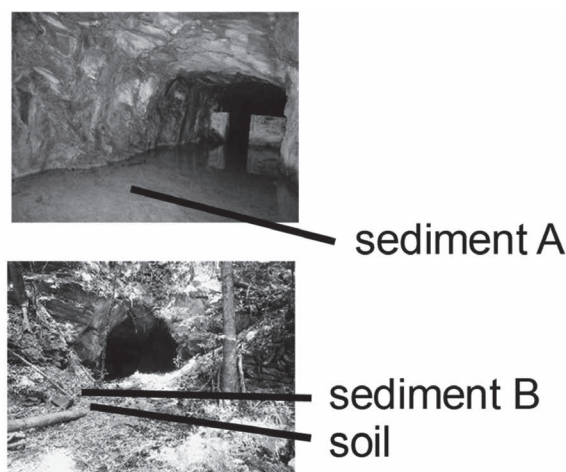
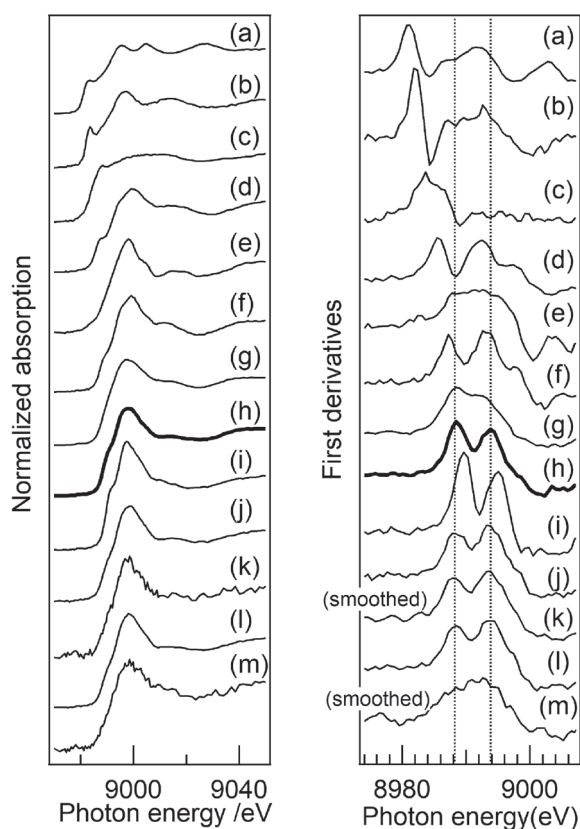


Fig. 1. Location and sampling point at abandoned copper mine.



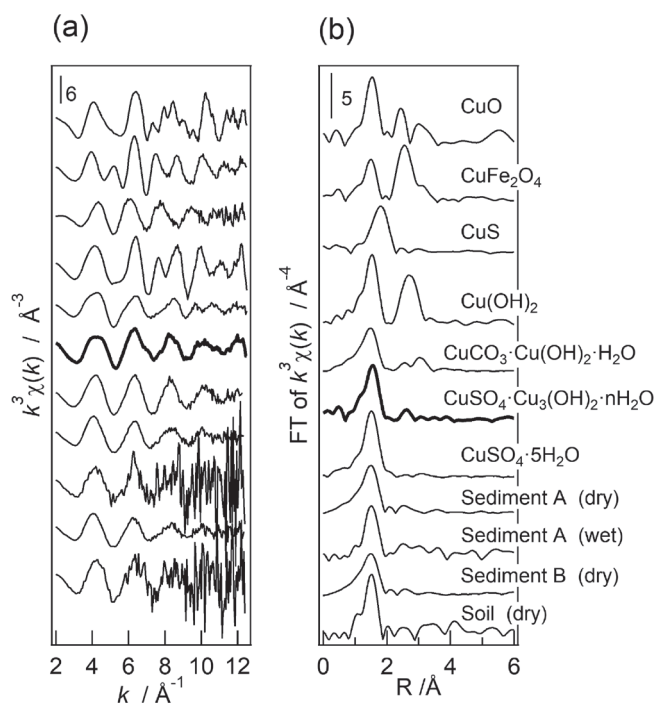


**Fig. 3.** Cu K-edge XANES spectra of sediment and reference samples, and the first derivatives. (a) Cu foil, (b)  $\text{Cu}_2\text{O}$ , (c) CuS, (d) CuO, (e)  $\text{CuFe}_2\text{O}_4$ , (f)  $\text{Cu}(\text{OH})_2$ , (g)  $\text{CuCO}_3 \cdot \text{Cu}(\text{OH})_2 \cdot \text{H}_2\text{O}$ , (h)  $\text{CuSO}_4 \cdot \text{Cu}_3(\text{OH})_2 \cdot n\text{H}_2\text{O}$ , (i)  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ , (j) Sediment A (dry), (k) Sediment A (wet), (l) Sediment B (dry), and (m) Soil.

derivatives are also shown. The  $k^3$ -weighted EXAFS spectra and the radial structure functions obtained by the Fourier transforms are shown in **Fig. 4**. Apparent absorption edge suggests that copper species in sediment and soil samples are divalent. The spectral features of the dried Sediment A sample could be regarded as the same as those of as-collected wet condition, and are similar to those of basic copper sulfate  $\text{Cu}_4(\text{OH})_6\text{SO}_4$ . Acid mine drainage water would contain dissolved copper and sulfate ions. Formation of basic copper sulfate may be responsible for precipitation from the drainage. Anazawa *et al.* precisely investigated behavior of heavy metals in river water and the sediment around another abandoned copper mine in Tokushima;<sup>20</sup> the place of which is close to the present Mochibe copper mine; and presumed the precipitation as  $\text{Cu}_4(\text{OH})_6\text{SO}_4$ .<sup>30</sup> The formation of basic copper sulfate from mine drainage has been reported.<sup>31,32</sup> Our XAFS characterization corresponds to the previous studies.

### 3.2. Atomic Emission Spectrometry

It has been reported that emission intensity in LEP-AES depends on the applied voltage<sup>10,11</sup> and the application time,<sup>11,13</sup> and so on. We confirmed the emission intensity increases with increasing interval of a pulse applied as well even in the same voltage applied and the time, as same as previously reported.<sup>13</sup> **Figure 5** shows the typical dependency of applied voltage pulse interval on emission intensity. Regarding to this increment phenomena, Kitano *et al.*



**Fig. 4.** Cu K-edge (a) EXAFS spectra of sediment and reference samples, and (b) the radial structure functions.

confirmed emission intensity for a flowing sample solution was about 10 times higher than that for the static solution.<sup>4</sup> They presumed that bubbles generated by heating caused together with high-voltage application influence on emission intensity if it remains at a narrow micro-channel of a chip filled with electrolyte solution. As similar to their proposal, we presume that bubbles existing in front of an optical fiber connected with a spectrometer would lead to reduction number of detectable atoms. We presume that the present increment behavior of emission intensity by elongation of the pulse interval is result of shrinkage and/or moving out of bubbles from the micro-channel.

Emission line of Cu (324.7 nm) for analysis overlaps with the tail of broad OH emission band. The lower limit of detection (LLD) was evaluated by the following equation:  $LLD = 3 \times (\text{standard deviation of blank at } 325 \text{ nm}) / (\text{slope of the calibration curve})$ . With increasing emission intensity by prolongment of applied pulse interval, background level of the Cu emission line raised as well. Then time of pulse interval did not so effective on the lower limit of detection for Cu because higher background increased in the statistical noise as shown in Fig. S1. Typically, it was evaluated to be  $8.0 \pm 2.5 \text{ ppm}$  ( $n = 6$ ) when applied pulse voltage and the time, the interval, and the iteration was 600 V, 3 ms, 5 ms and 10 times, respectively.

**Figure 6** shows emission spectra of leachate solutions and HCl-added mine drainage water. Atomic and/or molecular emission lines for Cu, OH, H, and Na species were confirmed in emission spectra of sediment samples. Additional emission lines for Mg, Ca and K existed in the spectrum of soil, whereas Cu was not detected in that of the drainage water.

The color of leachate solutions was brownish, suggesting that various kinds of inorganic and/or organic compounds are eluted. Preparation of a standard solution with the same

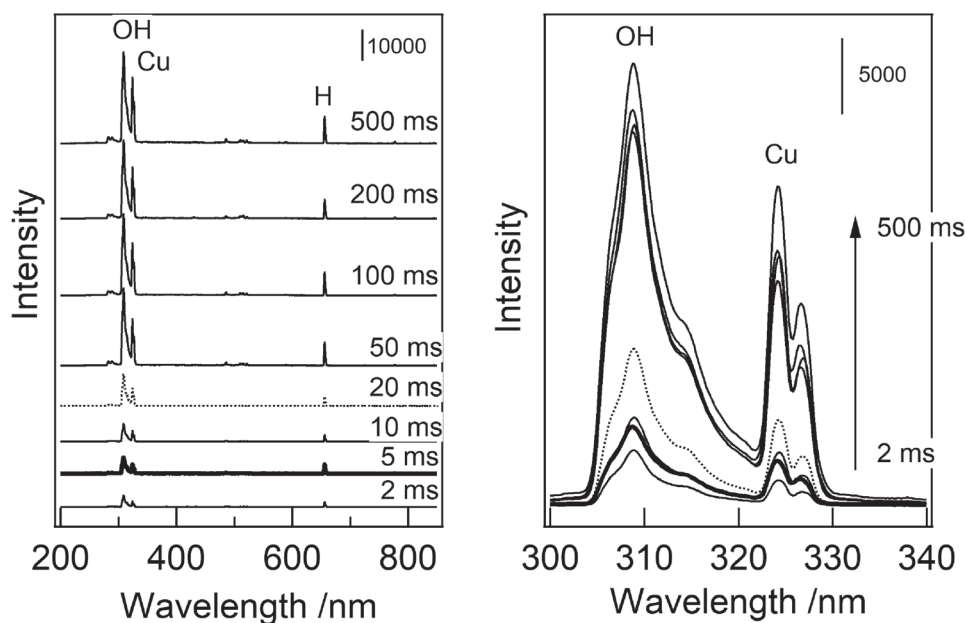


Fig. 5. Emission spectra of Cu 200 ppm standard solution in 1M HCl at different interval time of 3ms-pulsed DC600V application.

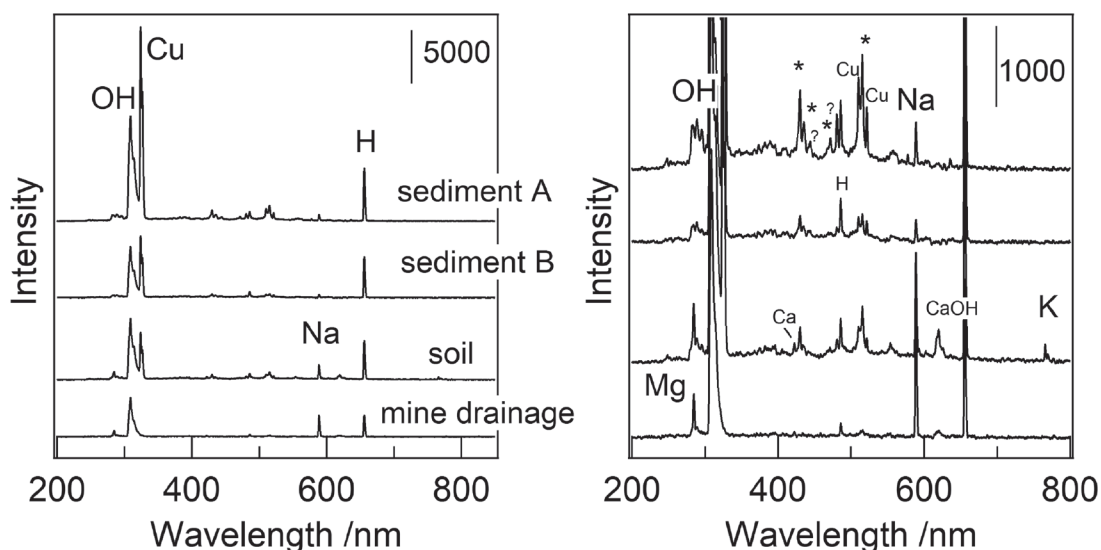


Fig. 6. Emission spectra of leachate and drainage samples. \* C2 and CH emissions from resin chip.

component are impractical, and a somewhat matrix effects in their quantitative analysis such as various chemical and/or spectroscopic interference would certainly occur. Then quantitative analysis of leachate samples was carried out for the diluted solution by the standard-addition method combined with self-internal standard method using hydrogen emission line at 656.3 nm. **Figure 7** shows the result. The linearity of each point suggests that a reliable qualitative analysis was done, where relative standard deviations of each point was  $11.2 \pm 4.6$  ( $n = 5$ ). Flame atomic absorption spectrometry (FAAS) was utilized for their validation. In quantitative analysis by LEP-AES, internal standard method was also carried out using conventional calibration curve. Results of quantitative analyses are summarized in **Table 1**. It should be noted that the evaluated Cu contents in leachate from sediments determined by the standard addition method were almost identical to those obtained by FAAS within 10% deviation. The correlation efficiency for

soil sample shown in Fig. 7 was slightly lower than those for sediment samples. The second data point corresponding to 100 ppm-addition in LEP-AES might lead to underestimation of the Cu content by about 30% comparing to that for FAAS. Note that quantitative values evaluated by the internal standard method were underestimated as large as 40% compared to those obtained by the standard addition method, probably due to matrix effects. The copper content of the drainage was determined to be 0.65 ppm by FAAS. Although the value was lower than that of lower limit of detection for LEP-AES, the content would be detectable using solid-phase extraction technique.

In the present study, we utilized a hand-operated centrifuge during preparation of a leachate sample solution. The utilized handy elemental analyzer could also work by six AA batteries (9 V). Our results suggest that the present handy analyzer could be applicable for various on-site quantitative elemental analysis without any external power

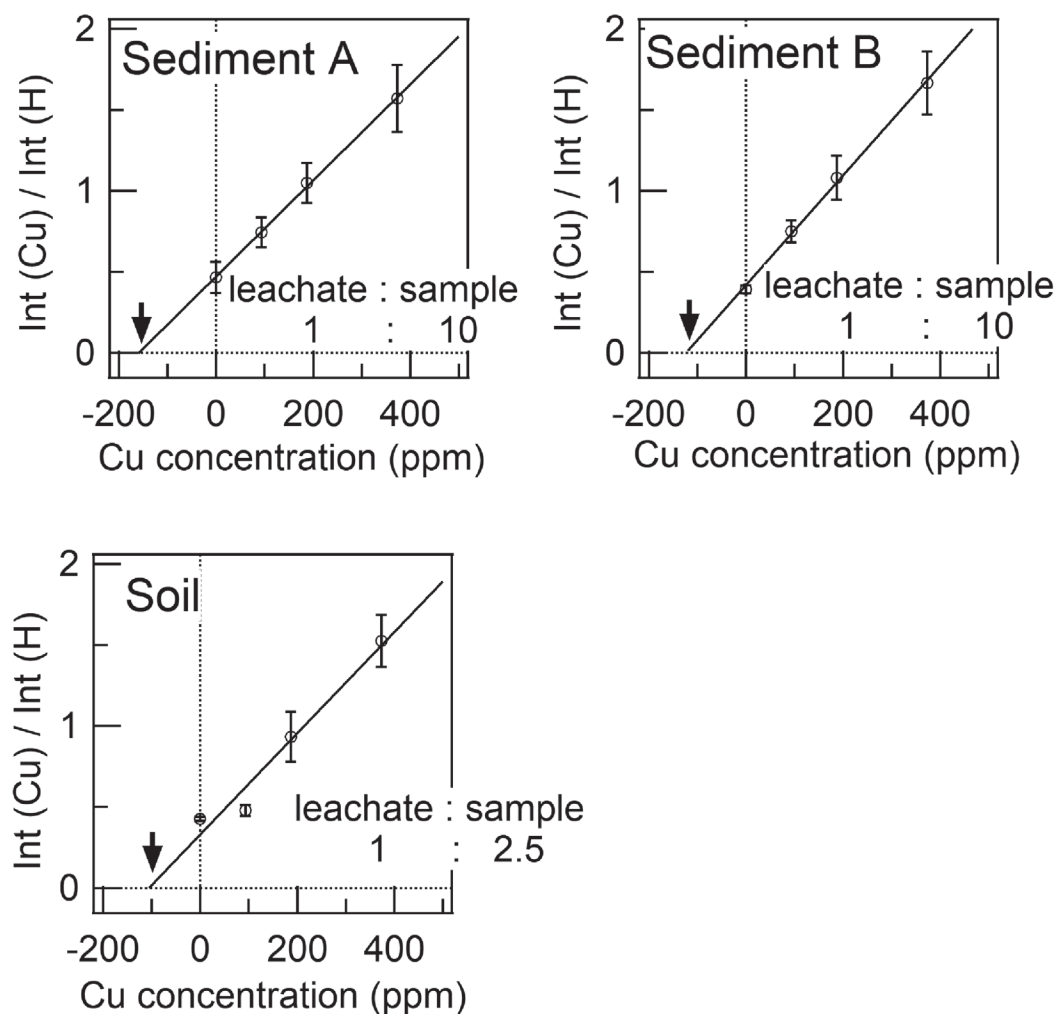


Fig. 7. Emission line intensities of diluted leachate samples with different concentration of added copper ( $n = 5$ ). Dilute leachate: 100  $\mu\text{l}$ , Cu 1 000 ppm standard: 0–40  $\mu\text{l}$ , 10M HCl: 90  $\mu\text{l}$ ,  $\text{H}_2\text{O}$ : 810–770  $\mu\text{l}$ ; total: 1 000  $\mu\text{l}$ . The value extrapolated to zero corresponds to copper concentration in the sample.

Table 1. Results of quantitative analysis of Cu in leachate and mine drainage.

Sample	Concentration (ppm)		
	LEP-AES		FAAS ( $n = 3$ )
	SA <sup>a</sup>	IS <sup>b</sup> ( $n = 5$ )	
Sediment A	1 482	826 $\pm$ 101	1 453 $\pm$ 0.11
Sediment B	1 410	775 $\pm$ 35	1 434 $\pm$ 0.13
Soil	300	213 $\pm$ 5.5	431 $\pm$ 0.02
Mine drainage	–	<i>nd</i>	0.65 $\pm$ 0.01

<sup>a</sup> Standard addition method, <sup>b</sup> self internal standard method.

supply. In the present study, a disposal chip made of resin was utilized for LEP-AES experiments. Repetition of several independent measurement was needed for a reliable quantitative analysis of real samples with standard addition method. We guess even a single spectrum measurement would be sufficient for qualitative or simple quantitative analysis. It has been reported that analytical precision and sensitivity in LEP-AES could be improved by use of a quartz chip instead of a resin-chip.<sup>4,16)</sup>

#### 4. Conclusion

Leachate Cu from sediment at an abandoned mine site was qualitatively analyzed by a handy elemental analyzer based on liquid electrode plasma atomic emission spectrometry. Repetition of several independent measurements with standard addition method combining with self internal standard method enabled to reliable quantitative analysis even by use of disposal sample chip. The elongation of interval of pulsed applied voltage in LEP-AES measurement enhanced intensities of emission line intensities, but limit of detection for Cu was not so improved because the emission line for detection overlaps with tail of intense emission bands of OH. Cu species in sediment were confirmed to be divalent basic copper sulfate by XANES/EXAFS characterization.

#### Supporting Information

Interval time dependency of applied pulsed voltage on lower limit of detection and signal intensity. This material is available on the Journal website at <https://doi.org/10.2355/isijinternational.ISIJINT-2021-406>.

## Acknowledgment

TY acknowledges to Professor J. Kawai (Kyoto University) for providing LEP-AES spectrometer. R. Yamaoka and K. Yamashita (Tokushima University) are acknowledged for their cooperation in collecting sediment samples.

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