The reductive coprecipitation with palladium has been reported for separation and pre-concentration of trace elements in high-purity metals. In order to evaluate the chemical forms of precipitate by this method, precipitates from acidic solution containing Se, Te, Au, Ag and Pd (only or mixture) were produced under the condition of quantitative precipitation and measured by X-ray diffraction and electron diffraction. The precipitates from solutions including single element were confirmed by X-ray diffraction or electron diffraction. In measurement of Te and Pd precipitate, X-ray diffraction peaks of each element were increase as leaving time lengthens. In measurement of Se precipitate, no X-ray diffraction patterns were found independent of leaving time in the acidic solution. But when leaving time was 24 h, electron diffraction spots of Se were found. The precipitates from solutions including mutual elements (mixture of Pd and the other elements (Se, Te, Au and Ag)) were confirmed by X-ray diffraction or electron diffraction. In measurement of Pd–Se or Pd–Te precipitate, it was found that palladium selenide (Pd₅Se₃) or palladium telluride (Pd₅Te₃) was product.

Keywords: coprecipitation with palladium, trace analysis, high-purity metals, X-ray diffraction, electron diffraction
2.2 Reagents

Standard solutions of palladium, selenium, tellurium, gold and silver (1 kg m\(^{-3}\)) were prepared by dissolution of these metallic elements in acid. All the used reagents were analytical-reagent grade and distilled water was used for all preparation procedures.
2.3 Procedure

The outline of experimental procedure is shown in Fig. 1. The standard solutions of these elements (single or mutual) and 10 cm³ of 18 kmol·m⁻³ sulfuric acid were transferred into an Erlenmeyer flask and the solution was heated to fumes. After cooling to room temperature, the solution was diluted with 90 cm³ of water. 3.0 g of ascorbic acid was added, and the solution was left at room temperature with ground stopper. The product precipitate was collected by filtration and measured by XRD and ED. The employed leaving times were adopted 3 h, 24 h, and 72 h. Weight of the precipitate was 10 mg. In spite of leaving time length, these elements in standard solutions were quantitatively precipitated by the procedure described above.

3. Results and Discussion

3.1 Evaluation by X-ray diffraction

3.1.1 Single element precipitate

Pd, Se and Te precipitate was respectively measured by XRD and these XRD patterns are shown in Fig. 2. No diffraction patterns were found in leaving for 3 h in measurement of Pd and Te precipitate. Diffraction patterns of each element were found in leaving for 24 h. In measurement of Se precipitate, no diffraction patterns were found in spite of leaving time length.

3.1.2 Precipitate from Pd–Au and Pd–Ag solution

Precipitate samples from a mixed Pd and Au (1:1), and a mixed Pd and Ag (1:1) solution were respectively evaluated by XRD and these XRD patterns are shown in Fig. 3. In measurement of both samples, diffraction peaks were increased as leaving time lengthens.
Table 3  Electron diffraction patterns of precipitates from Pd–Se and Pd–Se–Te solution.

<table>
<thead>
<tr>
<th></th>
<th>Pd–Se, 24 h</th>
<th></th>
<th>Pd–Se–Te, 3 h</th>
<th></th>
<th>Pd–Se–Te, 24 h</th>
</tr>
</thead>
<tbody>
<tr>
<td>R (cm)</td>
<td>d (nm)</td>
<td>R (cm)</td>
<td>d (nm)</td>
<td>R (cm)</td>
<td>d (nm)</td>
</tr>
<tr>
<td>0.760</td>
<td>0.3228 Pd$<em>{17}$Se$</em>{15}$</td>
<td>0.765</td>
<td>0.3207 Pd$<em>{17}$Se$</em>{15}$</td>
<td>0.755</td>
<td>0.3250 Pd$<em>{17}$Se$</em>{15}$</td>
</tr>
<tr>
<td>0.860</td>
<td>0.2853 Pd$<em>{17}$Se$</em>{15}$, Pd$_7$Se$_4$</td>
<td>0.855</td>
<td>0.2870 Pd$<em>{17}$Se$</em>{15}$, Pd$_7$Se$_4$</td>
<td>0.850</td>
<td>0.2887 Pd$<em>{17}$Se$</em>{15}$, Pd$_7$Se$_4$</td>
</tr>
<tr>
<td>0.895</td>
<td>0.2741 Pd$_7$Se$_4$</td>
<td>0.950</td>
<td>0.2583 Pd$_7$Te$_4$</td>
<td>0.945</td>
<td>0.2596 Pd$_7$Te$_4$</td>
</tr>
<tr>
<td>0.975</td>
<td>0.2516 Pd$<em>{17}$Se$</em>{15}$</td>
<td>0.995</td>
<td>0.2466 Pd$<em>{17}$Se$</em>{15}$, Pd$_3$Te$_2$</td>
<td>0.990</td>
<td>0.2504 Pd$<em>{17}$Se$</em>{15}$, Pd$_3$Te$_2$</td>
</tr>
<tr>
<td>1.185</td>
<td>0.2071 Pd$<em>{17}$Se$</em>{15}$, Pd$_4$Se$_4$</td>
<td>1.065</td>
<td>0.2304 Pd$<em>{17}$Se$</em>{15}$, Pd$_3$Te$_2$, Pd$_7$Te</td>
<td>1.070</td>
<td>0.2293 Pd$<em>{17}$Se$</em>{15}$, Pd$_3$Te$_2$, Pd$_7$Te</td>
</tr>
<tr>
<td>1.265</td>
<td>0.1940 PdSe</td>
<td>1.285</td>
<td>0.1909 PdSe, Pd$_2$Te</td>
<td>1.285</td>
<td>0.1909 PdSe, Pd$_2$Te</td>
</tr>
<tr>
<td>1.315</td>
<td>0.1866 Pd$<em>{17}$Se$</em>{15}$</td>
<td>1.390</td>
<td>0.1765 PdSe</td>
<td>1.385</td>
<td>0.1772 PdSe</td>
</tr>
<tr>
<td>1.380</td>
<td>0.1778 PdSe</td>
<td>1.390</td>
<td>0.1765 PdSe</td>
<td>1.385</td>
<td>0.1772 PdSe</td>
</tr>
</tbody>
</table>

Fig. 6  Electron diffraction of precipitate from Pd–Se solution; Leaving time is 3 h.

Fig. 7  Electron diffraction of precipitate from Pd–Se solution; Leaving time is 24 h.

of Pd and Au were respectively found. Similarly, diffraction peaks of Pd and Ag were respectively found in measurement of the Pd–Ag precipitate. Therefore, when Au or Ag was precipitated together with Pd, these elements were respectively precipitated as an elementary substance.

3.1.3  Precipitate from Pd–Se, Pd–Te and Pd–Se–Te solution

Precipitate samples from a mixed Pd and Se (1:1), a mixed Pd and Te (1:1), and a mixed Pd, Se and Te (2:1:1) solution were respectively evaluated by XRD and these XRD patterns are shown in Fig. 4. In measurement of Pd–Se and Pd–Se–Te precipitate, no diffraction patterns were found in spite of leaving time length and chemical forms of these precipitates could not be evaluated.

In measurement Pd–Te precipitate, diffraction patterns of palladium telluride were found and these elements were precipitated as compounds. The chemical forms of precipitates were different as difference of leaving time length. It is considered that a chemical form of precipitate is changed or a different compound is accidentally produced. But the reason is unknown for this phenomenon.

3.1.4  Precipitate from several ratio of Pd–Te solution

Precipitate samples from several ratios of mixed Pd and Te solutions were evaluated by XRD. The samples were produced from solutions, which the ratio of Pd and Te was changed from 9:1 to 1:9 in leaving for 72 h and measured by
XRD, respectively. These XRD patterns are shown in Fig. 5. When the Pd–Te ratio was changed, several different diffraction patterns were found.

These evaluation results are listed in Table 2. Palladium and some palladium telluride compounds were simultaneously produced when the Pd–Te ratio was 9:1 or 4:1. Tellurium and some palladium telluride compounds were simultaneously produced when the Pd–Te ratio was 1:9. In the other Pd–Te ratios samples, several palladium telluride compounds were respectively produced. The chemical forms of product precipitates were different when the ratio of palladium and tellurium was changed.

3.2 Evaluation by electron diffraction

3.2.1 Precipitate from Se, Pd–Se and Pd–Se–Te solution

Because XRD patterns could not be found in measurement of the Se, Pd–Se and Pd–Se–Te precipitates, the chemical forms of these precipitates were evaluated by using ED. The ED picture of Pd–Se precipitate in leaving for 3 h is shown in Fig. 6, and that for 24 h is shown in Fig. 7. No diffraction spots were found in leaving for 3 h. But diffraction spots could be found in leaving for 24 h. Therefore, it is considered that the precipitate in leaving for 3 h is amorphous state and the crystallization of precipitate progressed as the leaving time lengthens. Similar results were obtained in measurement of Se precipitate. In measurement of Se–Te–Pd precipitates, diffraction spots were found in spite of leaving time length.

The evaluation results of ED measurement are listed in Table 3. Several palladium selenide compounds were produced in Pd–Se precipitate and Palladium selenide and palladium telluride were simultaneously and respectively produced in Pd–Se–Te precipitate.

In spite of leaving time length and chemical forms, these elements were quantitatively precipitated.

4. Conclusions

The chemical forms of product precipitates by the reductive coprecipitation were evaluated by using X-ray diffraction and electron diffraction. As a result, crystallization of the precipitate in acidic solution progressed as leaving time lengthens. The chemical forms of the precipitates were evaluated as follows: Palladium selenide was produced when Se was precipitated with Pd. Palladium telluride was product when Te was precipitated with Pd. Moreover, palladium selenide and palladium telluride were respectively produced when Se and Te were simultaneously precipitated with Pd. However, when gold or silver was precipitated with Pd, the compounds were not produced but these elements were precipitated as the elementary substance, respectively.

REFERENCES