

## Valence Control of Technetium and Ruthenium for Anion Exchange Chromatographic Separation

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Analysis of  $^{99}\text{Tc}$  in LiCl molten salt sample is required to calculate source terms to prepare for the recovery of metal uranium from uranium oxide spent nuclear fuel in LiCl molten salt medium by reduction with lithium metal.<sup>1</sup> Technetium-99, which is formed by thermal neutron fission of  $^{235}\text{U}$  and  $^{239}\text{Pu}$ , is a beta emitter with a long half-life of  $2.1 \times 10^5$  y. The content of  $^{99}\text{Tc}$  in spent pressurized water reactor (PWR) fuel, after a cooling period of 10 years, is estimated at about 800 g per ton of uranium.<sup>2</sup>

To determine  $^{99}\text{Tc}$ , using a liquid scintillation counter (LSC), the beta emitting nuclides, such as  $^{99}\text{Mo}$  and  $^{106}\text{Ru}$ , have to be removed from technetium solutions. While  $^{99}\text{Mo}$  is negligible in the spent nuclear fuel with a long cooling period due to its relatively short half-life of 66 hours, the amount of  $^{106}\text{Ru}$  is 46 times as large as that of  $^{99}\text{Tc}$ , on the basis of beta activity, in the 10-year cooled spent nuclear fuels.<sup>2</sup> Moreover, since the solubility of Tc-bearing alloys in LiCl molten salt is low, preconcentration and chemical separation of the technetium from LiCl molten salt samples are required for beta counting of  $^{99}\text{Tc}$ .

As reported previously, any combination of ion exchange, solvent extraction, precipitation, and distillation has been used to remove the interfering beta activity nuclides, such as  $^{106}\text{Ru}$ , from  $^{99}\text{Tc}$  samples.<sup>3,9</sup> Although anion exchange techniques have been widely used to separate technetium from ruthenium, they are frequently combined with other separation methods. Therefore, thermodynamic data, which are useful to eliminate ruthenium from technetium solely by anion exchange, are not commonly available. This may be largely due to the fact that the anion exchanges were employed without proper valence control, specifically of ruthenium.<sup>3-6</sup> Valence control of technetium and ruthenium is indispensable for the successful separation of the elements from each other by anion exchange techniques.

The present study was designed to establish an effective procedure to control the valences of technetium and ruthenium that is particularly suitable for the anion exchange separation of  $^{99}\text{Tc}$  from LiCl molten salt samples from the uranium metalization process of spent nuclear fuel under development in the Korea Atomic Energy Research Institute.<sup>1</sup>

### Experimental Section

**Reagents and instruments.** Analytical grade reagents and deionized water were used throughout this study.

$\text{K}_3\text{RuCl}_6$ ,  $(\text{NH}_4)_2\text{RuCl}_6$ ,  $\text{RuCl}_3$ , sodium hypochlorite (NaOCl) solution and HCl were purchased from Aldrich Chemical Co., USA. The chlorine content of the NaOCl solution was determined by iodometric titration.<sup>10</sup> Anion exchange AG 1  $\times$  8 (200-400 mesh) in chloride form and cation exchange resin AG 50W  $\times$  8 (200-400 mesh) in hydrogen form were used for the experiments. The aqueous solution of ammonium pertechnetate, of which  $^{99}\text{Tc}$  purity was more than 99%, was obtained from the An Eckert & Ziegler Co., USA. Insta-gel XF (Packard) was used as a scintillator in liquid scintillation counting. The absorption spectra of solutions were measured with a Varian CARY5 UV-Vis-NIR spectrophotometer, using a 1.0 cm semi-micro quartz cell (Hellma). Determination of ruthenium was performed using a Jobin Yvon JY38 PLUS inductively coupled plasma atomic emission spectrophotometer (ICP-AES). Beta counting was made using a Packard 2500TR/AB, TRI-CARB liquid scintillation counter.

**Valence control of Ru and Tc.** A stock solution of 0.03 M  $\text{K}_3\text{RuCl}_6$  was prepared by dissolving an appropriate amount of solid  $\text{K}_3\text{RuCl}_6$  in 5.0 M HCl, then diluted to 0.05 M HCl solution with deionized water. An aliquot of 0.12 N NaOCl, as much as 10 to 30 times more than the moles of ruthenium, was added to the diluted ruthenium solution followed by the addition of a few drops of 95%(V/V) ethanol. The absorption spectra of this solution were obtained with various time intervals in the range of 200-600 nm. For  $(\text{NH}_4)_2\text{RuCl}_6$  and  $\text{RuCl}_3$ , the same experiments were performed.

A solution of Tc(IV) was prepared by adding concentrated hydrochloric acid to the aqueous solution of ammonium pertechnetate. The solution stood 40 days, with pertechnetate ion ( $\text{TcO}_4^-$ ) being converted to  $\text{TcCl}_6^{2-}$ . A portion of this solution was diluted to 0.022 mM Tc(IV) in 0.05 M HCl with deionized water. To the diluted Tc(IV) solution, an aliquot of 0.12 N NaOCl solution and a few drops of 95% (V/V) ethanol were added in succession, and the absorption spectra of the solution were measured in the same manner as above.

**Separation of ruthenium species.** Cation exchange resin was pretreated by a common procedure and slurry-packed to 0.7(i.d.)  $\times$  3.0 cm in a polyethylene column, where the resin bed was held in place by glass wool plugs at the top and bottom. An anion exchange resin column of 0.7(i.d.)  $\times$  3.0 cm was prepared by the same procedure. The resin columns

were preconditioned before use by passing 3 mL of 0.05 M HCl.

Ten minutes after addition of 0.1 mL of 0.3 N NaOCl solution to 5.0 mL of 3 mg/L Ru (as a form of  $K_3RuCl_6$  in 0.05 M HCl) solution, one drop of 95%(V/V) ethanol was added to this combination. Fifteen minutes later, the solution was loaded on the AG 50W  $\times$  8 resin column. Nonadsorbed ruthenium on the resin was washed off with 5.0 mL of 0.05 M HCl, and adsorbed ruthenium was eluted with 10 mL of 5 M HCl. The effluent was collected fractionally, and the ruthenium concentration in each fraction was determined by ICP-AES. The same procedure was performed on the AG 1  $\times$  8 resin column.

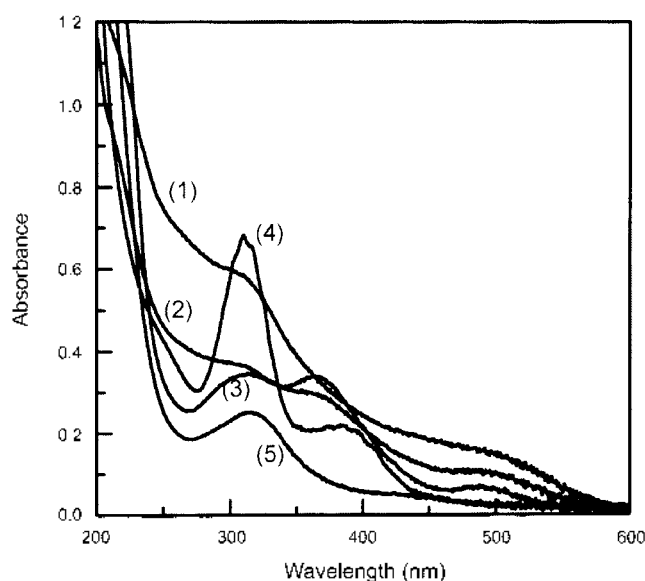
**Application of valence control technique.** Two milliliters of 0.05 M HCl solution containing 30  $\mu$ g Ru (as a form of  $K_3RuCl_6$ ) and 3.4 nCi  $^{99}Tc$  (as a form of  $TcCl_6^{2-}$ ) were treated with 0.2 mL of 0.3 N NaOCl and 3 drops of ethanol sequentially, and the solution was loaded on the AG 1  $\times$  8 resin column [0.7(i.d.)  $\times$  3.0 cm], which was preconditioned by passing 3 mL of 0.05 M HCl. The column was then washed with 10 mL of 1.0 M  $HNO_3$  and 10 mL of 10 M  $HNO_3$ , in succession. The effluent was collected in fractions of 1.0 mL, and the concentration of ruthenium and  $^{99}Tc$  was measured by ICP-AES and LSC, respectively. The flow rate of the AG 1  $\times$  8 column was 0.3 mL/min.

A synthetic solution containing 0.05 M HCl, 17 nCi  $^{99}Tc$ , 3.0  $\mu$ g Ru and 100 mg LiCl was treated with 0.05 mL of 0.3 N NaOCl followed by the addition of one drop of ethanol. The resulting solution was diluted to 10 mL with 0.05 M HCl. A 0.5 mL aliquot of this solution was loaded on the AG 1  $\times$  8 resin column [0.7(i.d.)  $\times$  3.0 cm]. After washing the column with 10 mL of 1.0 M  $HNO_3$ , technetium was eluted with 10 mL of 10 M  $HNO_3$ . A milliliter portion of 10 M  $HNO_3$  effluent was taken and mixed with 14 mL of scintillation liquid followed by LSC of  $^{99}Tc$  for 50 minutes. Experiments for the AG 1  $\times$  8 resin column were performed three times.

## Results and Discussion

**Valence control of Ru and Tc.** Technetium and ruthenium produced from the fission of uranium have been known to exist as a form of alloy in spent PWR nuclear fuels.<sup>11</sup> When the uranium oxide powder from spent nuclear fuels is fed into LiCl molten salt at 650  $^{\circ}C$ , the alloy is expected to dissolve, at least in part, in the molten salt, and to be converted to the chloride forms. When these chlorides are dissolved in concentrated hydrochloric acid, various chlorocomplexes of the elements are formed in the solution. Thus, the ruthenium chlorides in different oxidation states of ruthenium, such as  $K_3RuCl_6$ ,  $(NH_4)_2RuCl_6$  and  $RuCl_3$ , were selected in this study. Reports indicate that the average oxidation state of  $RuCl_3$  is closer to Ru(IV) than Ru(III).<sup>12</sup> It was also reported that no ionic chlorine is found in freshly prepared aqueous solutions of solid  $RuCl_3$ .<sup>13</sup>

Figure 1 summarizes the absorption spectra of ruthenium species [ $K_3RuCl_6$ ,  $(NH_4)_2RuCl_6$  and  $RuCl_3$ ] present in the



**Figure 1.** Absorption spectra of Ru-chlorocomplexes and  $RuO_4$  in 0.05 M HCl; (1) 0.3 mM  $(NH_4)_2RuCl_6$ , (2) 0.3 mM  $RuCl_3$ , (3) 0.3 mM  $K_3RuCl_6$ , (4) 0.3 mM  $RuO_4$ , (5) 0.3 mM Ru(III) (a mixture of neutral and cationic chlorocomplexes).

initial solutions of 0.05 M HCl, as well as the absorption spectrum of the  $K_3RuCl_6$  solution in 0.05 M HCl measured 5 minutes after the addition of NaOCl. As might be expected, the absorption spectrum after the addition of NaOCl to the  $K_3RuCl_6$  solution is much like that of ruthenium tetroxide ( $RuO_4$ ), as reported in the literature.<sup>12</sup> We observed no additional increase in the intensity of the 310 nm absorption band of  $RuO_4$  after the NaOCl-treated  $K_3RuCl_6$  solution stood 5 minutes, concluding that the ruthenium in a low valence state was instantaneously oxidized to  $RuO_4$  under this experimental condition. In the cases of  $(NH_4)_2RuCl_6$  and  $RuCl_3$  solutions treated with NaOCl as described above, their absorption spectra were nearly identical to that of the NaOCl-treated  $K_3RuCl_6$  solution. These results led us to conclude that the ruthenium present as various chlorocomplexes of Ru(III) and Ru(IV) in 0.05 M HCl solutions was instantaneously oxidized to  $RuO_4$  by NaOCl.

A small amount of ethanol was added to the ruthenium solution treated with NaOCl in an attempt to convert  $RuO_4$  to neutral or cationic chlorocomplexes of ruthenium. The change in the absorption spectrum of  $RuO_4$  due to the addition of ethanol to the NaOCl-treated  $K_3RuCl_6$  solution can be seen in (5) of Figure 1. Based on the suggestion by Cady and Connick,<sup>13</sup> the broad absorption spectrum with a maximum at 315 nm can be attributed to the formation of  $RuCl_3$ ,  $RuCl_2^+$ , and  $RuCl^{2+}$  from the reduction of  $RuO_4$  by ethanol. By employing NaOCl and ethanol in sequence, ruthenium can be rapidly and completely adjusted to the cationic and neutral species, which are not adsorbed on anion exchange resins.

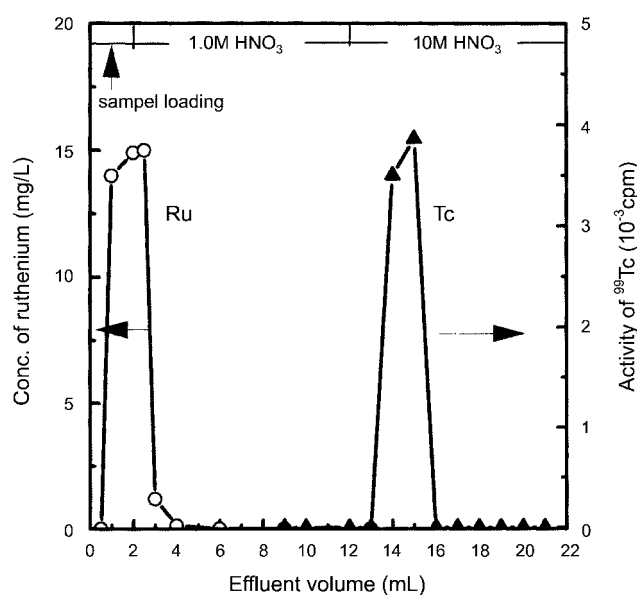
To separate technetium from the interfering elements in LSC by anion exchange chromatography, the interfering elements should be converted to the species that are not adsorbed or weakly adsorbed on the resin, while technetium

is converted to the strongly adsorbed  $\text{TcO}_4^-$ . It was necessary to confirm that the valence control procedure for ruthenium would also be effective in the oxidation of  $\text{TcCl}_6^{2-}$  to  $\text{TcO}_4^-$ . Absorption spectrophotometric observations of the oxidation of  $\text{TcCl}_6^{2-}$  by NaOCl in 0.05 M HCl revealed that  $\text{TcO}_4^-$  was produced as an oxidation product at 245 nm and 290 nm in agreement with the literature.<sup>14</sup> The oxidation reaction was completed within 5 minutes. We also found that the addition of ethanol to the 0.05 M HCl solution did not affect the stability of  $\text{TcO}_4^-$ .

**Identification of ruthenium species.** To understand the behavior of ruthenium on anion exchange resin column, it is necessary to know the distribution and properties of individual species of ruthenium. Ion exchange methods cannot only be applied to the separation of ions, but can also provide information relevant to the properties of complexes formed between ion and ligand. To identify the species of ruthenium chlorocomplexes formed when treating ruthenium solution with NaOCl and ethanol in sequence, the species were isolated by cation and anion exchange techniques. When the treated solution was loaded on AG 50W  $\times$  8 cation exchange column, about 70% of the ruthenium was found to be adsorbed by the resin from 0.05 M HCl solution, which could be eluted by 5.0 M HCl, whereas the rest of the ruthenium was not adsorbed and thus easily washed off by 0.05 M HCl solution. This means that 70% of the ruthenium in the treated solution was present as a cationic species and 30% as the neutral and/or anionic species. In case of AG 1  $\times$  8 anion exchange resin, all ruthenium species in the treated solution were not adsorbed from 0.05 M HCl solution, which indicates that no anionic species of ruthenium was present in the solution treated with NaOCl and ethanol. These results support the conclusion from the absorption spectrophotometric observations that ruthenium in 0.05 M HCl solution was converted to the neutral species  $\text{RuCl}_3$  and the cationic species, such as  $\text{RuCl}_2^+$  and  $\text{RuCl}^{2+}$ . It can also be concluded that the valence-controlled ruthenium species remained virtually unchanged on the resin column from the fact that the absorption spectra of the treated solution were identical with those of the effluent from AG 1  $\times$  8 resin column.

**Effectiveness of valence control.** When ruthenium in 0.05 M HCl solution treated with only NaOCl was applied on AG 1  $\times$  8 resin column, we observed that the color of the upper part of the resin bed changed from pale white to black. The black precipitation on the resin bed remained intact during washing stages with 1.0 M  $\text{HNO}_3$  and 10 M  $\text{HNO}_3$  solution. We found that most of the  $\text{RuO}_4$ , a strong oxidant, was reduced to ruthenium hydroxides on the column by the ion exchange resin. This indicates that single use of NaOCl is not suitable for the valence control of ruthenium and technetium in anion exchange resin.

On treating the ruthenium in 0.05 M HCl solution with NaOCl and ethanol in sequence, neutral and cationic chlorocomplexes of ruthenium were formed, which were not adsorbed on anion exchange resins. On the other hand, we found that, under the same condition, technetium was controlled to  $\text{TcO}_4^-$ , which was strongly adsorbed on anion



**Figure 2.** Separation of technetium from ruthenium on anion exchange resin; bed: 0.7(i.d.)  $\times$  3.0 cm, resin: AG 1  $\times$  8 (200-400 mesh), loaded amounts: 30  $\mu\text{g}$  Ru and 3.4 nCi  $^{99\text{m}}\text{Tc}$  in 2.0 mL of 0.05 M HCl, wash solution: 10 mL of 1.0 M  $\text{HNO}_3$ , eluent: 10 mL of 10 M  $\text{HNO}_3$ .

exchange resins. This valence control was evaluated in terms of the effectiveness of the anion exchange procedure for the separation of technetium from ruthenium. Figure 2 shows a typical chromatogram obtained from AG 1  $\times$  8 resin column operation with the NaOCl-ethanol treated 0.05 M HCl solution containing ruthenium and  $^{99\text{m}}\text{Tc}$  (as a form of  $\text{TcCl}_6^{2-}$ ). Ruthenium was washed off the column with 1.0 M  $\text{HNO}_3$  solution, and then with 10 M  $\text{HNO}_3$  to obtain the technetium portion. As the ruthenium was not adsorbed, it was substantially passed through the column until the first 1 mL portion of 1.0 M  $\text{HNO}_3$ , and technetium was completely eluted by less than 5 mL of 10 M  $\text{HNO}_3$  solution. Thus, 10 mL of 10 M  $\text{HNO}_3$  was sufficient to recover completely the technetium from the column. In addition, no technetium was found in the 10 mL effluent of 1.0 M  $\text{HNO}_3$ . Moreover, ruthenium was not found in the technetium eluate by ICP-AES, which confirms that ruthenium was completely removed from the resin column by the 1.0 M  $\text{HNO}_3$  washing step. This result indicates that separation of technetium from ruthenium can be achieved by combining the valence control technique with the anion exchange technique without the aid of other separation methods.

To examine the recovery of technetium and the reliability of the proposed procedure, three replicate experiments were performed with AG 1  $\times$  8 resin columns on the synthetic solution containing  $^{99\text{m}}\text{Tc}$  and ruthenium. Lithium chloride medium solution has to be considered in this study, since this procedure is to be used for samples from LiCl molten salt process of uranium metal production. It was found that technetium recovery from AG 1  $\times$  8 was 100.6% with a relative standard deviation of 2.3%. This result shows that complete recovery of technetium on AG 1  $\times$  8 columns can be achieved using the valence control procedure.

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