

Coprecipitation of Radio Ruthenium with Hydrous Manganese Dioxide

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Removal of radio isotope ruthenium-106 as nitrosyl complex species, from aqueous solutions, by coprecipitation on hydrous manganese dioxide has been studied under different conditions of pH and amounts of Mn(IV) oxide precipitated. Precipitation has been carried out by the action of hydrogen peroxide on potassium permanganate in basic media and influence of electrolytes, aging of ruthenium solutions in contact with permanganate, on coprecipitation yields has been discussed. Conclusions regarding the nature of the processes responsible for coprecipitation are drawn and a mechanism is outlined. Coprecipitation yields to the extent of 98% and more have been obtained suggesting its use in the treatment of radioactive waste waters.

NITROSYLRUTHENIUM(II) (RuNO^{2+}) ion is the most common form of radio ruthenium (^{106}Ru) present in radioactive waste waters produced during reprocessing of spent nuclear fuels. Decontamination of radioactive nitrosyl-ruthenium complexes by coprecipitation on some metal sulphides and lead periodate have been reported¹⁻⁴, but the use of former is limited to acid solutions whereas the latter gives partial removal. Hydrous manganese dioxide which is known for its affinity to fix a number of metal ions on its surface, has been used for the elimination of radium from uranium mill effluents⁵ and concentration of radionuclides from sea water⁶. Coprecipitation of a number of trace elements with Mn(IV) oxide have been reported and some useful separations proposed⁷. Elimination of nitrosylruthenium complex species from aqueous solutions by coprecipitation on hydrous Mn(IV) oxide have been studied in detail and the results are reported in this paper.

Materials and Methods

Tracer—Stock solutions of nitrosylruthenium(II) nitrate were prepared by distilling carrier free ruthenium tracer (^{106}Ru) from a solution of sulphuric acid and cerium(IV) sulphate and collecting the volatile ruthenium tetraoxide into 10% nitric acid solution. Nitrogen(II) oxide was simultaneously introduced in the collecting media^{8,9}. Nitrosylruthenium solution prepared in this manner was neutralized with sodium hydroxide and further diluted with distilled water. The activity of the stock solution was of the order of 10^{-2} $\mu\text{C/ml}$. To maintain uniformity, same stock solution was used throughout.

Carrier free ^{106}Ru in the form of ruthenium chloride was obtained from Isotope Division of Bhabha Atomic Research Centre. All other chemicals used were of analar grade.

Procedure—To nitrosylruthenium stock solution known volumes of standard potassium permanganate solution were introduced with constant stirring. Manganese dioxide was precipitated by the drop-

wise addition of hydrogen peroxide. pH adjustments were made using sodium hydroxide or nitric acid solutions. After allowing the precipitates to settle for about 2 hr, a 5 ml portion of the supernate was filtered through Whatman No. 42 filter paper. The filtrate was counted for gamma activity in a well type NaI(Tl) detector connected to a single channel analyser. Errors due to losses of the tracer activity by sorption on filter paper, increase in volume of the tracer due to the addition of potassium permanganate, hydrogen peroxide, alkali and acid solutions were taken in to account. Coprecipitation yields were computed and are expressed in terms of percentage of radionuclide in the precipitate.

Effect of electrolytes on the coprecipitation yields was studied by introducing known amounts of sodium sulphate to the tracer stock solution before treating with permanganate and precipitating the oxide.

Results and Discussion

The results are expressed in terms of coprecipitation yield, Y (%) represented by the relation

$$Y = \frac{I_s - F_s}{I_s} 100$$

where I_s is the initial activity of the test solution, F_s is the residual activity of the aqueous phase after precipitation.

Coprecipitation yield remains unaffected in the pH range 8 to 10. Coprecipitation yields as high as 98% and more were obtained under these conditions. A gradual decrease in coprecipitation was observed with the increase in pH beyond 10. As the low and medium active waste waters are near neutral², only alkaline pH was studied.

Aging of nitrosylruthenium in contact with permanganate prior to precipitation has significant effect on its ultimate precipitation with manganese dioxide (Fig. 1). At room temperature a minimum of 4 hr contact time is found necessary for obtaining maximum coprecipitation yields. Aging period is

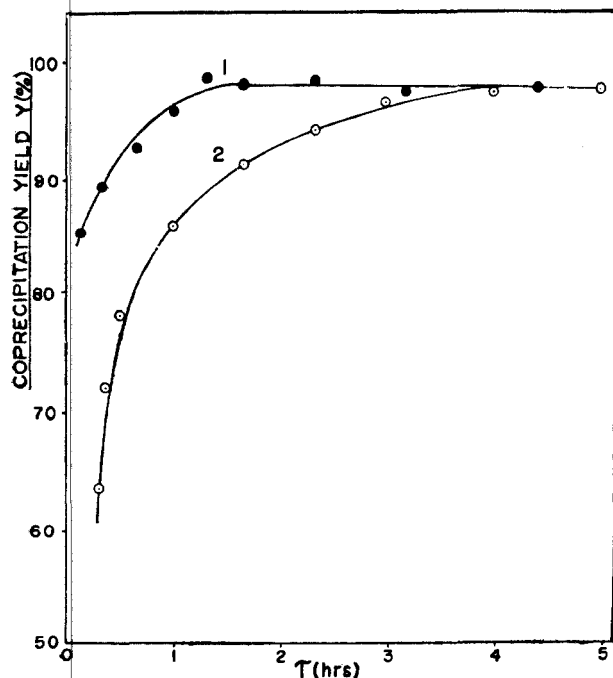


Fig. 1 — Aging of nitrosyl ruthenium in contact with potassium permanganate 'T' time in hours [1, at 60°C temperature; 2, at 28°C temperature]

considerably reduced with increase in temperature. At least 100 mg of manganese are required to be added as permanganate and subsequently precipitated as oxide for the scavenging process to be effective.

The problem of mechanism of coprecipitation is rather complex, there being only few methods for distinguishing between the various mechanisms of sorption of trace elements both on performed and preformed precipitates. One of the methods involves studying the influence of electrolytes on the coprecipitation yield. This method gives information on the probability of ion-exchange in sorption or coprecipitation. Added sodium sulphate is practically without effect on the extent of coprecipitation. For instance at sodium sulphate concentration of 0.0005, 0.001, 0.005, 0.01, 0.1 and 1.0M the coprecipitation yields are 97.1, 97.01, 96.81, 96.12, 95.68 and 93.54% respectively, thus ruling out the ion-exchange mechanism. Direct fixation of nitrosylruthenium complex species by surface adsorption has been tested with the help of externally formed precipitates obtained by the action of H_2O_2 on $KMnO_4$. Precipitates were centrifuged, washed with distilled water and then suspended in nitrosylruthenium tracer stock solution. Only a small fraction (~20%) of the total activity was taken up by the precipitated Mn(IV) oxide, indicating the inability of Mn(IV) oxide to directly fix the complex species on the surface. This implies that permanganate plays an important role in the overall process of coprecipitation. Role of permanganate may be considered as similar to the action of sodium hypochlorite which has been reported to oxidize nitrosylruthenium to ruthenates and perruthenates in alkaline media¹⁰. Oxidation of nitrosylruthenium by permanganate

has been tested with the help of ion-exchange resin. A column of 2 g of dry deacidite FF-IP (NO_3^- form) was used for this purpose. Nitrosylruthenium tracer stock solution (50 ml) was kept in contact with $KMnO_4$ (equivalent to 100 mg/litre Mn) for about 4 hr at room temperature and then passed through the column at the rate corresponding to the specific load of 5. Radio ruthenium tracer was completely retained by the column, indicating the quantitative change of nitrosylruthenium into negatively charged species. Ruthenates and perruthenates are analogous to the corresponding manganese compounds and yield hydrous dioxide on reduction. Hydrogen peroxide would thus generate Ru(IV) oxide together with Mn(IV) oxide from solutions containing mixture of permanganate and the corresponding species of the tracer. This implies that hydrous dioxide is the ultimate product derived from nitrosylruthenium through the oxidation-reduction cycle and it is in this form that ruthenium is finally precipitated with manganese. To further understand the nature of process responsible for the ultimate precipitation of the tracer, another series of experiments were conducted. In these studies, after having allowed the nitrosylruthenium tracer to age in contact with permanganate, the extent of manganese precipitated was varied by varying the amounts of hydrogen peroxide added and the corresponding amounts of the tracer activity removed from the liquid phase was determined. The values of λ , the heterogeneous enrichment factor and D , the homogeneous distribution factors were calculated using following expressions^{11,12}.

$$\lambda = \log \frac{\text{Initial tracer}}{\text{Tracer in soln}} / \log \frac{\text{Initial carrier}}{\text{Carrier in soln}}$$

$$D = \left(\frac{\text{Tracer}}{\text{Carrier}} \right)_{\text{solid}} / \left(\frac{\text{Tracer}}{\text{Carrier}} \right)_{\text{soln}}$$

Data in Table 1 show that within the limits of experimental errors, D values obtained are fairly constant in the whole range, when fraction of manganese precipitated is varied. The constancy of D values indicates that tracer is finally removed by way of isomorphous mixed crystal formation. The occurrence of isomorphism can be expected only from similar compounds and is true in the case of dioxides of the two elements as RuO_2 is reported to

TABLE 1 — DISTRIBUTION OF NITROSYLRUTHENIUM IN HYDROUS Mn(IV) OXIDE

Manganese precipitated (%)	Tracer in precipitate (%)	D	λ
28.60	90.50	23.78	6.98
42.00	94.88	25.60	5.42
43.40	95.00	24.77	5.26
46.20	95.68	25.78	5.06
50.00	96.29	25.96	4.75
71.20	98.48	26.21	3.36

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behave similarly to MnO_2 (ref. 10). This supports the formation of hydrous dioxide of the tracer via ruthenates and perruthenates, as the ultimate product. Thus it may be concluded that permanganate plays a dual role both as an oxidant as well as a source of hydrous Mn(IV) oxide. Nitrosylruthenium on undergoing oxidation-reduction process is ultimately precipitated as hydrous dioxide.

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