

**Charge and Nature of Technetium Species Produced  
In the Reduction of Pertechnetate  
by Stannous Ion**

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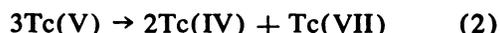
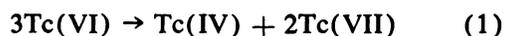
*By using a cation-exchange distribution technique, the net charge of the technetium species produced in the reduction of pertechnetate by stannous ion at  $\text{pH} \leq 2$  has been determined to be +2. The species carrying this charge is either the dihydroxy technetate ( $\text{Tc}(\text{OH})_2^{2+}$ ) ion or the oxotechnetate ( $\text{TcO}^{2+}$ ) ion. These species are hydrolysed to technetium dioxide dihydrate ( $\text{TcO}_2 \cdot 2\text{H}_2\text{O}$ ) at higher pH.*

*The advantage of the ion-exchange distribution technique for these studies is that they can be done with carrier-free technetium rather than at the high concentrations required for the more conventional methods of ion-charge determination. The results, therefore, are more likely to be applicable to the situation existing in the routine preparation of Tc-99m radiopharmaceuticals.*

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The first data on the chemistry of technetium were published by Perrier and Segré in 1937 and 1939 (1,2). Interest in technetium chemistry centered around its separation as  $\text{TcO}_4^-$  from the fission products of U-235 (3-6). The extraction of lower-valence compounds as complex anions, however, led to studies of other Tc valence states. The various physical methods employed included spectrophotometry (3,7-12), polarography (3,7,13-16), potentiometry (3,17,18), coulometry (3,7,15,19,20), electrophoresis (21), and solvent extraction (22).

Through these and other studies, it was established that Tc(VII) and Tc(IV) are the most stable oxidation states of technetium. In halide solutions (3,7, 23-25) and in the absence of complexing agent, Tc(VI) and Tc(V) disproportionate as shown below:



Gorski and Koch (21) and Guennec and Guillau-

mont (22) were among the few workers who sought to identify the reactive intermediate of reduced  $\text{TcO}_4^-$ . On the basis of electrophoretic and solvent-extraction behavior they proposed formation of  $\text{TcO}^{2+}$  and  $\text{TcOOH}^+$  at pH 1 and pH 2, respectively.

With the widespread application of Tc-99m in the formulation of a variety of radiopharmaceuticals (26), it has become important to study both the valence state of technetium present in these radiopharmaceuticals and the net charge on the reactive intermediate of the reduced technetium species. Eckelman and co-workers (27) have proposed the formation of Tc(IV)-diethylenetriaminepentaacetic acid (DTPA), while Steigman and Richards (28)

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proposed the formation of mixed Tc(III)-Tc(IV)-DTPA and also Tc(IV) citrate.

The present study deals with determination of the charge on the technetium species produced in the reduction of pertechnetate ion using stannous ion. We have chosen to use the technique of ion-exchange distribution because with this method studies can be carried out with carrier-free technetium. Other more conventional methods of charge determination require chemical amounts of compounds and may not reflect the true situation in typical radiopharmaceutical preparations.

### THEORY

Determination of the charge on a cation, anion, or complex species has been the objective of much research. Potentiometric, polarographic, coulometric, solvent-extraction, and ion-exchange methods (depending on the nature of the system under investigation), have been found useful for this purpose (29,30). In this study, an ion-exchange distribution method introduced first by Schubert (31) and developed further by Y. Marcus (32) was used to determine the Tc charge following reduction of the  $TcO_4^-$  ion. The method has the advantage of being applicable to solutions containing very low concentrations or carrier-free concentrations (as in this investigation) of technetium.

With this method we measure the equilibrium distribution of a cation, anion, or complex species present in trace quantity between an ion-exchange resin (cation or anion) and different concentrations of bulk neutral electrolyte. The distribution of the trace ion,  $D_o$ , is defined as follows:

$$D_o = \frac{\text{Activity in 1 g dry resin}}{\text{Activity in 1 g solution}} = \frac{[\bar{M}^{y+}]^n}{[M^{y+}]^n} \quad (3)$$

In the examination of the valence of a cationic species by this method, the trace species,  $M^{y+}$ , of charge ( $y$ ) is exchanged with the bulk cation,  $C^{n+}$ , of known charge ( $n$ ) and concentration as shown:



Bars are placed above a component to represent the resin phase. The equilibrium quotient,  $Q_o$ , for this reaction is given by:

$$Q_o = (D_o)^n \frac{[C^{n+}]^y}{[\bar{C}^{n+}]^y} \quad (5)$$

On rearrangement of eqn 5:

$$D_o = (Q_o^{1/n}) \frac{[\bar{C}^{n+}]^{y/n}}{[C^{n+}]^{y/n}} \quad (6)$$

$$\text{hence, } \log D_o = \frac{1}{n} \cdot \log Q_o + \frac{y}{n} \cdot \log [\bar{C}^{n+}] - \frac{y}{n} \cdot \log [C^{n+}] \quad (7)$$

Since  $Q_o$  and  $\bar{C}$  are constant:

$$\log D_o = \text{constant} - \frac{y}{n} \cdot \log [C^{n+}] \quad (8)$$

The slope of a plot of  $\log D_o$  against  $\log [C^{n+}]$  is thus  $y/n$  where  $y$ , as previously stated, is the charge on the unknown cationic species and  $n$  is the well-defined charge of the bulk cation species.

When the bulk electrolyte is monovalent—e.g., sodium perchlorate or perchloric acid—equation (8) reduces to:

$$\log D_o = \text{constant} - y \log [C^+]; \quad (9)$$

the slope of  $\log D_o$  against  $\log [C^+]$  then equals the charge,  $y$ , on the trace ion.

When the bulk electrolyte is divalent—e.g., stannous perchlorate—equation (8) becomes:

$$\log D_o = \text{constant} - \frac{y}{2} \cdot \log [C^{2+}], \quad (10)$$

and the slope of a plot of  $\log D_o$  against  $\log [C^{2+}]$  equals one half the charge,  $y$ , on the unknown ion.

### MATERIALS AND METHODS

**Chemicals and their preparation for use.** The radionuclide Tc-99m was obtained in the form of  $TcO_4^-$  ion in a saline solution\*. The carrier-free  $^{99m}TcO_4^-$  was extracted from Mo-99 in 5N NaOH solution using a modified version of the methyl-ethyl ketone (MEK) extraction method of Lathrop and co-workers (33). Before the extraction, two or three drops of hydrogen peroxide were added to the solution of Mo-99 to ensure the complete oxidation of all lower-valence states of technetium to  $TcO_4^-$ , which is easily extracted by MEK (34). The MEK layer was separated and evaporated to dryness in a water bath. The sodium pertechnetate was redissolved in 0.9% saline solution, sterilized by membrane filtration (0.2  $\mu$ ), and then autoclaved. The small amounts of Tc-99 in the "carrier-free" Tc-99m do not affect the results of this study. They are well below the resin saturation level.

Carrier-free zirconium-95 was obtained in 0.92 N oxalic acid†. One ml of 1 N nitric acid was added to the vial containing 0.05 ml of the Zr-95; then 0.5 ml was pipetted into a 10-ml separatory funnel, to which 1 ml of 10 M nitric acid was added. Potassium permanganate (0.1 N) was added dropwise to the solution in the funnel until the solution turned pink, indicating the complete oxidation of oxalic acid. Further purification and removal of  $HNO_3$  was

done by extracting the Zr-95 into benzene-trifluoroacetic acid solution. The Zr-95 was back-extracted into a small volume of 2.0 M HClO<sub>4</sub>.

To ensure complete reduction of <sup>99m</sup>TcO<sub>4</sub><sup>-</sup> ion, stannous perchlorate [Sn(ClO<sub>4</sub>)<sub>2</sub>] was the preferred bulk electrolyte. The Sn(ClO<sub>4</sub>)<sub>2</sub> was prepared by the method of Noyes and Toabe (35). Cupric oxide was slowly added to equal volumes of boiling HClO<sub>4</sub> and triply distilled water in a well-ventilated hood. The deep-blue cupric perchlorate solution was cooled and the supernatant solution decanted. Excess tin metal (30 mesh) was added to the above solution. The copper was completely displaced as a spongy deposit leaving a clear colorless Sn(ClO<sub>4</sub>)<sub>2</sub> solution. This was filtered through an asbestos column in an atmosphere of nitrogen. It was stored in a glass-stoppered bottle over metallic tin in a nitrogen atmosphere. The concentration of the Sn(ClO<sub>4</sub>)<sub>2</sub> was determined by titration with iodine using starch indicator.

To prepare the cation-exchange resin AG-50W-X8, 50–100 mesh (hydrogen form) for the distribution studies, it was first converted with at least a ten-fold excess of 0.05 M Sn(ClO<sub>4</sub>)<sub>2</sub> solution of predetermined Sn<sup>2+</sup>/H<sup>+</sup> concentration ratio. It was then washed with triply distilled water until the pH of the eluent equalled the pH of the elutriant. The resin, air-dried at room temperature, was isopiesticly equilibrated with a saturated solution of ammonium chloride under nitrogen to define its moisture content.

In order to study the hydrolytic tendency of the species produced in the reduction of TcO<sub>4</sub><sup>-</sup> ion by Sn<sup>2+</sup>, it was necessary to vary the pH of the bulk electrolyte in the distribution studies. To keep the variation of pH from affecting the value of Q<sub>0</sub>, which must remain invariant for Eqs 9 and 10 to be valid, the ratio [H<sup>+</sup>]<sup>2</sup>/[Sn<sup>2+</sup>] was kept constant at 1.0 in all stannous-ion solutions, including the one used to prepare the stannous resin. To determine the hydrogen-ion concentration in the Sn(ClO<sub>4</sub>)<sub>2</sub> solution, a portion of this solution was diluted and its pH measured. From the measurement, the hydrogen-ion concentration in the Sn(ClO<sub>4</sub>)<sub>2</sub> solution was calculated and appropriate adjustment of the perchloric acid was made in each of the Sn(ClO<sub>4</sub>)<sub>2</sub> solutions used in the distribution studies.

**Experimental procedure.** In the distribution experiments, the stannous form resin prepared as described above was weighed into polyethylene vials previously flushed with nitrogen. The vials were immediately capped. About 10 ml of the bulk electrolyte at the several different concentrations selected for study (previously bubbled with wet nitrogen) were then pipetted into each of the vials. The trace

amount of Tc-99m as TcO<sub>4</sub><sup>-</sup> was introduced next into each vial, which was immediately recapped and reweighed. To establish the time to reach equilibrium, the decrease of activity in the solution phase of duplicate vials was determined after periods of 1, 3, 6, 9, 12, 18, and 21 hr. No change in the activity of the solution was observed after 18 hr, and all experiments were subsequently equilibrated for 24 hr. Also, the H<sup>+</sup> ion concentration was measured by titration with standardized sodium hydroxide, both before and after equilibration, to show that there was no change in the hydrogen-ion concentration of the Sn(ClO<sub>4</sub>)<sub>2</sub>-HClO<sub>4</sub> solution. This result is to be expected on the basis of Tobias's (38) examination of this aspect. In the pH range of this study, 2.5 × 10<sup>-3</sup> M Sn(ClO<sub>4</sub>)<sub>2</sub> was shown not to hydrolyze.

To demonstrate the validity of the method used, distribution experiments were carried out with trace Na-22 and Zr-95 ions of known charge with the Sn(ClO<sub>4</sub>)<sub>2</sub>-HClO<sub>4</sub>-AG-50X-8 resin system.

**General procedure for counting.** Disposable syringes were used to introduce the equilibrated solution into preweighed counting tubes. The tubes were reweighed. Although these aliquot weights varied, depending on the salt concentration, the solution always filled the counting tube to the same level. In this way, constant counting geometry of the samples in the crystal well counter was assured.

Activity in the equilibrated resin was determined separately after removal of the supernatant solution. Sample geometry was controlled as before. Removal of most of the supernatant solution was followed by suction filtration, and the resin was dried to a constant weight. To ensure that negligible solution had been absorbed by the resin, the resin weight after equilibration was compared with its weight before equilibration. The former never exceeded the latter.

## RESULTS AND DISCUSSION

**Net charge on technetium species.** Using tracer concentrations of sodium ion, zirconium ion, and the technetium species, the distributions, D<sub>0</sub>, between the resin and the solution phase were measured as functions of both stannous- and hydrogen-ion concentrations. These data are presented in graphical form in Figs. 1–6. The molar concentrations of stannous perchlorate and hydrogen ion were relatively low, and concentration has been taken as equal to activity.

With an ion of known charge, Na<sup>+</sup>, the measured slopes are 1.2 and 0.63 (Figs. 1 and 2) when log D<sub>0</sub> is plotted against log [H<sup>+</sup>] and log [Sn<sup>2+</sup>], respectively. Within experimental error, these slopes

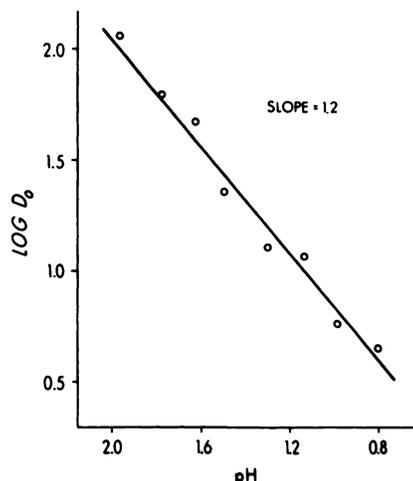


FIG. 1. Distribution,  $D_o$ , of Na-22 between resin and  $\text{HClO}_4$ - $\text{Sn}(\text{ClO}_4)_2$  solution phases plotted against pH.

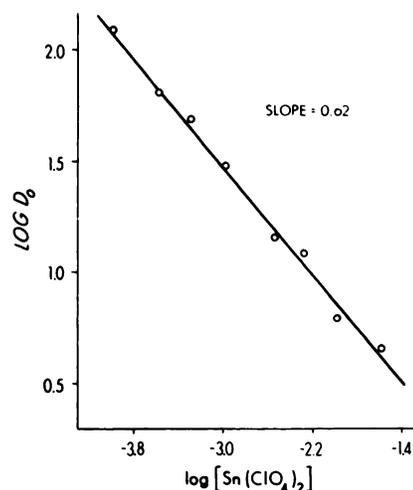
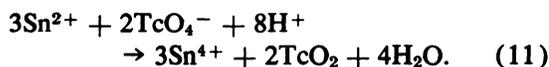


FIG. 2. Distribution,  $D_o$ , of Na-22 between resin and  $\text{HClO}_4$ - $\text{Sn}(\text{ClO}_4)_2$  solution phases plotted against  $\text{Sn}(\text{ClO}_4)_2$  concentration.

correspond to the known charge of +1 on  $\text{Na}^+$  ion, thus confirming the reasonable control of the value of  $Q_o$  by the experimental conditions.

The measured slopes in Figs. 3 and 4 are 2.18 and 0.98 respectively, indicating a technetium species with a charge of +2.0. The generally accepted redox reaction between  $\text{TcO}_4^-$  and  $\text{Sn}^{2+}$  at high concentrations is



With Tc(VII) reduced to Tc(IV) by  $\text{Sn}^{2+}$ , the most likely technetium species carrying a charge of +2 is either  $\text{Tc}(\text{OH})_2^{2+}$  or  $\text{TcO}^{2+}$ .

Gorski and Koch (21) have studied the net charge of tetravalent technetium produced by the reduction of  $\text{NH}_4^{99}\text{TcO}_4$  in  $\text{HClO}_4$  by hydrazine, using the electrophoresis method. At pH 1 they determined the charge on the Tc(IV) ion in solution to be +2. They suggested that the Tc(IV) species is  $\text{TcO}^{2+}$ , which hydrolyzes to  $\text{TcOOH}^+$  and finally to  $\text{TcO}(\text{OH})_2$  (or  $\text{TcO}_2 \cdot \text{H}_2\text{O}$ ). Guennec and Guillaumont (22), using a solvent-extraction method, have proposed the existence of  $\text{TcOOH}^+$  at pH 1. Some of the extraction coefficients obtained in these experiments, however, were very low and subject to sizeable error. At any rate, these two studies point to the existence of cationic species in solution resembling those pro-

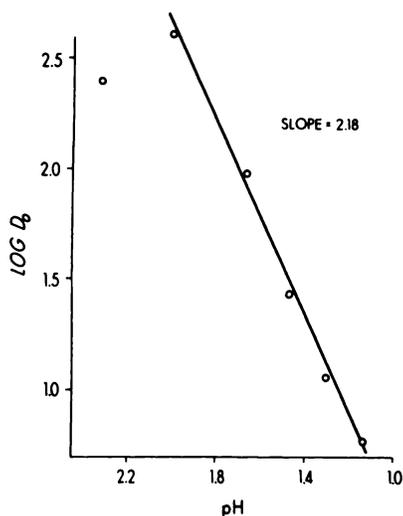


FIG. 3. A reduced technetium-99m species is produced by reduction of pertechnetate with  $\text{Sn}^{2+}$ ; its distribution,  $D_o$ , between the resin phase and  $\text{HClO}_4$ - $\text{Sn}(\text{ClO}_4)_2$  solution is plotted against pH.

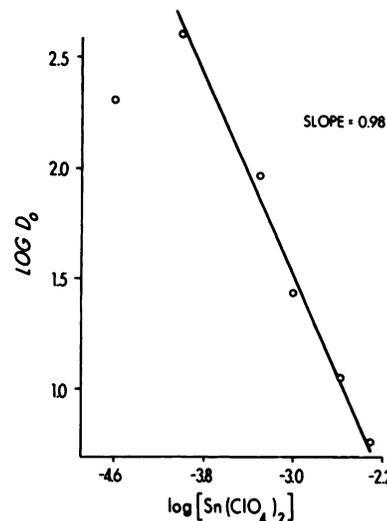


FIG. 4. The distribution,  $D_o$ , of reduced Tc-99m species (cf. Fig. 3) between resin phase and  $\text{HClO}_4$ - $\text{Sn}(\text{ClO}_4)_2$  solution is plotted against  $\text{Sn}(\text{ClO}_4)_2$  concentration.

**TABLE 1. APPROXIMATE CORRELATION BETWEEN DOMINANT SPECIES IN AQUEOUS SOLUTION AND FORMAL CHARGE OF METAL ION, Q, IN VARIOUS pH RANGES (Ref. 37)**

pH	Q							
	+1	+2	+3	+4	+5	+6	+7	+8
-1	H <sub>2</sub> O	H <sub>2</sub> O	H <sub>2</sub> O	H <sub>2</sub> O	OH <sup>-</sup>	OH <sup>-</sup>	OH <sup>-</sup>	O <sup>2-</sup>
7	H <sub>2</sub> O	H <sub>2</sub> O	OH <sup>-</sup>	OH <sup>-</sup>	OH <sup>-</sup>	O <sup>2-</sup>	O <sup>2-</sup>	O <sup>2-</sup>
15	H <sub>2</sub> O	OH <sup>-</sup>	OH <sup>-</sup>	O <sup>2-</sup>	O <sup>2-</sup>	O <sup>2-</sup>	O <sup>2-</sup>	O <sup>2-</sup>

posed in the present study.

We must point out that physical chemical techniques applied to solutions generally do not distinguish clearly between  $M(OH)_2^{2+}$  and  $MO^{2+}$  ions. In the present studies, the ion-exchange method used to determine the net charge on the technetium species does not discriminate between  $Tc(OH)_2^{2+}$  and  $TcO^{2+}$ . Using Jorgensen's approach (36) as modified by Selbin (37) and reproduced in Table 1, however, a reasonable judgment can be made as to which of the two ions,  $Tc(OH)_2^{2+}$  or  $TcO^{2+}$ , predominates at the pH under consideration. Table 1 shows the approximate pH intervals in which H<sub>2</sub>O, OH<sup>-</sup>, and O<sup>2-</sup> are the common ligands attached to a central ion with oxidation states varying from +1 to +8. Although this table suffers from several defects, as pointed out by Selbin, it appears that at the pH under consideration the Tc(IV) ion carrying the charge of +2 is  $Tc(OH)_2^{2+}$ . It is quite possible, however, that both  $Tc(OH)_2^{2+}$  and  $TcO^{2+}$  ions do exist in an equilibrium mixture.

**Hydrolysis of technetium (IV) species.** We mentioned that while studying the charge of the Tc species, we prepared the  $Sn(ClO_4)_2 \cdot HClO_4$  solution phase in such a way that the ratio of  $[H^+]^2/[Sn^{2+}]$  was kept constant, thus keeping  $Q_0$  invariant. As a consequence, it was also possible to examine the hydrolytic tendency of  $Tc(OH)_2^{2+}$  or  $TcO^{2+}$  ion.

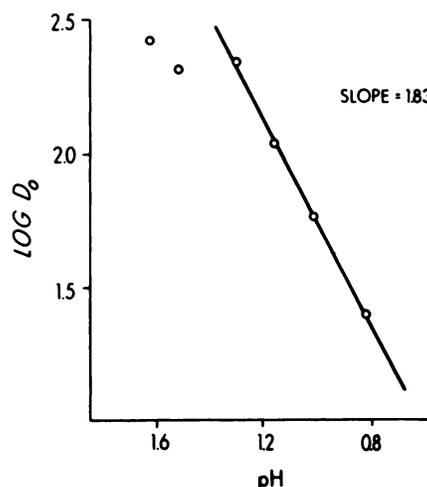
To enhance such interpretation of the distribution data, the parallel distribution behavior of Zr(IV), whose hydrolytic tendencies have been well studied (39-42), was examined to provide a basis for comparison.

Although zirconium belongs to subgroup 4b of the periodic chart of the elements, whereas technetium belongs to subgroup 7b, both elements are second-row transition (4d) elements. Zirconium (IV) has been shown to form dihydroxy or oxo cations (39-42) in solutions of the type proposed here for Tc(IV).

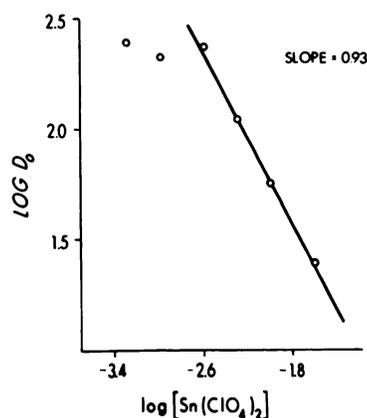
By using a solvent-extraction method and carrier-free Zr-95, Connick and McVey (39) have pro-

vided evidence that below pH 1, Zr(IV) exists as  $Zr(OH)^{3+}$ ; at pH 1 it exists as  $Zr(OH)_2^{2+}$ , and above pH 2 it undergoes further hydrolysis. In subsequent work using spectrophotometry, McVey (40) has also observed the presence of  $Zr(OH)_2^{2+}$  in dilute acid solutions. Lister and McDonald (41) have explained the exchange behavior of Zr in  $HClO_4$  by the presence of  $Zr(OH)_2^{2+}$  ion in solution. However, Larsen and Wang (42) in their cation-exchange studies have concluded the  $Zr^{4+}$  is unhydrolyzed in aqueous solution but is hydrolyzed in the resin to form the +2 and +3 ions.

Figures 3 and 4 [Tc(IV) species] and Figs. 5 and 6 [Zr(IV) species] exhibit the same log  $D_0$  slope pattern. The slope at low pH is identical for Tc and Zr. The breaks in the slope seen in the two systems occur at a lower pH in the Zr system, however. The



**FIG. 5.** Distribution,  $D_0$ , of Zr-95 between resin and  $HClO_4 \cdot Sn(ClO_4)_2$  solution phases plotted against pH.



**FIG. 6.** Distribution,  $D_0$ , of Zr-95 between resin and  $HClO_4 \cdot Sn(ClO_4)_2$  solution phases plotted against  $Sn(ClO_4)_2$  concentration.

charge of +2 (Figs. 5 and 6) determined in this work for Zr corresponds to the  $Zr(OH)_2^{2+}$  ion; the break in the slope of log  $D_0$ , above pH 1.5 indicates the initiation of further hydrolysis of the  $Zr(OH)_2^{2+}$  ion, corroborating the results of Connick and McVey (39).

It is suggested, therefore, that at pH 2,  $Tc(OH)_2^{2+}$  ion also begins to hydrolyze according to the following scheme:



The isolation of technetium dioxide dihydrate ( $TcO_2 \cdot 2H_2O$ ) is easily achieved by reduction of  $^{99}TcO_4^-$  using  $Sn^{2+}$  and centrifugation of the precipitate. A number of other workers (7,21,43) have reported the preparation of this compound. The colloidal form of this unreactive  $TcO_2 \cdot 2H_2O$  is found in many poorly prepared Tc-99m radiopharmaceuticals and is commonly referred to as "hydrolyzed reduced technetium" (27,28). This insoluble material may also include hydrolysis products of  $Sn^{2+}$ .

Numerous studies (41,42) have shown that Zr(IV) polymerizes in solution, but such studies were done with molar concentrations of Zr(IV) above  $5.0 \times 10^{-4}M$  (44) and at high acid ( $HClO_4$ ) concentrations. Such polymerization behavior for Tc(IV) may also occur under similar conditions. With "carrier-free" Tc-99m(IV), however, such polymerization behavior is unlikely to be due to the very low concentrations ( $10^{-9}$  to  $10^{-7}M$ ) of Tc-99m in solution and the high pH. This is true also for Zr(IV) (39,44).

#### CONCLUSION

By using the ion-exchange distribution technique, we have determined the net charge on the technetium species produced in the reduction of  $TcO_4^-$  by  $Sn^{2+}$  ion to be +2. The species most likely carrying this charge are either the dihydroxy technetate ion,  $Tc(OH)_2^{2+}$ , or the oxotechnetate ion,  $TcO^{2+}$ . Above pH 2 these hydrolyze to technetium dioxide dihydrate,  $TcO_2 \cdot 2H_2O$ .

#### FOOTNOTES

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