THE SOLUTION CHEMISTRY AND CHROMATOGRAPHIC BEHAVIOUR OF TECHNETIUM IN AQUEOUS HCl AND HBr

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INTRODUCTION

The literature on the solution chemistry and chromatography of technetium has been reviewed exhaustively in a number of recent articles[1–3] and several studies have been carried out on the behaviour of pertechnetate in HCl solutions. For example, reduction to $TcCl_6^{2-}$ was reported under various conditions and the formation of an unstable intermediate observed.

There seems to be no work so far on the solution chemistry of pertechnetate in HBr solutions, $Tc^{IV}Br_6^{2-}$ being usually prepared from $Tc^{IV}Cl_6^{2-}$ by evaporation with HBr.

The adsorption of pertechnetate on ion exchangers has been studied under various conditions and cationic character was even ascribed to pertechnetate owing to adsorption on cation exchangers.

In our recent work with ion exchange papers we have been able to distinguish between adsorption effects on resins and "true" ion exchange involving the charged groups on the resins and thought that data from ion exchange papers could explain the behaviour of pertechnetate better than column studies. This work is described in the first part of this paper.

While studying the adsorption of various species of Tc on cellulose paper we observed that the unstable intermediate (mentioned above) which seems to be pentavalent Tc is strongly adsorbed from dilute acid solutions and may thus be identified and studied in the presence of other Tc species.

Using this strong adsorption on cellulose paper of Tc(V) in combination with chromatography on cellulose anion exchange paper we were able to study the species present in HCl and HBr solutions. The solution chemistry of Tc in HCl could be amplified considerably and the behaviour in HBr observed. Finally the hydrolysis of $TcCl_6^{2-}$ and $TcBr_6^{2-}$ was investigated in dilute HCl and HBr (respectively). It was possible to show that $TcCl_6^{2-}$ is much more stable to hydrolysis than $TcBr_6^{2-}$.

EXPERIMENTAL

Chromatograms were all carried out by ascending development with small volume jars. Ion exchange papers were all first washed twice with acid (usually 2 N HCl) and distilled water and then converted to the required form by equilibrating for 30 min with a normal solution of the required cation or anion.

The technetium used in this work was a solution of ammonium pertechnetate (62.8 mg in 2 ml) supplied by the Radiochemical Centre, Amersham, England. This should be entirely the isotope mass 99 of half life $2.12 \cdot 10^5$ years and was found free of other radioelements by chromatography in various systems.

Two detection methods were used. A coloured spot was obtained by spraying with a solution of $SnCl_2$ and KCNS in 2 N HCl, the actual colour obtained depending on the other acids present on the paper, as well as the original valency of the Tc and the time of drying. The reagent also yields a coloured spot with perrhenate. Alternatively radioactive scans of 5 mm sections of the chromatograms were performed with a beta end-window counter. This has the advantage of giving quantitative results but has the disadvantage of not distinguishing closely moving bands which are readily perceived with the colour reagent.

The papers impregnated with inorganic exchangers were prepared by impregnating the paper with solutions of $Al(NO_3)_3$, $Fe(NO_3)_3$ and $ZrOCl_2$, respectively, and exposing these to an atmosphere of NH_3 followed by extensive washing with distilled water and drying in air.

In the work on the solution chemistry of Tc in HCl and HBr only two ion exchange papers were used, the strongly basic cellulose exchange paper of Macherey, Nagel & Co. (containing quaternary ammonium groups, capacity 0.3–0.4 mequiv./g) and the strongly acid cellulose exchange paper of Macherey, Nagel & Co. (containing sulphonic groups, capacity 0.4–0.7 mequiv./g). These were chosen in order to obtain separations of variously charged ions with only the adsorption properties of cellulose in addition to ion exchange effects. As will be seen in section (ii) this permitted the study of reversible complexing of Tc(V).

RESULTS

(i) The behaviour of pertechnetate and perrhenate on various exchange papers

Figure 1 shows the R_F values of perrhenate and pertechnetate on sulphonic resin paper, cellulose paper and quaternary ammonium resin paper.

It has already been shown by solvent extraction and paper chromatography with organic solvents that both $HReO_4$ and $HTcO_4$ strongly favour the non-aqueous phase and hence it is not surprising that they also adsorb strongly on the resin network of sulphonic as well as basic resins. This adsorption is highest with HCl and H_2SO_4 and lowest with HNO_3 and $HClO_4$. The separations obtained with perchlorate elution were explained so far by considering the competition between the strongly retained ClO_4^- ions for ReO_4^- and TcO_4^- ions. They may, however, equally well be explained by the competition of poorly hydrated ClO_4^- for adsorption sites on the organic network. The latter view is supported by the lower adsorption on cellulose paper in $HClO_4$ and HNO_3 as compared with HCl and H_2SO_4.

In the systems shown in Fig. 1 good separations were obtained either in moderately concentrated $HClO_4$, HNO_3 or in 8 N HCl. The latter is not likely to be due to a partial reduction in HCl as we could show that no reduction occurs in aqueous solution (*i.e.* in absence of the resin) when pertechnetate is allowed to stand in 8 N HCl for a time similar to that for development (*i.e.* about 1 h). This larger difference between the TcO_4^- and ReO_4^- spots in HCl is noteworthy as the difference in most other systems is almost constant.
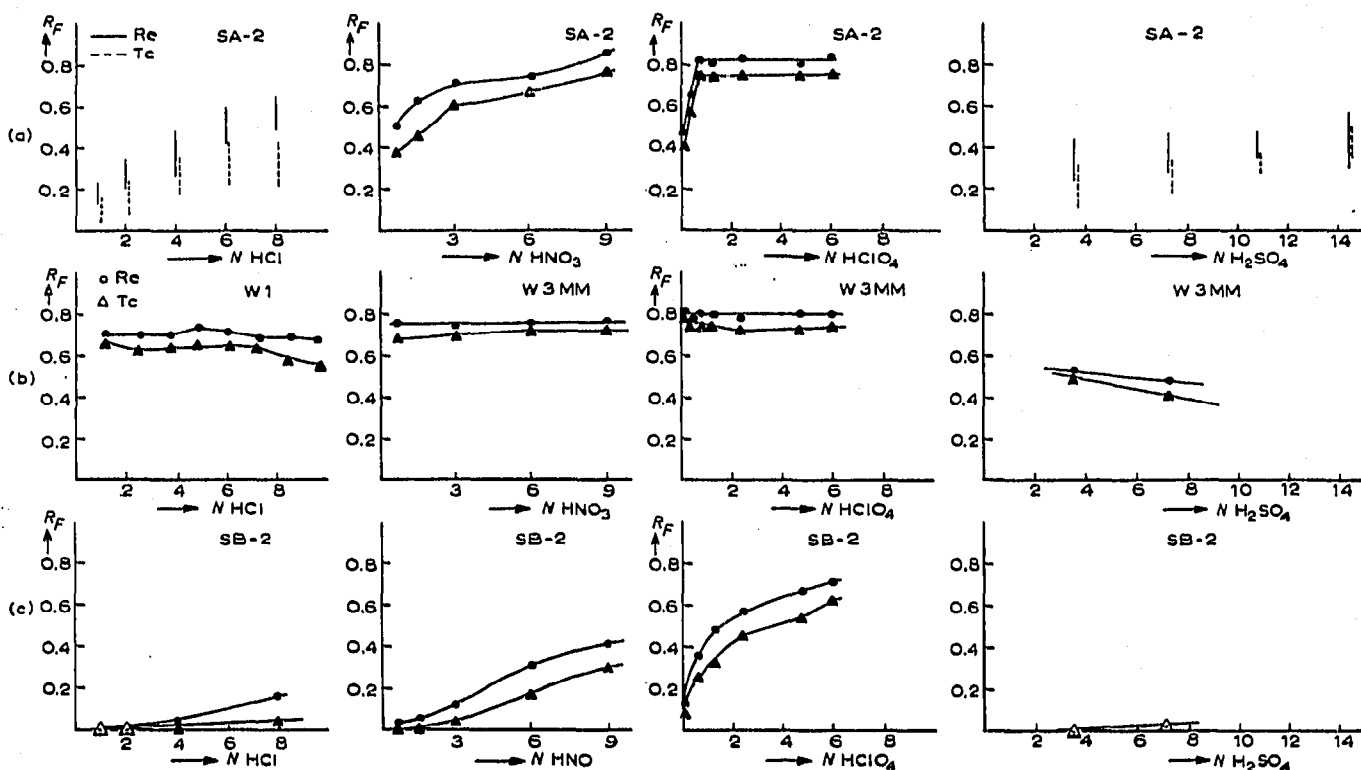
Fig. 1. R_F values of TcO_4^- and ReO_4^- plotted against the concentration of the eluant. (a) On sulphonic resin paper Amberlite SA-2; from left to right HCl, HNO_3, $HClO_4$ and H_2SO_4; (b) on Whatman No. 3MM cellulose paper, sequence as in (a); (c) on quaternary ammonium resin paper Amberlite SB-2, sequence as in (a). $\blacktriangle = TcO_4^-$; $\bullet = ReO_4^-$.

The salting-out effect on various resin and cellulose exchangers with $(NH_4)_2SO_4$ was studied as shown in Fig. 2. Here the differences in R_F values between Tc and Re seem to be almost constant while the adsorption is considerably increased with increased ammonium sulphate concentrations. This rather strong salting-out effect, which is opposite to the mass-action effect which may be expected in ion exchange, again shows that adsorption other than actual ion exchange plays a considerable role in the fixation of pertechnetate on to resins.

The adsorption on some inorganic oxides is shown in Fig. 3. Here papers impregnated with aluminium oxide, ferric oxide and zirconium oxide are compared with pure cellulose paper.

With various concentrations of neutral LiCl no differences between cellulose with and without inorganic oxides were noted and it may be concluded that adsorption in solutions more than 1 N in LiCl is negligible.

(ii) The chromatographic behaviour of Tc(V)

An unstable intermediate has been observed when TcO_4^- was reduced to $TcCl_6^{2-}$ in 6-8 M HCl at 100°[4]. According to CROUTHAMEL[5] this intermediate is most likely to be Tc(V) and while the present work does nothing to confirm this view we shall assume that this is correct and refer to the intermediate compound as Tc(V). In subsequent headings of this paper its stability in HCl and HBr will be discussed. For the studies described here solutions in HCl and HBr were used, in all of which high concentrations of Tc(V) were found during kinetic studies.
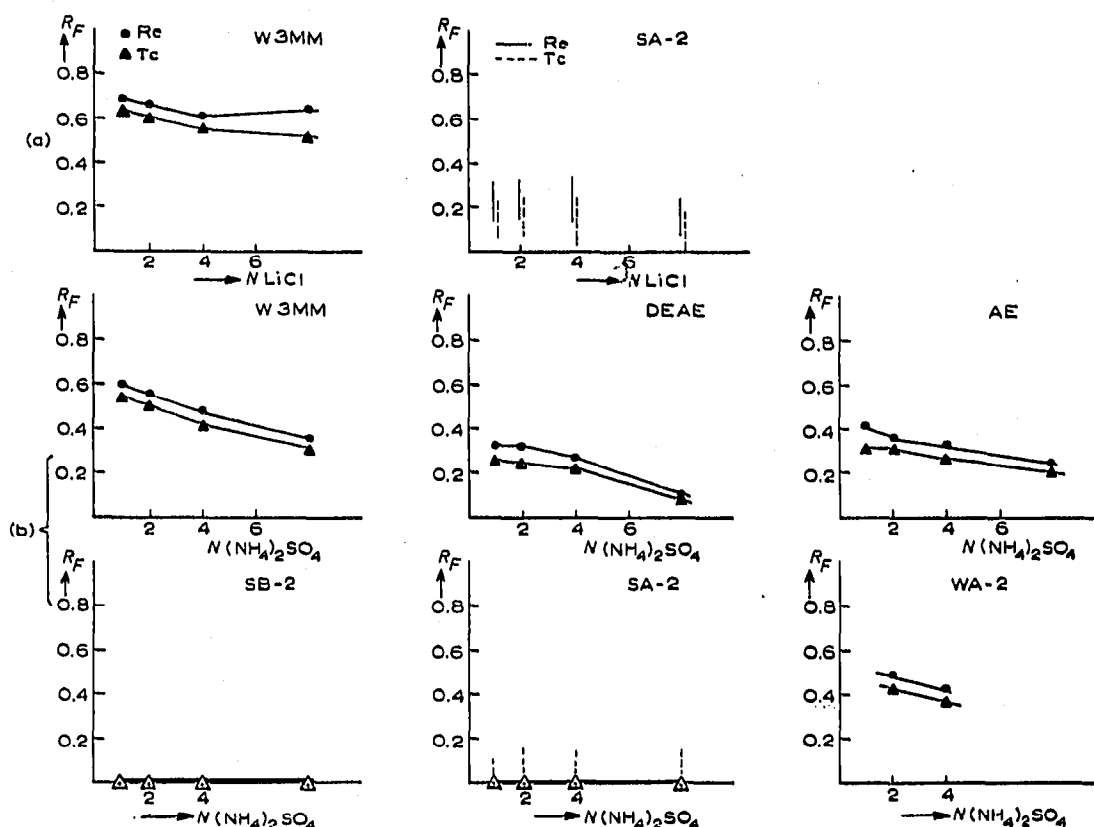
Fig. 2. R_F values of TcO_4^- and ReO_4^- plotted against the concentration of the eluant. (a) With LiCl on Whatman No. 3MM and Amberlite SA-2 paper; (b) with $(NH_4)_2SO_4$ on Whatman No. 3MM, Whatman DEAE paper, Whatman aminoethylcellulose paper, Amberlite SA-2 paper and Amberlite WA-2 paper. ▲ = TcO_4^-; ● = ReO_4^-.
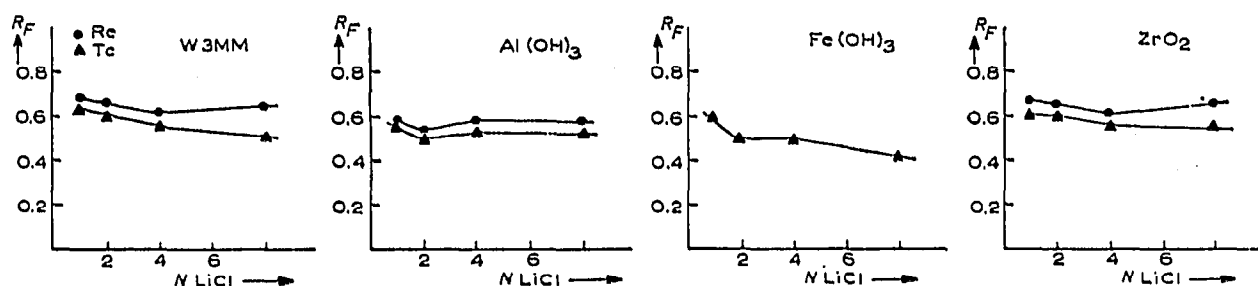
Fig. 3. R_F values of TcO_4^- and ReO_4^- on cellulose paper impregnated with inorganic oxides with LiCl as eluant. From left to right: cellulose paper, $Al(OH)_3$ paper, $Fe(OH)_3$ paper and ZrO_2 paper.

Fig. 4 shows the R_F values of Tc(V) in HCl, HBr and HClO$_4$. The increase in R_F values with the concentration of HCl and HBr would suggest complex formation with halide ions especially as such an increase does not occur with HClO$_4$. Thus the present results may be explained assuming that a neutral oxyhalide is present at low acid concentrations which may complex with halides.

If the R_F values on cellulose paper are correlated with those on the Macherey, Nagel strong anion exchange cellulose paper it is evident that a maximum of anionic behaviour is exhibited at about 1.8 N HBr and 1.2 N HCl (Fig. 4c).
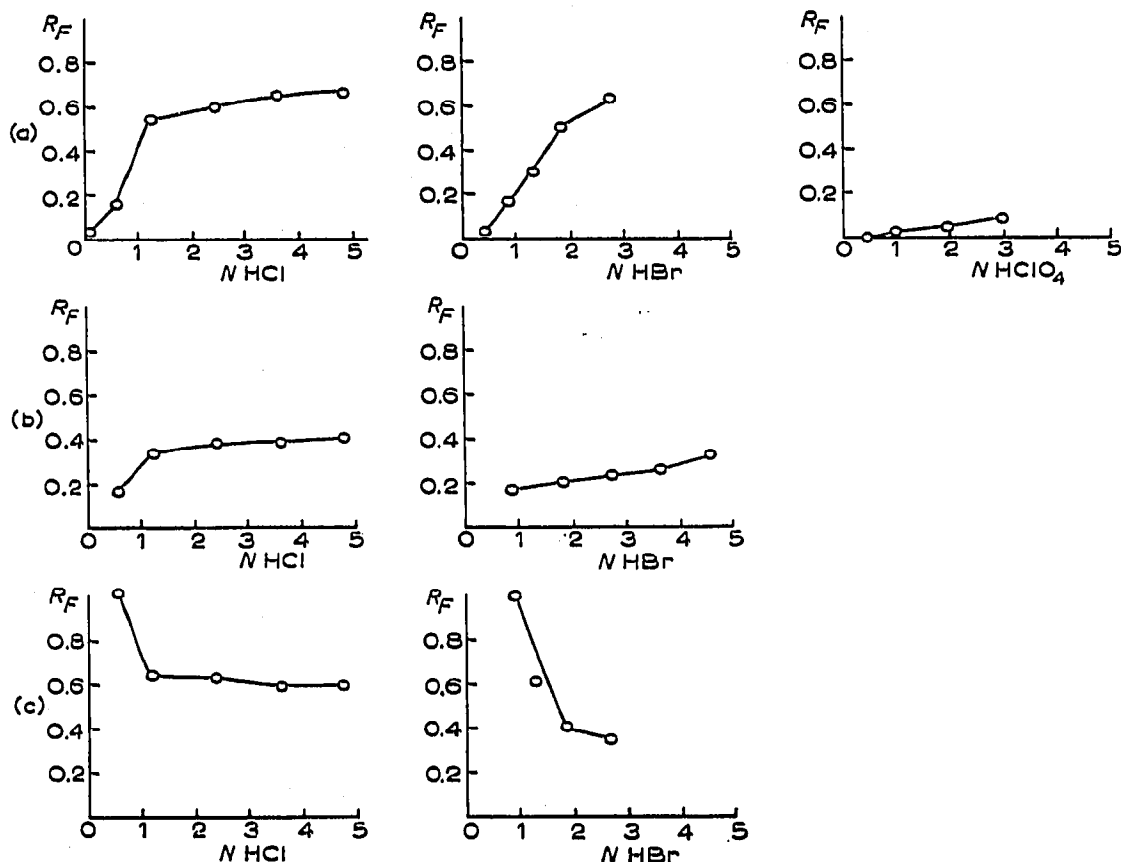
Fig. 4. R_F values of Tc(V). (a) On Whatman No. 3MM paper with HCl, HBr and HClO$_4$ as eluants; (b) on Macherey Nagel strong anion exchange cellulose paper with HCl and HBr as eluants; (c) R_F values on the anion exchange paper "corrected" for adsorption on the cellulose, *i.e.* R_F anion exchange paper/R_F cellulose paper.

The strong adsorption on cellulose paper from dilute acids is a unique feature of Tc(V), which permits its detection in the presence of TcO$_4^-$ as well as all of the Tc(IV) species so far studied which all travel well above R_F 0.5. Tc(V) when sprayed with SnCl$_2$-KCNS reagent instantaneously yields a colour like Tc(VII) while Tc(IV) only appears on standing.

(iii) The reaction of pertechnetate with conc. HCl at room temperature

Fig. 5 shows chromatograms of ammonium pertechnetate dissolved in conc. HCl developed with 0.6 N HCl on Whatman No. 3MM paper after 0, 1, 6, 24 and 48 h. Even after 48 h the preponderant species present is the slow-moving Tc(V). The solution turns yellow immediately on contact indicating that a small amount of Tc(IV) is already forming. While chromatograms on the anion exchange paper should have revealed the presence of Tc(VII), if still existent, there was no noticeable spot even at zero time. As the fast peak first decreases and then again increases after 1 hour we believe that a trace (*i.e.* less than 5 %) of Tc(VII) was perhaps present at the beginning but was already reduced after 1 h.

It seems thus that solutions in which about 80 % of the total Tc is present as Tc(V) may be prepared simply by dissolving pertechnetate in cold HCl, and these solutions are stable for at least 48 h.
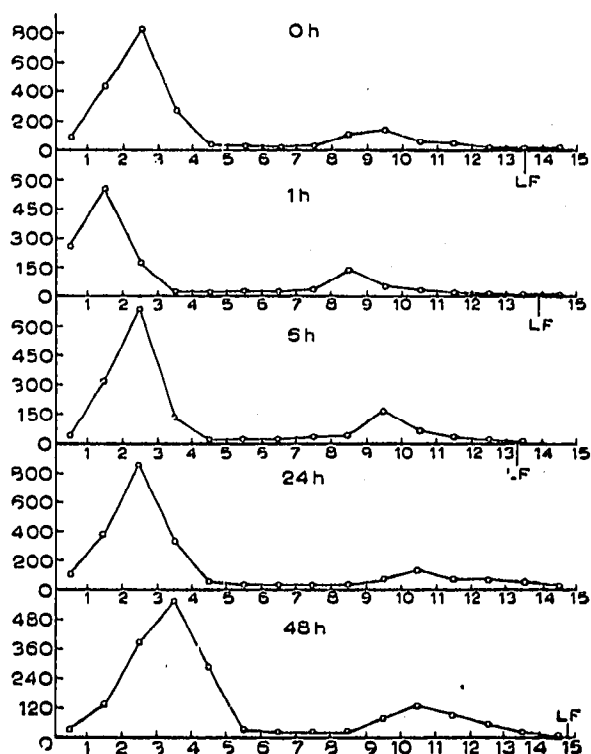
Fig. 5. The reaction of TcO_4^- with conc. HCl at room temperature. Chromatograms on Whatman No. 3MM paper developed with 0.6 N HCl and scanned for radioactivity. Ordinates: activity in counts/30 sec per cm. Abscissae: length of the chromatogram in cm. The point of application is on the left. The slow peak is Tc(V), the small fast peak all species of either Tc(VII) or Tc(IV). LF = liquid front.
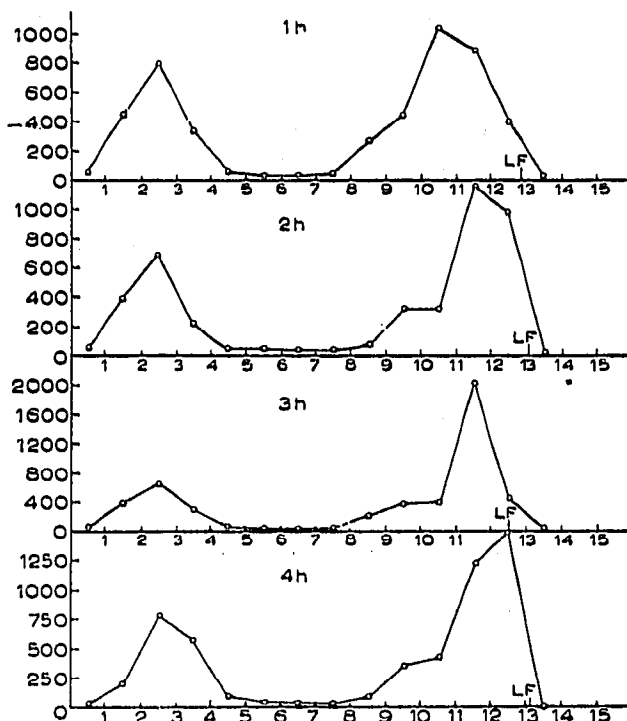

Fig. 6. Reaction of TcO_4^- with conc. HCl at 100°. Chromatograms on Whatman No. 3MM paper developed with 0.6 N HCl and scanned for radioactivity. Ordinates: activity in counts/30 sec per per cm. Abscissae: length of chromatogram in cm. The point of application is on the left. LF = liquid front.

Preliminary experiments in 8 N HCl showed that while no reduction of pertechnetate could be detected in one hour there was slow reduction. After 48 h the main species present is still Tc(VII) but both Tc(V) and Tc(IV) could also be detected.

During the work with HCl solutions we also tried to chromatograph on cellulose paper using 0.12 N HCl as solvent. After the strips had been dried and scanned for chromatography, the amounts did not correspond to those developed with higher concentrations of HCl. We believe that some Tc volatilised from the paper either during development or on drying. It is not clear which species becomes volatile under these conditions, and we intend to do further work on this problem.

(iv) The reaction of pertechnetate with conc. HCl at 100°

About 1 mg of ammonium pertechnetate was carefully dried in a vacuum desiccator and mixed with 0.25 ml conc. HCl in a micro-test tube and heated on a steam bath. Drops were withdrawn at intervals and chromatographed with 5 % HCl on Whatman No. 3MM paper. The chromatograms were scanned for radioactivity and the scans shown in Fig. 6 were obtained. It could be shown by chromatography on anion exchange paper that no pertechnetate was present after 30 min heating which was of course expected as it is reduced immediately even in the cold in conc. HCl to Tc(V). It is remarkable, however, that Tc(V) is present even after heating for 4 h.

These experiments were carried out three times and the amount of Tc(V) after 30 min was about 50 % and after 1 h about 30 %. The amount of Tc(V) seems to increase again after 3 h but this is due to the formation of crystals of $(NH_4)_2TcCl_6$ and not to a reoxidation of the Tc(IV) already formed.

Some reviews[1,2] quoting GERLIT[6] have stated that TcO_4^- is reduced in conc. HCl in one hour in the cold to $TcCl_6^{2-}$. This is of course not correct, nor was this claimed by GERLIT[6] who merely mentioned that TcO_4^- is completely reduced in one hour without mentioning specifically the valency of the reduction product.

(v) The reaction of pertechnetate with HBr at room temperature

As there seems to be no mention of the solution chemistry of pertechnetate in HBr in the literature so far, we have investigated this reaction in greater detail with various concentrations of HBr.

Fig. 7 shows the chromatograms obtained with Whatman No. 3MM paper using 0.9 N HBr as solvent.

In conc. HBr, Tc(V) does not exist any more after 24 h, while it is almost completely reduced in 80 % HBr only after 72 h, and in 60 % HBr begins to form after about 24 h. In up to 40 % HBr pertechnetate is not reduced even after 72 h.

In some HBr solutions Tc(IV), Tc(V) and Tc(VII) can exist in presence of each other and all 3 valencies may be separated on the anion exchange paper as shown in Fig. 8.

Tc(IV) separates here into two slow moving spots of which the slower seems to be $TcBr_6^{2-}$ and the faster $TcBr_5H_2O^-$ as will be shown in section (vii).

(vi) The reaction of pertechnetate with conc. HBr at 100°

Dry ammonium pertechnetate (about 1 mg) was dissolved in 0.25 ml of conc. HBr (Carlo Erba) and heated on a steam bath. After 30 min a sample was withdrawn and could be shown to contain only the $TcBr_6^{2-}$ ion by chromatography on anion exchange paper and Whatman No. 3MM paper.
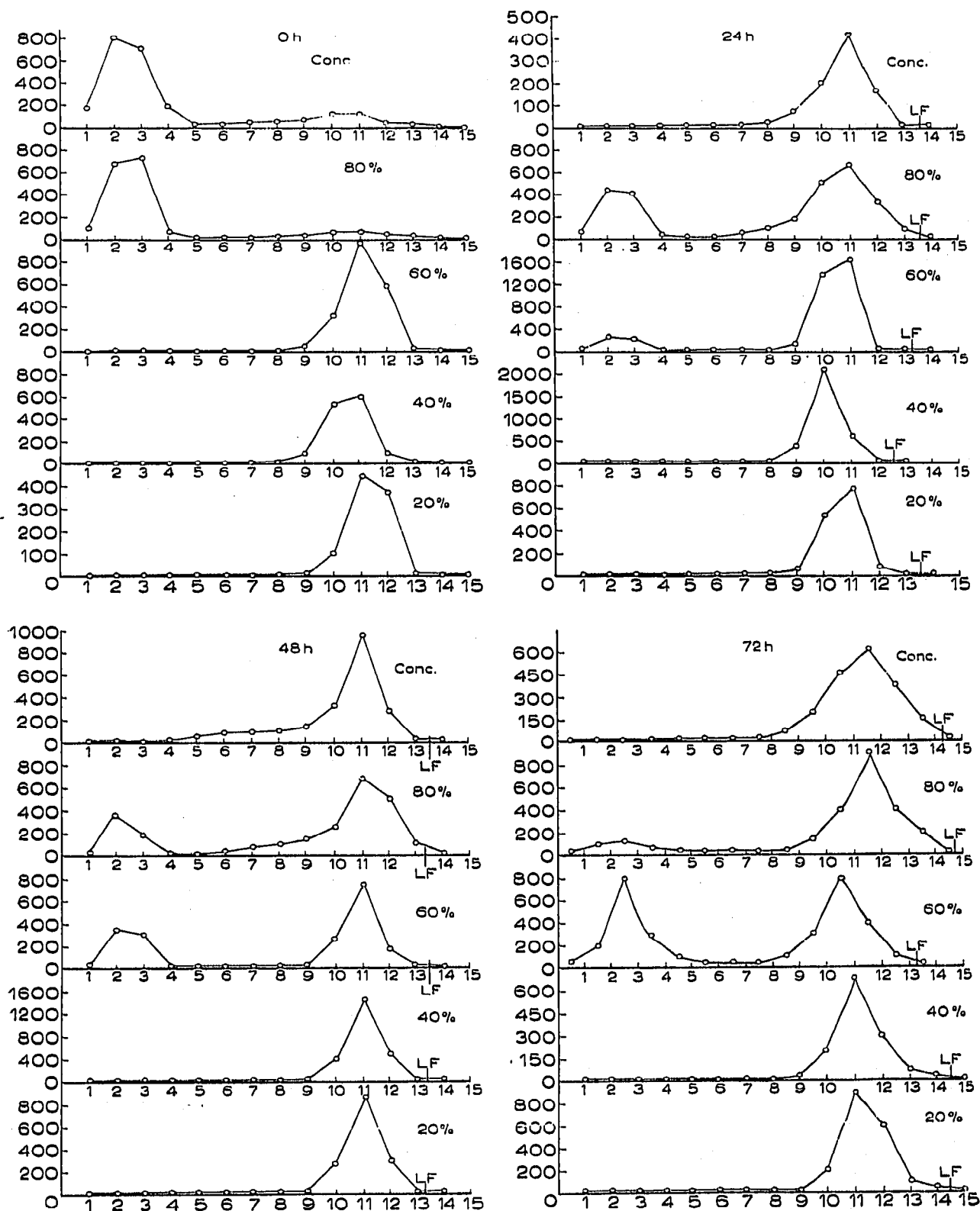
Fig. 7. The reaction of TcO_4^- with HBr at room temperature. Chromatograms on Whatman No. 3MM paper developed with 0.9 N HBr as solvent. Representation as in Figs. 5 and 6. From top to bottom: conc. HBr, 80 % HBr, 60 % HBr, 40 % HBr and 20 % HBr. On cellulose paper Tc(V) is separated from all Tc(IV) and Tc(VII) species. LF = liquid front.
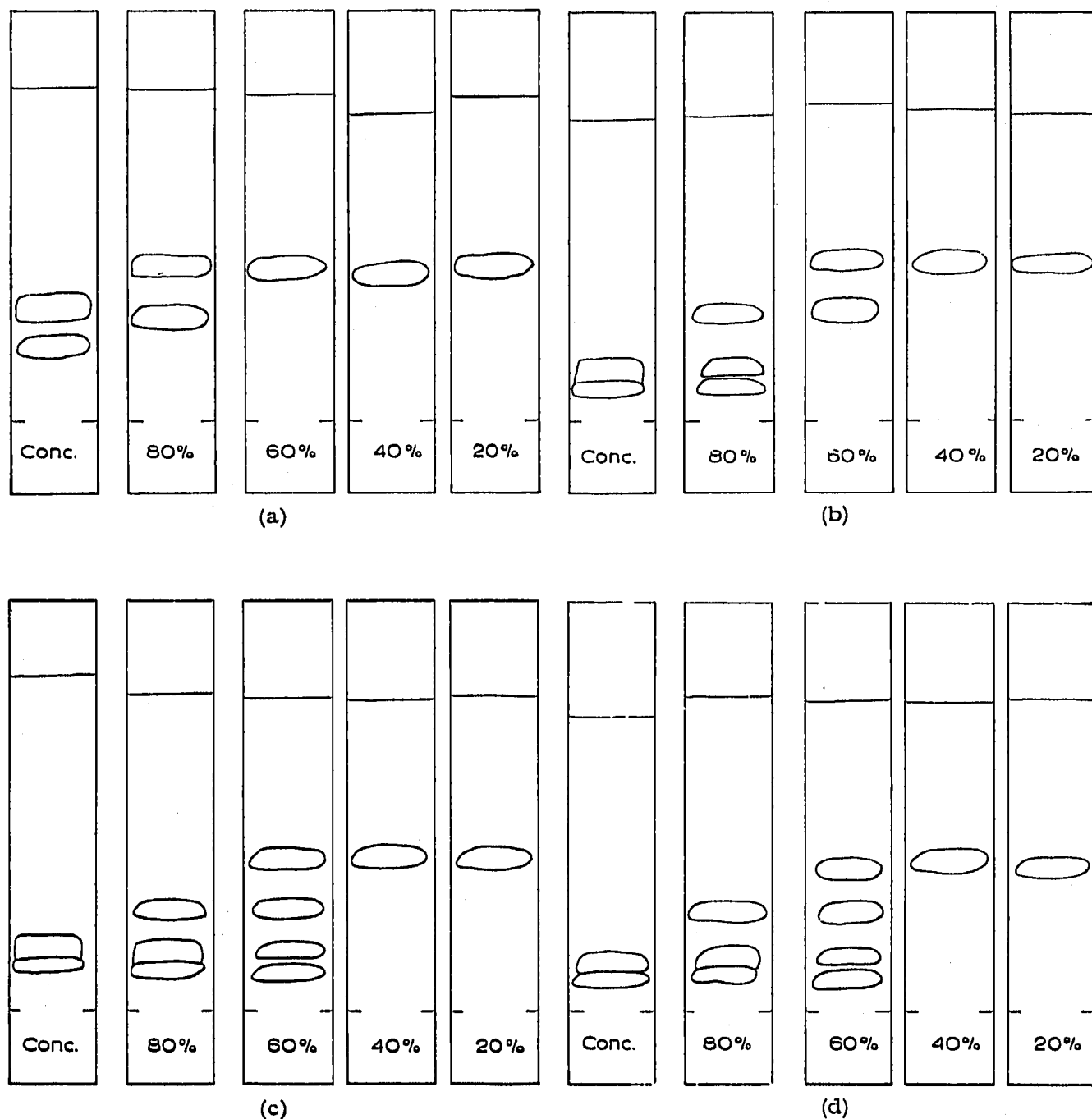
Fig. 8. The reaction of TcO_4^- with HBr at room temperature. Chromatograms on Macherey, Nagel strong anion exchange cellulose paper with 1.8 N HBr as solvent. Designs of chromatograms after spraying with $SnCl_2$–KNCS reagent (a) at o h, from left to right conc. HBr, 80 % HBr, 60 % HBr, 40 % HBr and 20 % HBr; (b) after 24 h; (c) after 48 h; and (d) after 72 h. The spot R_F 0.49 is TcO_4^-, the spot R_F 0.32 is Tc(V) while the two slow moving spots are species of Tc(IV).

(vii) *The hydrolysis of* $TcCl_6^{2-}$ *and* $TcBr_6^{2-}$

During the study of the reaction of pertechnetate with HBr as well as in some HCl solutions the intensely coloured halogeno Tc(IV) complexes were found to separate into two adjacent spots on chromatography with anion exchange paper.

It is already well known that both $TcCl_6^{2-}$ and $TcBr_6^{2-}$ undergo hydrolysis in aqueous solutions[7] and hence we suspected that the extra spot formed is due to a hydrolysis product. The study of the hydrolysis of $TcCl_6^{2-}$ and $TcBr_6^{2-}$ described below confirmed this and gave a general idea of the number of hydrolysed species which can be expected in dilute acid solutions.

(a) *The hydrolysis of* $TcBr_6^{2-}$ *in 0.9 N HBr at room temperature.* H_2TcBr_6 was prepared by heating pertechnetate with conc. HBr and diluting to 0.9 N. A chromatogram of this residue dissolved in 10 % HBr yielded one prominent peak of R_F 0.08 and traces only of other species when chromatographed with 20 % HBr on anion exchange paper. Fig. 9 shows scans of the radioactivity of chromatograms run after
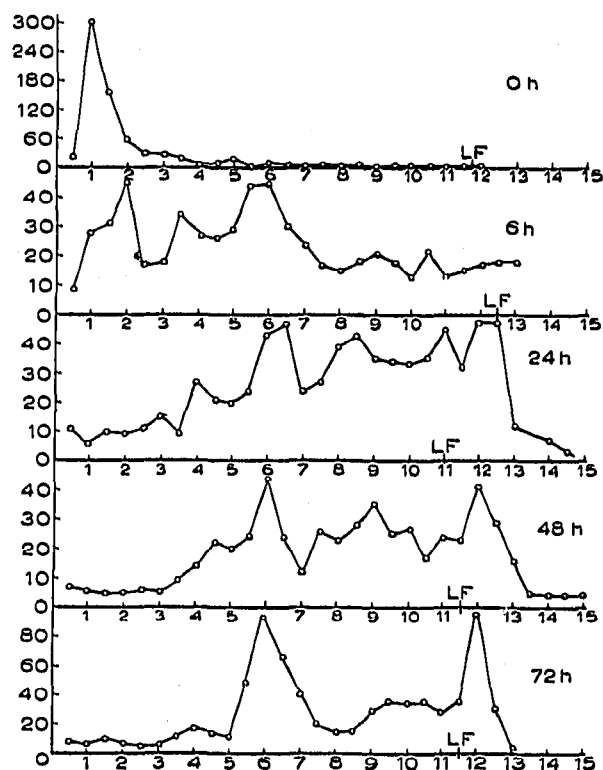

Fig. 9. Hydrolysis of $TcBr_6^{2-}$. Radioactivity scans of chromatograms on Macherey, Nagel strong anion exchange cellulose paper with 1.8 N HBr. Ordinates: activity in counts/30 sec per cm. Abscissae: length of the chromatogram in cm. From top to bottom: $TcBr_6^{2-}$ immediately after dissolution in 0.9 N HBr, after 6 h, after 24 h, after 48 h and after 72 h.

allowing the solution to stand for various times at room temperature. After 6 h two additional peaks (R_F 0.27 and 0.46) are prominent as well as a high background (elongated spot or series of spots) reaching up to the liquid front. After 24 h the initial spot of $TcBr_6^{2-}$ has practically disappeared and after 72 h also the spot of R_F 0.27 becomes small and there is a pronounced peak at the liquid front.

If it may be assumed that only aquo-bromo-complexes are present in 10 % aqueous HBr then the spot at R_F 0.27 is most likely the monoaquo-pentabromo technetate (IV) and the spot at R_F 0.46 the diaquo-tetrabromo-technetate (IV). The high activity in the upper portion of the paper would suggest the presence of neutral and cationic Tc(IV) species. These solutions were also tested for absence of Tc(V) by chromatography

with cellulose paper and no slow-moving species could be detected. The radioactivity scans shown here were made on chromatograms which were first sprayed with the reagent. The visible spots which were revealed had a compactness which is not given by the radioactive scans. The three slow moving spots were well recognised on all chromatograms while the upper portion of the bands gave indifferent colourations and hence the radioactivity scans are only reported here.

(b) *The hydrolysis of* $TcCl_6{}^{2-}$ *in 1.2 N HCl.* Ammonium hexachlorotechnetate (IV) was prepared according to DALZIEL *et al.*[8] by reducing ammonium pertechnetate with KI in conc. HCl and repeatedly evaporating with conc. HCl.

The yellow compound so obtained was dissolved in 1.2 N HCl and yielded on anion exchange paper, with 1.2 N HCl as solvent, one single spot R_F 0.07 with a slight forward comet.
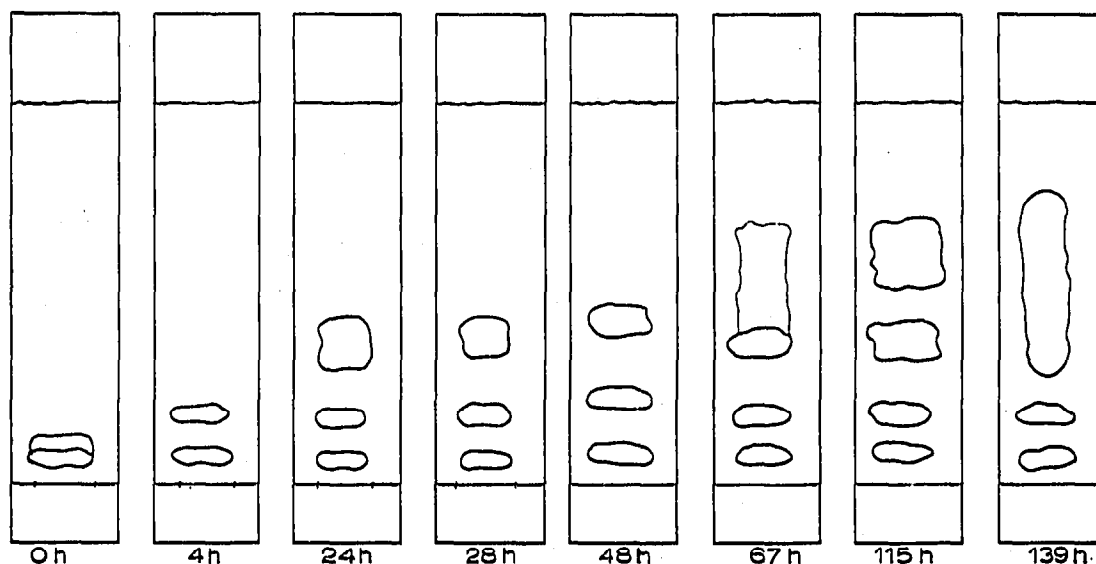

Fig. 10. Hydrolysis of $TcCl_6{}^{2-}$. Schematic drawings of chromatograms on Macherey, Nagel strong anion exchange cellulose paper developed with 1.2 N HCl. From left to right: $TcCl_6{}^{2-}$ immediately after dissolution in 1.2 N HCl and after 4 h, 24 h, 28 h, 48 h, 67 h, 115 h and 139 h.

On standing for various lengths of time at room temperature a number of faster moving spots are formed as shown in Fig. 10. If it may again be assumed that only mononuclear aquo-chloro-Tc (IV) complexes are formed then the spot of R_F 0.18 seems to be the monoaquo-pentachloro-technetate(IV) and the spot of R_F 0.39 the diaquo-tetrachloro-technetate(IV). Other spots are only formed after 67 h.

If Figs. 9 and 10 are compared it is evident that $TcCl_6{}^{2-}$ is much more stable to hydrolysis than $TcBr_6{}^{2-}$, the first still being preponderant after 139 h and the latter being absent after 24 h.

SCHWOCHAU[3] mentions that $TcF_6{}^{2-}$ is much more stable to hydrolysis than the other halotechnetates(IV). The order of stability to hydrolysis may thus be established as F > Cl > Br.

(viii) *The reaction of* TcO_2 *with dilute acids*

In studying the hydrolysis of hexahalotechnetates(IV) the presence of either cationic or neutral species was observed in aged solutions. We thus decided to attempt the

preparation of solutions with predominantly cationic species by dissolving TcO_2 in dilute acids.

These attempts were not crowned with success. TcO_2 proved to be practically insoluble in dilute HCl or HBr and only dissolved on prolonged heating on the water bath. The resulting solutions contained anionic species as well as cationic ones.

(a) *Reaction of TcO_2 with 0.9 N HBr.* TcO_2 was suspended in 10 % HBr and heated on the water bath as no reaction took place at room temperature. Almost complete dissolution took about 5 h. Samples were withdrawn earlier and chromatographed as shown in Fig. 11. The activity at R_F 0 is due to undissolved suspended TcO_2. When all has gone into solution the main activity seems to be due to the mono-aquo-pentabromo-technetate(IV) species.
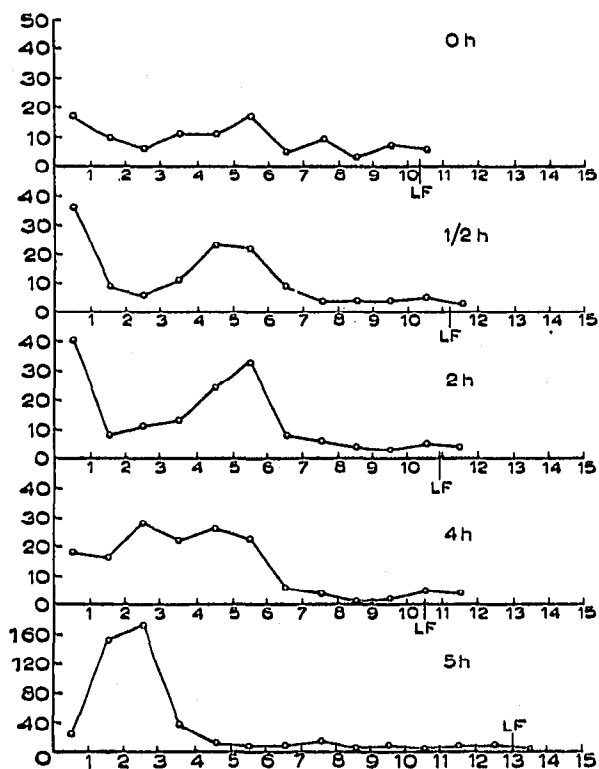

Fig. 11.

Fig. 12.

Fig. 11. Dissolution of TcO_2 in 0.9 N HBr. Radioactivity scans of chromatograms on Macherey, Nagel strong anion exchange cellulose paper developed with 1.8 N HBr. Ordinates: activity in counts/30 sec per cm. Abscissae: length of the chromatogram in cm. From top to bottom: immediately after suspending TcO_2 in HBr (supernatant is placed on paper), after 1/2 h, 2 h, 4 h and 5 h on the steam bath.
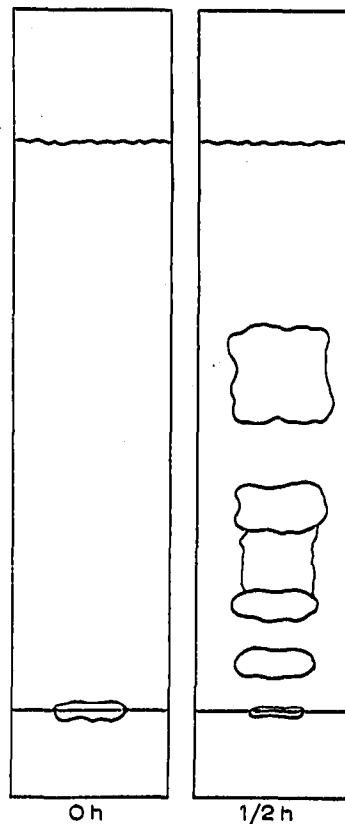
Fig. 12. Dissolution of TcO_2 in 1.2 N HCl. Schematic drawing of chromatograms on Macherey, Nagel strong anion exchange cellulose paper developed with 1.2 N HCl. From left to right: immediately after suspending TcO_2 in HCl and after 30 min on the steam bath. The spot at R_F 0 is undissolved TcO_2.

(b) *Reaction of TcO_2 with 1.2 N HCl.* Fig. 12 shows the chromatograms after 0 and 30 min of heating on a steam bath. First only suspended TcO_2 is found at R_F 0 and after 30 min there is an equilibrium mixture with several anionic species as well as fast moving species.

(ix) The reaction between Tc(VII) and Tc(IV) in dilute HCl solution

One remarkable feature of the solution chemistry of technetium is that in certain solutions three valencies (VII), (V) and (IV) can coexist for considerable periods of time. We thought it would be interesting to study the reaction between Tc(VII) and Tc(IV) in dilute HCl, in which both these species are stable, so as to have some idea of the speed of this reaction and of its possible influence on the chromatographic results obtained.

Pertechnetate and $TcCl_6{}^{2-}$ in a ratio of about 3:2 were dissolved in 1.2 N HCl. A chromatogram of this solution immediately after mixing gave only two fast-moving peaks, the faster due to $TcCl_6{}^{2-}$ and the slower due to $TcO_4{}^-$. After 24 h no measurable amounts of Tc(V) had yet been formed, however, the separation of Tc(VII) and Tc(IV) had become indistinct presumably owing to hydrolysis of the latter. After 43 h there is a small distinct peak of Tc(V) representing about 9 % of the total activity. This peak increases only to 12 % after 67 h. The chromatograms are shown in Fig. 13.
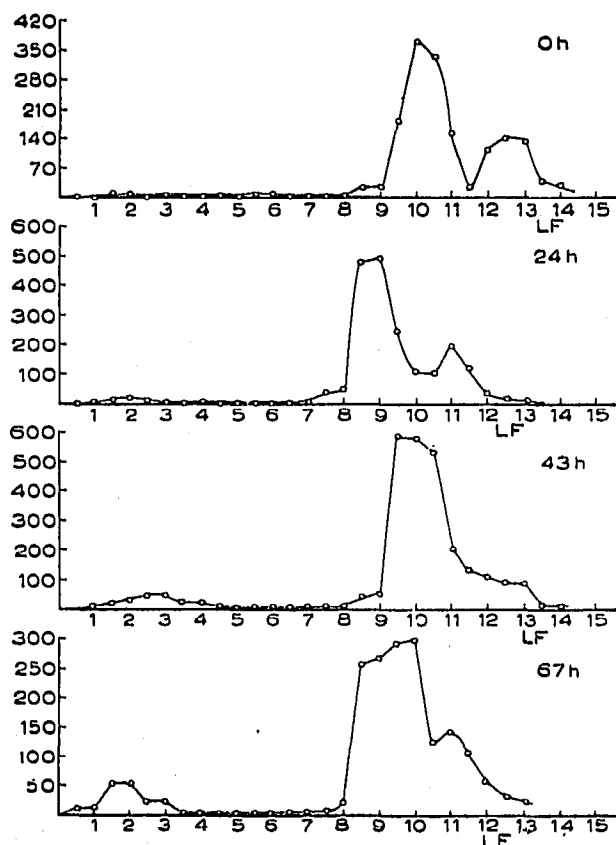

Fig. 13. The reaction between Tc(VII) and Tc(IV) in 1.2 N HCl. Radioactivity scans of chromatograms developed with 0.6 N HCl on Whatman No. 3MM paper. Ordinates: activity in counts per 30 sec per cm. Abscissae: length of the chromatogram in cm. From top to bottom: immediately after mixing, after 24 h, after 43 h and after 67 h.

DISCUSSION

The present work can be considered as a preliminary chromatographic investigation of the solution chemistry of technetium in HCl and HBr.

On several points further work suggested itself, such as the quantitative study

of the kinetics of the reduction of Tc(VII) in HCl and HBr. Both the long half-life of the radionuclide ^{99}Tc and the paper chromatographic techniques developed here lend themselves admirably to this purpose, and we intend to take this up in the near future.

Amongst the properties of technetium which were not well defined previously we would like to mention the rather unexpectedly high stability of Tc(V) in HCl solutions and the slow reaction between Tc(VII) and Tc(IV) in dilute HCl solution as well as the coexistence of the three different valencies in various concentrations of HCl and HBr.

The hydrolysis of hexahalotechnetates(IV) revealed a number of either neutral or cationic species which could not be investigated in detail by anion exchange paper chromatography. The work on the rather similar rhodium complexes (for a review see ref. 9) would suggest that these could be better resolved by paper electrophoresis and this will also be investigated in due course.

SUMMARY

The solution chemistry of technetium was studied in HCl and HBr employing paper chromatography and ion exchange paper chromatography. Techniques for the identification of TcO_4^-, Tc(V) and various Tc(IV) species were worked out.

REFERENCES

1 E. ANDERS, *Ann. Rev. Nucl. Sci.*, 9 (1959) 203.
2 E. ANDERS, *The Radiochemistry of Technetium*, Nuclear Science Series, National Academy of Sciences, National Research Council, Washington, D.C., 1960.
3 K. SCHWOCHAU, *Angew. Chem.*, 76 (1964) 9.
4 E. ALPEROVITCH, *Doctoral Thesis*, Columbia University, New York, 1954; quoted in ref. 1.
5 E. C. CROUTHAMEL, *Anal. Chem.*, 29 (1957) 1756.
6 J. B. GERLIT, *Proc. Intern. Conf. Peaceful Uses of Atomic Anergy, Geneva, 1955*, 7 (1956) 145.
7 G. E. BOYD, *J. Chem. Educ.*, 36 (1959) 3.
8 J. DALZIEL, N. S. GILL, R. S. NYHOLM AND R. D. PEACOCK, *J. Chem. Soc.*, (1958) 4012.
9 E. BLASIUS, *Metodi di Separazione nella Chimica Inorganica*, Corsi e Seminari di Chimica, Vol. 2, C.N.R., Rome, 1963, p. 141.