ION EXCHANGE PAPER CHROMATOGRAPHY OF Tc(IV), Tc(V) AND Tc(VII) IN HYDROCHLORIC ACID

S. K. SHUKLA
Laboratorio di Cromatografia del C.N.R., Istituto di Chimica Generale ed Inorganica, Roma (Italy)
(Received July 23rd, 1965)

A recent communication[1] from this laboratory has shown that the intermediate species, observed by previous authors during the reduction of the pertechnetate ion by concentrated hydrochloric acid, has the unique property of being strongly adsorbed on cellulose, especially in dilute hydrochloric acid of concentration below 1.0 *N*. A chromatographic method taking advantage of this property was developed for the separation of the intermediate species from the other two more stable valency states of the element, Tc(IV) and Tc(VII). The intermediate species was taken to be Tc(V), and its solution chemistry was studied by chromatography on cellulose and cellulose anion exchange paper. The present paper describes a detailed study of the ion exchange of the three valency states of technetium in hydrochloric acid using a wide variety of ion exchange papers.

EXPERIMENTAL

Chromatograms were obtained on the following papers:

1. Whatman No. 3MM, W-3MM.
2. Strongly basic cellulose exchange paper of Macherey, Nagel & Co. (containing quaternary ammonium groups, capacity 0.3–0.4 mequiv./g), MN-NR_4.
3. Strongly acid cellulose exchange paper of Macherey, Nagel & Co. (containing sulphonic groups, capacity 0.4–0.7 mequiv./g), MN-SO_3H.
4. Whatman anion exchange paper AE-30 (containing aminoethyl cellulose).
5. Whatman anion exchange paper DE-20 (containing diethylaminoethyl cellulose).
6. Amberlite ion exchange paper SA-2 (containing fine particle size Amberlite IR-120, a strongly acidic sulphonic acid type cation exchange resin).
7. Amberlite ion exchange paper SB-2 (containing fine particle size Amberlite IRA-400, a strongly basic, quaternary ammonium type anion exchange resin).

All the papers were washed with 2 *N* HCl followed by distilled water until they were free of HCl and then dried at room temperature.

Chromatograms were developed by the ascending technique in small jars, using 3 cm wide paper strips 20 cm long. Samples of the solution to be analysed were applied, with a micropipette, to the paper 3 cm from the extremity to be dipped in the developing solvent. The chromatograms were scanned for radioactivity by counting every 5 mm section of the paper under a thin-window Geiger-Müller counter. The

spots of the technetium species were also detected by spraying the chromatogram, after counting, with a solution of $SnCl_2$ and KCNS in 2 *N* HCl.

An aqueous solution of ammonium pertechnetate (supplied by the Radiochemical Centre, Amersham, Great Britain) was used, diluted, for studies of TcO_4^-, while the solutions of Tc(IV) and Tc(V) were in concentrated hydrochloric acid. Tc(IV) solution was obtained by repeated evaporation of a solution of $TcBr_6^{2-}$ with excess concentrated hydrochloric acid on a water bath, in order to convert the bromocomplex into the chlorocomplex and to remove the liberated bromine. The Tc(V) solution was a fresh solution of ammonium pertechnetate in concentrated HCl; this was light yellow because of some hexachlorotechnetate formed, but was found to contain more than 85% of technetium in the "pentavalent" state.

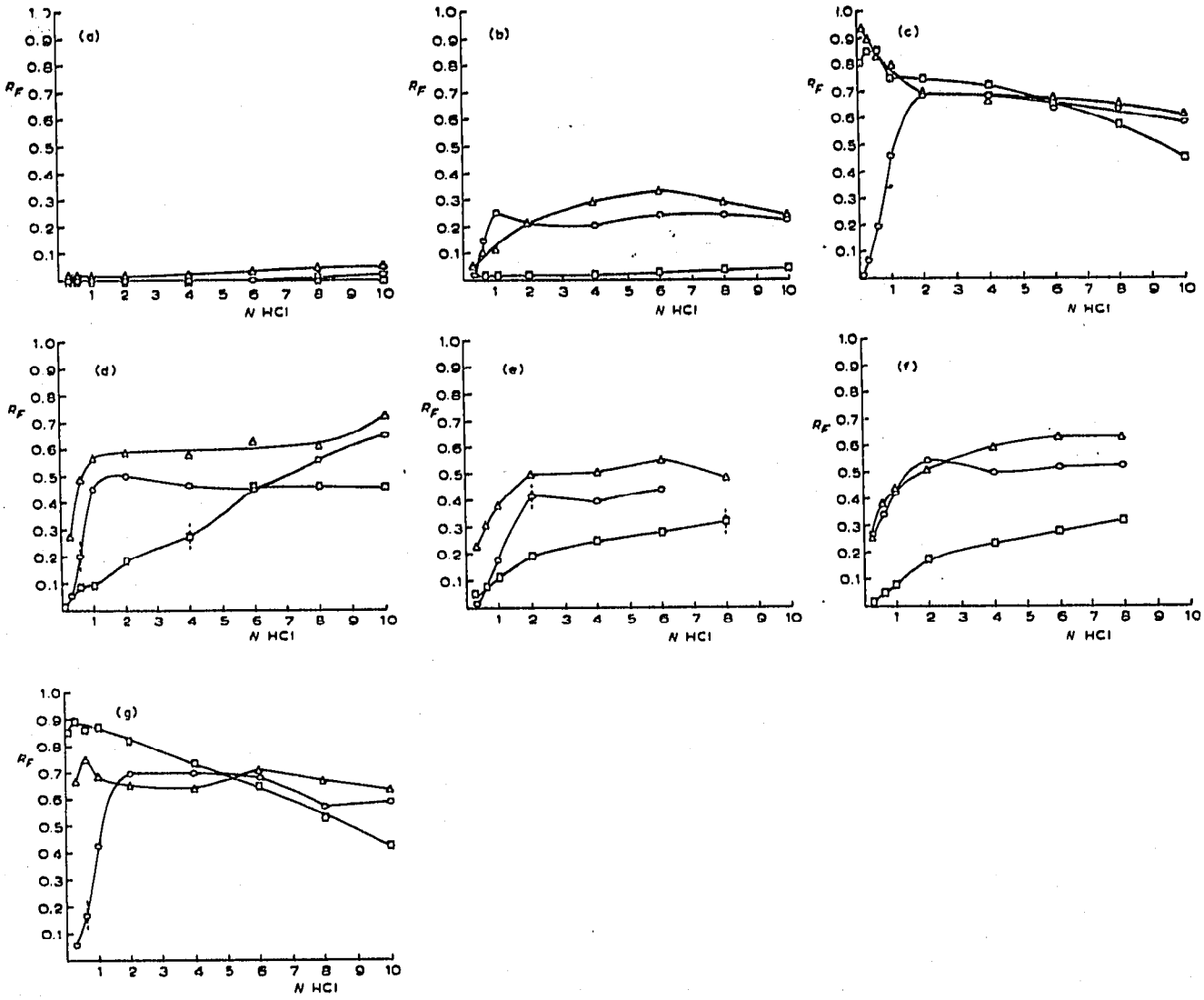

Fig. 1. R_F–HCl concentration plot of $TcCl_6^{2-}$ (□——□), Tc(V) (○——○), and TcO_4^- (△——△), on (a) SB-2 paper, (b) SA-2 paper, (c) MN-SO_3H paper, (d) MN-NR_4 paper, (e) AE-30 paper, (f) DE-20 paper, and (g) Whatman 3MM (pure cellulose) paper. (The dotted line intersecting the R_F–HCl concentration curves indicates the concentration below which the technetium species is hydrolysed and gives more than one spot on the radiochromatogram.)

RESULTS AND DISCUSSION

Fig. 1 shows the R_F values of TcO_4^-, Tc(V), and $TcCl_6^{2-}$ in the HCl, concentration range 0.3 to 10 N, on different papers. The concentration of HCl, below which the technetium species showed hydrolysis products (more than one spot), is marked by a dotted vertical line intersecting the R_F–HCl concentration curve.

Behaviour of Tc(IV), Tc(V) and Tc(VII) on SB-2 paper

On the basic anion exchange paper SB-2, $TcCl_6^{2-}$ is strongly adsorbed at the point of application as a yellow spot.

Tc(V) is hydrolysed in HCl more dilute than 2 N, giving a black tail from the point of application. The intensity of the tail decreases as the concentration of HCl is increased and it is no longer observed at HCl concentrations greater than 2 N. The displacement of Tc(V) on the chromatograms is small, the highest R_F value recorded being only 0.03 in 10 N HCl.

R_F values for TcO_4^- are higher than those for the other two valency states studied, but they are still too low to permit separation, With HCl concentrations higher than 4 N, a yellow spot is obtained, presumably due to the reduction of TcO_4^- by the resin in the presence of relatively concentrated HCl. The reduction of TcO_4^- by resins has previously been reported[2].

Behaviour of Tc(IV), Tc(V) and Tc(VII) on SA-2 paper

$TcCl_6^{2-}$ is strongly adsorbed at the point of application. With increase in concentration of HCl, it shows a little movement on the chromatogram, the highest R_F noted being 0.039 in 10 N HCl.

Hydrolysis of the Tc(V) species, which results in a black spot near the point of application, is observed in HCl concentrations less than 0.6 N. In 1.0 N HCl, Tc(V) has an R_F value of 0.25, which remains nearly constant for the higher concentrations of the solvent.

For solvent concentrations less than 0.6 N, TcO_4^- is adsorbed at the point of application. It begins to move as the concentration is increased and finally attains the maximum value of R_F 0.33 in 6 N HCl. Then a fall in R_F value is observed, which may be attributed to the reduction of Tc(VII) to lower valency states which have smaller R_F values.

The relatively small displacements of the three valency states of technetium, which are all anionic, may be attributed to adsorption on the resin network[1].

Behaviour of Tc(IV), Tc(V) and Tc(VII) on MN-SO_3H paper

$TcCl_6^-$ and TcO_4^- both move as fast bands, their R_F values being higher in solvent of lower HCl concentration.

In dilute developing solvent Tc(V) shows strong adsorption on cellulose. Its R_F increases rapidly to attain the maximum value of 0.68 in 2 N HCl, and then decreases. As is shown in Fig. 1, this paper can be used to separate Tc(V) from Tc(IV) and Tc(VII), using HCl concentrations of less than 2 N.

Behaviour of Tc(IV), Tc(V) and Tc(VII) on MN-NR_4 paper

The R_F–HCl concentration curve (Fig. 1) for $TcCl_6^{2-}$ shows three breaks, which

seem to be due to hydrolysis of the ion in dilute HCl. The chromatograms give two spots in solvents of concentrations less than 4 N, the main species always being the slower one.

Tc(V) is adsorbed more strongly in solvents of concentrations less than 1 N, and there is evidence of hydrolysis. The highest R_F value obtained for Tc(V) is 0.5 in 2 N HCl; it shows a decreases in R_F value in more concentrated acid.

The pertechnetate ion moves the fastest. Its R_F also increases with the HCl concentration. The presence of a yellow band on the chromatogram shows that it is reduced to a lower valency state on the paper in the presence of HCl of concentration $\geqslant 8$ N.

Separation of $TcCl_6^{2-}$ from the other two valency states of Tc was obtained in the concentration range 1 to 4 N HCl. TcO_4^- could not be separated from Tc(V), the concentration of the latter being too great in the mixture.

Behaviour of Tc(IV), Tc(V) and Tc(VII) on AE-30 paper

$TcCl_6^{2-}$ is more strongly adsorbed than Tc(V) or Tc(VII). There are two bands on the chromatogram for all concentrations of acid employed, the slower band being the more prominent one. The faster band gets progressively smaller in acid of higher concentration, and above 4 N HCl it gives only a small peak on the radiochromatogram.

Tc(V) moves faster than Tc(IV). It adsorbs in HCl of concentration less than 4 N, and for higher concentrations there is little change in its R_F value. In 0.3 N or less concentrated HCl, it hydrolyses to give a black spot at the point of application.

The movement of TcO_4^- is faster than that for the other two Tc species studied. It is reduced on the paper in HCl more concentrated than 6 N.

AE-30 paper is easily attacked by HCl. Even with 8 N HCl, the movement of the solvent front is very slow and is irregular, and the paper fragile. It permits separation of $TcCl_6^{2-}$ from Tc(V) and Tc(VII) in 1 to 6 N HCl, but the latter two could not be separated.

Behaviour of Tc(IV), Tc(V) and Tc(VII) on DE-20 paper

The variation of R_F of the three valency states of technetium with concentration of HCl on this paper is similar to that on AE-30 paper, with the sole difference that there is greater adsorption for Tc(IV), and less adsorption for the other two compounds. Tc(V) is hydrolysed more on DE-20 than on AE-30 paper under similar conditions.

Good separations of Tc(IV) from Tc(V) and Tc(VII) were obtained in HCl of concentrations higher than 2 N. The paper is attacked by HCl of greater concentration than 8 N.

Behaviour of Tc(IV), Tc(V) and Tc(VII) on Whatman 3MM (pure cellulose) paper

$TcCl_6^{2-}$ moves fast on the chromatogram, its R_F decreasing with concentration of HCl.

Tc(V) is highly adsorbed on cellulose in HCl of concentration less than 2 N. There is evidence of hydrolysis in HCl more dilute than 0.3 N, when a light black spot is observed near the starting line. It gives a constant R_F value in the range 2 to 6 N HCl and then the R_F falls, probably due to its reduction on cellulose in the presence of HCl.

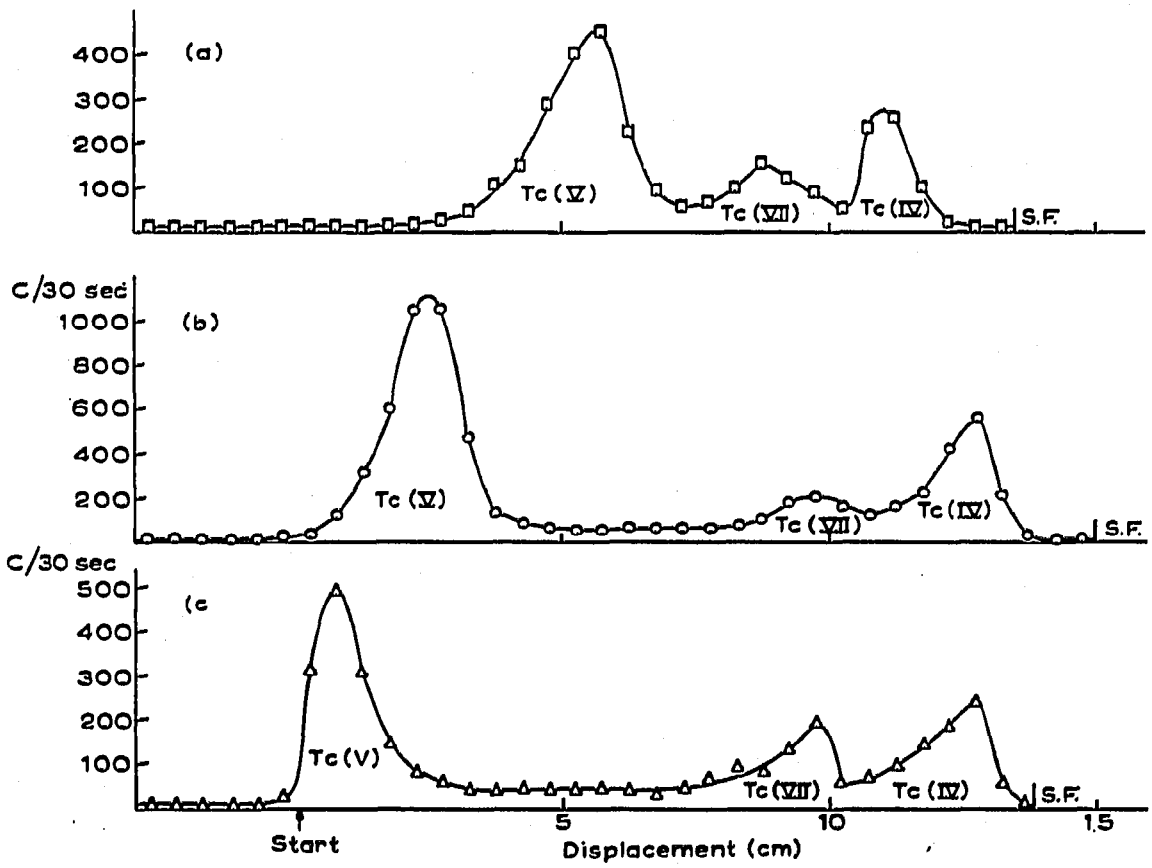

Fig. 2. Radiochromatograms of a solution of NH_4TcO_4 in concentrated hydrochloric acid (containing Tc(IV), Tc(V) and Tc(VII)) on Whatman 3MM (pure cellulose) paper in (a) 1.0 *N* HCl, (b) 0.6 *N* HCl and (c) 0.3 *N* HCl.

TcO_4^- moves more slowly than $TcCl_6^{2-}$ in HCl less concentrated than 5 *N*, but at higher concentrations it becomes the fastest of the three species. The presence of a yellow band on the radiochromatogram in HCl $\geqslant$ 8 *N* shows that it is reduced.

As can be seen from Fig. 1, this paper can give good separation of the three valency states in hydrochloric acid in the concentration range 0.3 to 1.5 *N*. Fig. 2 illustrates some of the separations obtained on this paper in HCl.

ACKNOWLEDGEMENT

This work was carried out under contract No. 265/RB with the International Atomic Energy Agency.

SUMMARY

The adsorption of Tc(IV), Tc(V) and Tc(VII) in 0.3 to 10 *N* HCl on Whatman 3MM cellulose paper, SA-2 and SB-2 resin papers, and MN-NR_4, MN-SO_3H, DE-20, and AE-30 modified cellulose exchange papers has been studied. The conditions under which a separation of the three valency states can be obtained using HCl as the solvent have been established. Only Whatman 3MM paper in the concentration range of 0.3 to 1.5 *N* HCl has been found to give complete separation.

REFERENCES

1 L. OSSICINI, F. SARACINO AND M. LEDERER, *J. Chromatog.*, 16 (1964) 524.
2 R. N. SEN SARMA, E. ANDERS AND J. M. MILLER, *J. Phys. Chem.*, 63 (1959) 559.