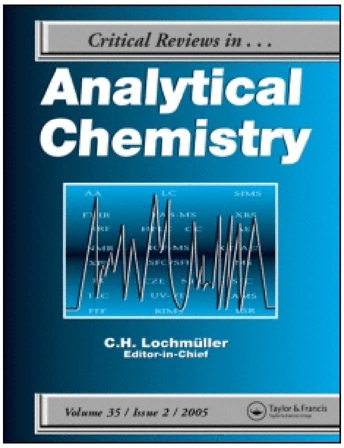

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RECENT DEVELOPMENTS IN THE ANALYTICAL CHEMISTRY OF RHENIUM AND TECHNETIUM

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I. INTRODUCTION

Rhenium is perhaps the least abundant of all the naturally occurring elements in the earth's lithosphere. Its richest occurrences seldom exceed concentrations of about 10 ppm. in certain molybdenites, sulfidic copper ores, or platiniferous materials. Its economic concentration and isolation, therefore, are dependent upon the existence of large-scale operations having other primary aims. The natural element of atomic mass 186.2 consists of the two isotopes Re^{185} (37.1%) and Re^{187} (62.9%).

It does not appear that any primordial technetium exists; the available artifact material is isolated from the partially-cooled fission products of uranium or plutonium reactors. Thermal fission Tc^{99} (from $Mo^{99} \xrightarrow[67\text{ hr}]{} Tc^{99m} \xrightarrow[6\text{ hr}]{}$) is relatively abundant (6% yield) and is monoisotopic with an atomic mass of 98.906. Its specific activity of 20 μc/mg ($t_{1/2}$ is 2.12×10^5 yr) is substantial, but it decays by a weak (0.29 Mev, maximum) beta emission to give an inactive Ru product.

Two interesting situations arise from these circumstances. The increasing use of nuclear energy sources may soon make man-made technetium the more abundant of the two elements. Meantime, increasing applications are being found for rhenium in specialty and high-temperature alloys, electrical and electronic contacts and filaments, thermocouples, and catalysts. Ironically, technetium might substitute for it for some of these purposes and is known to be a useful corrosion inhibitor, but its radioactivity precludes most practical applications (reactor-produced palladium of 1/200 this activity, however, is likely to have wide usage).

A second paradox is that, although some emphasis has been given in the literature to the *importance* of methods for separating technetium and rhenium, reflection indicates that this is an exercise of more academic than practical import. Technetium does not occur in nature with rhenium, and rhenium is not significantly present in fission products.

Chemical interest for compounds of these two elements and the literature that has resulted from that interest have increased greatly in the past decade.[1, 2] A large proportion of this literature concerns hydrides, carbonyls and π-compounds, mixed oxides in fused melts, (III) and (IV)-state cluster compounds, complex (V)-state chelates, and similar esoteric areas sometimes, but not very frequently, of analytical interest. At another extreme are numerous rather empirical reports of color-forming reactions of limited sensitivity and selectivity and some claims that rather unexciting separations have been effected by extraction, paper chromatography, etc. While analytical in character, many of these do not provide enough novelty or advantage to justify recounting them.

More than a decade ago it was shown that pertechnetate is rapidly reduced by concentrated hydrochloric acid to give a (V)-state; dilution and further standing form the (IV)-state, and the likelihood of oxo-species and of a photochemical dependence was also pointed out. Further studies confirming these aspects have since been reported. Nevertheless, a surprisingly large number of recent papers describe electrochemical studies, liquid-liquid extractions, chelations, paper chromatography, etc. of *pertechnetate* ion in such media as 8 and even 10 *M* hydrochloric acid. Other studies on the rate of hydrolysis of TcX_6^{-2} species seem to give no attention to the effect of light on such systems.

A similar difficulty concerns the fact that acidic pertechnetate solutions are rather rapidly reduced in contact with mercury. While this observation has been restated several times since it was first reported seven years ago, a number of subsequent electrochemical and polarographic studies are of dubious value because of its neglect. The loss of volatile $HTcO_4$ from acidic media suggests another obvious necessity for experimental precautions. The fact that these points require mentioning is illustrated by the appearance of more than a dozen papers in the past decade which suffer from their neglect. The magnitude of the "communications gap" is as frustratingly evident within this narrow area of chemistry as it is elsewhere.

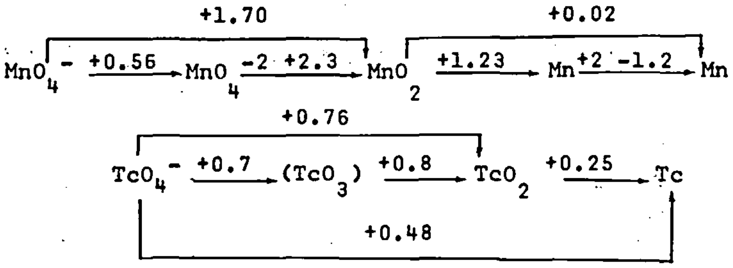
Some analytically significant new information has appeared, however, since the writing eight to ten years ago [3,4] of specialized treatments on the analytical chemistry of these two elements. At the same time, a really broad and flexible choice of good methods does not yet exist for either of these elements, and many of the older methods retain their importance. Evidently, a critical contemporary discussion of the analytical chemistry of these two elements should include reference to those useful older methods which have not been adequately displaced, as well as some attention to new chemistry which is potentially useful for analytical purposes.

II. ELECTROANALYTICAL

A. Redox Potentials

The redox behavior of technetium and rhenium species in solution is not very clearly or fully defined. Many pure compounds can be isolated representing the various oxidation states of these elements. Thermodynamic data for some of these compounds permit the calculation of idealized potentials. However, the oxidation states below (VII) exist in solution as covalently bonded chelates or complexes, cluster-ions, etc. rather than as simpler positive ions. The correct formulation of many of these species is not known with certainty and the (VI) and (V) states, especially, are prone to give disproportionation reactions. Polarographic and similar techniques clearly evince the irreversibilities of most of the redox couples whose potentials are observable in solution. Many such potentials are reasonably reproducible and have practical utility as formal potentials applicable for carefully specified media.

The following reduction potential diagrams rely largely on work by Cobble[5,6] and may be compared with the diagram for manganese.



$$\begin{tikzcd} ReO_4^- \arrow[r, "+0.768"] \arrow[rr, bend left, "+0.510"] \arrow[rrr, bend right, "+0.367"'] & ReO_3 \arrow[r, "+0.385"] & ReO_2 \arrow[r, "+0.260"] & Re \end{tikzcd}$$

Perrhenate and pertechnetate are very important and stable species in aqueous solution; they are not strong oxidants as is permanganate. Both (VI) and (V), generally in complex structures, can occur in solution; they often have only transient existence because they disproportionate to give the (VII) and (IV) states. All of the (IV) and higher states tend to retain some oxygenation; in the absence of complexing anions, the (IV) states separate as hydrous TcO_2 or ReO_2. Cluster ions and metal-metal bonding characterize most of the (III), and many (IV), state species. The (III) states of both elements can exist in solution but are rather strong reducing agents and subject to oxidation by air. No soluble representatives (excluding cluster species like $Re_3Cl_9^{-3}$) of (II) states, corresponding to manganous ion, are familiar in the aqueous chemistry of these elements. Technetium and rhenium hydrides while not impossible in alkaline media, are not likely to be of importance in aqueous solution chemistry. It is not yet clear if such known compounds as K_2ReH_9 possess even the short-term stability in dilute aqueous acid which is required to explain the "rhenide" of Lundell and Knowles.[7,8] The utility of the potential diagrams is somewhat limited by the absence of any (V) or (III) species and of any soluble ionic (VI) or (IV) species.

In the sense of practical formal potentials, Henze and Geyer[9] have reported data obtained with platinum indicator and saturated calomel reference electrodes for the rhenium 7/5/4 couples in 6 to 12 *M* hydrochloric acid, and the 7/4 couple in 2.5 to 10 *M* sulfuric acid. The components (below VII) of the couples were prepared by electrolytic reduction of 0.02 *M* perrhenate solutions and mixed in various proportions to test the Nernstian character of the results. The potential for (C_{Ox}/C_{Red}) = one is taken as the formal or standard value. All couples show more or less deviation from the Nernstian- behavior expected on the basis of the initial ratios of the concentrations of the species present. It was suggested that the species involved are ReO_3Cl, $ReOCl_5^{-2}$, $ReCl_6^{-2}$, and (in H_2SO_4) ReO_4^- and ReO_3^{-2}.

The results appear to be reasonable and to have some practical value in spite of the numerous issues which can be raised about their meaning and interpretation. The species, as formulated, may represent an oversimplification; the effects of such equilibria as 3(V) = (VII) + 2(IV) have not been evaluated, and it is improbable that many of these potentials represent equilibrium values. Referred to N.H.E., the measurements in 6 *M* hydrochloric acid give:

$$(6\ \underline{M}\ HCl,\ 25^\circ)\qquad \begin{tikzcd} Re(VII) \arrow[r, "+0.52"] \arrow[rr, bend right, "+0.46"'] & Re(V) \arrow[r, "+0.38"] & Re(IV) \end{tikzcd}$$

In 12 *M* hydrochloric acid, some values are +0.85 volt for $Re^{7/5}$and +0.56 for $Re^{5/4}$. An older value estimates 0.3 volt for the $Re^{4/3}$couple in hydrochloric acid.

No comparable data are available for technetium, but we may cite +0.72 volt for $Tc^{7/4}$in a medium 1 *M* in sulfuric acid and 3 *M* in hydrochloric acid. This is the 50% point in a one-step potentiometric titration of technetium (IV) with cerium (IV) and has the dubious virtue of lying near to one's best estimate of a reversible value. A comparable value of +0.73 volt may be estimated for $Tc^{7/5}$ in 1.3 *M* sulfuric acid and 0.4 *M* hydrochloric acid.

Accordingly, few reliable thermodynamic or reversible values are available that relate to definable solution species commonly encountered. This situation largely reflects the imperfections in our knowledge of the species actually present in various media for all oxidation states below (VII). The irreversibility or non-thermodynamic character of the potential measurements which are encountered in practice is well illustrated by the polarographic behavior of media involving these elements. Observable potentials will generally deviate by more than 0.5 volt from any reasonably-based estimate of the standard potential values (see Table 1).

B. Electrodeposition

It is possible to bright-plate either Tc or Re metal from an acidic solution of its MO_4^- salt; the current efficiency is generally poor but the deposition is reasonably quantitative (98% complete or better). In the absence of suitable complexing agents there is a strong tendency for the separation of insoluble MO_2 to intervene. The electrodepositions of these metals do not provide very promising weighing forms since both are subject to surface oxidation. Moreover, these depositions require the application of relatively energetic (i.e., negative) cathode potentials and are, therefore, very non-selective. Polarography indicates that the overpotentials for evolution of hydrogen on Tc and Re are rather low; hence macroelectrolyses from acidic media will always include concurrent discharge of hydrogen. It also seens to be quite difficult to realize completely quantitative deposition into (or onto) a mercury cathode, and it is doubtful that the product is a true amalgam.

Lundell and Knowles[7] and the Tomičeks[10] have described slow (or faster at 70° C) depositions from perrhenate in 5% H_2SO_4 solution on platinum electrodes at applied voltages of about 2.3 V. The first authors electrolyzed for 24 hours at room temperature and employed anode compartmenting. In spite of precautions in washing and drying, air oxidation of the deposited rhenium leads to high (*ca.* 4%) results. Henze and Geyer[11] studied the electrolytic reductions of ReO_4^- on platinum and on mercury, in hydrochloric and in sulfuric acid. They claim to have achieved reductions to metal, not necessarily quantitatively, on platinum from hydrochloric acid less concentrated than 6 *N*; and some separation of ReO_2, especially from sulfuric acid, was noted. Shropshire[12] examined the macroelectrolyses of ReO_4^- in 4 *M* sulfuric acid on platinum and on mercury cathodes at *ca.* −0.3 and −0.6 V, respectively. Reduction proceeded only to the (IV) state in both cases, giving colloidal ReO_2 on platinum and a violet-red ReO_3^{-2}(?) solution with mercury. This behavior was presumed to result from a disproportionation [3(VI) → 2(VII) + (IV)] that followed a one-electron reduction to (VI) in each case, but that was catalyzed on platinum. Commercial electrodepositions have usually employed sulfuric acid baths, which give largely metallic deposits from higher concentrations of acids, and more oxide at lower acidities. In either case, the deposits are annealed in hydrogen at 800° to 1,000° to produce pure metal.

The behavior of technetium is not conspicuously different. The isolation of the first gram of this element included an electrolytic deposition step from pertechnetate solution in sulfuric acid onto a platinum cathode, giving more dioxide than metal. Holt[13] has described the conditions for depositions from this electrolyte, noting the difficulties of obtaining a pure metal and of avoiding the formation of non-reactive intermediates. A patent (to the A.E.C.) by Box[14] describes the addition of oxalic acid, tartaric acid, or another

TABLE 1

Observed Redox Potentials vs. Estimated Standard Potentials

Polarographic Process		$E_{1/2}$ vs. S.C.E.	$E_{1/2}$ vs. N.H.E.	Estimated E°, vs. N.H.E.
Re(7/4)	4 *N* $HClO_4$	-0.38	-0.14	+0.5
(7/0?)	2 *N* KCl	-1.43	-1.19	+0.3
Tc (7/4 or 7/3)	1 *N* $HClO_4$	+0.06	+0.30	+0.8
	1 *N* HCl	-0.05	+0.19	
	1 *N* H_2SO_4	-0.12	+0.12	
(7/5)	1 *N* LiCl	-0.78	-0.54	
(7/0?)	2 *N* KCl	-1.14	-0.90	+0.5

polycarboxylic acid, to sulfuric acid for plating either as metal or oxide. On copper electrodes from 0.7 *M* oxalate and 0.45 *M* sulfuric acid, over 99% of technetium metal is plated at 1.0 to 1.3 A/cm^2 from a pertechnetate solution. But from 0.4 *M* oxalate and 1.9 *M* sulfuric acid it is the oxide that is deposited.

Detailed discussions of the behaviors of these elements in a mercury-cathode separation are not available. Apparently, extensive, but nonquantitative, depositions into mercury occur from dilute nonoxidizing acidic media in both cases. Older work of Furman et al.[15] showed erratic and incomplete depositions of rhenium from dilute sulfuric acid solutions of uranyl salts, but this electrolysis is strongly influenced by the potential-buffering effect of the uranium (IV/III) couple. Rulfs et al.[16–18] have commented on the extensive chemical reduction of pertechnetate by mercury in acidic media, which gives large amounts of soluble lower-oxidation states and some deposition of technetium metal. Technetium which is electrodeposited into mercury appears to have a particle size of the order of 500 Å diameter,[18] which is rather large to qualify as a true amalgam.

Majumdar and Bhowal[19] achieve reasonably quantitative deposition of rhenium metal onto a platinum cathode by electrolyzing a solution of a rhenium (IV) complex at pH 9–10. Perrhenate is prereduced to the (IV)-state in acid media by heating with iodide; an excess of EDTA is added and the pH adjusted. The (internal) electrolysis employs an attackable anode of pure zinc and is claimed to provide a separation from molybdenum. The deposited rhenium is rinsed with water, then ethanol. Weighing follows brief drying at 80 to 90° C with no special precautions noted.

Neither the rhenium nor the technetium which can be deposited more or less quantitatively on platinum or copper cathodes is attractive as a weighing form. The indirect measurement of the isolated deposit, which was suggested by the Tomičeks[10] for rhenium, might be applicable for either element. They dissolved the metal in preneutralized hydrogen peroxide solution giving $HReO_4$. This strong acid can be titrated with standard base. The preparation of uniform thin electrodeposits of Tc^{99} or of $Re^{186,\ 188}$ (resulting, for example, from neutron activation of natural rhenium) onto cathodes of confined area could be of interest for radiochemical counting. These isotopes are relatively weak beta emitters, and their radioassay in solutions containing fluorescing materials, highly colored species, or high concentrations of salts, presents some difficulties. Alternatively, if such deposits could be achieved on an appropriate cathode (pyrolytic graphite?), they might be used in concentrating these elements in preparation for such techniques as activation analysis.

C. Potentiometric Titrations

1. Miscellaneous Methods

The dissolution of electroplated Re metal in neutral hydrogen peroxide giving perrhenic acid may be followed by titration of this strong acid with a standard solution of base. Using internal indicators, much better results have been obtained by this procedure than by attempting to weigh the readily oxidized deposit of metal. Obviously, a glass electrode and pH-meter can be employed for the titration. Conductometric titration might be advantageous in other circumstances; the equivalent conductance of perrhenate ion is 54.95 at infinite dilution at 25°. A fresh deposit of technetium metal should be susceptible to assay by the same sequence of reactions, although it is slightly more resistant to attack by neutral hydrogen perioxide (insoluble in ammoniacal peroxide, and totally unattackable according to erroneous older reports).

It is possible to determine tetraphenylarsonium ion by titration with standard iodine solution in the presence of a moderate excess of iodide, using sodium chloride to decrease the solubility of the orange product:[20]

$$Ph_4As^+ + I_3^- \longrightarrow (Ph_4As)(I_3)$$

Using platinum and saturated calomel electrodes, a reasonably sharp ($\Delta E = ca.$ 140 mV) potentiometric end point is reported for this reaction. The indirect determination of perrhenate or pertechnetate, after precipitation by an excess of standardized tetraphenylarsonium reagent, can be based on such a potentiometric back-titration to measure the excess of reagent. This procedure has never become very popular, however.

2. Redox Methods for Rhenium

Many of the commonly available forms of the lower states (e.g., $ReCl_6^{-2}$, ReO_2) and $Re_3Cl_{12}^{-3}$)

can be determined by direct titration with such strong oxidants as cerium(IV) sulfate. But the reaction is very slow in most cases and it is more convenient to react with an excess of standard oxidant, followed by back-titration with a mild reductant solution such as iron(II). The principal alternatives for assay of the perrhenate(VII) state, by

(a) Prereduction to a well-defined lower state, removal of pre-reductant, titration with oxidant, or

(b) Direct titration to a reproducible lower state with a standard solution of reductant,

have been rather fully explored without conspicuously successful result.

The Tomičeks[21] studied a number of metals and metal amalgams as possible pre-reductants. The principal results of this study, portions of which were later examined by Lazarev,[22] are shown in Table 2. Mild reduction may yield approximately, rhenium (V) or an "equivalent" equilibrium mixture of this with the IV and VII states. Stronger reduction gives the (IV) state. There is little tendency to stop at the (III) level, but this might be favored by additions of phosphoric, pyrophosphoric, or polycarboxylic acids. "Apparent" lower states probably include the doubtfully characterized hydrido form, which can be obtained quantitatively (±2%) and which requires 8 equivalents per mole of rhenium for reoxidation to (VII).

None of these treatments results in the reproducible production of an integral lower oxidation level. It is known that such agents as zinc (Jones reductor) can lead to the partial deposition of insoluble ReO_2 from some of these media. The Walden silver reductor with 0.6 to 4 *M* hydrochloric acid and at 25° to 45°C gives no evidence of reduced product in the effluent but does give some evidence that insoluble Ag_2ReCl_6 is formed within the reductor. The separation of such insoluble forms, equilibrium mixtures of disproportionating species, the cluster-ion (III) forms, the presence of some hydrido species, and small initial losses of volatile $HReO_4$ are among the many reasons why apparent non-integral reductions may be found.

The reduction of perrhenate with standard solutions of very strong reducing agents, such as tin(II), titanium(III), vanadium(II), or chromium(II), in 1 to 4 *M* hydrochloric or in 0.5 *M* sulfuric acid has been claimed[23] to result in the more or less stoichiometric production of rhenium(IV). Stable potential readings on platinum are achieved only rather slowly, however; some workers prefer chromium(II) to tin(II) and this in turn to titanium(III) but claim that the reproducibility is good with either of the first two titrants.[24] Reduction with chronium(II) in 8 to 10 *M* hydrochloric acid is claimed to form rhenium(III);[23] brief aeration has been used to destroy an excess of added chronium(II) and evidently also oxidizes any rhenium(III) to rhenium(IV).[25] It is possible that one could select conditions under which this sequence of reactions could be made to yield rhenium(IV) quantitatively prior to titration

TABLE 2

Perrhenate Reductions

Reagent	Medium	Average Number of Equivalents Per Mole of Perrhenate
Bismuth amalgam	80% H_2SO_4	2.2 ±0.1
	45% H_2SO_4	3.1 ±0.1
Cadmium amalgam	35% H_2SO_4	3.1 ±0.3
Lead amalgam	10% HCl	3.1 ± 0.2
Zn amalgam (saturated)	40% H_2SO_4	4.7 ±0.1
(dilute)	40% H_2SO_4	3.0 ±0.1
(very dilute)	80% H_2SO_4	2.2 ± 0.1
(saturated)	10% HCl	7.8 ± 0.1
Metallic cadmium	5% H_2SO_4	2.9 ±0.1
Metallic zinc	5% H_2SO_4	8.0 ±0.2
	10% HCl	7.9 ± 0.2

with a standard solution of strong oxidant. The preparation and storage of standard solutions of any of these very powerful reducing agents is, of course, inconvenient. A more serious criticism is the fact that methods based on their use are necessarily somewhat non-selective.

3. *Redox Methods for Technetium*

Very much the same type of difficulties as those just enumerated surround the possibilities for redox titrimetry of technetium. This similarity is evident from the results of Rulfs and Pacer[26] who examined a series of prereductants (Table 3). Silver or zinc reductor-columns are inapplicable due to the separation of Ag_2TcCl_6 or TcO_2, respectively. The fact that iron(II) can reduce pertechnetate to (IV) and even to (III) in high concentrations of phosphoric acid[27] is not easily used, since

(a) a mixture of technetium(IV) and (III) is usually obtained.

(b) reoxidation with oxidants is very slow, and

(c) the technetium(III) is subject to partial air-oxidation.

There is little danger of reducing perrhenate with iron(II), but such a possibility (especially, if phosphate *is* present) must be borne in mind when ferrous ion is used as a back-titrant in indirect procedures for technetium, as when technetium(IV) is oxidized with excess cerium(IV) and the latter is back-titrated.

Reduction with sulfite in acidic solutions is inconveniently slow, but quantitative after some hours, giving an "equivalent (IV)" product [which could be a sulfito complex of technetium(III) or (V)]. Reduction by tin(II) may proceed below technetium(V), but any lower state can be potentiometrically titrated together with the excess stannous ion, after which technetium(V) is oxidized to (VII) by, for example, cerium(IV) as shown in Figure 1a. Equilibrium is not rapidly

TABLE 3

Behavior of Technetium(VII) with Reductants

Reductant	Medium	Oxidation State of Technetium in Product	Remarks
Ag column	1 *M* HCl 3 *M* HCl	(IV) (IV, III)	Ag_2TcCl_6 deposits in the column
Ascorbic acid	1–4 *M* HCl	(V, IV)	Red color, very slow reduction
$FeSO_4$	5–50% H_3PO_4	(IV)→(III)	Slow equilibrium
NH_4SCN	4 *M* HCl	(V)	Deep red, very slow
$NaNO_2$	2 *M* H_2SO_4, 3 *M* HCl, or 3 *M* H_3PO_4 + 1 *M* H_2SO_4	(VII)	No evidence of reduction in 30 min, or after heating
Na_2SO_3	2 *M* HCl + 0.8 *M* H_2SO_4	(IV)	SO_2 is boiled out after standing. Product is is a red (IV) complex; reaction is extremely slow but quantitative
$SnCl_2$	0.4 *M* HCl + 1.3 *M* H_2SO_4	(V)	Usable with potentiometry, see text
Zn column (10 mesh)	3 *M* H_2SO_4 1 *M* H_2SO_4 + 3 *M* HCl 4 *M* H_3PO_4	TcO_2, < (III) Tc°	Much material retained in column, widely variable results
Zn (30 mesh or powder)	3 *M* HCl 1 *M* H_2SO_4	(IV)	Quantitative, but $TcCl_6^{-2}$ is only sluggishly reoxidizable
Zn-Hg column	4.5 *M* HCl	(IV, III)	Green, partially reoxidized in air, TcO_2 in column

established during this titration, and the measurement requires reading the volume difference between two equivalence points.

It is possible to form technetium(IV) in mixed mineral acid by using finely divided (<30 mesh) zinc, and without the separation of TcO_2 which occurs in column reductors. This procedure is inconvenient, however, and the direct titrimetric reoxidation with cerium(IV) gives a sluggish potentiometric response, Figure 1b. It is much more convenient to add a measured excess of standard cerium(IV) and back-titrate with standard iron(II). This titration can be conducted rapidly (either potentiometrically, or using ferroin indicator) and without danger of beginning any reduction of technetium(VII) by iron(II) prior to the reaction of cerium(IV).

Crouthamel[28] described the potentiometric titration of technetium(VII) with titanium(III) in 12 *M* sulfuric acid. A transient potential break is obtained corresponding to the (V) state, which slowly disproportionates to (VII) and (IV). But the greater titrant consumption and a more securely located equivalence point correspond to the formation of the (IV) state.

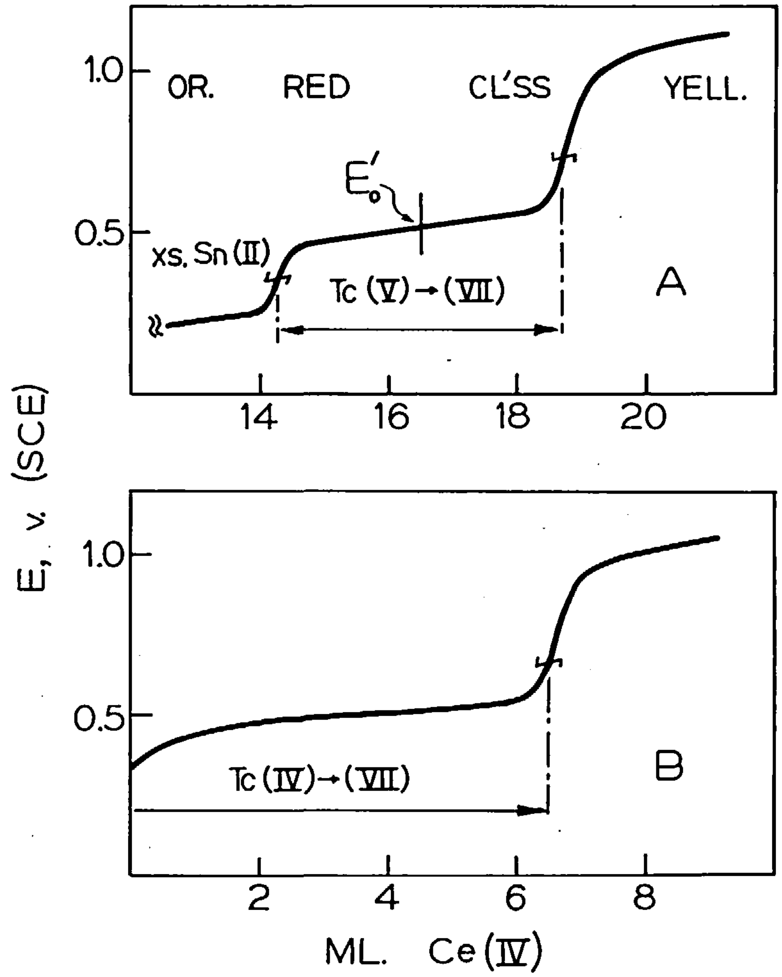


FIGURE 1. Titrations of reduced technetium species with approximately 0.05 *M* $Ce(SO_4)_2$, at platinum and saturated calomel electrodes: A. After prereduction of approximately 0.004 *M* technetium with excess stannous chloride in 0.4 *M* hydrochloric acid–1.3 *M* sulfuric acid medium. B. Preformed $TcCl_6^-$ in 1 *M* sulfuric acid–3 *M* hydrochloric acid medium.

D. Polarographic Methods

1. General Considerations

The polarographic behaviors of both elements have been rather fully explored. Useful (~ ± 1%) classical d.-c. polarographic methods exist for both of the MO_4^- forms in the usual concentration range (roughly 2×10^{-3} to 5×10^{-5} *M*). The initial 3- or 4- electron reduction waves occur in 4*N* to 1*N* mineral acid media at sufficiently positive potentials ($E_{1/2}$=*ca.* −0.4 to ±0.0 V vs. S.C.E.) to provide reasonably selective procedures. All of the observed reactions are irreversible; the mechanisms of some of these have been studied. The reliable use of these methods demands an understanding of some of their idiosyncrasies. It is especially important that precautions be taken to minimize the effect of the two sources of error which have already been mentioned.

The usual polarographic preliminary deaeration by bubbling nitrogen through the test solution can easily lead to losses from acidic media of 0.5 to 1.0% of the volatile HMO_4 forms of these elements. In the case of $HTc^{99}O_4$ this would represent an undesirable hazard and a contamination problem, as well as a serious source of error. Any contamination is easily eliminated by trapping the effluent in dilute alkaline solution. Some combination of the following measures may be adapted to lessen the error from this source:

(a) Thermostat the solution at 10 to 15°C and use a minimum amount of nitrogen bubbling.

(b) Trap the effluent and determine its technetium or rhenium content (e.g., colorimetrically) to be applied as a correction.

(c) Precondition the nitrogen by presaturating in a prebubbler containing a similar solution.

(d) Standardize the conditions of pretreatment, accurately measure the loss under these conditions, and apply a fixed correction factor to the data.

In view of the second serious source of error, it is important that mercury be carefully removed from the cell between runs and that the dropping electrode *not* be inserted during the deaeration process.

Salaria, Rulfs, and Elving[16] noted an apparently significant decrease in the height of the first polarographic wave of pertechnetate, especially in acids more concentrated than 1 *M*, after contact with mercury. Later experiments[17] showed a small amount of technetium metal in the mercury and a large decrease (or even the total disappearance) of the first wave; even a subsequent wave can be decreased by more than 20%. The situation is worsened in more concentrated acids, and for hydrochloric acid as compared to sulfuric acid. The same result obtains in perchloric acid media[18] and even led to the erroneous prior conclusion that pertechnetate in perchloric acid was not polarographically reducible to about −1.0 V vs. S.C.E.[29]

Evidently, reductions such as

$$TcO_4^- \xrightarrow[Hg,\ H^+]{} Tc(V,\ IV)$$

occur extensively and rather readily in approximately 1 *M* solutions of acids and also, though more slowly, in acids even more dilute than 0.1 *M*. They may yield still lower states (III, 0) on longer contact. The presence of hydrochloric acid, in particular, favors this reduction (by forming Hg_2Cl_2?). For this reason there should be no contact with mercury during pretreatments such as deaeration; polarography at a dropping mercury electrode should be conducted as expeditiously as is possible, and hydrochloric acid at a concentration of 0.1 *M* or above is not desirable as an electrolyte (obviously, serious leakage from S.C.E. junctions could be just as harmful when other acids are present). It is not known, and would not be expected, that perrhenate is subject to any similar reaction.

Some of the more important examples of the polarographic waves which will be discussed are shown in Figure 2.

2. Polarography of Rhenium

Lingane[30] and Rulfs and Elving[31] examined the reduction of perrhenate ion in acidic and neutral media, as well as the anodic oxidation[8,32] of Lundell's "rhenide." The latter retains considerable academic interest but has not yet been reexamined and interpreted in the light of present knowledge of hydrido species and cluster intermediates. It would rarely occur as a system of interest for analytical purposes. Some more recent studies have reexamined perrhenate reductions in acidic and in neutral salt media, as well as the reductions of $ReCl_6{}_{-}^{2}$ (IV) and of Re_3Cl_9(III) in hydrochloric acid.

The early studies showed that approximately 0.2 to 3 m*M* solutions of perrhenate in 2 *M*

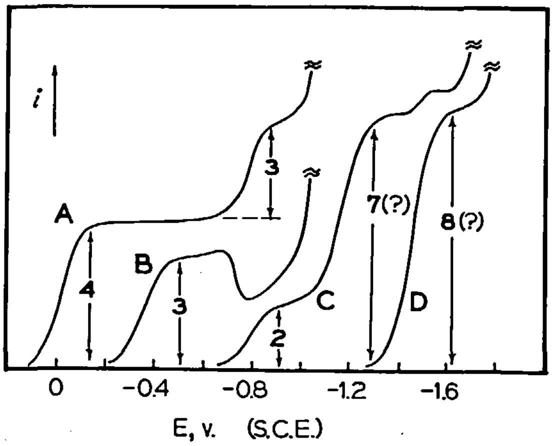


FIGURE 2. The general appearance of the polarograms of A. pertechnetate in 0.1 *M* perchloric acid; B. perrhenate in 4 *M* perchloric acid; C. pertechnetate in 2 *M* potassium chloride; D. perrhenate in 2 *M* potassium chloride. Most of these waves are diffusion-limited; all are irreversible. Numerals indicate the number of electrons transmitted; consult the text for details.

potassium chloride show a large wave at —1.42 V vs. S.C.E., which is closely followed by catalytic hydrogen-discharge. The plateau may be diffusion-limited, but the wave is highly irreversible ($E_{3/4}-E_{1/4}$ = -0.09 V). The *n*-value calculated from the classical Ilkovič equation is approximately eight but would lie closer to seven using the expanded forms of the Ilkovič relation.[33] Apparent values above eight are reported by these and later workers[29] for perrhenate concentrations below 0.2m*M*. Recent workers[34] report that the reduction involves seven electrons at —1.44 V in 1 *M* KCl and 0.5% gelatin. They include concentrations as low as 0.02 m*M* and calculate a transfer coefficient of 0.135.

In the light of all of these studies it seems reasonable to conclude that an irreversible but diffusion-limited seven-electron reduction of ReO_4^- to the metal does occur at about —1.43 V vs. S.C.E. in 1 to 2 *M* KCl. The overpotential of hydrogen on rhenium (or on mercury partially coated with rhenium) is undoubtedly much less than on pure mercury. Therefore, neither the graphical extrapolation and subtraction of residual current (especially on an irreversible wave where the potential may be 0.2 volt more negative on the plateau than at the toe) nor a subtraction based on a run in pure background electrolyte (with no rhenium on the electrode surface) will give an appropriate correction. The relative effect of the failure to subtract the current which can result from the reduction of water or hydrogen ion at potentials on the plateau is greater with low concentrations of perrhenate, thus giving apparent *n*-values as high as 10 and more. Actually, the effect of this factor is difficult to predict quantitatively since:

(a) The surface concentration or activity of the reduced rhenium will vary with the concentration of perrhenate in the solution, and

(b) The local concentration of available hydrogen ion is also affected by the reaction

$$ReO_4^- + 8H^+ + 7e^- \rightarrow Re^\circ + 4H_2O$$

and may be affected seriously if its bulk concentration is small.

More detailed studies of the comparable reduction of pertechnetate even suggest that differences exist between potassium and lithium chlorides as electrolytes, and clearly evince the expected complexity of such a multielectron process. Though the height of this wave is measurable prior to the subsequent rise of current, and despite the fact that it is fairly closely proportional to the concentration of perrhenate over a reasonable range, its application for analytical purposes is not to be recommended. In any case, the selectivity of a process which occurs at as negative a potential as —1.4 V would not be very attractive with many types of samples.

Van Ngoc[35] has described perrhenate reductions in sodium acetate at pH values between 6 and 12; in 1.3 *M* sodium acetate at pH 7.5 the waves are at —1.42 and —1.64 V. Compared with the use of neutral KCl media, this system seems to give smaller waves at equally negative potentials and a behavior which is even more variable with environmental changes. Unbuffered solutions are well known to be ill suited to work with half-reactions that consume hydrogen ions, as these must.

Early workers[30,31] and Ziemba[36] studied the reduction of perrhenate in hydrochloric, perchloric, and sulfuric acid media. All agree that a wave with an apparent *n*-value of 3 at —0.38 ±0.02 V vs. S.C.E. in 4 *M* perchloric acid is analytically useful. With any of these acids, the first polarographic reduction wave shifts to more positive potentials as the acid concentration is increased from 1 to 8 *M*. In general, the value of i_d/C is constant over a wide range of perrhenate concentrations if the acidity exceeds about 2.5 *M*. Surface-active agents, such as gelatin, suppress the wave.

The behavior in hydrochloric acid more concentrated than about 2.5 *M* is quite acceptable, but $E_{1/2}$ is about 0.1 V more positive than in equally concentrated perchloric acid media. This complicates the precise measurement of the wave height because of the poor definition of the toe of the wave due to early inception of the formation of calomel. Ziemba describes two waves at −0.16 and −0.36 V vs. S.C.E. in 4 *M* sulfuric acid, which might be an advantageous medium for some samples. These waves tend to show minima, especially at lower electrolyte concentrations, which distort the limiting current plateaus near the electrocapillary zero.[31,36] Nevertheless, the proper plateau level is clearly defined.

For most purposes, 4 *M* perchloric acid would seem to be the best supporting electrolyte. There is a small shift in $E_{1/2}$ with perrhenate concentration, from −0.360 V at 0.08 m*M* to −0.394 V at 1.00 m*M*. Although $i_d \propto h_{1/2}$, the temperature coefficient of the wave height is abnormally low.[31] It is not known to what extent a soluble (IV) product such as ReO_3^{-2} may exist in perchloric acid. It does not seem to be possible to obtain a full subsequent wave for the rhenium(IV) to (III) step, and the separation of some hydrous form of ReO_2[37] may account for some of the peculiarities of this wave. Oscillopolarographic studies in 2 *M* hydrochloric acid at a hanging-drop electrode[38] show the 3-electron reduction to be stepwise rather than smooth, and the overall diffusion control is complicated by rapid disproportionation of an intervening (VI) or (V) state to regenerate perrhenate. Yet its properties are suitable for analytical purposes:

Selectivity: $E_{1/2}$ = −0.38 V vs. S.C.E.
Sensitivity: I = 7.06 at 25° C
Reproducibility: $(i_d/C) < \pm 2\%$ relative (0.08 − 1.0m*M*)

The latter paper[38] also discusses the polarography of $ReCl_6^{-2}$(IV) in hydrochloric acid media.

Muenze[39] has examined the coulometric and the d.-c. and a.-c. voltammetric behaviors of the cluster (III) compound Re_3Cl_9 in solutions containing hydrochloric acid and sodium chloride, in which it is present as $Re_3Cl_{12}{}^{3-}$. On the d.-c. polarogram he finds as a primary process a wave involving two electrons per rhenium atom:

$$Re_3Cl_{12}{}^{3-} + 6e^- \quad Re_3Cl_9{}^{6-} + Cl^-$$

A secondary reaction is

$$Re_3Cl_{12}{}^{3-} + Re_3Cl_9{}^{6-} \rightarrow 2Re_3Cl_9{}^{3-} + 3Cl^-$$

In other words, the equivalent oxidation states of the rhenium in three variants of the cluster species are 3, 2, and 1.

3. *Polarography of Technetium*

The d.-c. polarographic reduction of pertechnetate from neutral salt solutions (0.1 − 2.0 *M* lithium chloride, potassium chloride, or potassium sulfate has been examined by a number of workers.[16,29,40] The observed behavior in neutral, and more alkaline, media has been further probed by coulometry.[16,17] a.-c. polarography,[40] and simple and double-potential-step chronoamperometry.[41]

In 2 *M* KCl it has been claimed that the reduction is similar to that of perrhenate:[1,29] there is an irreversible (slope) wave at a highly negative potential (but one about 0.2 V more positive than that for perrhenate), and its calculated *n*-value is about 8.5, assuming diffusion control, for pertechnetate concentrations below 0.1 m*M*. Indeed, the *n*-value is 7 if a better value is used for the diffusion coefficient of pertechnetate (see 18). Other work, however, shows that the value *n* = 7 does not clearly conform to the plateau which may be discernible prior to the hydrogen-discharge which follows.[40] This work shows a well-separated two-electron step at about −0.8 V, corresponding to (VII) → (V). A poorly defined (V) → (IV) step (sharper in alkaline media) may precede the subsequent reduction to metal.

In alkaline media Astheimer and Schwochau[40] found a rather well-defined two-electron wave at −0.8 V followed by a one-electron wave at −1.1 V:

$$(VII) \rightarrow (V) \rightarrow (IV).$$

This agrees with the report of Salaria, Rulfs, and Elving[16] that a coulometrically confirmed three-electron process occurs beyond −0.85 V, but these workers[16] also found that 4 electrons were transmitted at about −1.15 V. Kissel and Feldberg examined the mechanism of the early step, finding in the presence of gelatin

(1) $(VII) + e^- \rightarrow (VI)$ (primary, followed by

(2) $2(VI) = (VII) + (V)$ (rapid)

In the absence of gelatin, the two-electron step occurs directly. But coulometry and chronoamperograms confirm that $n = 3$ at potentials less negative than −1.0 V. Although insoluble TcO_2 tends to separate at this Tc(IV) stage, they also have found that an additional (fourth) electron is transferred near −1.1 V.

In neutral and alkaline media pertechnetate shows behavior still more complicated, and somewhat less reproducible, than that of perrhenate. Such supporting electrolytes are not very attractive for analytical purposes.

Reductions in acidic media give a rather well-formed first wave which shifts with pH:

$$E_{1/2} = A - 0.11_4 \text{ pH}, \qquad (1)$$

where A is +0.06, +0.05, and +0.12 V, respectively, for perchloric, hydrochloric, and sulfuric acid. Surprise has been expressed that the average shift observed with pH agrees so well with the value calculated from the dependence on $\frac{0.05915}{4}$ $\log(H^+)^8$, or 0.118 pH, predicted thermodynamically for the half-reaction $TcO_4^- + 8H^+ + 4e^- \longrightarrow Tc^{+3} + 4H_2O$, but as the reduction is irreversible, as shown by its slope, this means merely that the number of hydrogen ions consumed in the rate-determining step is very nearly equal to twice αn_a. Coulometrically, this wave accords with $n = 4$,[16, 18] but the (VII) ⟶ (IV) and (IV) ⟶ (III) stages are sufficiently resolved that with careful control of potentials one can obtain a coulometric n-value of 3. A subsequent wave at −0.93 continues the three-electron reduction to metal, $Tc(III) + 3e^- \longrightarrow Tc(0)$. As a result of rapid prior chemical reduction of pertechnetate to intermediate states by contact with mercury in acid, however, the data in hydrochloric and sulfuric acid media often show wave I (4 electrons) to be no larger than wave II (3 electrons). The comparison is further complicated by the fact that the (IV) ⟶ (III) stage may appear, in part, as a separate drawn-out wave between these two.[16] In perchloric acid media, however, the relative heights are in better agreement.[18] For five runs at pH 1 to 4 in perchloric acid,[42] the ratios of (II/I) were 0.70, 0.77, 0.72, 0.74, and 0.73 in good agreement with the expectation of 3/4. At pH < 1 the agreement is poorer for two reasons:

(a) The extent of chemical prereduction is greater, and

(b) There is a larger contribution from the reduction of hydrogen ion to the height of wave II (since H_+ is larger, and the presence of elemental technetium decreases the overpotential for hydrogen evolution).

At pH >4.5 only a single three-electron wave is found at about −0.8 V, although this tends to separate into (VII) ⟶ (V) followed closely by (V) ⟶ (IV), as discussed earlier. From other evidence, however, an initial four-electron step appears to persist up to about pH 6 in acetate-buffered tripolyphosphate media.[43]

The use of a background electrolyte containing 0.5 M potassium chloride together with enough hydrochloric acid to give pH=2 has been recommended[17] for pertechnetate concentrations within the range 0.2 to 0.01 mM. A well-formed first wave at about −0.17 V has a diffusion current constant of 11.9 ±0.1. In view of the less rapid occurrence of chemical prereduction,[42] approximately 0.1 M perchloric acid would seem to be a still better supporting medium. Even here,[18] the principal limitation on the accuracy and precision of measurements will relate, primarily, to the extent to which pre-contact of the solution with mercury has been avoided. Nevertheless, all indications are that such a procedure can be valid to at least ±1% relative. The peak-heights from a.-c. polarography may be less reproducible (and are mainly studied for the wave at −0.8 V in neutral media), but could be advantageous in terms of their better resolution from some interferences.[40]

E. Amperometric Titration

Nitron perrhenate and pertechnetate are too soluble to provide a good basis for amperometric precipitation titrations. The use of tetraphenylarsonium chloride for this purpose is more promising but has not been conspicuously successful. Rulfs and Mitchell[44] attempted the amperometric titration of 0.03, 0.3, and 1.2 mM pertechnetate using 4.7 to 50 mM solutions of tetraphenylarsonium chloride in a variety of supporting electrolytes. Typical conditions employed 0.4 M potassium chloride and 0.1 M hydrochloric acid at a fixed potential near −0.4 V vs. S.C.E. The best end points seemed to be more than 2% premature and the reproducibility was often poorer than ±5%. Precipitation is inconveniently slow at 15°, 25°, or 40°, and the behavior of the dropping electrode is erratic: the capillary tends to become plugged and the drop time to alter. The tetraphenylstibonium salt is more insoluble and might provide a better basis for such a method.

In a series of papers,[45-48] Gallai, Rubinskaya, et al. have described amperometric titrations of rhenium (VII) with chromium (II), titanium (III), iron (II) in phosphoric acid, and vanadium (II). While the methods appear to give relatively crude results, two variants will be briefly described here. The principles involved would appear to permit some degree of selectivity and the methods should be susceptible to refinement.

In a solution containing 2 *M* sulfuric acid and 2 *M* phosphoric acid, vanadium (II) reduces perrhenate to rhenium(IV). With a graphite indicator electrode potentials of 0.5 to 0.8 V vs. S.C.E. permit one to see the anodic (oxidation) current of the excess vanadium (II) titrant beyond the equivalence point. At +0.8 V the anodic reoxidation of the rhenium (IV) product also contributes, and a potential of +0.5 V is preferable. The presence of an eight fold excess of vanadium (IV) can be tolerated if one uses 2 *M* sulfuric acid containing EDTA as a medium. The precision shown, however, is only ±6% for 0.5 mg, and ±2% with 5 mg, of rhenium.[48]

Perrhenate is reduced to rhenium (V) by iron (II) as the titrant in several electrolytes, but a mixture containing 8 *M* phosphoric acid and 10 *M* sulfuric acid is recommended. At a platinum or graphite microelectrode the anodic current from excess iron (II) titrant is observed at +0.8 V vs. S.C.E. At this potential there is no need to remove dissolved oxygen, and the presence of a relatively large amount of iron (III) in the sample is not detrimental. It is also claimed that the presence of equivalent amounts of molybdenum (VI) is permissible and can also be measured since this is titrated stoichiometrically to give a "break" prior to the Re titration. Generally, the results reported are as poor as ±30% for 0.1 mg of rhenium or ±3% for 2 mg, but a precision as good as ±0.12% is claimed with 5mg. These comparisons include variations in the supporting-electrolyte composition which affect the sharpness of the end point.

F. Coulometry

A number of workers have studied the direct coulometric reduction of pertechnetate,[16-18,27,41,43,49] and the reduction of perrhenate with electrogenerated titanium (III) has been reported.[50] For analytical purposes the use of acidic media, usually containing phosphate or polyphosphates, has been favored.

Sheytanov, Chavdarova, and Konstantinova[50] describe the indirect coulometric reduction of rhenium (VII) to rhenium (IV) with cathodically generated titanium (III). The supporting electrolyte contains 8 *M* sulfuric acid, 0.2 *M* phosphoric acid, and about 0.6 *M* $TiOSO_4$, and is maintained at a temperature of 85°. Unfortunately, it is necessary to pregenerate about two-thirds of the requisite amount of titanium (III) in the cell before adding the rhenium sample. Such a restriction virtually dictates the need for a preliminary trial run prior to each determination on a new sample. The relative error is less than 1% with 0.4 mg of Re and less than 0.2% with 4 mg.

The controlled-potential coulometric reduction of acidic pertechnetate solution giving a three-electron or (at very slightly more negative potentials) a four-electron process, has been examined rather closely in relation to elucidating polarographic behavior.[16-18,24,49] Since it is difficult to cleanly discriminate the three- from the four-electron process, especially in the presence of complexing anions such as phosphate, it seems desirable to select conditions to insure complete four-electron reduction to the (III) state; this in spite of the tendency for this product to react with dissolved oxygen to regenerate (IV). The need for thorough deaeration of the test solution by bubbling inert gas invites some loss of volatile $HTcO_4$. The use of a stirred mercury cathode, even in weakly acidic media, invites the occurrence of some direct chemical reduction:

$$\text{Tc(VII)} \xrightarrow[H^+]{Hg^\circ} \text{(VI, V, IV, ...0?)} + Hg_2^{+2} \qquad (4)$$

Conceivably, coulometric conditions can be chosen such that subsequent electrochemical reduction of the resulting mercurous ion will take place during the run. This should result in a perfect compensation for any error from (4), *providing* that no products below the (III) state were formed. (This is not always the case; see 17). In dilute non-complexing acidic media, TcO_2 rather than Tc_2O_3 separates at the conclusion of a four-electron reduction due to reoxidation of the (III) state by hydronium ion or air[27] which occurs very readily in the absence of strong (III) complexation.

Terry and Zittel[43] describe the study of a specific coulometric system for analytical purposes. As a background medium they recommend a buffer system of pH 4.7 containing about 1 *M* ammonium acetate with 5% (w/v) of tripolyphosphate ($Na_5P_3O_{10}$). A controlled potential of −0.70 V vs. S.C.E. is suitable and falls well out on the plateau of the four-electron wave at this pH value. The authors employ 5 ml of stirred mercury as cathode with about 13 ml of test solution. Inert gas is passed throughout the electrolysis, due to the sensitivity of the (III) product to air reoxidation to (IV). The (IV) $\rightleftharpoons$ (III) transition in the buffered polyphosphate appears to behave almost reversibly, and $E_{1/2}$ is −0.48 V at pH 4.7.

Procedurally, the deaerated supporting medium is pre-electrolyzed at −0.70 V until the background current drops to 0.1 mA. The test solution is added and pre-reduced at −0.20 V until the current again drops to 0.1 mA. It is this step which eliminates possible interference by oxidizing agents such as cerium (IV), chromium (VI), and manganese (VII). The coulombic requirement for reduction at −0.70 V is then measured until the current again falls to the 0.1-mA. residual level. The time *t* for reduction is also noted and a background correction equal to $10^{-4}t$ coulombs is deducted from the total quantity of electricity consumed.

The presence of equal or larger amounts of perrhenate, or of many other ions, is not harmful. Fluoride and nitrate interfere seriously, however, as do iron (III), molybdenum (VI), ruthenium (IV), uranium (VI), and vanadium (IV). A preliminary distillation of Tc_2O_7 from sulfuric or perchloric acid would eliminate most of these interferences, as well as the strong-oxidant types mentioned above. With 0.5 to 5 mg of technetium, the authors modestly claim merely that the relative error is less than 1% and that the relative precision is better than ±0.5%, although the possibility for appreciably better performance is also evident from their data.

Some of the experiments described in connection with the development of this method are of interest in relation to interpretations of polarographic behavior. In unbuffered tripolyphosphate, the observed shift in $E_{1/2}$ between pH 4.0 and about 6.0 (first three runs of Table 1, ref. 43) would be consistent with an equation very similar to one given above for reductions from mineral-acid solutions:

$$E_{1/2} = 0.0 - 0.11_2 \text{ pH}$$

which would correspond to a reversible four-electron process requiring eight protons. From pH 6.5 to 9.0, however, some transition occurs and above pH = 9, a pH-independent wave is found at $E_{1/2} \cong -0.80$ V. The data of Table 2[43] show a diffusion current constant, *I*, of the order of 12 to 13, which is reasonable for a four-electron process. However, the values of i_d/C vary by more than 15% for tenfold changes in pertechnetate concentration (in the absence of the acetate buffer), which also reflects the tendency (which is borderline at the pH of 6 used here) for an alternative (three-electron?) process to occur. The *I*-value is lowest for the highest concentrations of pertechnetate.

This interpretation is consistent with other observations[16-18] for d.-c. polarography in mineral acid media, except that the comparable transition in processes occurred over a different pH range. In the other mineral-acid media (sulfuric, hydrochloric, or perchloric acid), a pH-dependent four-electron wave is found at pH < 3.5. Above pH = 4.0 this is replaced by a pH-independent three-electron wave with a half-wave potential near −0.80 volt.

The data of Terry and Zittel (Table 3) show a *decrease* of pH (e.g., from 7.0 to 5.5) upon electrolysis of about 6 μeq of pertechnetate in $Na_5P_3O_{10}$ media. An *increase* of pH would be anticipated with the occurrence of reaction (3). A part of the decrease could result from liberation of the protons associated with the phosphate species present at pH 7.5, when an uncharged $Tc^{III}PO_4$ product (or its cluster-ion analog) is formed. Other work[27] does indicate the existence of an uncharged Tc(III) species in (ortho)phosphoric acid. In the experiment cited, a gain of only about 0.08 μeq of proton is involved. Equally plausible, however, is the leakage of some 1 *N* H_2SO_4 through the frit of the compartmented working anode.

Minor modifications in the procedural details of this method might well result in significant improvement in its reliability. It is probable that a safer alternative could be found to the use of commercial grade tripolyphosphate, although there is no clear indication that its use is a source of any serious difficulty. As the authors point out, background current of 0.1 mA for a 10-minute reduction corresponds to a blank correction of 0.06 coulomb. This is a substantial fraction on the 1.56 coulomb needed, e.g., to reduce 0.5 mg of Tc (VII). It is not likely, however, that it can be very substantially decreased at −0.7 V on a cathode of good area. Trace impurities such as iron, which can cause cyclic consumption of current, should certainly be absent. A neutral pertechnetate solution could be more safely deaerated (without loss of $HTcO_4$) just prior to addition to the deaerated buffer, *and out of contact with mercury*.

The time for deaeration within the cell and pre-electrolysis at −0.2 V *in contact with mercury* could be detrimental to the accuracy of the method. The chemical reduction (Equation 4) which may occur would not be self-compensated if any resulting Hg_2^{+2} is pre-reduced at −0.2 V prior to the "run" at −0.7 V. From this point of view, elimination of this pre-electrolysis (*not* of the electrolyte buffer, but *after* the sample addition) may be advisable. For 13 runs using 2 to 10 mg of Tc the authors' data (Table 4[43]) would seem to show a definite negative bias averaging 0.66% relative. The error for 25 runs with 0.5- to 1.5-mg samples appears to be much smaller and random in direction. It does not exceed the relative standard deviation which is as good as ±0.2%. Some experience[51] with the chemical reduction of pertechnetate on mercury surfaces, especially in very dilute acids or at pH 3 to 4, indicates that a small but disproportionately greater extent of reduction occurs with higher concentrations of pertechnetate. This method would appear to be capable of refinement such as to give a relative error and/or standard deviation smaller than 0.2% with 0.5 to 5 mg of technetium.

III. SPECIES AND SPECTROPHOTOMETRY OF (VII) AND LOWER STATES

A. Miscellaneous Chemistry and Spectrometry

The solution chemistry of rhenium and technetium species is relatively complicated, and the numerous species already established and postulated are rapidly being added to and reinterpreted by newer studies. Some of the effect of these advances on the interpretation of electroanalytical behavior is evident from the prior discussion, but their effects on the reevaluation of older spectrophotometric data are even more drastic. In this section a concise discussion of the ultraviolet and visible spectrophotometry of the important (VII)-state species of these elements will be preceded by some comment on newer species formulations affecting the interpretation of spectra of states other than (VII), some analytically important spectrophotometric methods, and some developments in the infrared region.

Older data on the vapor pressures of Re_2O_7 and $HReO_4$[52] and of Tc_2O_7 and $HTcO_4$[53] have been supplemented by additional measurements on H_2O-$HReO_4$ systems.[54-56] One paper[56] would be of some interest in connection with the distillation of $HReO_4$ from sulfuric acid. Another[55] indicates that an aqueous solution containing 41 weight percent of $HReO_4$ boils at 103.5°; and significant amounts of rhenium were not detected in the vapor when the concentration of $HReO_4$ in the liquid phase is lower than about 65 weight percent. However, 9% of $HReO_4$ is found in the vapor when its concentration in the liquid phase is 93 weight percent. The danger of loss of $HReO_4$ from hot aqueous acids appears to be much less than with $HTcO_4$. The heptaoxides M_2O_7 avidly acquire water to form the very strong HMO_4 acids.

At concentrations below 1 *M* and within the pH range 0 to 14, there is little evidence for aqueous species other than the normal tetrahedral MO_4 ion.[27] The per-yl ion MO_3^+ may exist in strongly acidic media, associating with halide when present, as MO_3X. Bromide or iodide, however, results in rather rapid reduction to give MX_6^{-2}. In the case of Tc (but not in that of rhenium), 12 *M* hydrochloric acid reacts almost quantitatively to form a (V) state, possibly $TcOCl_5^{-2}$. It is possible that an intermediate equivalent to (VI) exists as $(TcO_3)_2$ $(TcOCl_5)$, accounting for the transient blue color when impure TcO_3Cl is prepared by addition of hydrochloric acid to pertechnetate in 18 *M* sulfuric acid.[27] Recently, Colton[57] has reported the preparation (in the "dry" way) of the compound $TcOCl_3$.

Intermediate (V)-state sales containing rhenium as $ReOCl_5^{-2}$ can be isolated using stronger reducing agents than chloride ion. With such agents (e.g., iodide or limited amounts of hypophosphite), or by dilution of the hydrochloric acid in the case of technetium, the reaction

$$3\ \mathrm{Tc(V)} \longrightarrow \mathrm{Tc(VII)} + 2\mathrm{Tc(IV)}$$

occurs and yields the (IV) state as the ultimate product. Stronger reduction is necessary to form the (III) state which is not common in aqueous chemistry (recall, however, the cases cited under Polarography and Coulometry), but is best known as variants of cluster-ion species like Re_3Cl_9. Species like $ReCl_6^{-2}$ can be supported in relatively dilute acid, but $TcCl_6^{-2}$ rapidly forms $TcO_2 \cdot 2H_2O$ in hydrochloric acid more dilute than 0.1 *M*.

Rulfs and Meyer followed the gradual titration of aqueous $ReCl_6^{-2}$ with dilute sodium hydroxide solution, observing the changes in conductance and in pH throughout the titration.[37] The pH remains relatively constant until four equivalents of hydroxyl ion have been added and rises sharply thereafter. The conductance rises more or less steeply during the addition of three equivalents, is nearly constant from this point until four equivalents are added, and then rises steeply again. The latter increase may be ascribed to the addition of uncombined hydroxyl ion, but the almost equally sharp increase of conductance (with *constant* pH) for the first three equivalents of OH^- must be explained in terms of other ions.

The behavior is illustrated in Figure 3 and can be rationalized in terms of the following sequence of reactions:

$$
\begin{array}{ll}
1. & ReCl_6^{-2} \xrightarrow[H_2O]{KOH} [ReCl_4(OH)(H_2O)]^- + K^+ + 2Cl^- \\
2. & \xrightarrow[H_2O]{KOH} [ReCl_2(OH)_2(H_2O)_2]^\circ + K^+ + 2Cl^- \\
3. & \xrightarrow[H_2O]{KOH} [Re(OH)_3(H_2O)_3]^+ + K^+ + 2Cl^- \\
4. & \xrightarrow[H_2O]{KOH} [Re(OH)_4(H_2O)_2]^\circ + K^+ + H_2O \\
 & \qquad\qquad\qquad \downarrow\uparrow \\
 & \qquad\qquad\qquad ReO_2 \cdot 2H_2O + 2H_2O \\
5. & \xrightarrow{KOH} K^+ + OH^- \ (\text{excess})
\end{array}
$$

The introduction of K^+ and OH^- beyond stage 5 contributes a total 272 units to the equivalent conductance, which is not much different from the total of 226 resulting from K^+ and 2 Cl^- in stages 1 to 3. Smaller distinctions within the first three stages result from the differences of equivalent conductance among the successive complex species of rhenium, stage (2) in particular showing a smaller increase of conductance since the resulting complex is uncharged. Step 4 involves little change in conductance since it merely substitutes the equivalent conductance of potassium ion for that of the univalent complex ion that it replaces.

The quantitative formation of $ReCl_6^{-2}$ by reduction with hydrazine in hot hydrochloric acid[58] or with chromous chloride[25] permits its spectrophotometric determination ($\epsilon = 1.2 \times 10^4$ at 281.5 nm); if necessary, this may be preceded by a cupferron extraction of molybdenum.[58] The procedure is rapid and reasonably sensitive and selective, and the reproducibility of the $ReCl_6^{-2}$ spectrum seems to be very good. For the comparable Tc species ϵ -values near 1.9×10^4 and 1.1×10^4 at 234 and 338 nm, respectively, have been given. Older concern for some possible tendency for photocatalyzed air oxidation[59] has been examined by Kanchiku.[60-62] It is concluded that photoaquation occurs, giving a series of mixed aquochlorocomplexes of technetium (IV) which have distinctively different absorption behavior. The technetium (IV) initially formed by these reductants (in contrast to the technetium (V) that is the main product of direct reduction by hydrochloric acid alone) retains the $TcCl_6^{-2}$ structure in 12 *M* hydrochloric acid, but exposure to ultraviolet light in 8 to 3 *M* hydrochloric acid results in gradual stepwise transitions down to $[TcCl_3(H_2O)_3]^+$. Some difficulties will therefore attend any attempts to reproduce such spectra for analytical or other purposes. Figure 4 shows the main features of the spectra of $ReCl_6^{-2}$ and the comparable $TcCl_6^{-2}$ in contrast with the spectrum of the aquated Tc(IV) species, $[TcCl_4(H_2O)_2]^0$, though it may be noted that this spectrum of $ReCl_6^{-2}$ differs from that now accepted by some authors.[68]

Despite the occasional interference of molybdenum, the thiocyanate spectrophotometric methods for rhenium and technetium have good sensitivity and remain widely used. It is clear that both (V) and (IV) state compounds exist for both elements, and many different formulations have been advanced for the major species. Bailey and Kozak[63] prepare the (V) form $[Re(SCN)_6]^-$ in a fused melt and recognize only this and the (IV) form $[Re(SCN)_6]^{-2}$ as products of aqueous reductions of (VII), either by thiocyanate alone or with tin (II). They find no evidence of oxythiocyanates. The detailed study of Crouthamel[28] recommends use of the more intensely colored (V) forms ($\epsilon = 4.5 \times 10^4$ at 430 nm for rhenium and 5.2×10^4 at 513 nm for technetium) in approximately 60% acetone.

The α-furildioxime reaction with a (?) lower state of rhenium, proposed by Meloche, Martin, and Webb[64] is about as sensitive as the thiocyanate method and is equally useful. It involves reduction with stannous chloride in 0.8 *N* hydrochloric acid

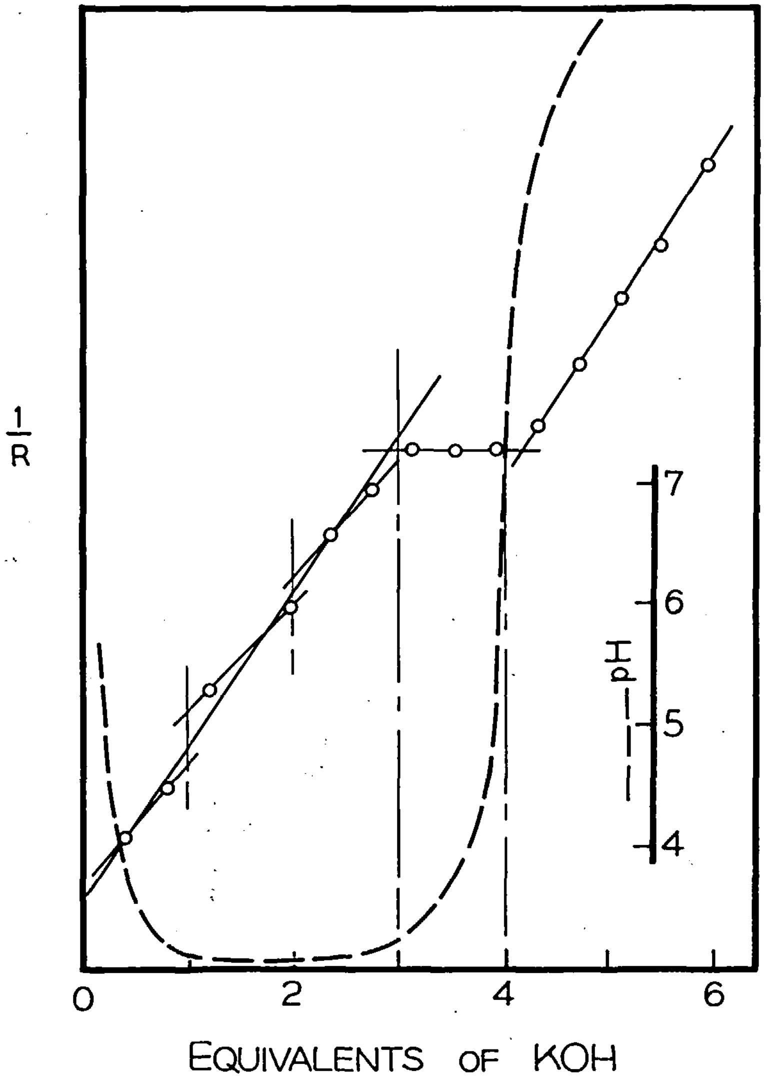


FIGURE 3. Conductance and pH during titration of K_2ReCl_6 with potassium hydroxide solution.

and 26% acetone, and gives a red-purple complex absorbing near 532 nm with $\epsilon = 4.1 \times 10^4$. The interference of molybdenum is obviated by extracting that element with ethyl xanthate into chloroform. Dahlby and Waterbury[65] include a separation by distillation and determine 0.01 to 0.2% of rhenium in plutonium with relative standard deviations of 1.4 to 0.4%, respectively. They have also applied the method to samples containing rhenium at concentrations as high as 8%.

In recent years, the reactivities of many dyes (including Orange R, toluidine blue, and methyl green, among others) with perrhenate have been noted.[66] The resulting complexes are soluble in benzene or ethylene chloride and have molar absorptivities of the order of 10^5. Tarayan and Vartanyan[67] form a methylene blue complex with perrhenate at pH 4 to 5 using a twenty fold excess of reagent. The complex can be extracted into ethylene chloride and has a molar absorptivity of 1.1×10^5 at 645 nm. To date, a comparable reactivity with pertechnetate (which seems most likely to exist) has not been reported.

Jezowska-Trzbiatowska et al.[68] contribute some interesting observations and interpretation concerning the magnetic and spectroscopic properties of the d^0, d^2, and d^3 (VII, V, and IV state) structures. The $ReCl_6^{-2}$ is interpreted as being the strongest (with $MnCl_6^{-2}$ being the weakest) complex of the (IV) series, and the discussion emphasizes the weak crystal field bands more than the analytically familiar strong charge-transfer absorptions. The octahedral (IV) d^3 structures have paramagnetic susceptibilities explained by the three unpaired electrons of the half-filled lower t_{2g} orbital. The weak visible-region absorptions of the d^2 (V)-species, $TcOCl_5^{-2}$ and $ReOCl_5^{-2}$, are shown. One of the weak (ϵ - *ca.* 5) $TcOCl_5^{-2}$ absorptions at 16,700 cm^{-1} would appear to be coincident with the strong 595-nm band of "impure" TcO_3Cl,[27] and some other similarity is noted (recall earlier discussion, paragraph 2). The hexacoordinate d^2 (V) compounds of rhenium and

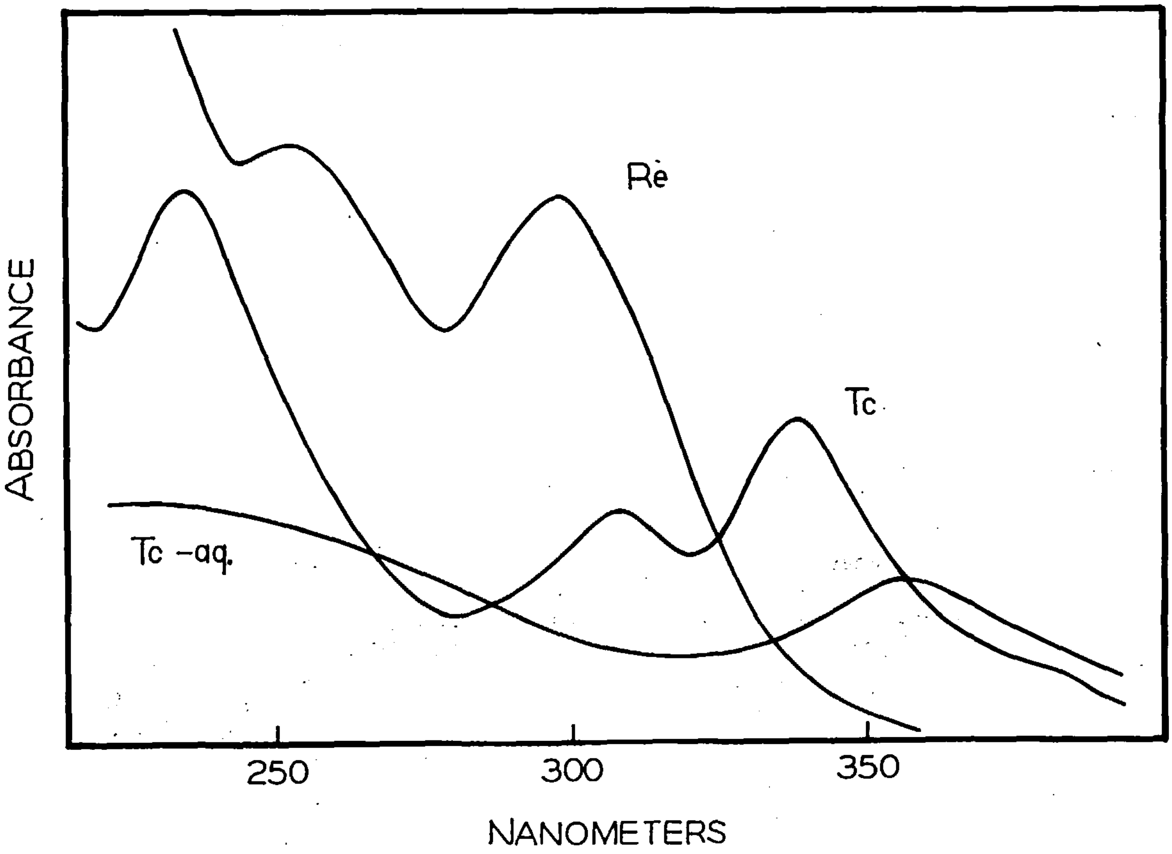


FIGURE 4. Absorption spectra of MCl_6^{-2} solutions and the diaquotetrachloro Tc(IV) species.

technetium are uniformly spinpaired and diamagnetic, although ReO_2^+ types may have a very weak paramagnetism. This is also true of K_2ReOCl_5, which was formerly claimed to exhibit considerable paramagnetism. The tetrahedral d^0 (VII) ions are but weakly paramagnetic.

While rarely of special value for quantitative *inorganic* analyses, spectrophotometry in the infrared region possesses potentialities for imparting *structural* (as opposed to simple qualitative analytical) information on inorganic compounds that are similar to those it has for organic ones. Especially with respect to rhenium and technetium structures, recent improvements in this area must, however, be characterized as being more numerous than real. The literature contains many contradictory interpretations, and the number of reliable ancillary x-ray structural determinations is just beginning to become adequate to clarify some of these conflicts. The subject remains too full of unresolved issues to permit giving it more than a passing notice here.

There is a long history of Raman-infrared studies of crystalline perrhenates and pertechnetates and comparisons of their spectra with "perturbed" spectra in concentrated solutions. Busey and Keller.[69] offer one explanation for the appearance of only two, of four, Raman lines in aqueous pertechnetate. Peacock (ref. 2, p. 37) lists some older assignments. The following examples may be cited:

Vibrational wave-numbers, cm^{-1}

	ν_1	ν_2	ν_3	ν_4
TcO_4^-	912	(very weak)	(913)	326
ReO_4^-	971	(331)	918	343

None of these values should be used without consulting the contemporary literature.[69, 70] Canterford, Colton, and Tompkins[71] have summarized some useful generalizations on the positions of terminal M=O as compared with bridging M—O frequencies. Recent x-ray structural data by Krebs et al. for Re_2O_7[72] and Tc_2O_7[73] can now be compared with interpretations of the infrared and Raman spectra of Re_2O_7[74] and $HReO_4$[75] A profusion of rather contradictory infrared data has been reported for rhenium and technetium (V) chelates and complexes. It has rather tenuous analytical interest and is too inconclusive to be usefully presented here.

B. Spectrophotometry of (VII) Species

The principal features of the familiar visible spectrum of MnO_4^-, the doublet at 525 and 545 nm with a shoulder near 565 nm, are reflected in the absorptions of TcO_4^- and ReO_4^- in the ultraviolet region (the 310- and 202-nm permanganate peaks are important but less familiar). The pertechnetate doublet at 244 and 248 nm is well enough resolved to be recognized as being composite, and the 287.5-nm peak is clearly separated. The perrhenate doublet at about 204 and 206 nm will be observed as a single peak at 205 nm on most instruments; the higher wavelength peak, at 227 nm, is rather well defined. The important features of these spectra are shown in Figure 5, although the characteristic vibrational (fine) structure is not shown. The electronic transitions responsible for the principal bands have been assigned by Viste and Gray[76] and are listed elsewhere.[68] A few comments on (VII)-spectra, including infrared spectra, have been included in section A above.

It seems well established that technetium (V), probably as $TcOCl_5^{-2}$, is a principal and rapidly formed product of the reaction of pertechnetate with 12 *M* hydrochloric acid. It is likely, therefore, that the formation of pertechnetyl, which is reported to occur on addition of hydrochloric acid to pertechnetate in concentrated sulfuric acid, gives rise to some contamination by technetium (V). Accordingly, the reported spectrum[27] of the compound prepared in this manner is not likely to represent that of the pure material (see comments in section A). The bulk of this preparation, however, can be back-extracted from chloroform into dilute aqueous base, reverting to pertechnetate in the process.

Measurements[27] based on the rates of acid-catalyzed sucrose hydrolysis, of the acid strengths of $HReO_4$ and $HTcO_4$ give acid dissociation constants greater than 10^8. In earlier attempts to measure the more moderate values which had been anticipated for these constants, the spectrophotometric behaviors of the MO_4^- species were examined in increasingly concentrated solutions of perchloric or sulfuric acid. Significant transitions in the spectra begin to occur with acid concentrations greater than about 7 *M*. Transitions to MO_3^+, including $MO_3(OH)$, may be involved. But a large proportion of the change is ascribed to the formation of Re_2O_7 or Tc_2O_7.

No significant changes occur in the ultraviolet spectra of aqueous pertechnetate or perrhenate over wide (approximately 10^{-5} to 0.2 M) concentration ranges, nor over the range of pH from 0.3 to 12.[27] This extensive "Beer's law" study involved the use of 0.01 mm to 5 cm cell paths, the use of absorbance readings from 0.1 to 1.0, and some differences in slit-width settings between runs. Hence, the reproducibility (e.g., of *ca.* ±1% relative), for the 244- and 248-nm peaks of pertechnetate of the molar absorptivities is certainly not directly indicative of the optimum precision or accuracy which should be expected of analytical applications confined to a more restricted concentration range. There is but limited justification, however, for reporting experimentally measured ε-values in the literature with the implication that they have absolute meaning within, say, one part in 6,000. This is especially true for the doublet peaks, for which the data are critically dependent on band width.

Within these restrictions, we may cite the following generally accepted values of molar absorptivity for aqueous solutions of perrhenate: 5940 ±60 at 205 nm and 3600 ±50 at 227 nm; for pertechnetate the corresponding values are 6190 ±40 at 244 and/or 248 nm and 2340 ±20 at 287 nm. The very low wavelength of the perrhenate peak makes for a large number of potential interferences in its measurement. Still, it has some utility, to better than ±1%, when applied to relatively pure rhenium materials.

The selectivity is appreciably better in the case of pertechnetate, and accuracy and precision within 0.5% relative is obtainable. Obviously, one should read the maximum from the continuous curve between 240–250 nm, rather than rely on a single reading at a fixed wavelength setting. The concentration is best based upon careful calibration using one's own instrument. Calibrated 1- to 10-cm cells with solutions giving absorbances greater than 0.15–0.20 but not above about 1.0, would define the preferred concentration range. For many research and some routine analytical uses, the characteristic shape of this curve is rather

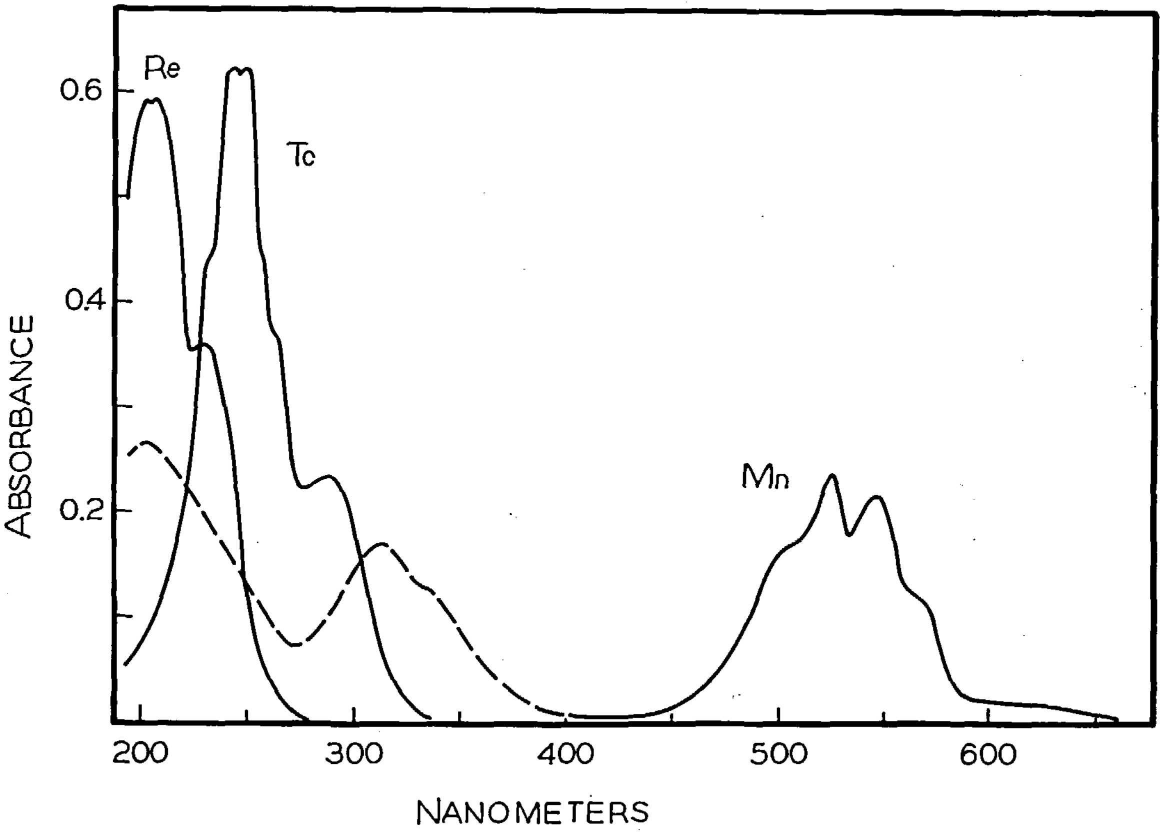


FIGURE 5. Absorption spectra of approximately 10^{-4} M MO$_4^-$ solutions in 1 cm cells.

favorable for good resolution in multicomponent spectrophotometry in the presence of impurities. For the assay of high or low concentrations of pure technetium materials, the method competes very favorably with the limited alternatives which are available. For example, low-energy beta counting of Tc^{99} is difficult to reproduce better than ±2%.

As early as 1933, B. Scharnow reported the isolation from strongly alkaline perrhenate solutions of the relatively insoluble salt $Ba_3(ReO_5)_2$. The extent to which any MO_5^{-3} meso-forms of rhenium or technetium (VII) may exist in alkaline aqueous media is obviously of general interest and of special concern for spectrophotometric measurements. A recent interpretation[77] of the changes in perrhenate spectra observed in 15 *M* sodium hydroxide concludes that only 35% of the perrhenate is converted to a meso-species in this medium. Estimated molar absorptivities of the mesoperrhenate peaks are 6400 at 260 nm and 1400 at 308 nm. The effect of strong base on the spectrum is illustrated in Figure 6. The extent of meso-formation would be negligble in aqueous solutions containing less than 1 *M* base.

In the case of pertechnetate, no evidence for detectable meso-conversion was found at any attainable alkalinity of aqueous solutions. In fused sodium hydroxide, however, two new higher-wavelength absorptions do appear: one near 345 nm and the other, which is half as intense, at 420 nm (a much weaker peak at 570 nm may be due to an ortho-form). The low solubility of the barium mesoperrhenate permits another indirect test of the conclusion regarding the distinct differences between the behaviors of technetium (VII) and rhenium (VII) in aqueous base. About 100-mg amounts of rhenium (VII) in approximately 12 *M* aqueous sodium hydroxide were successfully precipitated by barium ion in the presence of 0.5 to 1 mg of technetium (VII). Less than 0.5% of the Tc^{99} was carried on the $Ba_3(ReO_5)_2$ precipitate. However, carbon dioxide should be excluded, as a subsequent precipitation of barium carbonate can

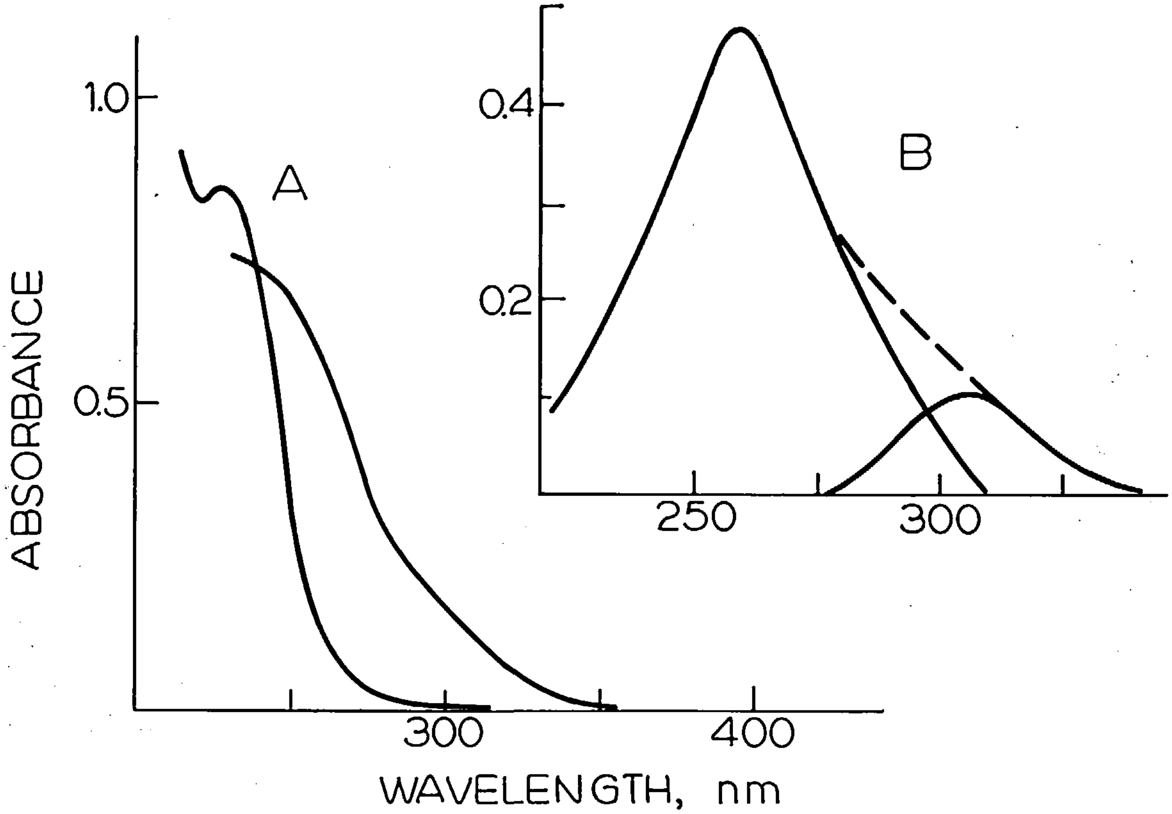


FIGURE 6. A. Absorption spectra of 2 x 10^{-4} *M* perrhenate in water and (to the right) in 15 *M* sodium hydroxide; B. the resolved features due to 35% of meso form in strong base.

carry up to 4–6% of the technetium.[78] Evidently, such a procedure could provide the basis for a separation of rhenium from technetium.

IV. (V)-STATE SPECIES: THE TECHNETIUM 8-QUINOLINOLATES

A. General Background

The significances of the intermediate (V)-state in certain polarographic reductions and in the important colorimetric thiocyanate methods for rhenium and technetium have been noted in prior discussions, but analytical chemists have been especially slow to recognize the fact that rhenium and technetium occur almost as frequently in the (V) as in the (IV) state. Unfortunately, it is not easy to prepare and isolate these in pure forms. They are often synthesized by air-oxidizing the (IV)-state compounds in the presence of suitable chelating agents,[79] but many such reactions give modest yields and impure (V) products. While many strong reducing agents will reduce (VII) to (IV) or (III) states, few of these reactions seem to permit trapping and recovering the (V) intermediates with chelating agents added to the reaction mixtures. But it is likely that many of the color-forming reactions of (VII) with reducing chelating agents (or with chelating agents in the presence of reducing agent) involve (V) compounds.

The reaction of a solution of rhenium (VII) at pH 1 with tin (II) *in the presence of o*-mercaptobenzoic acid (SB) is claimed[80] to lead to an $Re(SB)_2$ chelate of Re(V); however, the molar absorptivity is only 6100 at 395 nm. Similar reductions in the presence of dioximes lead to (V) chelates; but with pyridine ligands present, rhenium (IV) and (III) salts are formed.[81] In the case of technetium (VII), workers continue to agree[82] that technetium (V) is a prompt and major product of simple reaction with 12 *M* hydrochloric acid.

The analyst concerned with the general problem of separating technetium or rhenium from other elements soon recognizes one particularly dismaying void in the available literature: there is almost no reliable information on the behavior of the various oxidation states of these two elements with such common and important reagents as EDTA, 8-quinolinol, and cupferron.[83]

Cotton[84] proposed a classification of the better-characterized chelates of rhenium and technetium (V) into five major categories. When considered with other known (V)-state compounds of these elements, it is evident that the chemistry and structural possibilities for this state are extremely varied. Somewhat less is known with certainty about the technetium than about the rhenium compounds. One interesting series of water-soluble rhenium (V) chelates was first reported by Ivanov-Emin.[85] In 1963, Murmann[86] reported the acid association (here expressed as dissociation) behavior for this system,

$$[Re(OH)_2en_2]^{+3} \underset{}{\overset{10}{\rightleftharpoons}} [ReO(OH)en_2]^{+2} \overset{10^{-3}}{\rightleftharpoons} [ReO_2en_2]^{+}.$$

In 1965, Trzebiatowska[87] claimed to have isolated two rhenium (V) chelates from the fusion of 8-quinolinol in air with ReO_2 and characterized them as being $[ReO(OH)Ox_2]$ and $[ReO_2Ox(H_2O)_2]$. These are assumed to be octahedral; both are diamagnetic and insoluble in chloroform. Hirsch[88] confirmed that no technetium (VII) is extracted by 8-quinolinol in chloroform from aqueous media over the pH range 0–12. He also found evidence for intermediate (VII-IV) state chloroform-soluble 8-quinolinol chelates of both rhenium and technetium.

The composition of the solvated uranyl "oxinate" (8-quinolinolate) chelate, $UO_2Ox_2 \cdot HOx$ normally obtained by precipitation from solution has been known for many decades. Its ultraviolet and visible spectra,[89,90] "acidity,"[90] and infrared spectrum[91] were examined. The existence of a comparably unusual oxinate of PuO_2^{+2} and other abnormal types of oxinates is recognized. Further reports of infrared spectra[92, 93] and thermal stabilities[94, 95] have appeared, and several structural proposals are current.[96]

Hall et al.[97] present a most interesting x-ray crystallographic structure for the $UO_2Ox_2 \cdot HOx$ compound (Figure7). The trans-uranyl oxygens lie at right angles to the three oxine molecules, which are essentially coplanar. Two of the molecules of oxine are biligated in a normal fashion, but the third is monoligated to the metal via a phenolic oxygen. The charge-balance of this heptacoordinate structure and the "acidity" of the chelate result from the presence of a quinolinium proton on the nitrogen atom of the third oxine, which

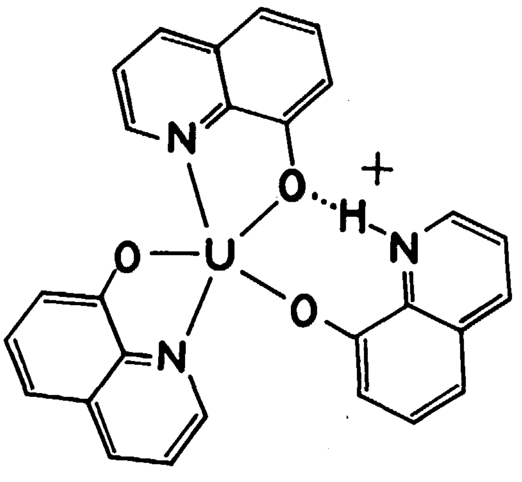


FIGURE 7. Hall's structure for uranyl *tris*-8 quinolinolate. The *trans* uranyl oxygens are normal to this plane.

forms a strong hydrogen bond between this atom and the phenolic oxygen of an adjacent biligated oxine. The U–N distance of 4.1 in the monoligated oxine contrasts with 2.6 A in the case of the two normal ligands.

This background will serve to introduce a summary of the present status of a study of the technetium (V)–8-quinolinol system. This study is a portion of work supported by an Atomic Energy Commission Contract AT(11-1)-1483. Major portions of the experimental work were carried out by Drs. Santosh K. Majumdar, Roland F. Hirsch, and Mohammed S. Rahaman. It will be obvious from the useful properties of this system (e.g., a distribution coefficient of 760 between chloroform and an aqueous solution of pH=0 and a molar absorptivity of about 1.1 X 10^4), as well as those of many other chelates of technetium and rhenium (V), that this general class of compound has great importance in analytical chemistry.

B. Technetium (V) 5,7-dichloro-8-quinolinolates

1. Synthesis, Composition, and Molecular Weight

For a "large-scale" preparation a pertechnetate solution containing no more than 10 mg of Tc^{99} is taken to dryness (to avoid subsequent dilution of acid) in the apex of a separatory funnel and treated with 1 ml of 12 *M* hydrochloric acid. Excess chlorine is swept out by passing nitrogen *over* the solution for 1 minute. Two ml of 4 *M* hydrochloric acid is added *with* 75 ml of chloroform containing about 60 mg (3 Ox/Tc) of 5,7-dichloro-8-quinolinol reagent, corresponding to 3 moles of reagent per mole of technetium, and the mixture is stirred or shaken while 23 ml of 0.5 *M* hydrochloric acid is slowly added over a 5- to 10- minute period. After an additional 10–15 min with intermittent mixing, the layers are separated, the aqueous phase is washed with 5–10 ml of chloroform, and the combined chloroform layers are rinsed with 10–15 ml of 0.1 *M* hydrochloric acid and dried overnight in contact with 5–6 g of anhydrous sodium sulfate. The solution is then decanted through a filter into a clean vessel and the chloroform is evaporated (at slightly elevated temperature and reduced pressure, if desired); the last 20–25 ml of concentrate may be transferred to a final storage vessel for taking to dryness. The solution is finally placed in an Abderhalden chamber over desiccant for 1 hour at 80–90° under reduced pressure. This gives a partially "acidic" form I, with some conversion to another form II_2 due to concentrating.

For "alkaline" preparations of form II_2, begin as above, including the washes. Treat the solution of chelate in about 80 ml of chloroform with three successive 80-ml portions of an aqueous solution of pH 12.4 ± 0.2, shaking for 10 min during each extraction. Rinse the chloroform phase once with 15–20 ml of water, dry over sodium sulfate, evaporate, etc., as before.

More than 96% of the technetium can be recovered in the acid product, but recovery in the alkaline form is usually no better than 80% because of partial decompositions and losses to the alkaline aqueous phases. Similar preparations, attempted with amounts of reagent limited to two moles per mole of technetium, give lower yields. For analytical, rather than preparative, purposes one proceeds as in the "acid" preparation but uses some excess of reagent and much smaller volumes of chloroform. The combined chloroform extracts are diluted to some definite volume (such as 25 or 50 ml) for spectrophotometric measurement at 420 nm, where the molar absorptivity is 1.104 X 10^4. The conversion and extraction are at least 98% complete. The initial concentration of hydrochloric acid must be 12 *M* and the solution must not be prematurely diluted if the conversion to technetium (V) is to be complete. There is no advantage in ultimate dilution to an acidity below about 2 *M*, since the extraction into chloroform is essentially quantitative from even more concentrated acid. The selectivity of the method is compromised by such dilution.

This synthetic route has been used because it is virtually quantitative and because it introduces no foreign metals that would complicate matters by reacting with oxine. The choice of the 5,7-dichloro reagent for an initial study of the system is then dictated by the fact that the chlorine produced during the reduction with 12 *M* hydrochloric acid would result in partial mono- and di-chlorination of unsubstituted 8-quinolinol if this were used, and would thereby lead to a confusing mixture of products having different extraction and spectrophotometric properties. Low-temperature (750°) Dumas nitrogen runs on I or II gave 5.4 ±0.5% N for eight products. The Tc^{99} assays were usually based on comparative counting on evaporated aliquots of known solutions and showed 13.1 ± 0.2% technetium. A special semimicro wet-combustion assembly for the determination of carbon was tested, and blanks were determined, with pure reagent and reagent plus added technetium. Van Slyke oxidant was used, and the train included a cold trap for Tc_2O_7.

The chelates were surprisingly camphor-soluble, permitting a Rast molecular-weight determination. Repeated remelting and freezing did not seem to result in any drift in the readings; hence the thermal stability of the chelates near 175° is good. The results found for (n) runs were:

	Experimental (n)			Theory for TcO_2Ox_3*
N	5.4	± 0.5%	(8)	$5.4_5\%$
Tc	13.1	± 0.2%	(10)	13.0%
C	42.0	± 0.5%	(4)	42.1%
MW	764	±35	(2)	770

* We shall later distinguish between O and OH in this composition.

The selective removal (or back-extraction) of any excess reagent from the chelate itself is difficult. In justifying the unexpected composition of the chelate, it is important to establish that the third mole of oxine is combined. The Rast molecular-weight determination indicates that this is the case up to the melting point of camphor, and also that a dimeric variant (II_2) is completely dissociated at this temperature.

Thermal stability was checked by slowly heating the chelate in a Pregl regenerating block under dried air at slightly reduced pressure. There was little weight loss below 240° C and less than 8% after 30 minutes at 275°. The pure reagent sublimed rapidly at 210° in the same apparatus. Several samples were examined by mass spectroscopy, showing the peak at $m/e = 770$ and expected fragment peaks as well as the doubly-charged peak at $m/e = 385$. This interesting example of mass spectrometry of a chelate will be mentioned in section V.

2. *Liquid - Liquid Extraction*

The partitioning of this chelate system between chloroform and aqueous media of a wide pH-range is shown in Figure 8. It will facilitate our attempts to rationalize this pattern of behavior if we permit ourselves to formulate the species somewhat euphemistically as shown in Figure 9. We shall deal with further interpretation of the meaning and possible structures of the system in a later section.

The partitioning behavior of the Tc (V) 5,7-dichloro-8-quinolinolates can be described in terms of the existence of a series of increasingly basic species such as,

$$[Tc(OH)_2Ox_2]^+ \xrightleftharpoons{K_1}$$

$$[TcO(OH)Ox_2]^\circ \xrightleftharpoons{K_2} [TcO_2Ox_2]^-,$$

where "Ox" represents the 5,7-dichlorooxinate anion. In the absence of large organic cations, the third species is exclusively water-soluble. The chloroform-soluble forms of each of the first two species include a third mole of monoligated oxine. In the present discussion these two forms may be taken as equivalent to,

$$\text{I.}\ [Tc(OH)_2Ox_2]^+\,[Ox]^- \rightleftharpoons$$

$$\text{II.}\ [TcO(OH)Ox_2]^\circ \cdot HOx, \qquad (1)$$

where the latter exists in both a monomeric and a dimeric form, II_2.

The partition coefficient of the dichloroxine reagent into chloroform is very high, about 7200, and its water solubility is low. The successive acid dissociation constants for the quinolinium – quinolinol – quinolinate transitions are 1.5 × 10^{-3} and 2.3 × 10^{-8}, respectively. The solubility of the *tris*-oxine chelate in chloroform is less than 0.01 *M*. Back-extractions from approximately 5 × 10^{-5} *M* solutions of the chelates in chloroform were used in most of the extraction studies. Solutions of *a priori* "acidic form" are reasonably stable at this concentration. "Alkaline forms" are readily converted to "acidic" ones in contact with aqueous acid and/or dissociate to monomer on simple dilution. The opposite conversion tends to be slow for low concentrations of chelate in contact with aqueous phases of pH $\leqslant 12$. The "acidic" to "alkaline monomer" transition may be viewed as a transition that is tautomeric but slow to reach equilibrium.

A system of *bis*-oxinate species is postulated for the aqueous forms, which are present at very low concentrations. Decomposition of the chelate by air-oxidation and/or disproportionation tends to occur in aqueous phases of pH > 13. Comparative counting of the Tc^{99} in evaporated aliquots from the two phases defined the distribution of the technetium, which is identifiable with that of the chelate (in other than highly alkaline media). In measuring *D*-values as high as 760, or even 100, the aqueous phases obtained after initial separation in the ordinary way were also centrifuged prior to withdrawing aliquots for counting. Some behavior of interest occurs at "pH numbers"

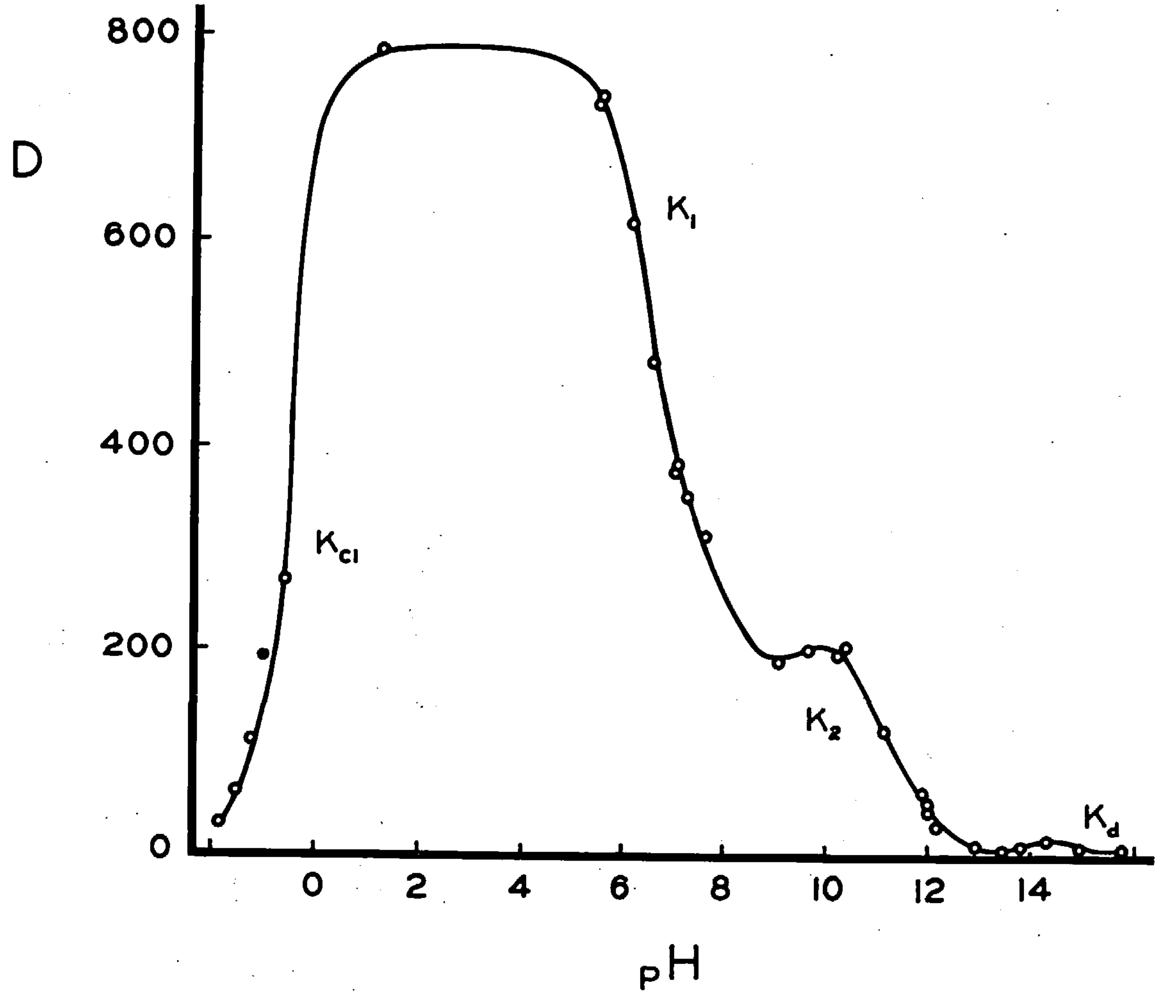


FIGURE 8. Partitioning into chloroform of the technetium(V) *bis*-oxo-*tris*-(5,7-dichloro-8-quinolinolate) system.

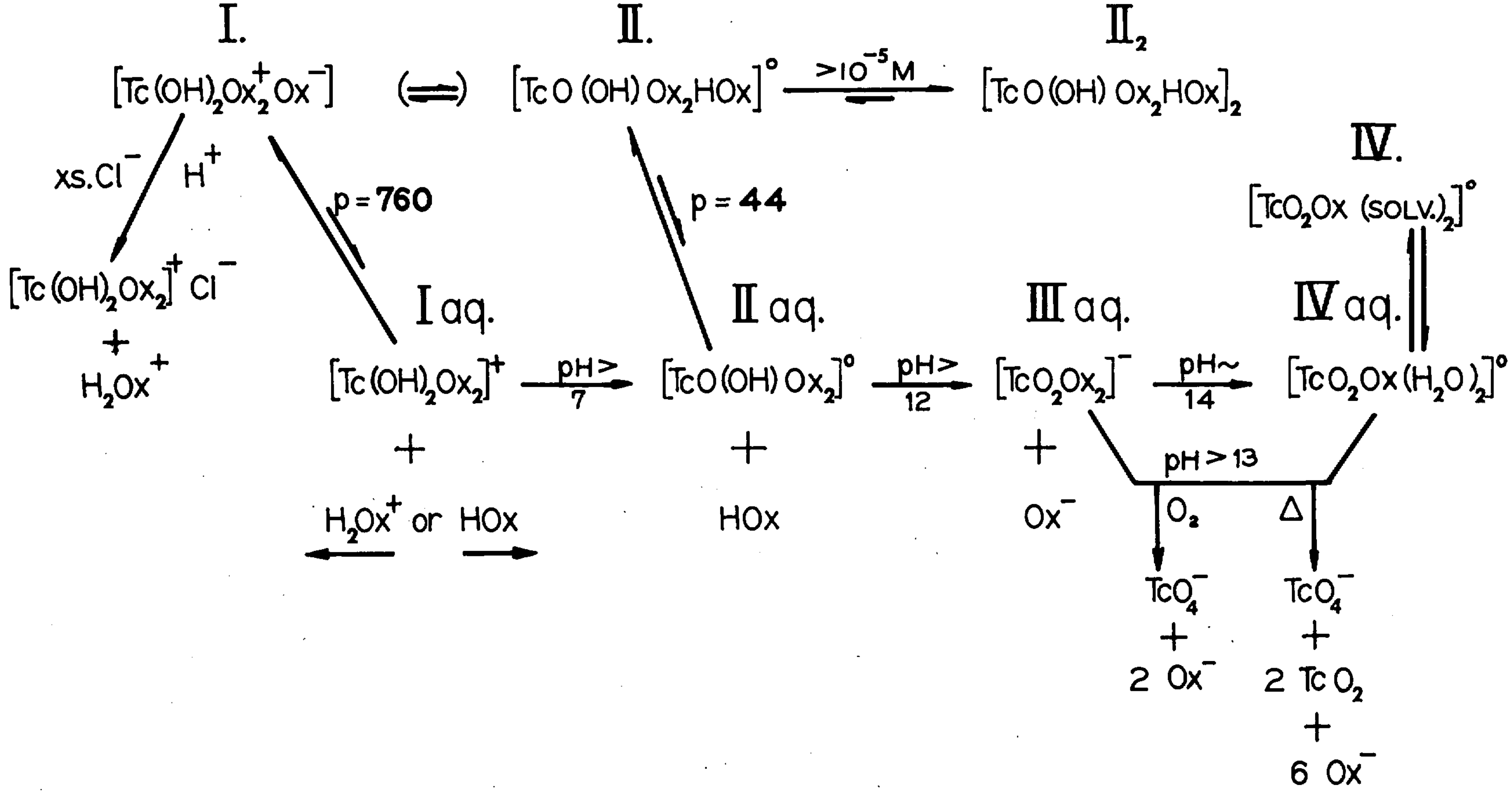


FIGURE 9. Schematic representation of the chloroform (upper) and aqueous (lower) species transitions for the technetium(V) oxinates.

below −1 and above 15. Such figures are only calculated from literature data on the mean activity coefficients of strong electrolytes.

The partition coefficient for the acidic form I is 760 ± 20, and this form is almost wholly in the chloroform phase even below pH 1. Aqueous hydrochloric acid at concentrations of 3, 6, 8, or 10 *M* (mean ionic activities of about 4, 19, 40, and 70 *M*, respectively) lowers the distribution as shown. If the water-soluble species were formed from the chloroform-soluble one by proton addition and if the protonated form had a dissociation constant K_a, then

$$D = 760/\{L+([H^+]/K_a)\}$$

The experimental *D*-values for the four concentrations give calculated values of 2.3, 3.3, 2.9, and 2.9 for K_a.

This consistency is impressive, but the resulting value is over 7 orders of magnitude higher than that for the dissociation of the next proton (see K_1 on the figure). A more plausible transition is

$$[Tc(OH)_2Ox_2]^+[Ox]^-_{CHCl_3} \rightleftharpoons [Tc(OH)_2Ox_2]^+[Cl]^-_{aq}$$

although the third oxine is actually monoligated to the metal. The equilibrium constant of this reaction is related to the reciprocal of the association constant of a monochloro complex. Using mean ionic activity coefficients for hydrochloric acid, one can as well refer to a pCl as to a pH scale. A fifth point on this curve refers to an aqueous phase which was 0.1 *N* in hydrochloric acid (pH = 1) *and* 5 *M* in lithium chloride (pCl = −1). The consistency of this point with the data for solutions of hydrochloric acid alone supports this interpretation. Although these data are necessarily approximate, they would seem to exclude a possible dependence on the square or any higher power of the chloride-ion activity, which would result in any displacement involving more than one chloride ion.

At pH 7 the measured *D*-value is 380 and the assumption that the extraction is controlled by a transition

$$[Tc(OH)_2Ox_2]^+ \rightleftharpoons [TcO(OH)Ox_2]^0$$

such that,

$$D = 760/\{1 + (K_1/[H^+])\},$$

provides a good fit from pH = 5 up to this point. A constant value for K_1 of 1.0 ± 0.1 × 10^{-7} fits the data. If this portion of the curve is extended and symmetrically turned at the toe (as if the more alkaline form were water-soluble), it would intercept the $D = 1$ level at a pH of approximately 9.7 ± 0.3. The calculated pH for "half-extraction" should be,

$$\begin{aligned} pH_{1/2} &= pK_1 + \log 760 \\ &= 7.0 + 2.9 = 9.9 \end{aligned}$$

The concept is reasonable, and the asymmetry beyond pH 7.5 is interpretable in terms of a chloroform-soluble dimer.

A plateau region extends from pH = 8 to 10.0 and defines the partitioning of a more "alkaline" species II. However, the partition coefficient for the monomeric species is $P_{II} = 44 \pm 2$, and not 200 as it might seem from the figure. The *D*-value found at the plateau is sharply dependent on the concentration of chelate present. Its behavior in the range between 0.02 and 0.12 m*M* conforms to the occurrence of dimerization in the chloroform phase.

The extraction between pH = 10.0 and 12.5 (and even beyond that to 13.3 if correction is made for decomposition in the aqueous phase) can be described in terms of P_{II} for the monomer, K_2 for the equilibrium II ⟶ $[TcO_2Ox_2]^-$ in the aqueous layer, and a dimerization constant $K_{dim.}$ for the reaction $2(II) \rightleftharpoons (II)_2$ in the organic layer. In this range of concentrations and pH-values, the total analytical concentration of chelate, C_t, provides a good approximation to the sum of the concentrations of all of the species in the organic phase. One of several ways of describing the relationship is

$$D = P_{II}(1 \pm \sqrt{1 + 8K_{dim.}C_t})/2\{1 + (K_2/[H^+])\}$$

Values for the other constants are $K_2 = 1.1 \pm 0.1_6 \times 10^{-12}$ and $K_{dim.} = 1.1_5 \pm 0.1_0 \times 10^5$. The latter value is confirmed by spectrophotometric dilution studies, which yield 1.1 ± 0.3 X 10^5.

It is increasingly difficult to obtain experimentally reproducible values of D beyond pH 13. At least three types of decomposition or transition which contribute to this situation are indicated on the flow diagram. In view of the tentative character of some of the prior interpretations, we will not elaborate on the requirements for calculations involving the pH-interval from 7.5 to 10. The above premises provide a satisfactory basis for such calculations, but an evident violation of the principle of microscopic reversibility is inherent in the premises. The violation is easily lifted only if one assumes that, despite the good experimental reproducibility of these results, the tautomeric I $\rightleftharpoons$ II equilibrium is only *very* slowly established. Near pH 10, the values of D decrease on decreasing the total concentration of the chelate, and asymptotically approach a lower limit of 44 ± 2, the partition coefficient of the monomeric alkaline form. Spectrophotometric dilution studies imply that the dimer – monomer transition, $II_2 \longrightarrow 2II$, is relatively facile.

3. Spectrophotometric Properties

Chloroform solutions containing the acidic or dimeric alkaline chelate at concentrations of about $10^{-4}M$ such as are used in the extraction studies, are well suited for examination of the ultraviolet and visible absorption spectra (Figure 10). Throughout most of the pH range, however, the corresponding equilibrium concentrations of chelate in the aqueous phase are too low for spectrophotometric measurement. Higher concentrations of modified species can be obtained in aqueous solutions, but, unfortunately, examination in the sodium chloride infrared region is also not feasible at the saturation-limit concentrations of the chelate in chloroform solution. Obviously, the examination of solid chelates isolated by concentration from chloroform solutions may not directly reflect the species originally present in $10^{-4}M$ solution.

The most characteristic feature of both chelate forms in chelate solutions is a strong absorption band near 420 nm (see Figure 10). The utility of this peak for analytical purposes has already been mentioned. The molar absorptivity of the completely "acid" form of the chelate at this wave-

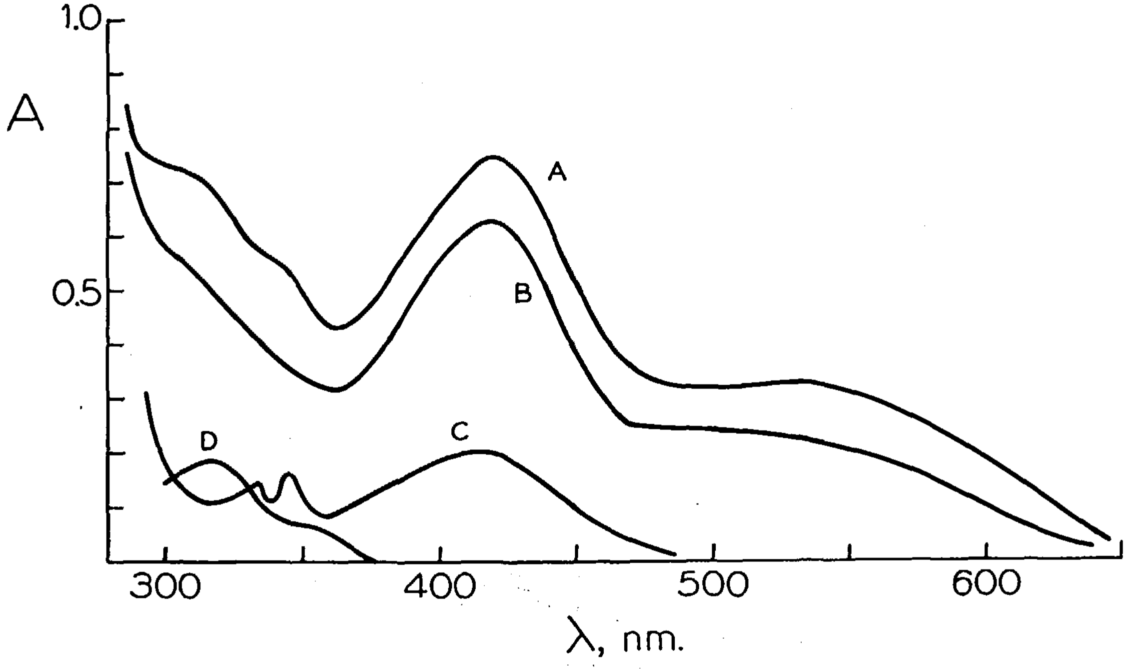


FIGURE 10. Absorption curves of the technetium(V) dichloro-oxinates and reagent forms in chloroform solution. A. acido chelate form I; B. dimeric alkaline chelate form II_2; C. quinolinium tetraphenylborate; D. the dichloro-8-quinolinol reagent.

length is 11040 ± 60, while that of the (completely dimerized) more alkaline form is 9250 ± 50. Only the latter form can be isolated, essentially free of other forms, by concentrating and evaporating solutions of it in chloroform. Initially acidic forms, after treatment in this fashion, redissolve in chloroform to give molar absorptivities of only about 10400–10700, but the full value of 11040 can be restored after contacting with aqueous acid.

By analogy with many well-known cases of metal oxinates, this absorption is to be ascribed to the ligated oxines. The previous observations already suggest that molar absorptivity (expressed with reference to moles of technetium, whether dimeric or not) of 9250 belongs to the normal *bis*-biligated oxines, while an additional 1790 in the acidic form may be loosely ascribed to a contribution from the third mole of oxine which has some different (e.g., "quinolinium-like") status in this form. This interpretation can be further pursued in terms of the other spectral differences found at lower wavelengths (see the figure), and some interesting analogies with $UO_2Ox_2 \cdot HOx$. The absorption spectra of $(Ph_4As^+)(Ox^-)$ and $(H_2Ox^+)(Ph_4B^-)$ in chloroform solutions provide "models" for these forms of quinolinol.

The liquid-liquid distribution studies (and electrical conductivities) indicate the desirability of a spectrophotometric dilution study of the dimeric alkaline form in chloroform solution. Both because of the concentration range in which monomerization occurs and because of the modest difference in absorption of the two forms, the accuracy is somewhat limited, even with a path length of 10 cm. The value of the dimerization constant which fits a spectrophotometric dilution curve (A_{420} vs. C) is $1.1 \pm 0.3 \times 10^5$, in good agreement with that deduced from the extraction data. The lower concentration (monomer) data can be extrapolated to give the ϵ of pure monomer as 10980 ± 150. While not precisely definable, this value lies suggestively close to that of the pure acidic form.

Infrared spectra of potassium bromide pellets containing the reagent, the (dimeric) alkaline form, and the purest isolable acid form all show the characteristic oxine ligation absorption at 1110 cm^{-1}. The absence from both preparations of the "free oxine" peak, which lies at 715 cm^{-1} for the dichloro compound, is also significant relative to the status of the third mole of ligand. The comparable peak is also absent in the spectrum of $UO_2Ox_2 \cdot HOx$. The fundamental O-H and N-H regions overlap and show added broad peaks due to extensive hydrogen-bonding. In the region from 1000 to below 600 cm^{-1}, the ligand contributes many bands. The locations of the vibrations expected from an approximately *trans* O=Tc—OH structure are difficult to identify amidst the other features.

In the latter region the location of Tc=O near 980 cm^{-1} is reasonably unambiguous, but the assignment of Tc—OH is less certain (e.g., between bands at 890, 685, or 650 cm^{-1}).[71] For the technetium (V) dichlorooxinates a unique phenomenon appears in the ligand ring-deformation and other modes. Not only are the usual 5 30 cm^{-1} ligand shifts to higher frequency observed, but also a comparably shifted band appears at a *lower* frequency. While this is not reported for the coplanar, *tris*-oxinate of UO_2, it may result from the non-coplanar and hydrogen-bonded oxine postulated in our case.

In the near-infrared region we find some distinction between the "acidic" and "alkaline-dimeric" technetium (V) chelate forms at concentrations above about 10^{-4} *M* in chloroform solutions and with path lengths of 1 cm or above. Corsini[98] cites 2600 cm^{-1} as characteristic for the N-H-O intramolecular bond, as in $UO_2Ox_2 \cdot HOx$. Our acidic (and/or monomeric) form in solution shows this band near 5200 cm^{-1} (the harmonic), while it is very much weaker for the dimer. It shifts as expected on deuteration. Corsini also notes the absence of this band for UO_2^{+2} with 7-substituted oxinates because of steric inability to form the *tris*-compound. The observation adds credence to our assumption that the *tris*-5,7-dichloro chelates of technetium have a non-coplanar oxine.

4. *Interpretation and Postulated Structures*

The prior discussion indicates the many unusual features of this system and its potential for separation and measurement. Since pertechnetate (VII) is *not* extracted by 8-quinolinol reagents into chloroform, a highly selective two-stage (oxidized, then reduced) separation of technetium from most other elements is possible.

Our present interpretation of both the extraction and spectrophotometric behavior of the system must be regarded as tentative. The system delineated in Figure 9 satisfies most of the experimental observations but does not resolve the non-equilibrated tautomerism question nor suggest actual structures.

Evidently, all three oxinates in these chelates are strongly bound, and three remain bound after scission of the dimer. Molecular-weight determinations and mass spectra on the isolable II_2 solid demonstrate:

1. The need for two hydroxyl ions as well as three molecules of oxine,
2. The complete retention of the third mole of oxine up to 175°, the melting point of camphor, and its substantial retention *in vacuo* at 220–250° C, the probe temperature in mass spectroscopy, which show that this ligand must be bound to the metal, and
3. The complete dissociation of the dimer to give monomer by 175° C.

Evans' indirect NMR technique[99] was used to estimate the magnetic susceptibility as being less than 0.6 B.M. Solubility limitations preclude any closer specificiation.

Recognizing the zwitterion character of the 8-quinolinol reagent, the structure established for $UO_2Ox_2 \cdot HOx$, and the implications of such distinctions between technetium and uranium as the difference between their radii and the difference between the "acidities" of $Tc(OH)_2$ and UO_2, our data lead us to postulate the structures indicated in Figure 11. All forms are heptacoordinate and the third, monoligated, oxine is rotated out of the plane of the normal *bis*-biligated oxines (not shown on the sketches). In chloroform, the acidic and monomeric alkaline forms differ only in the position of one proton (tautomers), but hydrogen-bonding is possible in both cases. The shorter Tc=O double bond, however, makes this less feasible (internally) with the monomeric more alkaline form, resulting in extensive dimerization and *intermolecular* hydrogen-bonding. Dimerization is almost complete at concentrations above 10^{-4} *M*.

V. MISCELLANEOUS TECHNIQUES OF SEPARATION AND MEASUREMENT

A. Separation Methods

1. Liquid-Liquid Extraction.

Once again it is important to recall that the extraction behavior reported for technetium (VII) from such aqueous media as 8 to 12 *M* hydrochloric acid may actually reflect the presence of some Tc (IV) and (V) states. Moreover, the extent to which organic solvents, such as ethers, alone may tend to extract perrhenate, pertechnetate, or other species from aqueous media, must be kept in mind when considering those additional separations which are possible via more conspicuous chelations with other reagents dissolved in such solvents.

Boyd and Larson[100] reported the most extensive survey of the liquid-liquid extraction behaviors of technetium (VII) with a variety of organic solvents. The presence of a donor nitrogen or basic oxygen group in the organic solvents favors extraction.

We have found a partition coefficient of about 0.13 for pertechnetate into diethyl ether from 2 *M* sulfuric acid.[83] From aqueous hydrochloric acid, the partition coefficient ranges from 0.03 to 0.16 as the acid concentration is changed from 0.73 to 3.9 *M*.[27] Attrep[101] reported partition coefficients between 0.03 and about 1.0 for aqueous nitric acid solutions at concentrations from 0.5 to, or above, 6 *M*. From hydrochloric or sulfuric acid at concentrations up to and including 8 *M* or 4 *M*, respectively, negligible extraction is observed into solvents such as chloroform[83] or carbon tetrachloride.

Healy and McCabe[102] studied the extraction of Mo^{99} (as molybdate) from dilute aqueous acid using cupferron and chloroform. Quantitative extraction is possible down to microgram levels, and it is claimed that the distribution coefficient exceeds 200. Meyer and Rulfs[58] successfully extracted larger amounts of molybdate from milligram levels of perrhenate in 1 *M* sulfuric acid using cupferron in chloroform. Salaria, Rulfs, and Elving[83] report that significant (5 – 10%) extraction of pertechnetate begins to occur at comparable acidities and increases with higher concentrations of acids. Still more extraction of technetium occurs using ether as the solvent. Evidence was also given to show that the extraction of technetium (III), but not that of technetium (IV), is appreciably increased in the presence of cupferron.

Although molybdate does form an extractable compound with 8-quinolinol, neither pertechnetate nor perrhenate is extractable in the (VII) state. Technetium (V) does form extractable oxinates, however, as described in section IV. In contrast to the behaviors of the rhenium (V) compounds studied by Trzbiatowska[87] we have also found a significantly chloroform-soluble brown form of rhenium (V) oxinate which can coexist in equilibrium with a water soluble yellow-green form.

Kuznetsov et al.[103] describe the quantitative extraction of tracer-level perrhenate or pertechnetate by 0.01 M 8-mercaptoquinoline in chloroform. They claim that 10^{-3} to 10^{-1} M solutions of 8-quinolinol, 2-methyl-8-quinolinol, or 5,7-dibromo-8-quinolinol give no extractions from acidic to neutral aqueous media. It is surprising (in view of the behavior discussed in section IV) that for pertechnetate this claim is extended to include 10 M hydrochloric acid.

Several sets of Russian workers (e.g., A. N. Zelikman et al.[104,105] and K. A. Bol'shakov et al.[106,107] from 1967 to 1969) have reexamined and extended studies of the extraction of technetium (VII) and rhenium (VII) with tributyl phosphate TBP and alkyl amines. Campbell[108] described the isolation of pertechnetate from fission product using TBP. Rein et al.[109] define the distributions of 57 metallic ions between aqueous

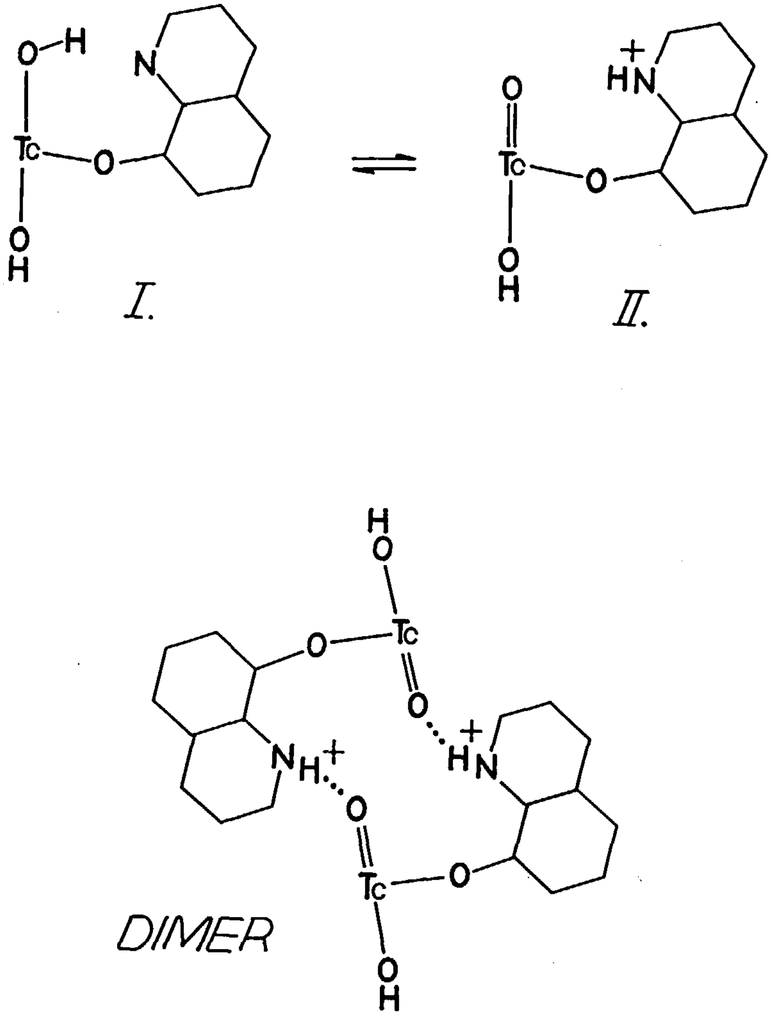


FIGURE 11. Postulated structures for the technetium(V) *tris*-oxinates in the plane of the third (monoligated) oxine. Not indicated are the ring unsaturation and the dichloro substitution. The *bis*-biligated oxines are essentially coplanar and lie normal to the features shown here.

solutions of acidities from 0.2 to 5 *M* and any of three different tetraalkyl amines in methyl isobutyl ketone.

Peterson, MacDuff, and Hovey[110] selectively extract small amounts of rhenium (VII) from alkaline media using 8% (w/v) methyltricaprylammonium chloride in chloroform. Salaria, Rulfs, and Elving[111] used millimolar concentrations of this extractant for the quantitative isolation of pertechnetate from dilute hydrochloric or sulfuric acid, neutral solution, or 0.1 *M* potassium hydroxide.

2. *Chromatographic and Ion-Exchange Methods*

For medical use as a diagnostic tracer Tc^{99m} is produced from Mo^{99}, which is bound as molybdic acid or molybdate to an alumina column. The metastable product, as pertechnetate, is eluted from the source columns using dilute acids or physiological saline solution. In the past five years, several dozen English, Russian, and German papers refer to empirical studies of variations in the technique surrounding this medically important procedure.

Anion-exchange resins, such as Dowex-1 or -2 or Amberlite IRA 400 or IR 120, have a long history of important applications to separations of rhenium (VII), technetium (VII), and molybdenum (VI). Faris and Buchanan[112] give a useful summary of the distribution behavior on Dowex-1 for 70 elements in 0.1 to 14 *M* nitric acid. Korkisch and Feik[113] describe some improvement in separation, especially that of rhenium and molybdenum, in such a system by using partially non-aqueous eluants.

Maeck, Kussy, and Rein[114] describe the behavior of 60 metal ions on hydrous ZrO_2 and zirconium salt columns.

Good separations of technetium, rhenium, molybdenum, and tungsten by thin-layer chromatography have been claimed using cellulose,[115] silica gel,[116-118] and alumina.[119]

B. Miscellaneous Measurement Techniques

1. *Emission Spectra and X-ray Methods*

Bozman, Meggers, and Corliss[120] recently recorded accurate wavelength data and relative intensities for 4500 TcI and TcII arc and spark lines in the 2000–9000 A region. Many of the TcI lines have been classified and their energy levels tabulated.[121]

Classical chemical procedures for the separation and determination of rhenium as a major constituent in present-day alloys and mixtures that also contain such elements as molybdenum, tantalum, zirconium, uranium, and tungsten are frustratingly complex and time consuming. The relative errors of about ± 1% that may be realized by x-ray absorption or fluorescence methods are often acceptable and are sometimes as good as those attainable by the best chemical method. Normally, the x-ray method requires no preliminary separation steps and is enormously time-saving by comparison with wet chemical approaches. Outlines of two such procedures will illustrate the nature and potentialities of these techniques. These methods were developed by E. A. Hakkila of Dr. C. F. Metz' Group CMB-1 at the Los Alamos Scientific Laboratories.[122]

Rhenium, in the concentration range between 0.10 and 10%, is determined in tantalum by x-ray fluorescence spectrometry using a solution technique. The sample is dissolved in 5.00 ml of hydrofluoric acid, irradiated using x-rays from a tungsten-target tube operated at 50 kV and 40 mA, and the intensity of the $L\alpha_1$ fluorescence line of rhenium, corrected for background, is compared with the intensities measured for samples of known composition. For samples containing between 0.1 and 1% of rhenium, 1.000-g aliquots are taken; for rhenium concentrations between 1 and 10%, 0.1000-g aliquots are used. Relative standard deviations of 5.6, 1.9, and 1.0%, respectively, were determined for 0.10, 1.00, and 10.0% of rhenium in tantalum. The standard deviation in the analysis of a blank, using a 1.0-g portion of tantalum containing no added rhenium, is $37 \mu g$ of rhenium. Copper and zinc interfere seriously with this determination of rhenium.[122]

Rhenium in rhenium-uranium-zirconium carbide is determined using an x-ray absorption edge method which provides the high selectivity generally associated with this type of analysis. Such a sample may be dissolved in mixed hydrofluoric and nitric acids without loss of volatile rhenium products. A bismuth-thallium alloy is irradiated with x-rays from a tungsten-target x-ray tube, and the secondary x-rays of bismuth and thallium are transmitted through an absorption cell filled successively with water, suitable known solutions, and the sample solution. An absorption edge for rhenium occurs between the $L\alpha_1$ lines for thallium and bismuth. Measured transmitted intensities are related to rhenium concentrations using accepted absorption principles. The procedure is applicable to the determination of rhenium concentrations of 20 to 100% with relative standard deviations in the range between 2.8 and 0.6%. Only gallium, ytterbium, lutetium, and hafnium have absorption edges between the x-ray lines used for analysis and, therefore, interfere.[122]

Solt et al.[123] distill Re_2O_7 from molybdenites and precipitate rhenium sulfide in the distillate prior to the x-ray fluorescence determination of 10^{-3} to 3 X 10 ° g of rhenium within about ±2%.

2. *Radiochemical Measurements and Activation Analysis*

Gemmill, King, and Molinski[124] isolate Tc^{99m} from its Mo^{99} precursor by extracting pertechnetate into methyl ethyl ketone from alkaline (2 *M* potassium carbonate) aqueous molybdate solution. Richards and O'Brien[125] employ readings with and without a shield using a Mediac dose calibrator to determine as little as 1 part of Mo^{99} present with 10^4 parts of product Tc^{99m}.

Johnson[126] describes a simple linear resolution, using count rates vs. time in two energy channels, for resolving binary mixtures of radionuclides. The application is described for the activation analysis of molybdenum, and involved the Mo^{101} Tc^{101} nuclides. Gureev et al.[127] separate molybdenum and rhenium on an ion-exchange column after neutron irradiation. The γ-activity of the separated $Re^{186,188}$ is measured and corrected for the efficiency of separation. Foldzinska[128] describes the neutron-activation determination of low concentrations of rhenium in molybdenites containing tungsten. Fusion of the ore with metallic calcium and potassium permanganate at 650° forms a soluble perrhenate; this is isolated by extraction into carbon tetrachloride of its complex with methylene blue.

The cross sections of Re^{185} and Re^{187} for (n,γ) and (n, 2n) reactions with fast (0.6, 0.8 and 14.8 Mev) neutrons have been measured by Druzhinin, Lbov, and Bilibin.[129]

Bogancs et al.[130] use neutron activation analysis to determine rhenium, aluminum, sodium, potassium, nickel, and silicon in tungsten filaments. Schmied and Ziffermayer[131] also use this method for vacuum-tube grids containing rhenium, molybdenum, tungsten, tantalum, and platinum. All of these elements provide γ-lines that overlap those of rhenium, and chemical separation is necessary. The alloys are dissolved in a 1 : 3 mixture of hydrofluoric and nitric acids and the solution is irradiated and cooled for two days. The products are bound to anion-exchange resin and successively eluted from the column using gradations of fluoride-ion concentration and acidity. Finally, the rhenium is eluted with 0.5 *M* perchloric acid.

Doctor and Haldar[132] subjected ferritic copper ores to neutron irradiation, then fused them with sodium peroxide spiked with potassium perrhenate, leached with water, extracted with pyridine, and precipitated the perrhenate as the nitron salt. The product is weighed and γ-counted on a planchet. A sensitivity of 10 ³µg is claimed, and the precision and accuracy are about 6% at the 5 µg-level.

Case et al.[133] use computer reduction of Ge(Li)-detector spectral data from neutron-activated rock and meteorite samples. They employed monitors on magnesium oxide beds; some radiochemical separation steps were necessary, after which yields were estimated by reirradiation. The elements determined were antimony, arsenic, bismuth, cesium, cobalt, gallium, germanium, gold, mercury, molybdenum, osmium, rhenium, scandium, selenium, tellurium, and zinc.

Many of these methods involve the counting of evaporated residues. Especially for the assay of materials such as Tc^{99}, liquid-scintillation counting has become very important. Finely divided dispersed forms may be used, but chelated or other soluble forms are usually available.

3. *Mass Spectroscopy*

The direct spark-excitation and mass spectrometry of solid inorganic materials containing traces of rhenium or technetium should be sensitive, as it is for most elements, to levels of 0.01 ppm or below. As additional applications are made of the increasingly abundant element technetium, the low-level contamination of surrounding and recycled media of all kinds will require inventory. The soft beta emission of Tc^{99} is not readily detected in company with high concentrations of many absorbers. Similarly, the occurrence of rhenium, usually at concentrations below 1 ppm, in molybdenites, copper ores, and platinum sources could be most readily determined by this technique.

Many volatile compounds such as Tc_2O_7, Re_2O_7, $HReO_4$, $HTcO_4$, oxyhalides, and carbonyls are obviously amenable to mass spectroscopic detection. Battles, Gundersen, and Edwards[134] used mass spectrometry to study the vaporization behaviors from the two-phase solid systems ReO_2 + ReO_3 and Re + ReO_2. With both systems the equilibrium vapor consists mainly of Re_2O_7 with less than 5% of ReO_3. The appearance potential of Re_2O_7(g) was measured as 13.0 ±0.5 ev.

Rinke, Klein, and Schaefer[135] report an interesting mass spectrometric study of rhenium and technetium halides. Mixtures of $ReCl_3$, $TcCl_3$, and other species were heated in the spectrometer inlet. Principal species found included all of the mixed possibilities (Re, Tc)$_3$Cl$_9$. The Tc_3Cl_{12} species was also present.

Excepting such cases as the carbonyls and acetylacetonates, one does not tend to think of most metal chelates as being adequately "volatile" (prior to extensive pyrolysis) to permit mass spectrometric examination. But an increasing number of such studies are now being reported, and these involve a wide variety of chelate types. Generally, samples are introduced directly into the system via heated inlet probes and, despite the evacuation, temperatures considerably in excess of 150° C are necessary. Several trial runs may be required to determine the conditions of scanning time and temperature level which will optimize the inclusion of undecomposed parent in balancing the minimal requirements of volatility against pyrolytic decomposition. Obviously, some indication of the course of pyrolytic behavior can be derived from studies at a series of temperatures.

An interesting example of this type of application involved the unusual technetium (V) chelate with 5,7-dichloro-8-quinolinol, as described in section IV. The composition of the "chloroxinate" appeared to be Tc(O,OH)Ox_3, with one mole of oxine being monoligated to the metal. In the vacuum of the spectrometer system large amounts of the chlorinated oxine (mass 213) already appear at probe temperatures below 200° C, but little of the highest-mass parent is detectable. With a probe temperature above 250° C and at 70 ev the parent of mass 770 is barely evident, but good indications are found of the doubly charged ion at $m/e = 385$ and the deoxygenated one at $m/e = 368$. Better definition of the parent is evident at 220° C and 40 ev. Prominent processes include the loss of OH (or H_2O) and the loss of entire chloroxine molecules, as indicated by the following relative intensities:

	TcO_2	TcO	Tc
3Ox	3	4.5	36
2Ox	8	24	50
Ox	9	27	100

The intensities of the doubly-charged [TcO_2Ox_3] and [$TcOx_3$] species were about 18. Loss of ring chlorine is also a prominent process: for example, for the $TcOx_2$ peak with but three chlorine atoms present (the fourth of the original ones having been lost) has an estimated intensity of 120.

One must recall that the *tris*-dichloroxinate species contain 6 chlorine atoms and give a set of seven peaks with $\Delta m = 2$. The 27 carbon atoms of a *tris*-oxinate also give an adjacent set of O^{13} satellites, with $\Delta m = 1$, having about 30% the intensity of their neighbor set. The nine sets of peaks tabulated above, e.g., should actually include 90 peaks. This profusion of data resulting from monoisotopic Tc^{99} compounds would be further complicated in the case of Re.[185, 187] Actually, the unambiguous interpretation of such data tends to be facilitated by the utilization of all such factors. For example, the number of chlorine-isotope satellite peaks and/or their pattern of relative intensity prevents possible confusion between $TcOx_2$ with four chlorine atoms and $Tc(OH)_2Ox_2$ with three chlorine atoms, etc. In a given scan where some peaks are just adequately developed while some others are off-scale in magnitude, the pattern of the latter may be estimated by using the smaller C^{13} satellite peaks.

DeJongh[136] has recently reviewed the applications of spark-excitation and of "volatile" metal chelates in inorganic analytical mass spectrometry.

VI. SUMMARY

It is possible to bright-plate both Re and Tc metals from aqueous media in a reasonably quantitative fashion, but the deposit is not favorable for weighing. The (VII)-states in 4 *M* perchloric acid undergo initial 4- or 3-electron reduction-steps in polarography at the d.m.e. These waves are suitable for analyses of 10^{-3} – 10^{-4} *M* solutions within ± 1% if necessary precautions are taken. The four-electron coulometric reduction of pertechnetate can probably be refined to better than ± 0.5%. Several usable amperometric techniques exist for the determination of rhenium. The direct chemical reduction of some technetium (VII) in aqueous acidic media by contact with mercury is an important consideration in many electrochemical techniques.

The available techniques for the determination of rhenium and technetium by redox potentiometry are not very selective. Precipitation of the tetraphenylarsonium MO_4^- salts remains the only good gravimetric determination which has been described for these elements; useful amperometric variants of this procedure have not been defined.

Older procedures for the separation of rhenium or technetium from other materials by volatilization are often supplanted by ion-exchange or liquid-liquid extraction methods. Most ion-exchange methods involve the MO_4^- ions on anion-exchangers and the use of acidic media, especially nitric acid. Many different liquid-liquid extraction systems are used, the majority employing the (VII)-species. Many complexed and chelated (V)-species would be amenable to extractions, but conveniently quantitative routes to the (V)-compounds are not easily found.

The normal tetrahedral MO_4^- species persist in aqueous media under most circumstances; their characteristic absorption in the ultraviolet region has some analytical utility, especially for the pertechnetate ion. The formation of meso-ions, MO_5^{-3}, in alkaline media is not very extensive in the case of rhenium and is virtually non-existent with technetium in aqueous media. Spectrophotometric measurement of $ReCl_6^{-2}$ provides a useful method; a comparable $TcCl_6^{-2}$ procedure would be complicated by the occurrence of photocatalyzed aquation. Study of the latter process explains some of the previous discrepancies regarding the spectrum of this ion. The (V)-thiocyanate procedures remain important for rhenium and technetium, as does the furildioxime chelate with rhenium. A number of dyes have been found to be reactive with perrhenate and extract into solvents like benzene; they have molar absorptivities that approach 10^5.

The very unusual properties of a technetium (V) system with a substituted 8-quinolinol are described. The system has important direct applications for liquid-liquid extraction and spectrophotometry. More importantly, it is probably representative of other (V)-chelates of analytical significance. Only a start has been made toward the full elucidation of this rather complex example of such a system.

Both the spark excitation of refractory solids and the volatilization of metal chelates will permit increasingly frequent application of mass spectrometry to inorganic analyses and studies of materials including rhenium and technetium. There is no question whatever that a more widespread use should be made of x-ray absorption and fluorescence methods in the routine analysis of such difficult samples as alloys containing rhenium and technetium.

Activation analysis is being widely applied for the determination of low levels of both rhenium and technetium. In addition, of course, the usual occurrence of the latter element is as either Tc^{99m} or Tc^{99}, which provide their own radioactivity.

There remains a relative paucity of good classical gravimetric, titrimetric, and simpler electrometric methods available for rhenium and technetium. But there does exist a good selection of bases for separations, and for sensitive and reliable measurements by spectrophotometry, radioactivity, and contemporary instrumental methods.

VII. REFERENCES

1. Colton, R., *The Chemistry of Rhenium and Technetium*, John Wiley & Sons, London, 1965.
2. Peacock, R. D., *The Chemistry of Technetium and Rhenium*, Elsevier Pub. Co., Amsterdam, 1966.
3. Rulfs, C. L., Part II, Volume 7, Rhenium, in *Treatise on Analytical Chemistry*, Kolthoff, I. M. and Elving, P. J., Eds., Interscience Publishers, New York, 1961.
4. Cobble, J. W., Technetium, in *Treatise on Analytical Chemistry*, Part II, Volume 6, Kolthoff, I. M. and Elving, P. Eds., Interscience Publishers, New York, 1964.
5. Cobble, J. W., Smith, W. T., Jr., and Boyd, G. E., *J. Amer. Chem. Soc.*, 75, 5777 (1953).
6. King, J. P. and Cobble, J. W., *J. Amer. Chem. Soc.*, 79, 1559 (1957).
7. Lundell, G. E. F. and Knowles, H. B., *J. Res. Nat. Bur. Stand.*, 18, 629 (1937).
8. Rulfs, C. L. and Elving, P. J., *J. Amer. Chem. Soc.*, 73, 3287 (1951).
9. Henze, G. and Geyer, R., *Z. Chem.*, 8, 349 (1968).
10. Tomicek, O. and Tomicek, F., *Trans. Electrochem. Soc.*, 76, 197 (1939).
11. Henze, G. and Geyer, R., *Z. Chem.*, 8, 437 (1968).
12. Shropshire, J. A., *J. Electroanal. Chem.*, 16, 275 (1968).
13. Voltz, R. E. and Holt, M. L., *J. Electrochem. Soc.*, 114, 128 (1967).
14. Box, W. D., (to USAEC), U.S. Patent 3,374,157 (March 19, 1968).
15. Furman, N. H. et al., cited by Casto, C. C., in *Analytical Chemistry of the Manhattan Project*, Rodden, C. J., Ed., McGraw-Hill, New York, 1950, 520.
16. Salaria, G. B. S., Rulfs, C. L., and Elving, P. J., *J. Chem. Soc.*, 2479 (1963).
17. Salaria, G. B. S., Rulfs, C. L., and Elving, P. J., *Anal. Chem.*, 35, 979 (1963).
18. Rulfs, C. L., Pacer, R., and Anderson, A., *J. Electroanal. Chem.*, 15, 61 (1967).
19. Majumdar, A. K. and Bhowal, G., *Anal. Chim. Acta*, 48, 192 (1969).
20. Willard, H. H. and Smith, G. M., *Anal. Chem.*, 11, 186, (1939).
21. Tomicek, O. and Tomicek, F., *Coll. Czech. Chem. Comm.*, 11, 626 (1939).
22. Lazarev, A. I., *Zhur. Neorgan. Khim.*, 1, 385 (1956).
23. Tribalat, S., *Ann. Chim.*, 4, 289 (1949).
24. Drwega, I., *Chem. Anal.* (Pol.), 13, 135 (1968).
25. Meloche, V. W. and Martin, R. L., *Anal. Chem.*, 28, 1671 (1956).
26. Pacer, R. A., Investigation of the Analytical Chemistry of Technetium, thesis, University of Michigan, Ann Arbor, 1965.
27. Rulfs, C. L., Pacer, R. A., and Hirsch, R. F., *J. Inorg. Nucl. Chem.*, 29, 681 (1967).

28. Crouthamel, C. E., *Anal. Chem.*, 29, 1756 (1957).

29. Colton, R., Dalziel, J., Griffith, W. P., and Wilkinson, G., *J. Chem. Soc.*, 71 (1960).

30. Lingane, J. J., *J. Amer. Chem. Soc.*, 64, 1001 (1942).

31. Rulfs, C. L. and Elving, P. J., *J. Amer. Chem. Soc.*, 73, 3284, (1951).

32. Lingane, J. J., *J. Amer. Chem. Soc.*, 64, 2182 (1942).

33. Macero, D. J. and Rulfs, C. L., *J. Amer. Chem. Soc.*, 81, 2942 and 2944 (1959).

34. Gross, M., Lemoine, P., and Brenet, J., *C. R. Acad. Sci.*, Paris, Ser. C. 267, 1384 (1968).

35. Van Ngoc, N., *Mater. Nauch. 1967 – Konf. Aspir., Rostovnadonu Gos. Univ.*, 6, 7, 62, (1968).

36. Ziemba, S., *Chem. Anal. (Pol.)*, 13, 487 (1968).

37. Rulfs, C. L. and Meyer, R. J., *J. Amer. Chem. Soc.*, 77, 4505 (1955).

38. Demkin, A. M. and Sinyakova, S. I., *Elektrokhimiya*, 3, 1175 (1967).

39. Muenze, R., *Z. Phys. Chem.*, 240, 135 (1969).

40. Astheimer, L. and Schwochau, K., *J. Electroanal. Chem.*, 8, 382 (1964).

41. Kissel, G. and Feldberg. S. W., *J. Phys. Chem.*, 73, 3082 (1969).

42. Rulfs, C. L. and Reutlinger, R. T., unpublished experiments (1966).

43. Terry, A. A. and Zittel, H. E., *Anal. Chem.*, 35, 614 (1963).

44. Rulfs, C. L. and Mitchell, T., unpublished experiments (1966).

45. Gallai, Z. A., Rubinskaya, T. Ya., and Fursova, A. V., *Zh. Anal. Khim.*, 21, 584 (1966).

46. Gallai, Z. A. and Rubinskaya, T. Ya., *Zh. Anal. Khim.*, 21, 961 (1966).

47. Gallai, Z. A. and Rubinskaya, T. Ya., *Zh. Anal. Khim.*, 22, 1378 (1967).

48. Rubinskaya, T. Ya., Khusid, L. B., and Gallai, Z. A., *Zh. Anal. Khim.*, 22, 1519 (1967).

49. Miller, H. H., Kelley, M. T., and Thomason, P. F., in *Advances in Polarography*, Vol. 1, Longmuir, I. S., Ed., Pergamon Press, New York, 1960, 716.

50. Sheytanov, Ch., Chavdarova, R., and Konstantinova, M., *C. R. Acad. Bulg. Sci.*, 19, 1147 (1966).

51. Rulfs, C. L. and Anderson, A., unpublished experiments (1966).

52. Smith, W. T., Jr., Line, E. E., Jr., and Bell, W. A., *J. Amer. Chem. Soc.*, 74, 4964 (1952).

53. Smith, W. T., Jr., Cobble, J. W., and Boyd, G. E., *Amer. Chem. Soc.*, 75, 5773 (1953).

54. Nisel'son, L. A., Nikolaev, R. K., Vasilevskaya, I. I., and Vasil'eva, A. G., *Zh. Neorg. Khim.*, 14, 1136(1969).

55. Bol'shakov, K. A., Plotinskii, G. L., and Bardin, V. A., *Zh. Neorg. Khim.*, 12, 189 (1967).

56. Bol'shakov, K. A., Gel'perin, N. I., Grishko, V. Z., Bardin, V. A., Rossner, F., and Plotinskii, G. L., *Zh. Neorg. Khim.*, 12, 2152 (1967).

57. Colton, R. and Tomkins, I. B., *Aust. J. Chem.*, 21, 1981 (1968).

58. Meyer, R. J. and Rulfs, C. L., *Anal. Chem.*, 27, 1387 (1955).

59. Busey, R. H., U.S.A.E.C., ORNL - 2782 (1959).

60. Fujinaga, T., Koyama, M., and Kanchiku, Y., *Bull. Chem. Soc. Jap.*, 40, 2970 (1967).

61. Koyama, M., Kanchiku, Y., and Fujinaga, T., *Coord. Chem. Rev.*, 3, 285 (1968).

62. Kanchiku, Y., *Bull. Chem. Soc. Jap.*, 42, 2831 (1969).

63. Bailey, R. A. and Kozak, S. L., *Inorg. Chem.*, 6, 2155 (1967).

64. Meloche, V. W., Martin, R. L., and Webb, W. H., *Anal. Chem.*, 29, 527 (1957).

65. Dahlby, J. W. and Waterbury, G. R., U.S.A.E.C., LA-3711 (1967).

66. Boltz, D. G. and Mellon, M. G., *Anal. Chem.*, 42, 16OR (1970).

67. Tarayan, V. M. and Vartanyan, S. V., *Dokl. Akad. Nauk. Arm. SSR*, 45, 121 (1967).

68. Jezowska-Trzebiatowska, B., Wajda, S., Baluka, M., Natkaniec, L., and Wojciechowski, W., *Inorg. Chim. Acta*, 1, 205 (1967).

69. Busey, R. H. and Keller, O. L., Jr., *J. Chem. Phys.*, 41, 215 (1964).

70. Cotton, F. A. and Wing, R. M., *Inorg. Chem.*, 4 867 (1965).

71. Canterford, J. H., Colton, R., and Tomkins, I. B., *Inorg. Nucl. Chem. Lett.*, 4, 471 (1968).

72. Krebs, B., Mueller, A., and Beyer, H. H., *Inorg. Chem.*, 8, 436 (1969).

73. Krebs, B., *Angew. Chem., Int. Ed. Engl.*, 8, 381 (1969).

74. Ulbricht, K. and Kriegsmann, H., *Z.Chem.*, 7, 244 (1967).

75. Petrov, K. I., Bardin, V. A., and Kalyuzhnaya, V. G., *Dokl. Akad. Nauk. USSR*, 178, 1097 (1968).

76. Viste, A., and Gray, H., *Inorg. Chem.*, 3, 1113 (1964).

77. Majumdar, S. K., Pacer, R. A., and Rulfs, C. L., *J. Inorg. Nucl. Chem.*, 31, 33 (1969).

78. Rulfs, C. L. and Brininger, C., unpublished experiments (1968).

79. Murmann, R. K., in *Inorganic Syntheses,* Vol. 8 , Holtzclaw, H. F., Jr., Ed., McGraw-Hill, New York, 1966, 173.

80. Tarayan, V. M. and Gaibakyan, A. G., *Arm. Khim. Zh.*, 19, 924 (1966).

81. Bailey, R. A. and Montillo, F. J., *J. Inorg. Nucl. Chem.*, 31, 2031 (1969).

82. Shukla, S. K., *Ric. Sci.*, 36, 725 (1966).

83. Salaria, G. B. S., Rulfs, C. L., and Elving, P. J., *Anal. Chem.*, 36, 146 (1964).

84. Cotton, F. A., Curtis, N. F., and Robinson, W. R., *Inorg. Chem.*, 4, 1696 (1965).

85. Lebedinskii, V. V. and Ivanov-Emin. B. N., *Zh. Obshch. Khim.*, 13, 253 (1943).

86. Murmann, R. K. and Foerster, D. R., *J. Phys. Chem.*, 67, 1383 (1963).

87. Przywarska-Boniecka, H. and Jezowska-Trzebiatowska, B., *Bull. Acad. Polon. Sci., Chim.*, 13, 67 (1965).

88. Hirsch, R. F.,Some Analytical Aspects of the Chemistry of Technetium, thesis, University of Michigan, Ann Arbor, 1965.

89. Moeller, T. and Ramaniah, M. V., *J. Amer. Chem. Soc.*, 76, 5251 (1954).

90. Bullwinkel, E. P. and Noble, P., *J. Amer. Chem. Soc.*, 80, 2955 (1958).

91. Charles, R. G. and Freiser, H., *Spectrochim. Acta*, 8, 1 (1956).

92. Magee, R. J. and Gordon, L., *Talanta*, 10, 851, 961, 967 (1963).

93. Tackett, J. E. and Sawyer, D. T., *Inorg. Chem.*, 3, 692 (1964).

94. Van Tassel, J. H. and Wendlandt, W. W., *J. Amer. Chem. Soc.*, 81, 813 (1959).

95. Wendlandt, W. W. and Horton, G. R., *Anal. Chem.*, 34, 1098 (1962).

96. Magee, R. J. and Woodward, I., *Talanta*, 13, 709 (1966).

97. Hall, D., Rae, A. D., and Waters, T. N., *Acta Crystallogr.*, 22, 258 (1967).

98. Corsini, A., Abraham, J., and Thompson, M., *Chem. Commun.*, 1101 (1967).

99. Evans, D. F., *J. Chem. Soc.*, 2003 (1959).

100. Boyd, G. E. and Larson, Q. V., *J. Phys. Chem.*, 64 988 (1960).

101. Attrep, M., Jr., *Anal. Chem.*, 34, 1349 (1962).

102. Healy, W. B. and McCabe, W. J., *Anal. Chem.*, 35, 2117 (1963).

103. Kuznetsov, V. I., Gudym, L. S., Rudenko, N. P., and Awad, H. K., *Radiokhimiya*, 11, 240 (1969).

104. Nerezov, V. M. and Zelikman, A. N., *Izv. Vyssh. Ucheb. Zaved. Tsvet. Met.*, 10, 113 (1967).

105. Zelikman, A. N. and Dregan, L., *Sb. Mosk. Inst. Stali. Splavov*, 45, 36 (1968).

106. Bol'shakov, K. A., Sinitsyn, N. M., Petrov, K. I., Travkin, V. F., and Rubtsov, M. V., *Zh. Neorg. Khim.*, 13, 3082 (1968).

107. Bol'shakov, K. A., Sinitsyn, N. M., and Travkin, V. F., *Dokl. Aka..Nauk. SSSR*, 185, 338 (1969).

108. Campbell, M. H., *Anal. Chem.*, 35, 2052 (1963).

109. Maeck, W. J., Booman, G. L., Kussy, M. E., and Rein, J. E., *Anal. Chem.*, 33, 1775 (1961).

110. Peterson, H. E. Macduff, J. S., and Hovey, M. W., Isolation and Colorimetric Determination of Rhenium, U. S. Dept. Interior, Bur. Mines, Washington, 1961, Report 5889.

111. Salaria, G. B. S., Rulfs, C. L., and Elving, P. J., *Anal. Chem.*, 35, 983 (1963).

112. Faris, J. P. and Buchanan, R. F., *Anal. Chem.*, 36, 1157 (1964).

113. Korkisch, J. and Feik, F., *Anal. Chim. Acta*, 37, 364 (1967).

114. Maeck, W. J., Kussy, M. E., and Rein, J. E., *Anal. Chem.*, 35, 2086 (1963).

115. Seiler, H., *Helv. Chim. Acta*, 52, 319 (1969).

116. Shoibara, Y., *Bunseki Kagaku*, 17, 1396 (1968).

117. Kuroda, R., Kawabuchi, K., and Ilto, T., *Talanta*, 15, 1486 (1968).

118. Mikulaj, V. and Dobias, M., *Acta Fac. Rerum Natur. Univ. Comenianae, Chim.*, 12, 125 (1968).

119. Gaibakyan, D. S., *Arm. Khim. Zh.*, 22, 13 (1969).

120. Bozman, W. R., Meggers, W. F., and Corliss, C. H., *J. Res. Nat. Bur. Stand.*, *A*, 71, 547 (1967).

121. Bozman, W. R., Corliss, C. H., and Tech. J. L., *J. Res. Nat. Bur. Stand.*, *A.*, 72, 559 (1968).

122. Hakkila, E. A., Metz, C. F. et al., The X-Ray Fluorescence Determination of Rhenium in Tantalum and The X-Ray Absorption Edge Determination of Rhenium in Re-U-Zr Carbide, Los Alamos Scientific Laboratory, Group CMB-1, Analytical Methods Nos. 801 and 839.

123. Solt, M. W., Wahlberg, J. S., and Meyers, A. T.; *Talanta*, 16, 37 (1969).

124. Gemmill, W. J., Kong, P. A., and Molinski, V. J., (to Union Carbide Corp.), Brit. Patent 1,131,910 (October 30, 1968).

125. Richards, P. and O'Brien, M. J., *J. Nucl. Med.*, 10, 517 (1969).

126. Johnson, R. A., *Radiochim. Acta*, 5, 231 (1966).

127. Gureev, E. S., Islamov, T., Miranskii, I. A., Muminova, M. F., and Miroshnikov, V. S., *Izv. Akad. Nauk. Uzb. SSR, Ser. Fiz.-Mat. Nauk.*, 11, 75 (1967).

128. Foldzinska, A., *Proc. Conf. Appl. Phys.-Chem. Methods Chem. Anal.*, Budapest, 2, 367 (1966).

129. Druzhinin, A. A., Lbov, A. A., and Bilibin, L. P., *Yad. Fiz.*, 5, 18 (1967).

130. Bogancs, J., Cseh, S., Elek, A., Sali, S., Simonits, A., Ordogh, M., and Szabo, E., *Atomtech. Tajek*, 11, 631 (1968).

131. Schmied, H. and Ziffermayer, G., *Microtechnic*, 22, 292 (1968).

132. Doctor, Z. K. and Haldar, B. C., *Proc. Nucl. Radiat. Chem. Symp., 3rd.*, 512 (1967).

133. Case, D. R., Laul, J. C., Lipschutz, M. E., and Schmidt-Bleek, F., *Radiochem. Radioanal. Lett.*, 1,143 (1969).

134. Battles, J. E., Gundersen. G. E., and Edwards, R. K., *J. Phys. Chem.*, 72, 3963 (1968).

135. Rinke, K., Klein, M., and Schaefer, H., *J. Less-Common Metals*, 12, 497 (1967).

136. De Jongh, D. C., *Anal. Chem.*, 42, 178-180R (1970).

Author's Correction

The following corrections should be made in the printed text of the article Estimation of Medium Effects for Single Ions in Non-Aqueous Solvents, *C.R.C. Crit. Rev. Anal. Chem.*, 1 (1), 73 (1970):

1. On p. 90, col. 2, line 7, "Table 14" should read "Table 12".

2. In Table 12, p. 109, the values obtained by Alexander and Parker for K^+, Cs^+, and Ag^+ should be 0.0, -0.1, and (-5.9^b, -5.7^c), respectively.—Orest Popovych