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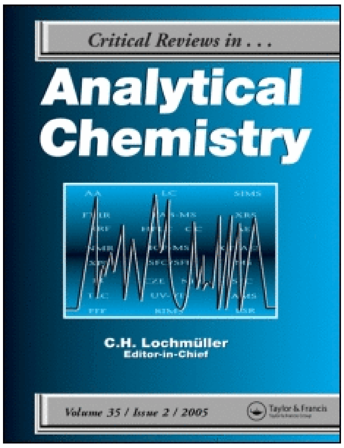

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THE APPLICATIONS OF HYDROFLUORIC ACID AND FLUORIDES IN ANALYTICAL CHEMISTRY

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I. INTRODUCTION

For a long time hydrofluoric acid was not as widely used in analytical chemistry as hydrochloric, nitric, or sulfuric acids. This was partly because it is both a moderately weak and nonoxidizing acid, having a pK_a-value of 2.9 in 0.5 *M* sodium perchlorate. Other deterrents to its use have been the facts that it attacks glassware and that, particularly when concentrated, it produces nasty burns when brought into contact with the skin.

Nowadays, however, the ready availability of laboratory ware made from such materials as polyethylene, polypropylene, and Teflon® (polytetrafluoroethylene) makes it easy to solve the perennial problem of finding containers for the acid, and makes it possible to take advantage of certain unique and analytically advantageous properties of hydrofluoric acid and fluorides.

Under the proper conditions, which will be discussed later, hydrofluoric acid is a very convenient solvent for silicates, since it reacts with them to form the stable water-soluble fluosilicate anion. Indeed this use of the acid was mentioned by the Swedish chemist Bergman (1735 to 1784).[1] Solutions containing hydrofluoric acid are also useful solvents for species such as zirconium (IV), niobium (V), tantalum (V), and tungsten (VI), which also form stable and soluble fluoro complexes.

Because hydrogen fluoride is very volatile (boiling at 19° C), it is used as a concentrated aqueous solution. Commercial hydrofluoric acid is an approximately 48% (w/v) solution. Since hydrofluoric acid is a relatively weak acid, many fluoro complexes are at least partly dissociated in strong acids such as hydrochloric or sulfuric acid. However some fluoro complexes, such as those of titanium (IV), zirconium (IV), and niobium (V), are very stable and persist even in the presence of strong acids. Because hydrofluoric acid volatilizes from aqueous solutions at about 110° C, these complexes can be broken down by heating strongly with perchloric or, preferably, sulfuric acid. Prolonged heating is essential if the last traces of fluoride are to be removed. The fluorides most widely used in analytical chemistry are those of ammonium, sodium, and potassium.

Since hydrofluoric acid and fluorides are mainly used in analytical chemistry because of their complexing ability, the next section of this review deals with the stability of fluoride complexes.

There have been no startling advances in the uses of hydrofluoric acid and fluorides during the past 20 years, but progress has been steady. Their uses fall into 5 categories. First, the unique properties of aqueous solutions containing hydrofluoric acid as solvents have already been mentioned. There has been much activity in this field within the last decade, particularly with Teflon®-lined bombs used at temperatures in excess of 110° C. Second, the use of fluoride ion as a complexing agent has been exploited in the development of separation procedures such as ion-exchange and partition chromatography and solvent extraction, of which the last is sometimes followed by absorption spectrophotometric determination of the extracted element. The fundamental advances in these fields were made between 1945 and 1965; since then most of the progress that has been made has involved the improvement of existing methods rather than the development of new ones. Third, fluoride ion is used as a precipitant for certain cations, with which it forms insoluble salts. This is a long-established use of fluorides, but because gravimetric methods are being replaced by faster instrumental ones there is little activity in this area at the present time. Fourth, like all complexing agents, fluoride has a profound effect on the formal potentials of certain redox couples, and these effects have been used to develop methods for the determination of many elements by titration, polarography, and so on. This is a field in which there was much interest in the 1960s. Finally, there have been a number of miscellaneous applications of fluoride ions; these include its use as a masking agent and as a reagent to improve the sensitivity with which elements such as zirconium and tantalum can be determined by atomic absorption spectroscopy. All of these fields are reviewed in the following pages.

II. THE STABILITIES OF FLUORIDE COMPLEXES

A. Stability Constants

The fluoride ion is the smallest of the halide anions, having an ionic radius of 1.33 Å and it is not readily polarized. It coordinates most readily with cations of high charge and small radius, the bonding in many instances being mainly electrostatic in nature. These considerations alone would account for the formation of strong fluoride complexes in aqueous solution by Be^{2+}, (B^{3+}), Al^{3+}, Ga^{3+}, In^{3+}, (Si^{4+}), Sn^{2+}, (Sn^{4+}), Sc^{3+}, Y^{3+}, (Ti^{4+}), (Zr^{4+}), Th^{4+}, (V^{5+}), (Ta^{5+}), Cr^{3+}, Mn^{3+}, Fe^{3+}, and Co^{3+}. This is borne out by the stepwise stability or formation constants of fluoride complexes shown in Table 1. This information is reproduced from the Chemical Society's publication on "Stability Constants".[2] In the list shown, the species in parenthesis are, of course, partly or completely hydrolyzed in aqueous solutions in the absence of complexing agents.

The stability constants for the monofluoro complexes of many elements are shown more clearly for comparison in Figure 1. Most of these were taken from Table 1, but a few have been estimated mostly from the data of Babko.[3]

Equilibrium data for the formation of the fluoro complexes of several metallic ions have been presented by Goldstein[4] in the form of useful distribution diagrams. These are plots of fraction of each species present versus fluoride concentration.

B. Inhibition of Hydrolysis

One of the most useful properties of the fluoride ion is its ability to complex with inorganic species such as silicon (IV), zirconium (IV), niobium (V), and tungsten (VI) to form soluble fluoro complexes. These species have high affinities for the hydroxyl ion, whose ionic radius is similar to that of the fluoride ion. Because the hydroxyl ion frequently acts as a bridging ligand, the resulting hydroxide complexes tend to poly-

TABLE 1

Stepwise Stability Constants of Fluoride Complexes

Species	Medium*	Temp.(°C)	Stepwise Stability Constants†
Be^{2+}	0.5 NH_4ClO_4	25	K_1 4.7, K_2 3.6, K_3 2.8, K_4 2.3
Al^{3+}	0.53 KNO_3	25	K_1 6.1, K_2 5.0, K_3 3.9, K_4 2.7, K_5 1.6, K_6 0.5
Ga^{3+}	var	20	K_1 4.5, K_2 3.8, K_3 2.8, K_4 1.5, K_5 0.3
In^{3+}	1 $NaClO_4$	25	K_1 3.7, K_2 2.6, K_3 2.3, K_4 1.1
Tl^{+}	0 corr	25	K_1 0.1
Si^{4+}	0.5 HCl		K_6 4.0
Ge^{4+}	0.5 HCl		K_6 3.9
Sn^{2+}	0.85 $NaClO_4$	25	K_1 6.3, K_2 2.5, K_3 0.5
Pb^{2+}	1 $NaClO_4$	25	K_1 1.5
Bi^{3+}	1.89 $HClO_4$	25	K_1 4.7, K_2 3.6
Sc^{3+}	0.5 $NaClO_4$	25	K_1 6.2, K_2 5.3, K_3 4.1, K_4 2.9
Y^{3+}	0.5 $NaClO_4$	25	K_1 3.9, K_2 3.2, K_3 3.2
La^{3+}	0.5 $NaClO_4$	25	K_1 2.7
TiO^{2+}	3 $NaClO_4$	25	K_1 > 5.4, K_2 4.4, K_3 4.0, K_4 3.7
Zr^{4+}	0 corr	25	K_1 9.8
	1 $NaClO_4$	25	K_4 2.8, K_5 1.9, K_6 1.4
Th^{4+}	0 corr	25	K_1 8.7
VO^{2+}	1 $NaClO_4$	20	K_1 3.3, K_2 2.3, K_3 1.6, K_4 ~ 0.7
Ta^{5+}	1(H,Na)ClO_4	25	K_5 4.8, K_6 3.6, K_7 3.3, K_8 3.0, K_9 3.6
Pa^{5+}	1 $NaClO_4$	25	K_1 5.4, K_2 5.0, K_3 4.9, K_4 4.8, K_5 4.5, K_6 4.4, K_7 3.7, K_8 1.7
Cr^{3+}	0.5 $NaClO_4$	25	K_1 4.4, K_2 3.3, K_3 2.5
Mn^{2+}	1 $NaClO_4$	25	K_1 0.8
Fe^{3+}	0.5 $NaClO_4$	25	K_1 5.2, K_2 3.9, K_3 2.9
	var		K_4 2.0, K_5 0.4
Ni^{2+}	0.5 $NaClO_4$	15	K_1 0.7
Ag^{+}	0 corr	25	K_1 0.4
Zn^{2+}	2 $NaClO_4$	25	K_1 0.9
Cd^{2+}	1 $NaClO_4$	25	K_1 0.5, K_2 0.1
Hg_2^{2+}	0 corr	25	K_1 < 0.5
Hg^{2+}	0 corr	25	K_1 0.1
U^{4+}	2 $HClO_4$		K_1 7.2, K_2 5.3
	0.12 $HClO_4$	25	K_3 4.2, K_4 4.3, K_5 1.6, K_6 2.3
UO_2^{2+}	1 $NaClO^4$	20	K_1 4.6, K_2 3.3, K_3 2.6, K_4 1.4
Pu^{4+}	0 corr	25	K_1 7.9

*The number before the salt is concentration which in the original paper is usually expressed in mole l^{-1} (M), but occasionally as mole kg^{-1} (m).

The entry 'var' means that the ionic strength was varied.

The entry '0 corr' means that the constant(s) have been corrected to zero ionic strength.

†The numbers given are the logarithms to the base 10 of the appropriate equilibrium constant. For example, 'K_1 5.9' means '$\log K_1 = 5.9$.'

(From *Stability Constants*, Special Publication No. 17, The Chemical Society, London, 256. With permission.)

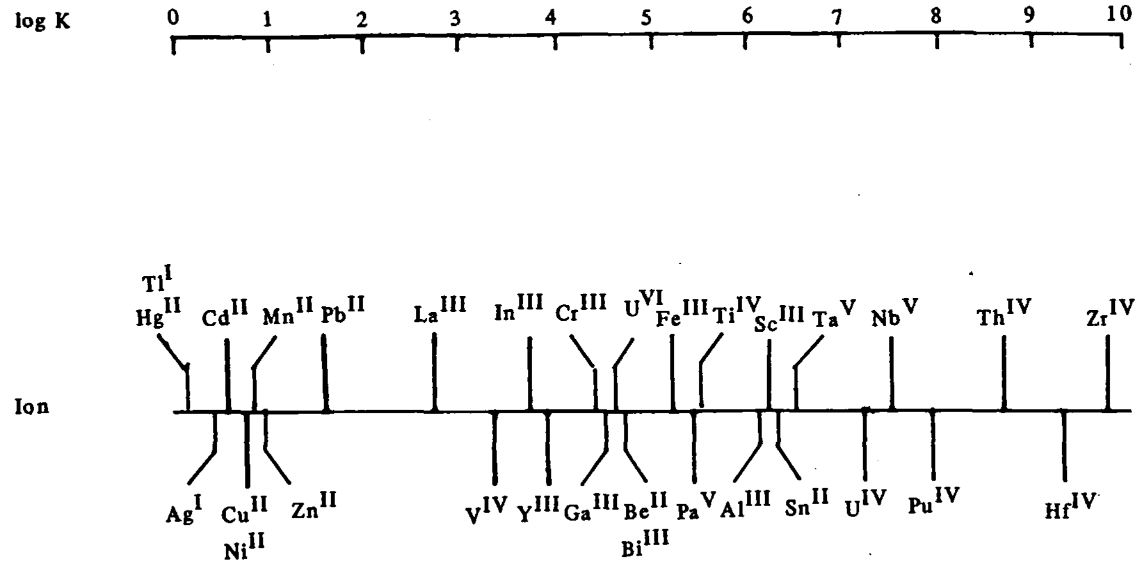

FIGURE 1. Stability constants of some monofluoride complexes. The values of log K for titanium(IV), tantalum(V), niobium(V), and hafnium(IV) have been estimated.

merize readily, and precipitation will result if the polymerization number becomes sufficiently high. In the presence of fluoride ion, this hydrolytic polymerization is inhibited because hydroxyl ions in coordination positions are replaced by fluoride ions, which are much less effective bridging ligands than hydroxyl ion.

Therefore, it is frequently desirable to add hydrofluoric acid to solutions of silicon (IV), zirconium (IV), hafnium (IV), niobium (V), tantalum (V), or tungsten (VI) so that these may be retained in true solution prior to separating them or determining them by techniques such as solvent extraction, ion-exchange chromatography, titrimetry, and atomic absorption spectroscopy.

III. THE DISSOLUTION OF MATERIALS IN FLUORIDE MEDIA

A. Decomposition using Hydrofluoric Acid

1. Metals

Easily oxidized metals such as magnesium and zinc readily dissolve in hydrochloric acid, while more noble metals such as copper, mercury, and platinum are dissolved by nitric acid alone or together with hydrochloric acid. However, nitric acid will not dissolve zirconium, hafnium, niobium, and tantalum. Fortunately, these elements form very stable fluoro complexes and may be conveniently dissolved by a mixture of hot hydrofluoric and nitric acids. In fact, they will dissolve slowly in hydrofluoric acid alone. The presence of hydrofluoric acid in the dissolving medium is also particularly useful for the dissolution of metallic samples containing tungsten, for a soluble fluotungstate complex is produced. In the absence of such a complexing agent the tungsten is converted to insoluble tungstic acid.

When the metal to be analyzed also contains appreciable amounts of niobium or tantalum, it is common practice to add hydrofluoric acid to the acid mixture used in dissolving the metal. However, only a few examples will be quoted to illustrate these points. Nickel-base[5] and cobalt-base[6] alloys have been analyzed for major alloying elements including niobium, tantalum, and tungsten by atomic absorption spectroscopy after dissolving the alloys in a mixture of acids including hydrofluoric acid. Headridge and Taylor[7] dissolved ferrotungsten in a mixture of hydrofluoric acid, hydrochloric acid, and hydrogen peroxide as the first step in a method for the titrimetric determination of the iron, tungsten, and molybdenum contents. Kakita and Gotô[8] dissolved niobium metal or ferroniobium in a mixture of hydrofluoric and nitric acids in a method for the spectrophotometric determination of tantalum in these matrices.

Langmyhr and Paus[9] have determined silicon, aluminum, magnesium, calcium, titanium, manganese, chromium, copper, nickel, cobalt, lead, and tin in ferrosilicon by atomic absorption spectroscopy after dissolving the material in hydrofluoric and nitric acids in a Teflon®-lined bomb by heating at 110° C for 30 min. Further details on such bombs are given in Section III A3 of this review, dealing with silicates and other minerals. Price and Roos[10] have also employed hydrofluoric acid in determinations of silicon by atomic absorption spectroscopy in cast irons and aluminum alloys. In the presence of this acid, silicon is held in solution as the fluosilicate anion.

2. *Oxides, Carbides, Nitrides, and Borides.*

Hot hydrofluoric acid is also very useful for dissolving the oxides of titanium, zirconium, hafnium, niobium, and tantalum, although the time that is required to effect solution depends on the previous heat treatment that the oxide has received. An oxide that has been heated for a long period at temperatures above 1,000° C takes longer to dissolve than one that has been dehydrated at lower temperatures. Willard and Rulfs[11] have stated that a mixture of hydrofluoric and nitric acids will dissolve the carbides of titanium, zirconium, niobium, tantalum, and tungsten; the nitrides of titanium, zirconium, niobium, and tantalum; and the borides of zirconium and probably titanium, niobium, tantalum, and tungsten. Nitric acid alone would decompose these compounds much less readily.

3. *Silicates and Other Minerals.*

Hydrochloric, nitric, and perchloric acids decompose silicates containing high proportions of the alkali and alkaline earth elements. However, silicates containing only small proportions of elements with basic oxides are not appreciably attacked by these acids. On the other hand, hydrofluoric acid is most useful for decomposing many silicate minerals. This is so because silicon(IV) reacts with fluoride to form the stable fluosilicate anion, SiF_6^{2-}, and other constituents of many silicate rocks, such as iron(III) and aluminum, also form stable fluoro complexes. Heating with hydrofluoric acid speeds up the decomposition process, and Langmyhr and Sveen[12] have shown that the decompositions of quartz (SiO_2), staurolite ($FeAl_4Si_2O_{10}(OH)_2$), and epiodote ($Ca_2(Al,Fe)_3(SiO_4)_3OH$) are as effective with hydrofluoric acid alone as with its mixtures with hydrochloric, sulfuric, and perchloric acids. Dissolution of silicate minerals with hydrofluoric acid, either alone or in mixtures with other acids, usually leads to the formation of precipitates of slightly soluble fluorides or complex fluorides. These are readily brought into solution by adding an excess of aluminum ions. An extensive review of the use of hydrofluoric acid in the decomposition of minerals has been written by Doležal, Povondra, and Šulcek.[13]

It has been shown that there is no loss of silicon as volatile silicon tetrafluoride when silica is dissolved in concentrated hydrofluoric acid, even at 100° C, if an appreciable volume of solution is maintained.[14] However, the solution must not be evaporated to small volume or loss of silicon does occur. Evaporation of solutions containing silicon in the presence of hydrofluoric acid and higher-boiling acids such as sulfuric or perchloric acid does, of course, result in the loss of silicon as the tetrafluoride. When silicon in hydrofluoric acid solution is to be determined spectrophotometrically, the fluosilicate anion can be dissociated and fluoride ion bound by adding an excess of aluminum ions, the stable fluoaluminate ion being produced.

However, it must be stressed that there are numerous silicates that are not decomposed entirely by treatment with hot hydrofluoric acid or with acid mixtures containing hydrofluoric acid in an open beaker. Willard and Rulfs[15] state that kyanite (Al_2SiO_5), beryl ($Be_3Al_2Si_6O_{18}$), zircon ($ZrSiO_4$), topaz ($Al_2F_2SiO_4$), andalusite (Al_2SiO_5), and some tourmalines ($XY_3B_3Al_3[(Al,Si)_3O_9]_3(OH,F)_4$, where X = Na, Ca and Y = Mg, Fe, or Li) are resistant to such treatment.

When minerals are decomposed in boiling hydrofluoric acid certain elements can be lost partially as volatile fluorides. These include boron, arsenic, and selenium(IV). From a mixture of perchloric and hydrofluoric acids at 200°C, boron, silicon, and arsenic are lost entirely by volatilization and varying amounts of germanium, antimony, chromium, selenium, manganese, and rhenium are lost as well.[16] When silicates are decomposed with a mixture of nitric and hydrofluoric acids, no loss of selenium occurs,[17] presumably because selenium(VI) is formed and is nonvolatile. The loss of boron through volatilization as boron trifluoride during the dissolution of silica in hot hydrofluoric acid is prevented by the addition of mannitol.[18]

When hydrofluoric acid alone or in mixtures with other acids is used to decompose minerals, very stable fluoro complexes of elements such as titanium and zirconium are produced. It is essential to dissociate these compounds and remove fluoride from the solution before determining these elements spectrophotometrically. This is usually done by adding sulfuric acid if it is not already present and evaporating the solution to dense white fumes of sulfur trioxide. Strong heating is necessary to remove all fluoride and it is often advisable, after obtaining the first fumes of sulfur trioxide, to cool the beaker or crucible, wash down the side with a little water, and reheat until sulfur trioxide is again evolved. Indeed, in order to expel the last traces of fluoride, Langmyhr[12] reports that it is necessary to evaporate twice, not only to dense fumes of sulfur trioxide, but to complete dryness at a final temperature of 280±10° C.

Of course, the volatilization of silicon tetrafluoride from a strongly heated mixture of hydrofluoric and sulfuric acids is the method used for removing silica from a silica precipitate before recovering the small amount of mixed oxides that accompanies silica in the wet chemical method for the analysis of a silicate. It is also used to remove the small amount of silica accompanying the mixed oxides in this classical method.

For the determination of iron(II) in silicates, decomposition with hydrofluoric acid is particularly useful. Since hydrofluoric acid is a nonoxidizing acid, the iron(II) passes unchanged into solution, where it can be subsequently titrated with a standard solution of an oxidizing agent or determined spectrophotometrically.[19] However the formal potential of the iron(III)/iron(II) couple is so far displaced toward less positive values in the presence of hydrofluoric acid, which strongly complexes iron(III), that iron(II) may be readily oxidized by oxygen from the air. For this reason the decomposition is best carried out under an inert atmosphere.

Alternatively, the rock sample can be decomposed by hydrofluoric acid in the presence of a known excess of oxidizing agent, such as vanadate, dichromate, or permanganate, which oxidizes iron(II) to iron(III). The excess of oxidant can then be determined by titration. This method is inapplicable in the presence of sulfide. In rocks iron(II) can also be determined by decomposing the rock with boiling hydrofluoric and sulphuric acids in the presence of potassium iodate.[20] Iodine, the reduction product, is volatile in the steam and is removed. The unreacted iodate is determined by adding excess iodide and titrating of the resulting iodine with standard sodium thiosulfate solution. The decomposition can be carried out in a Pyrex® flask.

Minerals of niobium and tantalum, with the exception of the rare simpsonite ($Al_2Ta_2O_8$), are decomposed by heating with a mixture of hydrochloric and hydrofluoric acids under mild pressure.[21] This is done by adding the sample and acid mixture to a polyethylene beaker, which is then covered with a piece of thin polyethylene sheet held tightly against the outside of the beaker with a rubber band. The beaker is heated on a steam bath for about 2 hr with occasional mixing by swirling. Zircon is not attacked, and cassiterite (SnO_2) is only slightly attacked, by this treatment.

It was stated earlier that certain silicate minerals are not completely decomposed by hot hydrofluoric acid, alone or in a mixture with another acid, in an open beaker. Ito[22] has achieved very effective decomposition by heating samples for 3 to 4 hr at 240°C in a Teflon® liner in a stainless steel bomb, using equal volumes of 1:1 sulfuric acid and 48% hydrofluoric acid. His work was directed toward the determination of iron(II) by titration of the final solution with standard permanganate and the determination of alkalis by flame photometry. Complete decomposition occurred with tourmaline, axinite ($H(Ca,Fe,Mn)_3Al_2B(SiO_4)_4$), and staurolite, as well as with more easily decomposed minerals. The minerals named were incompletely decomposed by conventional acid attack in an open beaker. Nonsilicate minerals are often difficult to dissolve in acids and a longer period of heating (up to 16 hr) is required to decompose them completely even in the Teflon® bomb. With the above acid mixture in the bomb, complete decomposition has been achieved with magnetite ($FeO \cdot Fe_2O_3$), ilmenite ($FeO \cdot TiO_2$), chromite ($FeO \cdot Cr_2O_3$), columbite and tantalite ($(Fe,Mn)(Ta,Nb)_2O_6$), baddeleyite (ZrO_2), rutile (TiO_2), and corundum (Al_2O_3). Zircon is only partly decomposed with the mixed acids but decomposes completely when heated for 10 hr at 240° C with hydrofluoric acid alone. Pyrite (FeS_2) is only partly decomposed.

Langmyhr and Sveen[12] have carried out further work on the decomposition of minerals using a 1:1 (v/v) mixture of concentrated hydrofluoric and perchloric acids for 1 hr in a Teflon®-lined aluminum bomb at 250 ± 10° C. Certain minerals that do not decompose on heating in an open beaker are decomposed in the bomb. These include beryl, kyanite, staurolite, pyrite, chalcopyrite ($CuFeS_2$), and pyrrhotite (Fe_nS_{n+1}). Topaz was only partially decomposed by this treatment.

May and Rowe[23] have also used a metal bomb containing a removable Nichrome-cased platinum crucible to decompose samples of minerals with hydrofluoric acid or with a mixture of hydrofluoric and sulfuric acids. Temperatures of 400 to 450° C and pressures as high as 6000 psi could be maintained for 24 hr. Complete decomposition was achieved for minerals such as zircon, which are not decomposed in open beakers at the boiling point of the acid. The great advantage of Teflon®-lined bombs is that elements with volatile fluorides such as silicon tetrafluoride are unable to escape from the bombs and subsequently may be determined spectrophotometrically or by other means. This is particularly useful in the case of silicon.

As a preliminary step in analyses by atomic absorption spectroscopy, Langmyhr and Paus[24] have decomposed silicate rocks by treatment with hydrofluoric acid, either at about 100° C, in plastic bottles or, for more resistant materials, in a Teflon®-lined bomb at 150 to 250° C. They describe a general procedure to be adopted when nothing is known about the ease of decomposition of the material to be analyzed. An atomic absorption finish has been used to determine silicon, aluminum, total iron, magnesium, calcium, sodium, potassium, titanium, and manganese. Any insoluble fluorides or fluoro complexes that remain after the decomposition procedure are brought into solution by heating with boric acid.

In an important series of papers, hydrofluoric acid decomposition procedures and atomic absorption spectroscopic finishes have also been described by these authors for the determination of many elements in a wide variety of materials. These determinations are listed in Table 2.

Bernas[32] has also reported on the decomposition of samples of granite, diabase, and tektite by treatment with aqua regia and hydrofluoric acid in a Teflon®-lined vessel at 110°C, followed by treatment with excess of boric acid to dissolve insoluble fluorides and determination of silicon, iron, aluminum, titanium, vanadium, calcium, magnesium, sodium, and potassium by atomic absorption spectroscopy.

B. Decomposition Using Fused Potassium Hydrogen Fluoride or Ammonium Fluoride

Potassium hydrogen fluoride or ammonium hydrogen fluoride may be used as a flux for the decomposition of minerals containing elements such as beryllium, zirconium, niobium, tantalum, and silicon, which form very stable complexes with fluoride ion. A good account of the use of these fused fluorides as reagents for the decomposition of minerals is given by Doležal and co-workers.[33] Fusion with these reagents should be made in platinum crucibles.

Potassium hydrogen fluoride melts at 239° C

TABLE 2

The Determinations of Elements in Various Materials by Atomic Absorption Spectroscopy after Decomposition with Hydrofluoric Acid

Material analyzed	Elements determined	Ref.
Silica	Al, Fe, Mg, Ca, Ti	25
Bauxite	Si, Al, Fe, Mg, Ca, Na, K, Ti, Mn, Cr	26
Cements, clinkers, raw mixes, and siliceous limestones	Si, Al, Fe, Ca	27
Iron ores	Si, Al, Mg, Ca, Na, K, Ti, Mn	28
Slags	Si, Al, Fe, Mg, Ca, Ti, Mn, C·	28
Felspars	Si, Al, Fe, Mg, Ca, Na, K	29
Silicate minerals and rock reference samples	Si, Al, Fe, Mg, Ca, Na, K, Ti, Mn	30
Sulfide minerals and ores	Fe, Pb, Si, Al, Mg, Ca, Na, K, Ti, Mn, Zn, Cu	31

and readily loses hydrogen fluoride when heated. Since the presence of hydrogen fluoride is essential in the decomposition process, it is necessary to mix the powdered mineral intimately with excess potassium hydrogen fluoride and to heat the mixture very slowly so as to give time for the hydrogen fluoride to attack the mineral matrix. The temperature of the crucible and contents is therefore raised very slowly to a dull red heat over a period of 15 min, after which decomposition of the mineral should be complete. Silicon is lost as volatile silicon tetrafluoride during the fusion. Minerals that are decomposed by this attack include beryl,[34] niobates, tantalates, and zircon.[33] It seems likely that other elements forming volatile fluorides, such as arsenic and boron, will be lost along with silicon tetrafluoride. With this fusion care must also be taken not to heat too strongly when elements that form somewhat less volatile fluorides are present. These include molybdenum, tantalum, and niobium.[35]

With the object of determining thoria, monazite sands have been decomposed by fusion with potassium hydrogen fluoride.[36] Insoluble rare earth and thorium fluorides were separated by centrifugation and then brought into solution by treatment with saturated aluminum nitrate solution. Thorium was separated from the rare earths by solvent extraction and determined spectrophotometrically.

Silicates that are resistant to decomposition by boiling acids, such as topaz and kyanite, can be decomposed by fusion with ammonium fluoride.[37] According to Erdey et al.,[38] ammonium fluoride decomposes on heating, yielding ammonium hydrogen fluoride with the evolution of ammonia, the rate of the reaction being greatest at 145° C. The ammonium hydrogen fluoride then decomposes to ammonia and hydrogen fluoride, the rate of this decomposition being greatest at 225° C. Ammonium hydrogen fluoride melts at 125° C with decomposition beginning at 80° C and reaching a maximum rate at 235° C.

IV. ION-EXCHANGE SEPARATIONS AND PARTITION CHROMATOGRAPHY

A. Ion-Exchange Separations

Since many elements form stable fluoro complexes, which are usually anionic in the presence of excess fluoride, it is understandable that extensive studies have been made on the separation of elements on columns of ion-exchange resins from solutions containing fluoride. Anionic fluoro complexes are usually absorbed from fluoride solutions on strongly basic anion-exchange resins, but elements that either do not form fluoro complexes or form only cationic or neutral fluoro complexes are not held strongly by the resin. On strongly acidic cation-exchange resins, uncomplexed cations and cationic fluoro complexes are generally held while neutral and anionic fluoro complexes are not absorbed.

Much pioneering work on the separation of elements on columns of ion-exchange resins was undertaken by Kraus and co-workers in the late 1940s and 1950s. Their early investigations included the separations of niobium and tantalum[39] and of niobium and zirconium[40] from hydrochloric acid - hydrofluoric acid media on the anion-exchange resin Dowex-1. Encouraged by these results, Hague and co-workers[41] in 1954 made preliminary investigations on the separation of titanium, tungsten, molybdenum, and niobium using various hydrochloric acid - hydrofluoric acid mixtures. The results of many publications by Kraus and co-workers on ion-exchange separations are collected together and discussed in an excellent review by Kraus and Nelson[42] published in 1958. In that review, separations using the hydrochloric acid-hydrofluoric acid system are discussed at length. This system was developed because, in their work with the hydrochloric acid system,[42] they found that species such as zirconium(IV), hafnium(IV), niobium(V), tantalum(V), and protactinium(V) tended to hydrolyze, polymerize, or precipitate even in fairly concentrated hydrochloric acid solutions. In the presence of fluoride this hydrolysis was prevented because of the formation of stable fluoro complexes. The ion exchange behaviors of many elements in hydrochloric acid solution are modified by the addition of hydrofluoric acid. The extent of complexing of various metals by fluoride ion in hydrochloric acid solutions has been calculated by Kraus et al.[43] and such data are shown in Table 3.

The original paper[42] should be consulted for details, but the behavior of a metal on a column of anion-exchange resin can be ascertained from a plot of the logarithm of the distribution coefficient of the metal between the resin and solution against the molarity of hydrochloric acid

TABLE 3

Complexing of Various Metals by Fluoride Ions in Hydrochloric Acid Solutions (Containing 1 M Hydrofluoric Acid)

Element	Fraction of element as fluoride complexes in hydrochloric acid of various molarities						
	0.5	1	2	4	6	8	11
Sn(II)	0.98	0.96	0.9	0.7	0.2	N[a]	→
Fe(III)	←	>0.98	0.98	0.8	0.1	N	→
Ga(III)	←	>0.98	0.98	0.9	0.5	0.3	N
Sb(III)	←	(-)[b]	>0.99	0.7	N	→	→
Ti(IV)	←	←	(-)	←	←	←	>0.97
Zr(IV)	←	←	(-)	←	←	←	>0.999
Hf(IV)	←	←	(-)	←	←	←	>0.999
Ge(IV)	←	←	(-)	←	←	←	>0.994
Sn(IV)	←	←	(-)	0.9	0.5	0.1	N
U(IV)				←	←	0.99	
Pa(V)	←	←	(-)	←	←	←	>0.99
Sb(V)	←	←	(-)		0.95	0.9	
Mo(VI)	←	←	(-)	0.9	0.7	0.4	N
W(VI)	←	←	(-)	←	>0.9	0.8	0.6
U(VI)	←	(-)	>0.88	0.4	N	→	→

[a] N means that the fraction of element as fluoride complexes is negligible.

[b] (-) means that there is evidence for the predominance of negatively charged fluoride complexes.

(From Nelson, F., Rush, R. M., and Kraus, K. A., *J. Amer. Chem. Soc.*, 82, 339 (1960). With permission.)

in the presence of a fixed concentration of hydrofluoric acid, such as 1 *M*. Schemes for separating various elements can be devised forwardly from such data, and Kraus et al.[42,43] show a number of examples.

Faris[44] has presented extensive data on the absorption of elements from hydrofluoric acid (1 to 24 M) by Dowex 1-X10 anion-exchange resin. With the exception of niobium(V), the absorbability of every element forming an anionic complex in hydrofluoric acid decreases regularly with increasing molarity of the acid. The following species are strongly absorbed from dilute hydrofluoric acid solutions: beryllium(II), scandium(III), titanium(IV), zirconium(IV), hafnium(IV), niobium(V), tantalum(V), molybdenum(VI), tungsten(VI), rhenium(VII), palladium(II), platinum(IV), gold(III), mercury(II), boron(III), tin(IV), arsenic(V), antimony(V), and tellurium(IV). Many of these elements form highly stable anionic fluoro complexes in fluoride media (see Section II A), so it is to be expected that they will be absorbed strongly from dilute hydrofluoric acid solutions. However, it would appear that the hydrochloric acid - hydrofluoric acid system is a better system than the hydrofluoric acid system in that it provides more and better possibilities for column separations of elements for the analytical chemist. Many more useful separations can be achieved with the former system because many elements, in fairly concentrated hydrochloric acid, form stable anionic chloro complexes which are strongly absorbed by anion exchangers.

Cation-exchange separations of metal ions by elution with dilute hydrofluoric acid have been reported by Fritz and co-workers.[45] From Dowex 50W-X8 cation-exchange resin in the hydrogen form the following species are readily eluted with 0.1 *M* hydrofluoric acid: aluminum(III), cadmium(II), molybdenum(VI), niobium(V), scandium(III), tin(IV), tantalum(V), titanium(IV), uranium(VI), tungsten(VI), and zirconium(IV). It will be noted that many of these form stable anionic fluoro complexes and it is not surprising that they are eluted so readily.

Nikitin[46] has also used a cation-exchange resin column and hydrofluoric acid solutions of different concentrations to separate many inorganic species into groups.

Although these fundamental investigations with solutions of single ions and simple mixtures are most valuable and interesting, the analytical chemist in industry has to analyze "real" materials and is more interested in knowing if ion-exchange methods involving hydrofluoric acid and fluorides can be applied to analyses of complex alloys and other materials. In this direction worthwhile contributions have been made by Wilkins,[47] Hague and Machlin,[48] and Dixon and Headridge.[49,50]

Wilkins[47] has devised a scheme for the separation and determination of nickel, chromium, cobalt, iron, titanium, tungsten, molybdenum, niobium, and tantalum in a high-temperature alloy by anion exchange. The flow sheet for the analysis of the alloy is shown in Figure 2. The method was then applied with good results to a sample simulating a high-temperature alloy.

Titanium plus zirconium, niobium, and tantalum have been separated from an anion-exchange resin by elution with mixtures containing ammonium chloride, hydrochloric acid, and hydrofluoric acid in results reported by Hague and Machlin.[48] A preliminary precipitation with cupferron was required to isolate these elements from solutions of steels. The separated elements were determined in the column eluates by well-established gravimetric or photometric procedures. Good results were obtained when the method was applied to steels.

Headridge and Dixon[49] determined the distribution coefficients of many elements likely to be found in complex alloys between hydrochloric acid - hydrofluoric acid solutions and the ion-exchange resins De-Acidite FF® (anionic) and Zeo-Karb 225 (cationic). From a study of the results a scheme was proposed for the separation of these elements into more manageable groups. This was followed by a detailed study of the absorption of titanium, zirconium, niobium, tantalum, molybdenum, and tungsten on De-Acidite FF® from solutions containing mixtures of 2 or more of the compounds hydrofluoric acid, hydrochloric acid, ammonium fluoride, and ammonium chloride, with a view to obtaining a separation scheme for these elements that could be completed within 5 hr.[50] A completely satisfactory separation scheme was achieved, after determining the weight distribution coefficients of these elements between aqueous solutions of the above reagents and the resin, and after investigating numerous elution curves for these elements from columns of the resin.

Titanium(IV), zirconium, niobium(V), tantalum, molybdenum(VI), and tungsten(VI) were retained on the resin and separated from aluminum, vanadium(IV), chromium(III), manganese(II), iron(III), cobalt(II), nickel, and copper(II) by passing a solution of these elements in 1 M hydrofluoric acid through a column of 100 to 200-mesh resin in the chloride form. Titanium plus zirconium, tungsten, niobium, molybdenum, and tantalum were then quantitatively eluted from the resin with 0.01 M hydrofluoric acid - 9 M hydrochloric acid, 3 M hydrofluoric acid - 10 M hydrochloric acid, 0.2 M hydrofluoric acid - 7 M hydrochloric acid, 3 M hydrofluoric acid - 3 M hydrochloric acid, and 1 M ammonium fluoride - 4 M ammonium chloride mixtures, respectively. This separation is shown in Figure 3.

Good results were obtained when the scheme was applied to the separation of these elements in synthetic mixtures and alloys, spectrophotometric or titrimetric[51-53] methods being used for quantitatively determining the separated elements.

The volume distribution coefficients for 19 metals between Dowex 1-X4 resin and nitric acid - hydrofluoric acid mixtures (1 to 12 M in nitric acid, and 0.2 to 5 M in hydrofluoric acid) have been determined by Huff.[54] From these results a method was developed for the quantitative determination of trace elements in tantalum or trace amounts of tantalum in other matrices. Anion-exchange separations involving fluoride solutions have also been employed for the determinations of molybdenum, titanium, and zirconium in tungsten;[55] of niobium and tantalum in stabilized chrome-nickel steel;[56] and of nickel, cobalt, copper, iron, and zinc in molybdenum and tungsten.[57]

The absorptions of many ions arising from complex alloys on an anion-exchange resin from solutions containing hydrofluoric acid (0.1 or 1.0 M) and either nitric or sulfuric acid (0.1 or 1.0 N) have been studied by Danielsson.[58] The absorption behaviors of metal ions in some of these acid mixtures are shown in Table 4.[59] It can be concluded that these systems, which are fairly similar in behavior, are less versatile than the hydrochloric acid - hydrofluoric acid system for achieving separations.

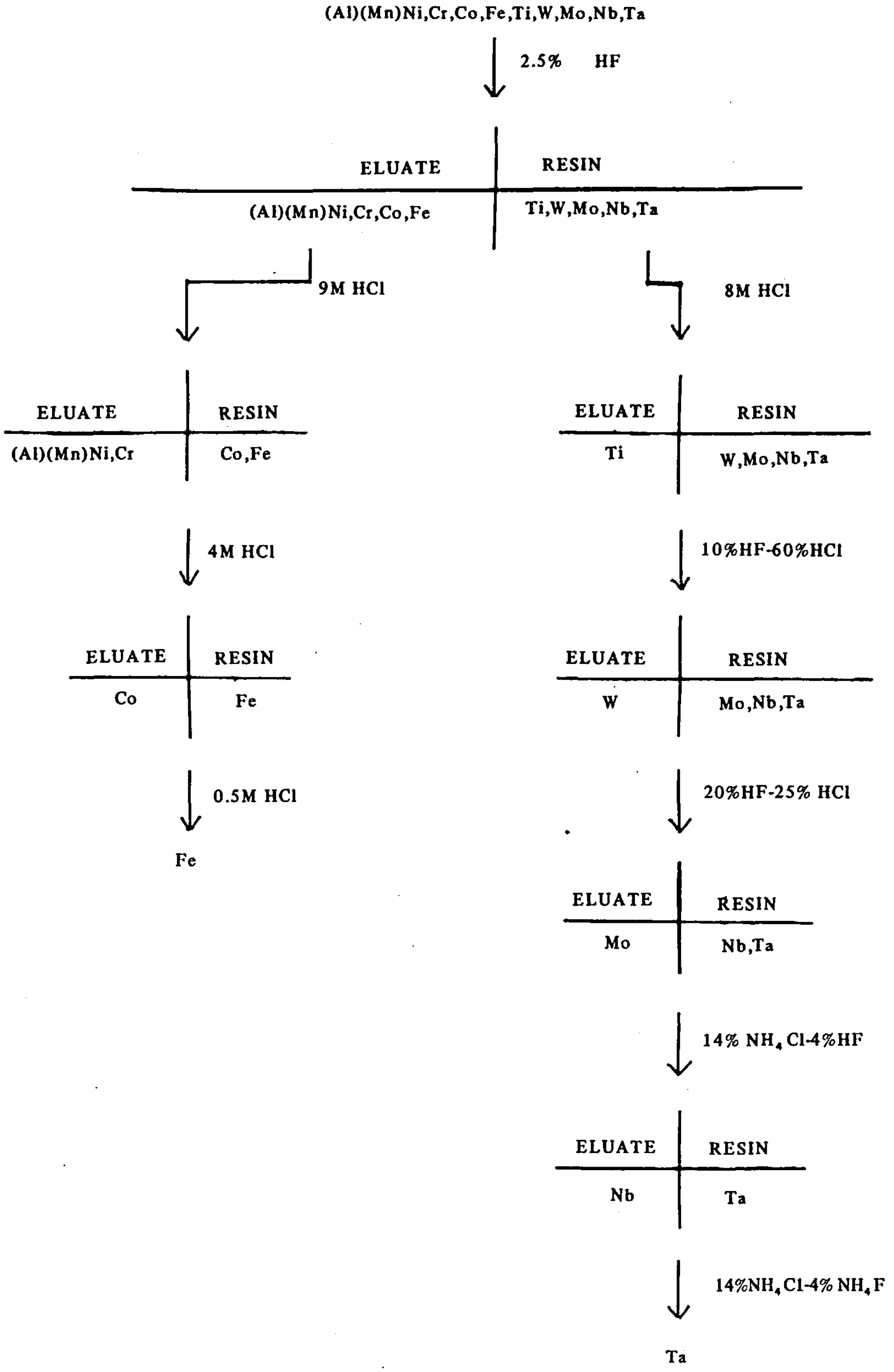

FIGURE 2. Flow sheet for the analysis of a high temperature alloy. (From Wilkins, D. H., *Talanta,* 2, 355 (1959). With permission.)

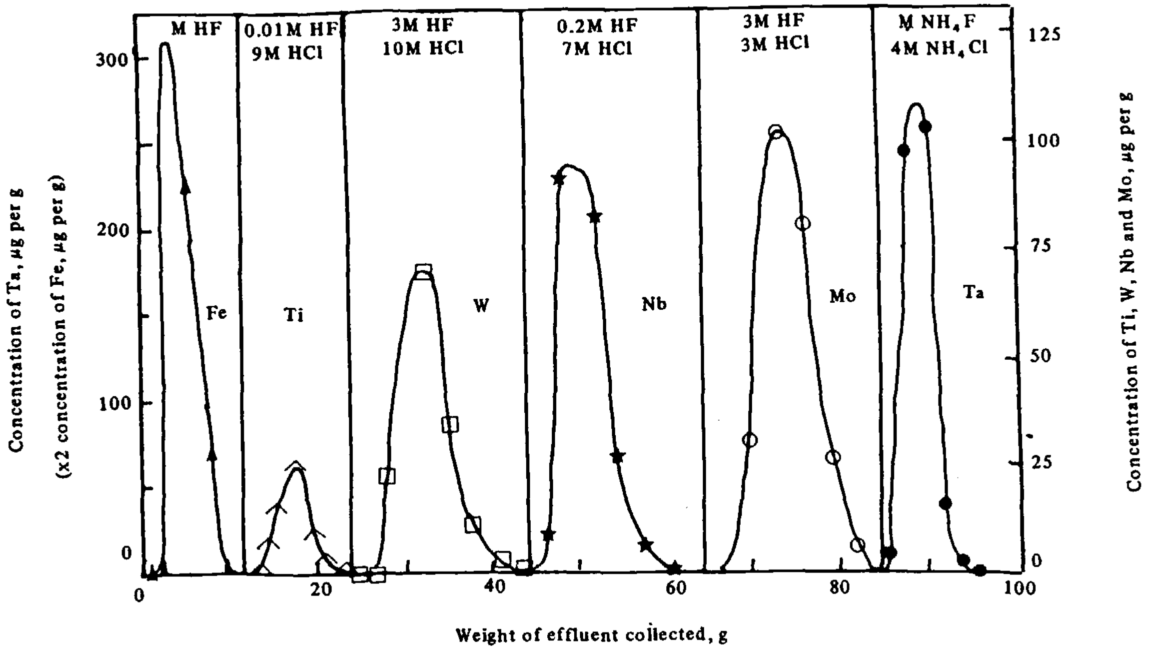

FIGURE 3. Elution curves for the separation of a mixture containing iron, titanium, tungsten, niobium, molybdenum, and tantalum; eluants as shown. (From Headridge, J. B. and Dixon, E. J., *Analyst*, 89, 185, (1965). With permission.)

Danielsson has also investigated the cation-exchange separations of traces of metals from large amounts of iron[60,61] or aluminum,[62] and the anion-exchange separation of traces of metals from large amounts of iron.[63] He summarizes studies on ion-exchange separations, with particular reference to the analysis of iron and steel, in a very useful review.[59]

Further examples of analytical methods involving a preliminary separation on a column of ion-exchange resin using solutions containing hydrofluoric acid are as follows. Lead has been separated from elements, including iron(III), that would interfere with its polarographic determination by absorption on a column of strongly acidic cation-exchange resin in the hydrogen form from 1 M hydrofluoric acid.[64] The lead was eluted with 2 M hydrochloric acid and determined by dc polarography. The method has been applied to the determination of lead in steels.

Niobium has been separated from iron and several other elements by absorption on an anion-exchange resin from a solution containing 1 M hydrofluoric acid and 0.05 M nitric acid. Niobium, held by the resin, was eluted with 4 M nitric acid - 1 M hydrofluoric acid and finally determined photometrically with 4-(2-pyridylazoresorcinol).[65]

Eluants containing hydrofluoric acid have also been used in schemes for the separations of lead, bismuth, and polonium;[66] zirconium, neptunium, and niobium;[67] and uranium, neptunium, and plutonium;[68] while uranium(VI) has been separated from rare-earth elements by elution of uranium(VI) with 1 M ammonium fluoride, sodium fluoride, or hydrofluoric acid from the mixture retained on a cation-exchange resin.[69]

Finally, Ferraro[70] has recently described an ion-exchange method involving eluants containing hydrofluoric acid for the determination of vanadium, zirconium, hafnium, titanium, molybdenum, tungsten, and tantalum in niobium alloys.

B. Separations by Cellulose and Paper Chromatography

Hydrofluoric acid has been incorporated in eluants used for the separation of niobium and tantalum on a column of cellulose. This separation is less convenient than an ion-exchange separation of these elements, but a typical procedure[71] involves the use of a column of activated cellulose in methyl ethyl ketone. A mixture of niobium and tantalum as fluoro complexes on the top of the column is treated by passing methyl ethyl ketone saturated with water down the column. Tantalum

TABLE 4

Approximate Absorption Behaviors of Metal Ions in Solutions Containing 1 M HF and 0.1 *N* H_2SO_4 or HNO_3

	Cation exchange
Weakly absorbed (D<10)[a]	Al(III), As(III), As(V), Cr(III), Fe(III)[b], Mo(VI), Nb(V), Sb(III), Sb(V), Sn(IV), Ta(V), Ti(IV), V(V), W(VI), Zr(IV)
Moderately absorbed (D = *10 to 100*)	Bi(III)[b], Fe(II)[b], V(IV)[b]
Strongly absorbed (D>100)	Ag(I), Cd(II), Co(II), Cu(II), Mg(II), Mn(II), Ni(II), Pb(II), Zn(II)
	Anion exchange
Weakly absorbed (D<10)	Ag(I), Al(III), As(III), Bi(III), Cd(II), Co(II), Cr(III), Cu(II), Fe(II), Fe(III), Mg(II), Mn(II), Ni(II), Pb(II), Sb(III), V(IV), Zn(II)
Moderately absorbed (D = 10 to 100)	As(V), V(V)
Strongly absorbed (D>100)	Mo(VI), Nb(V), Sb(V), Sn(IV), Ta(V), Ti(IV), W(VI), Zr(IV)

[a] D is the weight distribution coefficient.

[b] If the concentration of HF is decreased to 0.1 M these elements are strongly absorbed.

(From Danielsson, L., *Ark. Kemi*, 27, 467 (1967). With permission.)

is eluted, and niobium is then stripped from the column with methyl ethyl ketone containing 7.5% (v/v) of concentrated hydrofluoric acid.

Niobium and tantalum can be separated satisfactorily by paper chromatography using hydrofluoric acid and methyl isobutyl ketone,[72] and niobium, tantalum, and titanium have been separated on Whatman No. 1 paper using diethyl ketone saturated with 2.2 M hydrofluoric acid - 2 M nitric acid. The R_f-values are 0.05 for titanium, 0.55 for niobium, and 1.00 for tantalum.[73] The paper chromatographic behaviors of many inorganic substances with solvents containing hydrofluoric and hydrochloric acids have also been reported by Popa and co-workers.[74]

V. SOLVENT EXTRACTION

A. Basic Considerations

In the presence of excess hydrofluoric acid or fluoride, there are many elements that form stable anionic fluoro complexes. These anions may be extracted into organic solvents as ion-association complexes, in which the cation may be either the protonated solvent or some other bulky ion, such as a tetraalkylammonium ion. In actual fact, satisfactory extraction methods have only been devised for boron and tantalum, and to a much more limited extent for niobium and protactinium.

Early studies were made by Kitahara[75] and

TABLE 5

The Extent of Extraction of Elements into Diethyl Ether from 20 M Hydrofluoric Acid Solution

Percentage extracted	Elements in each class
< 1	Al, Ga, In, Tl(I), Si, Sb(V), Ti(IV), Cr(III), W(VI), Fe(II), Fe(III), Ni, Ag, Zn
1 to 10	Be, Ge(IV), Sn(II), Sn(IV), Sb(III), Zr(IV), V(V), Mo(VI), Mn(II), Co(II), Cu(II), Cd, Hg(II), U(VI)
10 to 50	P(V), As(III), As(V), Se(IV), Te(IV), V(III)
> 50	Nb(V), Ta(V), Re(VII)

Bock and Herrmann[76] on the solvent extraction of many elements into diethyl ether from hydrofluoric acid solutions. The extent of extraction increases with the concentration of hydrofluoric acid in the aqueous phase. Data on the extractions of many elements from 20 M hydrofluoric acid are presented in Table 5.[76]

From aqueous solutions containing 10 to 20 M hydrofluoric acid, this acid is extracted to the extent of approximately 38%.[76] Work on the solvent extraction of elements from fluoride solutions up to 1956 has been ably reviewed by Morrison and Freiser.[77]

It will be noted from Table 5 that niobium and tantalum are appreciably extracted into diethyl ether from 20 M hydrofluoric acid. Niobium(V) is nearly quantitatively extracted from 6 M hydrofluoric acid - 6 M sulfuric acid into diisobutylcarbinol[78] and from 10 M hydrofluoric acid - 6 M sulfuric acid - 2.2 M ammonium fluoride into methyl isobutyl ketone.[79] With this latter system the extraction of tantalum is also almost complete. This solvent-extraction procedure has been used in a method to determine niobium in titanium ores and pigments.[80]

Niobium and tantalum can be separated fairly effectively by extracting the tantalum into diisopropyl ketone from an aqueous solution 0.4 M in hydrofluoric acid and approximately 4 M in hydrochloric, nitric, sulfuric, or perchloric acid.[81] A double extraction procedure for the separation of tantalum from niobium, using a hydrochloric-hydrofluoric acid medium and methyl isobutyl ketone, has been devised by Theodore,[82] and a colorimetric determination of tantalum in niobium has been reported after separation of the tantalum by extraction into cyclohexanone from 0.4 M hydrofluoric acid - 2 M sulfuric acid solution.[83] Protactinium(V) is almost completely extracted into diisopropyl ketone from 8 M hydrochloric acid - 0.6 M hydrofluoric acid - saturated aluminum chloride.[84]

Maeck and co-workers[85] have investigated the distributions of 57 metallic ions between methyl isobutyl ketone and an aqueous phase containing 0.2 to 5 M hydrofluoric acid and tetrapropyl-, tetrabutyl-, or tetrahexylammonium ions. Distribution data are presented as plots of percent extraction versus molarity of hydrofluoric acid in the form of a periodic table. These plots show that, for these metals, the only important extractable fluoride complex is that of tantalum(V). Niobium(V) and protactinium(V) are scarcely extracted, but high percentages of technetium(VII) and rhenium(VII) are extracted. Tantalum is also extracted from 0.15 M hydrofluoric acid - 8 M hydrochloric acid using 10% (v/v) Amberlite LA-2® in benzene[86] and can be separated from niobium, titanium, and zirconium by solvent extraction of tetraphenylarsonium fluotantalate into dichloroethane or chloroform.[87]

Using a 3% (w/v) solution of triisooctylamine in carbon tetrachloride and an aqueous solution containing niobium(V) and tantalum(V) together with 1.33 M nitric acid and 0.24 M hydrofluoric acid, Marchart and Hecht[88] have shown that 98%

of the tantalum is extracted into the organic phase on shaking while 98% of the niobium remains in the aqueous phase. From 0.5 to 2 M hydrofluoric acid, with or without sulfuric acid, tantalum is extracted to the extent of 90 to 95% with 1 volume of tributylphosphate, while only 2.5 to 5% of the niobium is extracted.[89] From solutions 6 M in hydrofluoric acid and 8 M in sulfuric acid, 1 volume of tributylphosphate extracts 100% of the tantalum and 97.5 to 99.5% of the niobium. From 1 M hydrofluoric acid, tantalum is also extracted and may be separated from niobium by shaking with an equal volume of a solution consisting of tri-n-butylphosphate-kerosene (4:1,v/v).[90]

It would appear that tantalum is readily extracted from mildly acidic fluoride solutions, but that niobium is best extracted from strongly acidic solutions containing high concentrations of hydrofluoric acid. With the latter systems tantalum will usually be extracted also.

Another element that can be extracted as a fluoro complex is boron. At a pH less than 3.2 in the presence of fluoride and tetraphenylarsonium chloride, this element is extracted into chloroform as the tetraphenylarsonium tetrafluoborate ion-association complex.[91]

B. Solvent Extraction Followed by Spectrophotometric Determination

It has been seen that boron and tantalum are readily extracted as ion-association complexes from fluoride solutions into organic solvents. If the cationic part of an ion-association complex is a dyestuff such as methyl violet, then the extracted complex will be colored, providing the basis for a colorimetric determination of the extracted element.

1. Determination of Boron

Methods for the determination of boron are summarized in Table 6. There seems to be little

TABLE 6

Methods for the Solvent Extraction and Spectrophotometric Determination of Boron

Cationic Reagent	Solvent	Comments	Ref.
Methylene blue	1,2-Dichloroethane	In water, Si, and SiO_2; no interference from Al, Fe(III), and Si	92
		In steel	93,94,95 96,97,98
		In Al and its alloys	99
		In Zr and Zircaloy	100
		In rocks	101
Monomethylthionine (Azure C)	1,2-Dichloroethane	Preferred to methylene blue	102
Methyl violet	Benzene	pH 3.4	103,104
	Trichloroethylene	In steel	105
Brilliant green	Benzene	In steel	106
		In Ti and Zr metals	107
Crystal violet	Benzene	–	108
Malachite green	Benzene	Cl^-, I^- and NO_2^- interfere	109
Brilliant Cresyl Blue Capri Blue Nile Blue	1,2-Dichloroethane	–	110
Nile Blue A	Chlorobenzene or *o*-dichlorobenzene	In fertilizers, soil, plants, and water	111
Tris(1,10-phenanthroline) iron(II)	*n*-Butyronitrile	Measure at 520 nm	112
	Nitrobenzene	Alkylbenzenesulfonates and SCN^- interfere	113
Methyl green	Trichloroethylene	pH 2.5 to 5.0	114
Rhodamine B	Butyl acetate	Measure at 555 nm	115

ground for choice among these reagents for the spectrophotometric determination of boron.

2. Determination of Tantalum

Methods for the determination of tantalum are summarized in Table 7. The optimum pH-values for the extraction of fluotantalate from aqueous solution into benzene as ion-association complexes are 1.9 to 2.2 with methyl violet, 1.6 to 2.3 with crystal violet, 0.8 to 2.0 with malachite green and 0.6 to 2.0 with brilliant green.[122] Such triphenylmethane dyes form ion-association complexes with tantalum in the form of hexafluotantalate(V).[123] Again it would appear that any of the dyes in Table 7 and of those just mentioned can be satisfactorily used in a spectrophotometric method for tantalum.

In a highly sensitive method reported for the determination of tantalum in silicon dioxide and trichlorosilane, the tantalum is extracted from hydrofluoric acid solution into benzene, using rhodamine 6G, and the concentration of the complex is determined fluorometrically. Parts per hundred million of tantalum can be determined.[124]

3. Determination of Niobium

Butyl rhodamine B has been employed for the extraction into benzene of niobium from 5 M sulfuric acid containing hydrofluoric acid. A subsequent spectrophotometric determination of niobium could then be made. Conditions have been established for the determination of niobium in the presence of tantalum.[125]

C. Solvent Extraction Followed by Flame Photometry

Boron as tetrafluoborate has been extracted into methyl isobutyl ketone as an ion-association complex with tetrabutyl-ammonium ion and subsequently determined by flame photometry.[126] Niobium has been extracted from 6 M hydrofluoric acid - 6 M hydrochloric acid into methyl isobutyl ketone and determined in the organic phase by flame photometry. Tantalum is extracted along with niobium.[127] The method has been applied to the determination of niobium in steels. Finally, niobium and tantalum have been extracted into methyl isobutyl ketone from solutions of nickel-base[5] and cobalt-base[6] alloys in 10 M hydrofluoric acid - 6 M hydrochloric acid before determination by atomic absorption spectroscopy.

TABLE 7

Methods for the Solvent Extraction and Spectrophotometric Determination of Tantalum

Cationic Reagent	Solvent	Comments	Ref.
Methyl violet	Benzene	pH 2.3	103
	Toluene	pH 1.9 to 2.3; in Nb metal; no interference from Ti and Zr	116
Malachite green	Benzene	In Fe, steel, and Nb containing 0.005 to 0.5% Ta*;	8
		in B, U, Zr and U-Zircaloy-2; Ta is first coprecipitated with Fe(III) from aqueous ammoniacal solution	117
Butylrhodamine B			
Rhodamine 6G	Benzene		118
Nile Blue A	Chlorobenzene	In steel and Nb	119
Victoria Blue B	Benzene	$2 M$ H_2SO_4 to $0.5 M$ HF	120
Meldola Blue	Chlorobenzene	In Nb metal	121
Methyl Green	Benzene	pH 0.8 to 1.7	114

*Boron, which forms a similar complex, is removed by fuming with sulfuric acid in the presence of hydrofluoric acid to volatilize it as boron trifluoride.

VI. PRECIPITATION FROM FLUORIDE–CONTAINING MEDIA

Many elements form insoluble or sparingly soluble fluorides. These include lithium, magnesium, calcium, strontium, barium, lead, scandium, yttrium, and lanthanides and actinides in the +3 and +4 oxidation states. This fact has been used to develop separation methods for certain groups of elements. However, little use has been made of fluoride precipitates in direct gravimetric analysis, probably because fluoride precipitates are often gelatinous and difficult to filter. Precipitation from homogeneous solution should yield more compact precipitates. Most of the basic facts on insoluble fluorides were discovered before 1960 and few papers appear to have been published on the precipitation of fluorides in the last decade. The decreasing interest in gravimetric analysis as a field for research in recent years probably contributes to this fact.

It is stated that lithium can be determined gravimetrically as the fluoride,[128] but the method offers no advantages over better-established methods such as precipitation as a complex periodate.[129] Calcium has been determined by precipitation as calcium fluoride from homogeneous solution. The fluoride ion was produced by the hydrolysis of tetrafluoborate ion in the presence of ammonium chloride and urea at 95° C. Magnesium and lead interfere.[130] Apparently lead can also be determined gravimetrically as lead chlorofluoride.[131]

Scandium forms an insoluble fluoride and in dilute aqueous hydrofluoric acid solution can thus be separated from titanium, niobium, and tantalum.[132] However, care must be taken to see that the concentration of excess of fluoride is kept low because scandium trifluoride readily forms a soluble anionic fluoro complex in solutions containing high concentrations of fluoride. Indeed, this reaction has been used by Meyer and coworkers[133] to separate scandium fairly effectively from thorium. Its use has been further evaluated by Fischer and Bock.[134]

Rare earths are separated from niobium, tantalum, titanium, zirconium, and iron by precipitation as insoluble fluorides on addition of hydrofluoric acid. The other elements are held in solution as soluble fluoro complexes provided that the alkali metal ions, which form insoluble complex fluorides with these elements, are absent or present at only low concentration.[135] Thorium and uranium(IV) are precipitated as insoluble fluorides along with the rare earths, but calcium and lead are precipitated incompletely. Care must be taken to keep the concentration of excess fluoride fairly low, for there is a tendency to form soluble complex rare earth fluorides in media containing high concentrations of fluoride. The gravimetric determination of rare earths by collecting and weighing their precipitated fluorides does not appear to have been reported. Rare earth fluoride precipitates are usually dissolved by treatment with sulfuric acid or with a mixture of nitric and perchloric acids and the solution subjected to further analysis. Lanthanum fluoride has been produced by precipitation from homogeneous solution by boiling a nitric acid solution containing fluoboric acid and urea.[136] A good account of the precipitation of rare earth fluorides, with many references, is given by Ryabchikov and Ryabukhin.[137]

Thorium is precipitated as hydrated thorium tetrafluoride by the addition of hydrofluoric acid to soluble thorium salts at room temperature. At 300° C the anhydrous tetrafluoride is formed, but this is not a suitable weighing form because partial hydrolysis occurs on heating in the atmosphere. Small amounts of thorium fluoride are converted into thorium oxide when ignited at 1,000°C.[138] Yttrium and lanthanum fluorides are good carriers for the precipitation of trace amounts of thorium. Further details on the precipitation of thorium by hydrofluoric acid and alkali fluorides are reported by Ryabchikov and Gol'braikh.[138] Like thorium tetrafluoride, uranium(IV) fluoride is insoluble in aqueous hydrofluoric acid solutions, and this permits the separation of uranium(IV) from uranium(VI). The compound $UF_4 \cdot NH_4F \cdot 0.5H_2O$ may also be used for the quantitative separation of uranium(IV) from uranium(VI), iron(III), and vanadium(III).[139] An extensive account of the precipitation of uranium(IV) fluoride in the presence of other elements such as zirconium and tantalum is given by Palei.[140]

Neptunium, plutonium, and americium in the +3 and +4 oxidation states can be precipitated from solution as fluorides using lanthanum fluoride as a carrier. Insoluble fluorides of the rare earths and thorium accompany these actinides.[141] The transamericium elements in their +3 oxidation state are also coprecipitated along with rare earths by fluoride and thereby collected.[142] The insoluble double salt $NaPuF_5$ is formed when an excess of sodium fluoride is added to a nitric acid solution of plutonium(IV).[143] By using this reaction, plutonium could be separated from those elements such as iron(III) and titanium, which are present as soluble species under these conditions.

VII. TITRIMETRIC ANALYSIS

A. Redox Titrations

1. General Considerations

From a study of the data on stability constants in Section IIA, it is evident that, compared with most singly and doubly charged cations, the cations of higher charge form more stable complexes with fluoride ion. This is reflected in an appreciable lowering of the values of the formal potentials of M(III)/M(II) couples in fluoride media compared to the values in noncomplexing media. Some couples which one would expect to be affected are vanadium(III)/vanadium(II), chromium(III)/chromium(II), manganese(III)/manganese(II), iron(III)/iron(II), and cobalt(III)/cobalt(II). The measured values for certain formal potentials in 0.5 M ammonium fluoride - 0.5 M hydrofluoric acid are shown in Table 8 along with the corresponding formal potentials for the uncomplexed ions.[144]

By combining the estimated overall stability constants (β_6) of the hexafluomanganate(III) and hexafluoferrate(III) anions with the Nernst equation, Headridge and Taylor[145] calculated that the formal potentials of the manganese(III)/manganese(II), iron(III)/iron(II), and manganese(VII)/manganese(III) couples should be +0.86 V, +0.06 V, and +1.29 V, respectively, assuming that manganese(II), iron(II), and permanganate were not complexed by fluoride. These calculated results are in fairly good agreement with the experimental results reported in Table 8. Clearly, iron(II) in certain fluoride media is a powerful reducing agent. The formal potentials indicate that it should be possible to oxidize manganese(II) to manganese(III) with potassium permanganate in 0.5 M ammonium fluoride – 0.5 M hydrofluoric acid. The results that have been obtained with these systems will be described later. One would also expect chromium(II) and vanadium(II) in suitable fluoride media to be very powerful reducing agents, which would probably react rapidly with hydrogen ion to reduce it to molecular hydrogen. Cobalt(III) should be appreciably stabilized by complex formation with fluoride and it may be possible to devise an analytical method for the titrimetric oxidation of cobalt(II) to cobalt(III) in the presence of fluoride. The applications of some of these couples in titrimetric analysis are described below.

2. The Manganese(VII)/Manganese(III) System

As illustrated in Table 8 at pH-values around 3 permanganate becomes a more powerful oxidant in the presence of free fluoride ions than in their absence. However, it must be appreciated that the hydrogen-ion concentration has a pronounced effect on the formal potential of the manganese(VII)/manganese(III) couple.

$$MnO_4^- + 8H^+ + 6F^- + 4e \rightleftharpoons MnF_6^{3-} + 4H_2O.$$

TABLE 8

Formal Potentials in 0.5 M Ammonium Fluoride – 0.5 M Hydrofluoric Acid and in a Noncomplexing Medium

System	$E^{0\prime}$(fluoride medium) (V vs. N.H.E. at 25° C)	$E^{0\prime}$(uncomplexed ions)* (V vs. N.H.E. at 25° C)
Mn(III)/Mn(II)	+0.87	+1.51
Fe(III)/Fe(II)	+0.10	+0.77
Sn(IV)/Sn(II)	+0.05	+0.15
Mn(VII)/Mn(III)	+1.30	+1.13
Cr(VI)/Cr(III)	+0.95	+0.92
V(V)/V(IV)	+0.71	+0.62

*These values are calculated, where applicable, for the pH (3.15) of 0.5 *M* ammonium fluoride - 0.5 *M* hydrofluoric acid.

As the hydrogen-ion concentration is increased, the fluoride-ion concentration is decreased due to the formation of undissociated hydrofluoric acid. In strongly acidic solutions the addition of fluoride ion will have no pronounced effect on the formal potential of the manganese(VII)/manganese(III) couple.

Potentiometric end-point detection has been employed by Issa and Hamdy[146] in the titration of mercury(I) with permanganate in sulfuric acid solution in the presence of fluoride. The permanganate is reduced to manganese(III). A visual titration of mercury(I) is possible in the presence of copper sulfate, which is added to mask the color of the manganese(III) ion. The method has also been applied to the determination of tellurium(IV) in acidic fluoride solution by titration with standard permanganate solution,[147] after the addition of mercury(I), which presumably serves as a catalyst. Selenium(IV) in sulfuric acid solutions containing fluoride has been determined by adding excess potassium permanganate, waiting 30 min, and back-titrating the excess with mercurous nitrate solution.[148] It seems likely that mercury(I), selenium(IV), and tellurium(IV) could be determined equally well in the absence of fluoride.

Issa and Hamdy have also determined iron(II)[149] and chromium(III) and vanadium(IV),[150] by adding excess potassium permanganate in sodium hydroxide solution, allowing the solution to stand for 5 min, acidifying with sulfuric acid, adding sodium fluoride solution and then an excess of standard mercury(I) solution, and back-titrating the excess with permanganate in the presence of copper sulfate.

An interesting titration is that of manganese(II) with permanganate in the presence of fluoride. Zvenigorodskaya and Gotsdiner[151] performed this titration, employing potentiometric end-point detection; manganese(III) is both the product of oxidation of the manganese(II) and the product of reduction of the permanganate, so that the overall reaction is

$$MnO_4^- + 4Mn^{++} + 8H^+ + 30F^- = 5MnF_6^{3-} + 4H_2O$$

Visual determination of the end-point was also possible.[152] These titrations were used for the determination of manganese in ores and slags.

Headridge and Taylor[153] later investigated the accuracy and precision of the titrimetric determination of manganese(II) in 0.5 M ammonium fluoride – 0.5 M hydrofluoric acid with 0.02 M permanganate as the titrant. In the absence of colored ions, they found that 2.5 to 15 mg of manganese(II) in 100 ml of solution could be determined by visual titration with a mean error of 0.001 mg and a standard deviation from the mean of 0.020 mg. The manganese(III) fluoride complex anion is pale yellow-brown in color, but after a little practice the merest excess of permanganate can be readily detected by eye even if the titrand contains as much as, or even more than, 15 mg of manganese(II) per 100 ml.

Except for obvious reducing agents, it was considered that only cobalt(II), nickel(II), copper(II), and chromium(III) in fluoride solutions could possibly be oxidized to higher oxidation states by permanganate, but it was soon established that these species were not in fact, oxidized by permanganate, either in the presence or in the absence of manganese(II). The reaction, therefore, seems to be highly selective for manganese(II) in the presence of other elements.

Of course it is much more difficult to obtain accurate results when manganese(II) is titrated visually with permanganate in the presence of colored ions, and in these instances a photometric titration was preferred. A potentiometric titration should be equally satisfactory. Using this method, good results were obtained for the analysis of steels and other alloys containing manganese.

3. The Iron(III)/Iron(II) System

Mahr and Seeger[154] have determined copper(II) by adding excess potassium iodide in the presence of acetate buffer and potassium fluoride, and titrating the liberated iodine with standard ferrous sulfate solution. In the presence of fluoride ion, iron(II) becomes a powerful reducing agent. Variamine Blue, a redox indicator, was used. Alternatively a potentiometric end-point may be employed. The method was applied to the determination of copper in brass and bronze samples. However, it would appear that in the presence of fluoride iron(II) has no advantages over thiosulfate as a titrant for iodine.

From Table 8 it can be seen that iron(II) is a powerful reducing agent in 0.5 M ammonium fluoride – 0.5 M hydrofluoric acid. In fact, it is a more powerful reducing agent than tin(II) in 1 M hydrochloric acid ($E^{0\prime} = +0.14$ V vs. N.H.E.). In 50% (v/v) aqueous alcohol containing 0.5 M ammonium fluoride and 0.5 M hydrofluoric acid, the formal potential of the iron(III)/iron(II) couple is even less positive, -0.02 V vs. N.H.E., and in this medium the purities of many quinones were determined by Headridge and Wilson[155] by potentiometric titrations with standard iron(II) solution. Any quinone, that forms part of a couple whose formal potential in the aqueous alcoholic mixed fluoride solution is not less than +0.24 V vs. N.H.E. can be determined. These include almost all of the 1,4- and 1,2-benzoquinones and phenanthraquinones, as well as many naphthaquinones, but only a few anthraquinones.

4. Metal Reductors and Fluoride Solutions

In addition to the titrations so far considered, where the fluoride ion has had a pronounced effect on the oxidizing or reducing ability of the titrant or titrand, there are other titration systems where the presence of fluoride ion is desirable. These involve solutions that contain partially hydrolyzed species in the absence of fluoride. In Section IIB, a brief account was given of the beneficial effect of fluoride in inhibiting hydrolysis. The presence of hydrofluoric acid is particularly advantageous in achieving quantitative reduction of niobium(V) and tungsten(VI) with metal reductors before titrimetric determinations of the reduced species with a suitable oxidant as titrant.

Although the titrimetric determination of niobium had been studied by many workers since 1885, no completely satisfactory procedure was reported before the work of Headridge and Taylor[51] published in 1962. Methods for this determination are based on the titration of a solution of niobium after treatment with a metallic reducing agent to convert the element into the tervalent state. The earlier methods reviewed by Schoeller and Waterhouse[156] all yielded low results, probably because of the presence of colloidal niobic acid resulting from hydrolysis. A more satisfactory titrimetric method, proposed and used by Cunningham,[157] was studied in detail by Knowles and Lundell.[158] These workers examined the reduction of niobium(V) in sulfuric acid media and used succinic acid and hydrogen peroxide as complexing agents; their results indicated that reduction was almost complete, but lacked precision. As the most stable complex of niobium in aqueous media is probably the fluoro complex, Headridge and Taylor[51] examined the titrimetric determination of niobium in solutions containing fluoride. Niobium(V) in 6 M hydrochloric acid – 0.5 M hydrofluoric acid was reduced quantitatively in a Jones reductor to niobium(III). The niobium(III) solution was collected in ferric ammonium sulfate solution under oxygen-free nitrogen. An amount of iron(II) was produced equivalent to the amount of niobium(III) present. The iron(II) was determined by titration with 0.0167 M potassium dichromate, using barium diphenylaminesulfonate as indicator. It is essential to the success of this method that the volume of the delivery tube between the column of amalgamated zinc shot and the iron(III) solution be kept to a minimum, for the niobium(III) species is fairly rapidly oxidized by hydrogen ion and the residence time of the niobium(III) solution in the delivery tube should be no more than a few seconds. When this precaution is observed, quantitative reduction of niobium(V) is readily achieved either in the presence or in the absence of tantalum(V), which is not reduced under these conditions. The precision of the method is good.

Before 1950, attempts to determine tungsten by titration of tungsten(III), produced by reduction of tungsten(VI) with metals, were unsuccessful[159] because reduction was not quantitative. Some time later, Geyer and Henze[160] and Luke[161] showed that almost complete reduction can be achieved if strong hydrochloric acid solutions of tungsten(VI) are reduced. Headridge and Taylor[52] found that tungsten(VI) in 2 M hydrochloric acid – 0.5 M hydrofluoric acid can be reduced completely to tungsten(III) using a Jones reductor; the reduced species being collected in ferric ammonium sulfate solution under a nitrogen atmosphere. Thus, the iron(II) produced was titrated with standard dichromate solution as with niobium. Molybdenum(VI), is also reduced to molybdenum(III) under these conditions and, as expected, iron(III) is reduced to iron(II). To ensure that premature oxidation of tungsten(III) by hydrogen ion does not occur, it is again essential to employ a delivery tube of the smallest possible volume. In fact, tungsten(III) reacts with hydrogen ion even more readily than does niobium(III)[52] Neither molybdenum(VI) nor tungsten(VI) in 2 M hydrochloric acid – 0.5 M hydrofluoric acid is at all reduced on a silver reductor at 10°C, although iron(III) is quantitatively reduced to iron(II) under these conditions.[53]

On a silver reductor at 60° C in 0.2 M hydrofluoric acid – 1.5 to 2.0 M hydrochloric acid, molybdenum(VI) is reduced quantitatively to molybdenum(V); in 0.2 M hydrofluoric acid containing more than 4 M hydrochloric acid, it is reduced quantitatively to molybdenum(III). No reduction of tungsten(VI) in 0.2 M hydrofluoric acid – hydrochloric acid occurs on a hot silver reductor at a hydrochloric acid concentration below 5.5 M.

Solutions containing iron(III), molybdenum(VI), and tungsten(VI) but no other species capable of reduction can, therefore, be analyzed for all three metals by using the Jones and silver reductors. These methods have been applied to the analyses of ferromolybdenum and ferrotungsten.[53]

The behaviors of a few elements that can be quantitatively reduced to lower oxidation states on metal reductors in solutions free from fluoride, were investigated for the fluoride systems employed for iron, molybdenum, and tungsten.[53] The procedures used for the reductions and titrations were identical with those employed for iron, molybdenum, and tungsten. The results are shown in Table 9. As a summary, the results obtained for iron, molybdenum, and tungsten are also included in this table.

TABLE 9

Oxidation States of Titanium, Vanadium, Chromium, Molybdenum, Tungsten, and Iron after Passage through Various Reductors

	Oxidation states in the effluent from the reductor		
Species	Cold silver[a]	Hot silver[b]	Jones[c]
Titanium(IV)	+4.00	+4.00	+3.00
Vanadium(V)	+4.00	+4.00	+2.00
Chromium(III)	+3.00	+3.00	+2.83*
Molybdenum(VI)	+6.00	+3.00	+3.00
Tungsten(VI)	+6.00	+6.00	+3.00
Iron(III)	+2.00	+2.00	+2.00

[a] Using 2 *M* hydrochloric acid - 0.5 *M* hydrofluoric acid at 10°C.

[b] Using 4.5 *M* hydrochloric acid - 0.2 *M* hydrofluoric acid at 60°C.

[c] Using 2 *M* hydrochloric acid - 0.5 *M* hydrofluoric acid at 12°C.

*Chromium(III) is not reduced to a definite oxidation state on the Jones reductor in cold 2 *M* hydrochloric acid - 0.5 *M* hydrofluoric acid.

B. Precipitation Titrations

Calcium in an ethanolic solution of pH 2.5 to 3.5 may be determined by titration with standard sodium fluoride solution using ferric thiocyanate as indicator. The red color of the indicator disappears at the end-point as excess fluoride complexes the iron(III).[162] Likewise, lead in the presence of excess sodium or potassium chloride can be determined by titration with standard sodium or potassium fluoride solution. Insoluble lead chlorofluoride is produced. The end-point is determined potentiometrically when the solution contains low concentrations of both ferrous and ferric ions. A sharp drop in the potential of the indicating electrode occurs at the end-point as the ferric ions are complexed by fluoride.[163]

Using standard sodium fluoride as titrant, thorium may be titrated in the presence of SPADNS as indicator at pH 3. Zirconium, hafnium, molybdenum, and phosphate interfere.[164] Thorium has also been determined by titration in a 50% (v/v) alcoholic solution at pH 2 with standard sodium fluoride solution using Alizarin Red S plus Pyrocatechol Violet as indicator. Thorium may be determined in monazite using this method.[165]

These titrations with sodium fluoride solution are interesting, but determinations of these elements by complexometric titrations with EDTA are much more popular.

VIII. POLAROGRAPHY AND VOLTAMMETRY IN FLUORIDE MEDIA

A. Polarography

The analytical chemist is likely to use the simplest system consistent with his requirements and, therefore, in polarography he is unlikely to use base electrolytes containing fluoride if simpler base electrolytes can be employed. However, we have already seen that the fluoride ion, being a good complexing agent, has a pronounced effect on the formal potentials of certain couples. The use of fluoride in polarography is, therefore, advantageous if it produces separate waves for two species whose waves are superimposed in noncomplexing supporting electrolytes. With these objects in mind, detailed polarographic investigations have been undertaken by West and co-workers[166] and by Headridge and co-workers.[167,168] Data from these papers and a few others are presented in Table 10. The results for the similar supporting electrolytes 1 M ammonium fluoride[168] and 1 M sodium fluoride[166] are in reasonable agreement.

For polarography in 0.1 M hydrofluoric acid – 0.1 M ammonium fluoride, Headridge et al.[167] used a Teflon® dropping mercury electrode identical with the one described by Raaen.[172] Glass capillaries are not suitable for use as dropping mercury electrodes at pH < 4, for they are then attacked by hydrofluoric acid. If lead is to be determined in supporting electrolytes containing fluoride, Pyrex® rather than lead-glass capillaries should be used.

It can be seen from Table 10 that species strongly complexed by fluoride are indeed reduced at much more negative potentials in fluoride media than in noncomplexing media. The strong fluoride complexes are also often reduced very irreversibly. Well-formed waves with half-wave potentials less negative than −1.0 V vs. S.C.E. are, however, obtained for bismuth(III), cadmium(II), lead(II), antimony(III), and thallium(I) in these fluoride media, and the polarographic determination of, for example, bismuth in titanium-, zirconium-, niobium-, tantalum-, or tungsten-base material in acidic or neutral fluoride solutions should be straightforward. Hamza and Headridge[168] did, in fact, determine lead in a nickel-titanium alloy using 1 M ammonium fluoride at pH 7 as a supporting electrolyte. For the determination of trace amounts of such elements a differential cathode-ray or pulse polarograph should be employed.

Verbeek and co-workers[173] have shown that reduction waves due to ferric iron are not present up to a concentration of 0.05 M in neutral 0.75 M sodium fluoride provided that the pH of the iron solution is between 2 and 3 before addition of the fluoride. Presumably different iron(III)-fluoride complexes are formed when this procedure is adopted and when an iron(III) salt is dissolved in the base electrolyte directly, because when using the latter procedure with 1 M ammonium fluoride, Hamza and Headridge[168] obtained 2 reduction waves for iron(III). Using the former procedure, Verbeek et al.[173] were able to determine uranium(VI) polarographically in the presence of up to 400-fold excess of iron(III).

Headridge and Hubbard[174] also used polarography in 0.5 M hydrofluoric acid – 0.5 M sulfuric acid for the determination of molybdenum (about 5%) in niobium-base alloys that also contained 15% tungsten. In this supporting electrolyte, molybdenum(VI) produces two waves with half-wave potentials of −0.06 V ($E_{1/4} - E_{3/4} =$ 100 mV) and −0.52 V vs. S.C.E. ($E_{1/4} - E_{3/4} = 140$ mV). The first wave results from the reduction of molybdenum(VI) to molybdenum(V) and the second from the reduction of molybdenum(V) to molybdenum(III). For the analysis of the niobium-base alloys a polyethylene cell with a mercury-pool anode was used, and diffusion current measurements were made on the first wave at a potential 0.15 V more negative than the half-wave potential. The results obtained by this polarographic method and a thiocyanate spectrophotometric method were in good agreement.

B. Voltammetry

Using a rotating platinum electrode, Hamza and Headridge[175] have also investigated the voltammetric behaviors of 19 ions in 1 M ammonium fluoride. The voltammetric data are shown in Table 11.

The oxidation wave for manganese(II) to manganese(IV) is particularly interesting and has been used successfully to determine manganese in steels and cast iron of low cobalt content. Any interference from vanadium(IV) was obviated by oxidizing it to vanadium(V) with a slight excess of dichromate, which has no effect upon manganese(II).

IX. MISCELLANEOUS

A. Fluoride as a Masking Agent

Because fluoride forms stable complexes with the ions of such elements as beryllium, aluminum, silicon, germanium, tin, titanium, zirconium, hafnium, niobium, and tantalum, the reactions of these ions with many other analytical reagents can be prevented by the addition of fluoride ions. Species that are not strongly complexed by fluoride are able to react with the other analytical reagents in a more selective way. Fluoride is frequently used as a masking agent, but only a few examples will be given to illustrate this point.

Precipitation of tin(IV) as sulfide is prevented in the presence of fluoride ion, which forms a very stable fluoro complex with tin(IV). This serves as a means of separating lead and copper as insoluble sulfides from tin(IV)

TABLE 10

Polarographic Data for Inorganic Species in Fluoride Solutions

	Supporting Electrolyte					
Species	0.1 *M* HF - 0.1 *M* NH_4F (Ref. 167)		1M NH_4F (pH 7) (Ref. 168)		1M NaF (Ref. 166)	Others
	$E_{1/2}$ (V vs. S.C.E.)	$E_{1/4} - E_{3/4}$ (mV)	$E_{1/2}$ (V vs. S.C.E.)	$E_{1/4} - E_{3/4}$ (mV)	$E_{1/2}$ (V vs. S.C.E.)	$E_{1/2}$ (V vs. S.C.E.)
Ag(I)	Reduced chemically by Hg		> 0		> 0	
As(III)	-0.84; -0.88	waves cover 0.6 V	about -1.40^m	very irreversible		
As(V)	> 0; -0.8	second wave small and very irreversible	N.R.^{a}			
Bi(III)	-0.13	19	-0.27	35	-0.07 (pH 0.7 to 2.1)	
Cd(II)	-0.59	30	-0.61	27	-0.63 (pH 3.1 to 6.7)	
Co(II)	I.S.H.W.*		-1.32	110	-1.38 (pH 2.9 to 6.0)	
Cu(II)	+0.08; -0.07	waves cover 0.3 V	+0.02; -0.16	waves cover 0.35 V	0.00 (pH 5.1)	
Fe(II)	N.R.		about -0.06**; -1.44	incomplete sepn. from Hg wave; 63		+0.11** in 0.1 *M* KHF_2 (Ref. 169)
Fe(III)	-0.52 (III → II)	140	-0.77 (III → II) -1.47 (II → 0)	160 100		-0.74 (III → II) -1.44 (II → 0) in 1 *M* KF pH 7 (Ref. 170)
Ga(III)	N.R.		-1.50	about 120		
Mn(II)	N.R.		-1.55	about 40	-1.55 (pH 2.4 to 6.8)	
Mo(VI)	-0.53 (VI → V) I.S.H.W. (V → III)	130	N.R.			
Ni(II)	-1.00	61	-1.05	71	-1.12 (pH 4.3 to 6.4)	
Pb(II)	-0.40	28	-0.45	30	-0.41 (pH 1.1 to 2.8)	
Re(VII)	I.S.H.W.		about -1.44^m			
Sb(III)	-0.62	100	-0.74	95	small prewave -0.68 (pH 3.0 to 4.4)	

TABLE 10 (continued)

Sb(V)	Reduced chemically by Hg to Sb(III); –0.65	90	I.S.A.W.§			
Se(IV)			–1.28	100		
Sn(II)	–0.23**; –0.60	–33; 27	–0.41**; –0.70	–34; 29	–0.20**; –0.73 (pH 4.0 to 6.3)	
Te(IV)			–0.52	140	–0.48 (pH 4.4)	
Ti(IV)	I.S.H.W.		–1.37	95		
Tl(I)	–0.46	54	–0.46	54	–0.50 (pH 3.7 to 6.7)	
U(VI)	–0.51	270	–0.80; –1.11	v. irr. waves		–0.94 (VI → V) in 1M NaF (Ref. 171)
V(IV)	I.S.H.W.		–1.45; about –1.68 about -0.12^{m}; –0.79; –1.40 First 2 waves small	irr. waves v. irr.; 140; 100		
Zn(II)	–1.11	35	–1.15	54	–1.14 (pH 4.2 to 6.4)	

m means a maximum

[a] N.R. means no reduction

* I.S.H.W. means incomplete separation from H^+ wave

** oxidation wave

§ I.S.A.W. means incomplete separation from NH_4^+ wave

In 0.1 *M* HF - 0.1 *M* NH_4F, in addition to the information given above, waves incompletely separated from the H^+ wave were found for chromium(III), indium, and tungsten(VI). No reduction before the hydrogen ion wave occurred with tin(IV) and niobium(V). In 1 *M* NH_4^+ (pH 7), waves incompletely separated from the NH_4^+ wave were found for chromium(III), niobium(V), tin(IV), and tungsten(VI). No reduction before the NH_4F wave occurred with indium, selenium(VI), tantalum, and zirconium.
The polarographic ranges in 0.1 *M* hydrofluoric acid – 0.1 *M* ammonium fluoride and in 1 *M* ammonium fluoride (pH 7) were +0.1 to –1.2 V vs. S.C.E. and +0.1 to –1.8 V vs. S.C.E., respectively.

TABLE 11

Voltammetric Data for Inorganic Species in 1 M Ammonium Fluoride

Species	$E_{1/2}$, V vs. S.C.E.	$E_{3/4} - E_{1/4}$ mV
Ferrocyanide	+0.18	56
Silver(I)	+0.21	−32*
Antimony(V)	+0.34	−122*
Iron(II)	+0.46	185
Iodide	+0.47[m]	
Manganese(II)	+0.52	28
Vanadium(IV)	+0.56	158
Thallium(I)	+0.87	95

*Reduction wave

[m]Maximum present

The oxidation wave for cobalt(II) started at +0.85 V and was not completed before the final rise in current.

There were no oxidation or reduction waves for antimony(III), arsenic(III) or (V), bromide, chromium(III) or (VI), copper(II), iron(III), nickel(II), and vanadium(V) at potentials more positive than 0 V vs. S.C.E.

With the rotating platinum electrode in 1 M ammonium fluoride the final rise in current occurred at +1.1 V vs. S.C.E.

(From Hamza, A. G. and Headridge, J. B., *Talanta*, 13, 1397 (1966). With permission.)

In the complexometric titration of zinc with EDTA, aluminum, calcium, and magnesium are masked by the addition of ammonium fluoride.[176] Aluminum forms a stable fluoro complex, while calcium and magnesium are precipitated as insoluble fluorides.

In the spectrophotometric determination of cobalt as tetraphenylarsonium thiocyanatocobaltate after extraction from aqueous solution into chloroform, interference from iron(III) resulting from formation of the red ferric thiocyanate complex is prevented by adding ammonium fluoride to the aqueous phase.[177]

B. Atomic Absorption Spectroscopy

Hydrofluoric acid is widely used to hold elements such as niobium, tantalum, and tungsten in solution prior to determination by atomic absorption spectroscopy. This use has been mentioned in Section III A1. However, the presence in solution of fluoride ion, and particularly ammonium fluoride, also increases the sensitivities of the atomic absorption method for zirconium, hafnium, titanium, tantalum, and uranium using the nitrous oxide-acetylene flame.[178] These are the elements that form stable oxide molecules in flames, but that exist in aqueous fluoride solution as stable fluoro complexes and that form volatile fluorides. In the determination of zirconium the presence of 0.1 M ammonium fluoride leads to an eightfold improvement in the sensitivity and causes interference effects to be either eliminated or appreciably suppressed.

C. The Separation of Silicon by Volatilization as Tetrafluoride

Silicon can be separated from most other elements by microdiffusion as silicon tetrafluoride from a mixture of hydrofluoric and sulfuric acids. The diffusion is allowed to proceed for 6 hr at room temperature. The silicon tetrafluoride is absorbed in ethylene glycol and the silicon is determined spectrophotometrically by the molybdenum-blue method.[179,180] The speed of this method can be increased by transferring the volatile silicon tetrafluoride from the sample solution at 70° C to an absorbing solution of ammonium molybdate by a current of dry air.[181]

Stobart[182] has described a related method for the determination of traces of silicon in niobium, tantalum, molybdenum, and tungsten. The finely divided sample was dissolved in a mixture of hydrofluoric and nitric acids in a Teflon® distillation apparatus. Perchloric acid was then added and the silicon tetrafluoride was distilled into a boric acid solution, in which the silicon was subsequently determined spectrophotometrically by the molybdenum-blue method. The method can also be applied to the determination of silicon in steels and copper-base samples.[183]

X. CONCLUSIONS

It is noted from the previous pages that hydrofluoric acid and fluorides have been employed in analytical chemistry for well over a century. The chief use of the fluoride ion is as a complexing agent; when the time was ripe for the development of analytical techniques such as ion-exchange and solvent-extraction separations and inorganic polarography, it was only natural that investigators should try to use the unique complexing properties of that ion to develop new analytical methods involving these techniques. Of course, such work was inhibited to an appreciable extent until about 1955, when suitable plastic materials, unattacked by hydrofluoric acid, became readily available. By the use of fluoride, many satisfactory separation schemes involving ion-exchange resins have now been developed for the most complex materials containing elements such as zirconium, niobium, tantalum, molybdenum, and tungsten. By solvent extraction followed by a spectrophotometric finish, very selective methods have been developed for the determination of boron and tantalum.

The high stabilities of fluoro complexes provide the basis of many analytical methods and a reasonable amount of data on the stability constants of fluoro complexes is available. However, further research in this field would still be worthwhile to obtain a more comprehensive list of stability constants.

Work on the development of new redox titrations in fluoride media and on polarography and voltammetry in fluoride solutions is of interest to the analytical chemist as illustrating how theoretical predictions can be put to use in developing new methods of analysis. Undoubtedly, however, the most useful contributions in recent years have been in the dissolution of materials in fluoride media followed by atomic absorption spectroscopic analyses of the resulting solutions. The analytical chemist should be a realist and welcome anything that simplifies and speeds up an analysis. Dissolution procedures involving hydrofluoric acid and Teflon®-lined bombs followed by atomic absorption spectroscopy have greatly simplified silicate rock analysis and much activity in this field is to be expected in the future.

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