PROBLEMS IN SAMPLE TREATMENT IN TRACE ANALYSIS

Claude W. Sill

Health Services Laboratory
U.S. Atomic Energy Commission
Idaho Falls, Idaho 83401 U.S.A.

One of the most important — and most neglected — parts of any analytical procedure is the initial decomposition of the sample. Not only must the sample matrix be dissolved but the element sought must be converted reliably to the proper ionic form before chemical reactions characteristic of that element can be obtained. Complete dissolution is especially difficult with the quadrivalent and pentavalent elements which form very refractory oxides, carbides, *etc.*, particularly after having been heated. For example, the plutonium in the ash remaining from dry ashing large samples of soft tissue requires much more powerful treatment for its complete conversion to the ionic state than merely boiling with nitric acid. Fusion with molten potassium fluoride is one of the simplest and most effective methods for dissolving metallic as well as siliceous refractories because of the stability of the fluoride complexes and the high reaction rates available at its melting point of 846 °C. Inclusion of a small quantity of potassium nitrate even permits rapid and complete dissolution of refractory carbides such as Carborundum. The cake can then be transposed either with sulfuric acid to a pyrosulfate fusion with simultaneous volatilization of both hydrogen fluoride and silicon tetrafluoride, or with nitric and boric acids to give a solution free of sulfate. The procedure is neither difficult nor time-consuming as is generally supposed.

Extremely serious problems can be introduced by evaporating solutions of quadrivalent elements to dryness or by neutralizing them to too high a pH. Powerful sequestering agents can be produced from orthophosphates in the sample that will completely change the course of the analysis unless recognized and provided for. Standardizations are frequently carried out in a careless and inaccurate manner. Contamination is one of the greatest problems in trace analysis and needs to be avoided by good management and understanding of the causes. Preservation of both samples and standards can be vastly improved by application of a little more fundamental chemistry. Many other important "details" will be discussed which are frequently ignored or overlooked because of preoccupation with the more glamorous facets of the procedure, such as elegant separations or measurement techniques employed.

463

I. Introduction

An analytical procedure can be – and generally is – a very complicated combination of many individual unit operations. The number of different chemical reactions – both intended and inadvertent – that can occur from the time the sample is collected until the final measurement is made is enormous. While the analyst has his attention and interest focused on the unique separation or the exotic reagent or instrumental technique to be employed, millions of little chemical gremlins are busily at work, undermining the intended structure of the determination and, indeed, casting the deciding vote on its outcome. It seems fairly safe to say that there is probably more art involved in understanding and controlling the many secondary influences working against the desired course of events than in the primary chemical reactions desired. Chemical problems seem at times to increase almost exponentially with the charge on the metallic cation. While most monovalent and divalent elements are relatively free of problems due to solubility, hydrolysis, ion exchange, sorption, *etc.*, the tervalent and particularly quadrivalent and pentavalent elements require unrelenting care and attention to detail to achieve high and reproducible recoveries and accurate results. This paper will discuss a few of the basic chemical problems affecting the higher valent elements particularly, with some suggestions for their elimination or control.

II. Sample Preservation

A. SAMPLES

It is self-evident that the best analysis cannot possibly be any better than the sample on which the determination is made. Certainly, the sample must be representative of the population from which it was taken, and to which it must relate in some known fashion. However, even the small analytical sample received in the laboratory must be treated properly or erroneous results will be obtained. One of the biggest questions involves acidification and/or filtration of aqueous samples before removing an aliquot for analysis. Some organizations officially require aqueous sam-

ples to be filtered as received, and the analysis performed on the filtrate. This philosophy will certainly obscure the real contribution of radioactive and chemically toxic elements on environmental pollution.

The great majority of natural waters has a pH between 6 and 8, including seawater, lakes and rivers, with some rivers and ponds being much more alkaline yet. It is well known that most metallic elements except the alkalis and the alkaline earths form extremely insoluble hydroxides, and in fact most tervalent and quadrivalent elements can be removed quantitatively from solution at pH's above 6, particularly if a little carrier is present. Consequently, filtration of natural water samples as received before analysis will certainly make pollution of the aquatic environment appear to be much less severe than it really is. In some tests on river water containing liquid effluents from mills processing uranium ore, nearly 95 percent of the thorium-230 but only about 25 percent of the radium-226 were found in the residue filtered from an unacidified sample. If the distribution of activity between the filterable and nonfilterable components is desired, filtration of samples as received can be done, but certainly both fractions should be analyzed. Unfortunately, in many cases known to the present author, the residues are discarded because of some very superficial and tenuous argument that the only interest was the content "in" the solution, meaning soluble or nonfilterable, rather than "in" the solution, meaning within the bounds of the container in whatever form. From the standpoint of evaluating environmental pollution, and excepting special interests, water samples should be acidified to redissolve as much hydrolyzed material as possible, including that deposited on the walls of the container, and then the sample shaken vigorously immediately before removing an aliquot for analysis to include a representative portion of the undissolved floc or sediment in the analysis.

Unless the residue is analyzed separately, water samples should not be filtered with or without acidification to avoid severe losses of components that should be included in the analysis. Many elements are known to sorb strongly on silica, cellulose fiber, *etc.*, at pH's above about 4 and some of which, like protactinium, do so even from strongly acid solutions. Barium occurs widely in the environment, and barium sulfate is very insoluble in acid and will carry down most of the large tervalent and quadrivalent ions quantitatively under certain conditions [1]. One of the most severe and surprising problems was encountered in the analysis of aqueous samples of radiological wastes from operating nuclear reactors [2]. Even from 10 percent nitric or hydrochloric acid solutions, and with vigorous shaking immediately before pouring the solution from the bottle, most of the activity remained inside the empty bottle from which it was removed only

very slowly and incompletely by further vigorous treatment with concentrated acids, including hydrofluoric, prolonged vigorous shaking, ultrasonic vibration, *etc.* Zirconium is well known for its tendency to hydrolyze even from fairly strong acid and deposit on the walls of the container. However, containers in which zirconium has deposited hydrolytically can be cleaned simply and rapidly by a brief wash with hydrofluoric acid. The most surprising aspect was the fact that a large part of the activity was manganese-54, cobalt-58 and -60, iron-59, *etc.,* which are not particularly hydrolytic and would certainly not be expected to be hydrolyzed or long remain insoluble in such strong acids. Autoradiography showed that the activity occurred in very finely-divided discrete particles with no evidence of the large aggregated patterns to be expected from flocculant, hydrolytic precipitates. Apparently, these are particles of the original fuel elements or cladding materials of zirconium, stainless steel, ceramics, *etc.* that never were dissolved but are in their original form. This view is substantiated by the fact that addition of paper pulp is of material assistance in keeping the particles off the container surface, so that the particles can be removed with the suspension of paper fibers, particularly from polyethylene bottles. A more difficult but completely unequivocal solution to the problem is to insert a small polyethylene bag in the sample container as a removable liner, and wet-ash the entire bag.

B. STANDARD SOLUTIONS

Undoubtedly, a large number of analytical problems and inaccurate results are caused by improperly prepared standard solutions on which the entire determination depends. Most solutions can be stabilized adequately by simply adding sufficient acid to prevent incipient hydrolysis. An acidity larger than about $0.01N$ will suffice for most monovalent and divalent ions. Most of the work reported in the literature shows that such solutions remain fairly stable over long periods of time until the pH is allowed to go higher than 2. In some cases, such as with silver, mercury and polonium, acid alone does not produce stable solutions, probably caused by reduction of the relatively noble elements to the metallic state or to a volatile lower state, either spontaneously or due to traces of reducing agents present. Addition of a suitable oxidant such as dichromate for silver and mercury [3], or quadrivalent cerium or bromate for polonium [4] produces solutions that are stable over long periods of time.

With the higher valent elements, progressively higher concentrations of acid and/or addition of complexing agents are required to produce adequately stable solutions. In addition, both the order of addition of

water and acid and the exact manner in which they are combined can make the difference between a homogeneous stable solution and an in-homogeneous erratic one. For example, if 250 mg of Nb_2O_5 is dissolved in a pyrosulfate fusion, the cake then redissolved in concentrated sulfuric acid and diluted to 250 ml with water, a slightly turbid solution will usually result depending on the quantity of acid used, that becomes increasingly turbid on standing. In contrast, if the sulfuric acid solution is diluted with dilute sulfuric acid instead of water, a completely clear solution is obtained that does not develop turbidity with time. One such solution prepared in this laboratory is still perfectly clear after standing for 11 years. Obviously, pure water has a hydroxyl ion concentration a million times higher than even $0.1 N$ sulfuric acid, and is high enough to cause significant hydrolysis of the most hydrolytic elements.

The effect of manner of addition of reagents is exemplified by tin. If several milligrams of quadrivalent tin is fumed strongly with sulfuric acid, and the resulting solution is cooled to room temperature and diluted in an unparticular manner with water, the solution will exhibit a beautiful golden-yellow fluorescence when examined under short-wave ultraviolet light in a darkened room. The fluorescence becomes more intense with passage of time. If the fluorescent solution is reevaporated to fumes of sulfuric acid, and the cold solution is treated with individual drops of water with vigorous swirling and cooling between drops, so that the solution never warms up very much for very long, a completely non-fluorescent solution is obtained which develops the identical golden-yellow fluorescence on prolonged standing if cold, or more rapidly at higher temperatures. The transition apparently corresponds to the formation of a fluorescent hydrolytic polymer from the simpler sulfonated stannic ion.

Many elements require both high acidity and complexing agents to produce stable aqueous solutions. In particular, the sulfate ion is an excellent complexing agent in acid solutions that is yet mild enough to be relatively easily overridden by many extractants, *etc.* when necessary, and has not received the attention and use that it deserves. For example, protactinium has a reputation as being one of the most hydrolytic and capricious elements in the periodic table. The reputation is well-deserved because most investigators studiously avoid use of sulfate systems, preferring the extractions that are available from chloride or nitrate systems, and suffer the consequent hydrolytic depositions that inevitably occur with protactinium in such systems. In contrast, protactinium in a sodium sulfate-sulfuric acid solution will retain the same chemical characteristics for at least several years, showing not the slightest suggestion of the hydrolytic or capricious behavior so noticeable in other systems, due to the combination of high acidity and sulfate complexing [5,6]. Yet, the

sulfate complex can be easily converted to a chloride by addition of an equal volume of concentrated hydrochloric acid, and the protactinium can then be extracted quantitatively into disobutylcarbinol.

III. Sample Decomposition

One of the most important — and most neglected — parts of any analytical procedure is the initial decomposition of the sample. Not only must the sample matrix be dissolved, but the element sought must be converted reliably to the proper ionic form before chemical reactions characteristic of that element can be obtained. Complete dissolution is particularly difficult with the quadrivalent and pentavalent elements which form extremely refractory oxides, carbides, *etc.*, particularly after having been heated strongly. Many investigators attempt to leach the elements selectively from the sample matrix with various acids with varying degrees of success. The divalent and tervalent elements not bound up in acid-insoluble particles can frequently be leached fairly successfully; the higher valent elements more generally are not leachable, at least not quantitatively. If silica or some of the refractory silicates are involved, recovery of even the lower valent elements will be markedly incomplete unless hydrofluoric acid is employed. Consequently, methods based on such procedures are generally erratic and incapable of the highest accuracy and precision.

A. ALKALINE FUSIONS

Although fusion with sodium peroxide is undoubtedly one of the most powerful methods available for dissolution of a wide variety of sample types, it has many disadvantages. It is a relatively dirty flux, and its attack on the fusion container is so severe, whether of silica, iron, nickel, zirconium, *etc.*, that large additional quantities of impurities are added to the sample. When applied to large samples of siliceous materials, the silica is solubilized but requires a great deal of effort subsequently to eliminate satisfactorily. Sodium carbonate fusions are relatively much cleaner and can be carried out in platinum. However, the same objection about disposition of the soluble silicate is present, and the fusion itself is relatively mild, leaving some considerable uncertainty as to the completeness of dissolution of refractory compounds.

B. PYROSULFATE FUSION

Fusion with an alkali pyrosulfate is undoubtedly one of the most power-ful, clean and convenient methods available for the dissolution of non-siliceous refractory compounds. The flux can be prepared simply by heat-ing sodium or potassium sulfate with an equal molar quantity of concen-trated sulfuric acid. This is particularly convenient when concentrated sulfuric acid remains from wet oxidation of organic compounds or elimination of other volatile acids. The flux is virtually a molten acid that can be used at temperatures up to nearly 800 °C. The melting points of the pure potassium and sodium salts are about 300 °C and 400 °C, respective-ly. However, on heating, the pyrosulfate is decomposed with loss of sulfur trioxide, and the melting point of the mixture of sulfate and pyrosulfate in-creases progressively. The high acid concentration, the high temperature available for reaction, the high concentration of sulfate ion as an inorganic complexing agent for metals, and the relatively high solubility of metallic sulfates at the high temperature used are all partly responsible for its effi-ciency in dissolving metallic oxides.

The flux is also a relatively powerful oxidizing agent. The last traces of very resistant organic matter are oxidized more rapidly and completely in a pyrosulfate fusion than by treatment with perchloric acid. Quadrivalent cerium is thermally decomposed in boiling sulfuric acid containing sodium sulfate to the tervalent state. However, after the excess sulfuric acid has been driven off and a pyrosulfate fusion obtained, the cerium is reoxidized to the quadrivalent state nearly halfway to completion, the oxidation un-doubtedly being materially assisted by the strong complexing action of the high concentration of sulfate on the quadrivalent ion. Manganese is also oxidized to permanganate to the extent of only a few tenths percent, but even this small quantity is highly effective in producing oxidation of traces of other elements. For example, hexavalent plutonium is normally reduced quantitatively to the quadrivalent state in a pyrosulfate fusion due to thermal decomposition in a high sulfate system. In the presence of a few milligrams of either cerium or manganese, nearly half of the quadrivalent plutonium is reoxidized to the hexavalent state, apparently due to the oxidizing action of the oxidized forms of the two elements produced in the fusion. These examples show the complete reversal of chemical reactions that can be produced inadvertently by the presence of certain elements in the sample.

Although fusion with an alkali pyrosulfate has been widely used for many years, there are only scattered references to the consequences resulting from the choice of alkali metal used or to the effects of sulfate ion, both during the fusion and afterwards. The sodium salt is generally

recommended because "This salt melts more quickly and forms more soluble double salts with aluminum and some other metals" [7]. However, potassium is frequently present in the samples being analyzed, or its addition in other parts of the procedure might be necessary as in the potassium fluoride fusion in which the potassium salt has much greater solvent capacity and is generally much more effective than the other alkali fluorides. In some cases, the greater insolubility of the potassium salts can be exploited to the analysts' advantage. Consequently, some of the insoluble compounds need to be identified specifically, and some effects of sulfate ion described.

Most heavy metal sulfates except those of the alkali metals are extremely insoluble in concentrated sulfuric acid but become much more soluble in the presence of alkali metal sulfates, undoubtedly due to the formation of anionic sulfate complexes. For example, as little as 1 mg of tervalent iron, aluminum, or chromium is precipitated virtually quantitatively by fuming with 5 ml of concentrated sulfuric acid but remains completely in solution when 1 gram of sodium sulfate is present. The anhydrous sulfates of tervalent iron, aluminum, chromium, and quadrivalent vanadium are extremely difficult to redissolve in water or dilute acid even on prolonged boiling, probably due to the slowness of rehydration. The rapid dissolution of titanium dioxide in hot concentrated sulfuric acid containing ammonium sulfate is well known. Perhaps the most graphic demonstration of the effect of sulfate is provided by zirconium. If powdered zirconium metal is heated with concentrated sulfuric acid, evolution of hydrogen bubbles begins almost immediately, and the metal begins to dissolve. However, a white precipitate of zirconium sulfate soon forms, coating the unreacted metal, the evolution of hydrogen ceases, and the dissolution stops. If a few grams of sodium sulfate is added, the white precipitate clears up rapidly, evolution of hydrogen gas resumes, and the dissolution of the metallic zirconium proceeds to completion. Apparently, the sodium sulfate converts the insoluble zirconium sulfate to a sulfatozirconic acid, which is soluble in concentrated sulfuric acid, and dissolution of the uncovered metal proceeds. Heating with hot concentrated sulfuric acid containing sodium sulfate is a much simpler and convenient method of dissolving metallic zirconium than the more common one involving hydrofluoric acid.

A similar but much more subtle effect of sulfate and alkali metal ions is present during the fusion. If 50 mg of iron, aluminum or chromium is fused with 3 grams of anhydrous sodium sulfate and 2 ml of concentrated sulfuric acid, all three metal sulfates dissolve subsequently in water almost as fast as the cake itself disintegrates, giving completely clear solutions. In contrast, if the fusion is made with the potassium salt, the metal-

lic salts do not dissolve subsequently in dilute sulfuric or hydrochloric acids on prolonged boiling, even though the fusion itself was completely clear. Prolonged boiling with strong hydrochloric acid dissolves most, but frequently not all, of the insoluble anhydrous sulfates. Chromium is the most insoluble of the three elements, giving a very pale greenish white precipitate with very little discernible green color of the chromic ion in solution. However, if the fusion with the potassium salt is heated as hot as possible over the maximum heat from a blast burner for 15 or 20 minutes after the melt has cleared, the anhydrous sulfates will again dissolve in water almost as fast as the cake disintegrates. Apparently the prolonged high-temperature treatment decomposes much of the pyrosulfate to sulfate ion with loss of sulfur trioxide which increases formation of sulfate complexes that are more rapidly hydrated and solubilized during sub-sequent treatment with water. The same effect can be produced much more rapidly and conveniently by adding 1 or 2 grams of anhydrous sodi-um sulfate after most of the excess sulfuric acid has been driven off and the fusion has cleared. When presence of potassium is desirable or una-voidable, its insolubilizing effect can be largely overcome by adding two parts of sodium sulfate for each part of potassium sulfate present. For ex-ample, even 50 mg of chromium will dissolve in water giving a deep green solution almost as fast as the cake disintegrates if the fusion is made with a mixture of 6 grams sodium sulfate to 3 grams of potassium sulfate and the appropriate quantity of sulfuric acid. The exact cause of the dif-ferences caused by sodium or potassium is not clear. However, it is clear that a high concentration of sulfate ion is necessary to keep the metals present as water-soluble sulfato complexes and prevent formation of the very insoluble anhydrous sulfates.

The ability of sulfate ions to form anionic complexes with many metals that are soluble in hot concentrated sulfuric acid is of real practical im-portance in the complete dissolution of large samples of soil [8]. In sam-ples containing large quantities of aluminum and iron, decomposition of the potassium fluoride cake with concentrated sulfuric acid causes precipitation of iron or aluminum sulfates in a form that retains sulfuric acid tenaciously. The resultant slurry is virtually impossible to transpose to a pyrosulfate fusion because it is not possible to heat the thick mud hot enough to volatilize sulfuric acid without causing prohibitive spattering. However, if sodium sulfate is added, the thick intractable mud changes rapidly to a thin fluid consistency, which permits the excess sulfuric acid to be volatilized rapidly and smoothly without significant spattering until the pyrosulfate fusion is obtained [8]. The quantity of sodium sulfate required clearly relates to the quantity of excess sulfuric acid present, and

the effect is reversible. For example, a 10-gram sample of soil fused with 30 grams of potassium fluoride can be transposed smoothly with 30 ml of concentrated sulfuric acid and 10 grams of anhydrous sodium sulfate in the presence of an average quantity of iron and aluminum. If an additional 5 ml of sulfuric acid is added, the thin fluid slurry will be reconverted to the thick intractable mud essentially identical to that produced without addition of sodium sulfate. An additional 10 grams of sodium sulfate will neutralize the additional sulfuric acid and restore the thin fluid characteristics.

Other differences resulting from the use of sodium or potassium salts are encountered after the pyrosulfate fusion cake is dissolved in water. The incompatibility of perchlorate ions in a system containing potassium is well known. Similarly, the potassium salts of the anionic sulfate complexes formed with most quadrivalent elements, particularly thorium, titanium, tin, *etc.*, are much less soluble in dilute sulfuric acid than the corresponding sodium salts or the free acids, and many more solubility problems result when potassium is present. For example, not more than 5 or 10 mg of quadrivalent titanium will remain dissolved in 30 ml of solution containing 5 grams of potassium acid sulfate when the solution is cooled [1]. Similar solutions containing only sodium salts remain clear with several times as much titanium.

Apparently, double potassium-barium salts of much decreased solubility are formed in the presence of barium because the ability of barium sulfate to carry all the large tervalent and quadrivalent ions from lead to at least californium is markedly enhanced by the presence of potassium. In fact, even aluminum and tervalent iron in high concentrations are partially precipitated with lead or barium sulfates in the presence of potassium. Also, the solubility of potassium sulfate itself in solutions of low acidity is much less than that of sodium sulfate. Consequently, use of potassium salts should be avoided unless their use is specifically indicated. In this case, special precautions must be observed to keep the quantity of the quadrivalent ions forming insoluble salts with potassium sulfate below the permissible limit.

C. POTASSIUM FLUORIDE FUSION

Fusion with anhydrous potassium fluoride is probably the simplest, most effective and reliable method available for the complete dissolution of a wide variety of siliceous materials. The fusion can be carried out in platinum vessels with little or no attack on the container, keeping contamination with foreign materials at a minimum. The high melting point of

846 °C and the high concentration of fluoride ion, which forms some of the most stable inorganic complexes with many heavy metals, both contribute to high rates of chemical attack. Consequently, fusion with potassium fluoride is not only effective in dissolving silica and refractory silicates but most metallic oxides as well. In this respect, it is distinctly superior to pyrosulfate fusion, which is totally ineffective with siliceous materials. Other alkali metal fluorides are not as effective as the potassium salt because of either higher melting points and/or lower solvent capacity for metallic fluorides.

On heating potassium fluoride, the melt becomes progressively more alkaline due to slow but continuous loss of hydrogen fluoride produced by hydrolysis from water vapor from the air or from the combustion gases from the blast burner. Oxidation of organic materials in the slightly alkaline flux at the high temperature of fusion is very rapid, smooth and complete, particularly in the presence of a small quantity of nitrate. For example, simply pretreating soils or other basic materials with nitric acid will fix enough nitrate to provide for the subsequent smooth oxidation of organic matter. Similarly, addition of a small quantity of potassium nitrate to the potassium fluoride before or during fusion causes rapid oxidation and dissolution of very refractory carbides such as silicon carbide (Carborundum). Because of the increasing use of carbide refractories in the atomic energy industry, this method of sample decomposition will be most useful in the determination of various radionuclides in process and environmental samples. The increasing alkalinity becomes a disadvantage if the fusion is prolonged because insoluble hydroxides soon begin to precipitate and the dissolution action effectively ceases. However, this effect can be reversed or delayed by adding solid acids such as pyrosulfates or even silica, both of which can be added in solid form to the molten flux.

The effect of silica in a fluoride fusion is very interesting. In a procedure for the determination of the actinides in water, a ferric hydroxide scavenge is used to collect the precipitated hydroxides of the other elements. Because the precipitate also contains the siliceous sediments present, potassium fluoride fusion is employed for total decomposition of all materials present. Invariably, the molten flux is highly colored, turbid, and with almost black crystals of hydrolyzed iron compounds sticking to the sides of the platinum dish. The solvent capacity of the flux decreases rapidly, and the sample never does dissolve completely. If 0.5 gram of silica gel is added to 6 grams of potassium fluoride, at least 100 mg of iron will dissolve to give a completely clear, light yellow melt, identical to that obtained from siliceous samples. Apparently, the silica consumes alkali in being converted at least partly to metasilicate rather than fluosilicate and

keeps the iron and probably other metals in the form of soluble fluoride complexes.

After complete dissolution of the siliceous sample in the molten potassium fluoride, the cake can be transposed with concentrated sulfuric acid to a completely clear pyrosulfate fusion, with simultaneous elimination of both silicon tetrafluoride and hydrogen fluoride. This permits the remainder of the determination to be carried out in conventional glassware, completely demasked from the powerful complexing fluoride anion, and with complete elimination of silica by volatilization. This latter step eliminates the objection to alkaline fluxes mentioned earlier. Not only is the silica eliminated smoothly and simply, but it is done by volatilization so that no loss of other components of the sample occurs, and no retreatment of residues of any kind is required. About the only objection to this procedure is that the sample ends up in a sulfate system causing some additional problems in the presence of alkaline earths and the rare earths, and requiring that the rest of the procedure be worked out to be compatible with a sulfate system. However, this can be done very simply in most cases [8].

Many analytical chemists feel that there is something inherently difficult, dangerous or time consuming about procedures requiring fusions. The potassium fluoride fusion and pyrosulfate transposition mentioned above is described in detail elsewhere [8] and can be easily handled by technicians after one or two demonstrations. Figure 1a shows 10 grams of soil in a 250-ml platinum dish at the beginning of the analysis. The sample shown is a -200 mesh standard plutonium soil, but samples as coarse as -10 mesh have been dissolved successfully. Figure 1b shows the sample after a pretreatment with nitric and hydrofluoric acids and evaporation to near dryness. Figure 1c shows the potassium fluoride fusion after addition of 30 grams of anhydrous potassium fluoride. Most troubles encountered in fusions are due to use of too little flux or too little heat to do the job. By using a Fisher blast burner with the large grid to supply the amount of heat shown, the sample is completely dissolved giving a clear melt in 6 minutes, about 4.5 minutes of which is required to heat the sample, flux and dish to the fusion temperature. The clear melt is shown in figure 1d, with the wrinkles in the bottom of the platinum dish being clearly visible through the melt. After cooling to room temperature to permit association of all iron as the colorless ferric fluoride complex, the potassium fluoride cake generally has a light violet color, apparently due to manganese in the sample.

The potassium fluoride cake is then transposed to a sulfate system by addition of 35 ml of concentrated sulfuric acid and evaporation to dryness

on a hot plate as shown in figure 1e, with simultaneous elimination of silicon tetrafluoride and hydrogen fluoride. When heated over the blast burner, the salts melt but precipitation of the anhydrous sulfates of iron and aluminum produces a thick mud that retains the sulfuric acid so tenaciously that it is almost impossible to evaporate off the sulfuric acid to a pyrosulfate fusion without prohibitive spattering. On addition of sodium sulfate and further heating, the thick mud rapidly and very impressively clears to a thin suspension that is easily boiled without spattering. When most of the excess sulfuric acid has been volatilized, the insoluble salts begin to dissolve around the sides as shown in figure 1f. Further heating results in the completely clear pyrosulfate fusion shown in figure 1g, demonstrating conclusively the complete elimination of silica which would otherwise produce a turbidity because of its insolubility in sulfuric acid. On cooling, the pyrosulfate cake has a light yellow color due mainly to iron and is easily removed by flexing the sides of the platinum dish. Generally, the pyrosulfate cake dissolves completely in dilute hydrochloric acid as shown in figure 1h. (The upside-down thermometer is not indicative of the state of knowledge in this laboratory, but was done deliberately to get some calibration markings below the liquid level to demonstrate the clarity of the solution.) In the presence of barium or relatively high concentrations of calcium, a turbid solution due to precipitation of the insoluble alkaline earth sulfates results. This precipitate can be filtered off and retreated if necessary.

If a sulfate system is undesirable, as in analysis of samples containing high concentrations of alkaline earths or rare earths, the potassium fluoride cake can be transposed with nitric acid. However, the transposition is much more time consuming and certainly less neat when applied to the larger samples. Hydrofluoric acid cannot be removed efficiently by evaporation with nitric or even perchloric acids. Repeated evaporation is necessary followed by addition of boric acid or aluminum salts to reduce the concentration of fluoride ion sufficiently that the insoluble metallic fluorides will dissolve in nitric acid. Even then, the final aqueous solution will invariably still be slightly turbid. In addition, the original sample must be pretreated with acid to neutralize any alkaline components present or the alkaline cake will not even disintegrate completely on prolonged boiling with nitric acid. The potassium fluoride fusion has been used successfully with transposition by both sulfuric acid and nitric-boric acids on soil, soft tissue ash, vegetation ash, air dusts, water, etc.
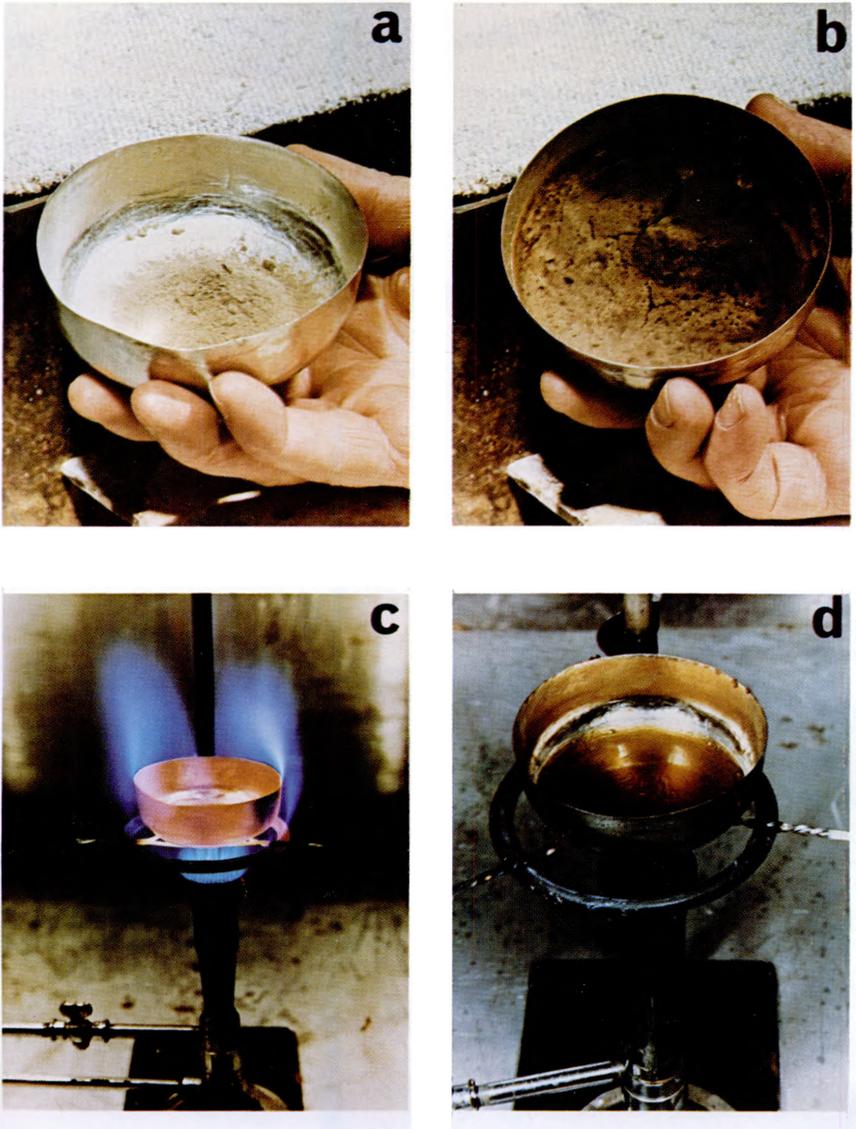
Figure 1. Potassium fluoride fusion and pyrosulfate transposition. a. soil sample in a Pt dish, b. evaporated to near dryness after pretreatment with HNO_3 and HF, c. potassium fluoride fusion, d. clear melt obtained with blast burner, e. transposed to a sulfate
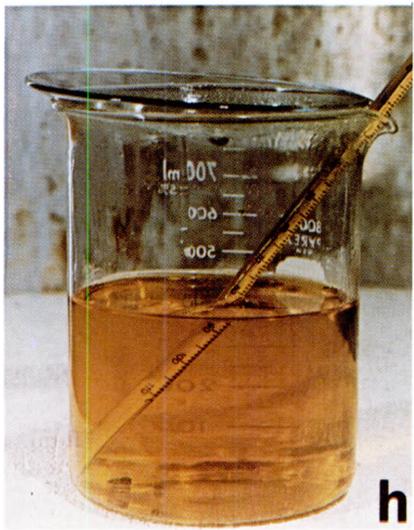
system by addition of concentrated H_2SO_4 and evaporated to dryness, f. excess H_2SO_4 volatilizes and salts begin to melt, g. further heating results in the completely clear pyrosulfate fusion, h. pyrosulfate cake dissolved in dilute HCl.

D. PHOSPHORIC ACID

Orthophosphoric acid is known to form relatively stable complexes with a wide variety of elements. Mixtures with perchloric acid are remarkable solvents for iron and steels, including stainless steel, high-speed tungsten tool steels and even metallic tungsten. On dehydration, orthophosphoric acid forms a variety of more highly condensed chain and ring phosphates whose complexes with metals are generally even more stable. These very powerful sequestrants are produced from ortho-phosphates present in the sample during such common analytical operations as ignition of bone, evaporation of urine and feces to dryness, pyrosulfate fusion of phosphatic materials, and even fuming with perchloric acid in the presence of enough salts to give very high temperatures. Consequently, every sample that might conceivably contain any kind of phosphate compounds must be given deliberate treatment to prevent profound changes in the course of the desired chemical reactions caused by the inadvertent production of these powerful complexing agents. In most cases, the condensed phosphates can be converted to the less powerful orthophosphates by boiling, the hydrolysis being strongly catalyzed by acid.

The powerful complexing action of condensed phosphates can be utilized analytically to dissolve even refractory metallic oxides in such highly phosphatic materials as bone ash, urine, feces, *etc*. This is very fortunate because those are the very types of samples on which pyrosulfate fusion is impossible or undesirable because of their high calcium content. For example, samples of bone ash are preferably dissolved in boiling 72 percent perchloric acid to oxidize the last traces of unburned carbon and then evaporated until most of the perchloric acid has been volatilized and the solution has a thick syrupy consistency. Evaporation should not be carried to the point at which the solution begins to solidify on the hot plate. Even beryllium, thorium and protactinium present in bone during ignition are easily solubilized under these conditions. The same effect can be observed visibly by evaporating several milligrams of the high-fired oxides with 85 percent phosphoric acid to a syrupy consistency and observing how easily and completely the turbid suspension clears. However, the cake must be dissolved in dilute acid and boiled for 15 minutes or so to hydrolyze the condensed phosphates before any chemical reactions are attempted. Protactinium has been removed to the extent of 98 percent in a single diisobutylcarbinol extraction from a solution of 100 grams of bone ash in $8M$ hydrochloric acid after such treatment.

The extraction of beryllium into acetylacetone from a solution of bone

ash illustrates the principles involved and the great potential for perturbations in the analytical scheme if not provided for. Under the proper conditions [9], beryllium can be extracted into acetylacetone to better than 99 percent in a single extraction. The presence of 0.5 ml of 85 percent phosphoric acid produces no significant effect on the extraction, but addition of 0.5 gram of sodium pyrophosphate, which contains less than one-third as much phosphorus, reduces the extractability to about 0.9 percent under the same conditions. Boiling the solution for 15 minutes in $1M$ hydrochloric or perchloric acids restores the original complete extractability. Sulfuric acid is not as efficient as the strong acids.

Similarly, if bone ash is dissolved in a slight excess of 72 percent perchloric acid and the heating is stopped as soon as the ash dissolves, ionic beryllium can be extracted quantitatively. The condensed phosphates produced during ignition of the bone are rapidly hydrolyzed by the boiling with strong acid used to dissolve the ash, and the subsequent extraction proceeds normally. On the other hand, if the solution is evaporated to a syrupy consistency to ensure complete dissolution of refractory beryllium oxide or phosphate, the condensed phosphates are reformed and subsequent extraction of beryllium is reduced to less than 30 percent, even though the cake was dissolved by boiling with water for 15 minutes without added acid. If the solution is boiled for 15 minutes after having added enough perchloric or hydrochloric acids to make the solution about $1M$, the subsequent extractability of beryllium goes back up to better than 99 percent.

Similar competing reactions of condensed phosphates in many other systems have been observed repeatedly. Samples containing both calcium and phosphate, such as vegetation or soft tissue ash, and dissolved by pyrosulfate fusion will frequently dissolve in dilute hydrochloric acid completely at first and then suddenly precipitate profusely after a few minutes boiling which destroys the sequestering agent. The efficiency of carrying large polyvalent ions on barium sulfate is decreased drastically if the solution from pyrosulfate fusions of phosphatic samples is not boiled extensively with strong acid before the precipitation is carried out. It may confidently be predicted that condensed phosphates produced *in situ* from orthophosphates present in the sample by strong heating will cause severe deviations from the expected chemistry in most analytical procedures.

One other perturbing characteristic of phosphoric acid needs to be emphasized. If carrier-free thorium-234 tracer is evaporated to complete dryness on a hot plate with a few drops of 85 percent phosphoric acid, a bone-white amorphous powder is obtained which is almost totally insoluble in even boiling concentrated hydrochloric acid and which will contain

over 95 percent of the total thorium tracer present. The material can be dissolved and the thorium released by fusing with pyrosulfate. The white, insoluble material is obviously a phosphoric acid polymer of some un-known composition because only phosphoric acid was present. It is to be expected that heating phosphatic samples such as urine, feces, *etc.* to dry-ness will certainly produce these acid-insoluble residues, and severe losses of almost any element being sought will occur. For example, more plutonium was found in the acid-insoluble residue from a fecal sample that had been dry-ashed in a muffle furnace than was found in the acid-soluble portion. These experiences again emphasize a cardinal rule for analytical chemists: Be extremely careful about discarding any insoluble residues!

IV. Evaporation to Dryness

One of the most common operations performed at least once in many analytical procedures is that of evaporating aqueous solutions to dryness. Whether for purposes of eliminating acids or other unwanted volatile materials, the evaporation is all too frequently carried out with almost total disregard for whether or not the residue will redissolve on sub-sequent treatment with water or even strong acids. Obviously, if the proper ionic condition is not restored, severe deviations from the ex-pected chemistry will result. If part of the residue remains firmly attached to the walls of the container, additional problems will be introduced in subsequent samples due to contamination if proper cleaning methods are not employed.

One of the outstanding characteristics of tervalent and particularly quadrivalent ions is their ability to form extremely insoluble hydroxides at very low hydroxide concentrations. When an acidic solution containing a metallic salt of a volatile acid is evaporated to dryness, the excess acid is volatilized, and the remaining neutral salt undergoes progressive hydrolysis in its own water of crystallization. The number of hydroxyl ions taken up depends greatly on the charge of the metallic ion. For each hydroxyl ion taken up by the metal ion, an additional molecule of the volatile acid is formed, which is immediately driven off. On prolonged heating, complete conversion to a refractory oxide occurs in many cases that is redissolved very incompletely or not at all on subsequent treatment even with strong acids.

To permit this effect to be observed visibly, four solutions each contain-ing a few milliliters of water and about 100 mg of thorium nitrate were evaporated just to dryness on a bare electric hot plate. The four residues

dissolved completely within about 1 minute by heating with a few milliliters of concentrated hydrochloric, nitric, perchloric, and sulfuric acids, respectively. However, after reevaporating the four different acid solutions just to dryness so that no residual nitrate remained and each residue was then treated with its respective acid, only the nitrate dissolved in concentrated nitric acid. The chloride, perchlorate and sulfate residues did not dissolve completely in hydrochloric, perchloric and sulfuric acids, respectively. In contrast, addition of about 1 gram of sodium hydrogen sulfate before evaporation to dryness with any of the acids gave a residue that dissolved completely and almost instantaneously in cold water. Another run with 1.5 grams of sodium hydrogen sulfate was evaporated, and the residue was heated over a blast burner until the bottom of the Pyrex flask sagged and evolution of sulfuric acid fumes had completely stopped. The residue dissolved almost but not quite completely either in cold water or on subsequent boiling, probably due to partial hydrolysis at the low acidity resulting from such severe heating. The turbidity does clear up on addition of a few drops of nitric acid.

These tests show that sodium hydrogen sulfate is remarkably effective in preventing hydrolytic deposition of quadrivalent thorium. The reasons are obvious. Sulfate forms a relatively stable complex with thorium, requiring significant hydroxide concentrations before even a monohydroxo thorium ion forms to any significant extent. Furthermore, unlike hydrochloric, nitric and even sulfuric acids, which are volatile, sodium hydrogen sulfate is virtually nonvolatile, acting as a buffer in preventing the acidity from going any lower on strong heating than that of the sodium hydrogen sulfate itself. In fact, strong heating converts sodium hydrogen sulfate to molten pyrosulfate, which is a powerful solubilizing flux for the very oxides that are being produced on heating the other systems containing volatile acids. When only small quantities of elements are present, the quantity of sodium hydrogen sulfate required is so small as to be compatible with almost any system except in the presence of those elements forming very insoluble sulfates.

Four solutions of thorium in hydrochloric, nitric, perchloric and sulfuric acids were again evaporated to dryness, but the residues were allowed to remain on a bare electric hot plate for several hours. None of the residues – not even the nitrate – dissolved significantly on boiling with concentrated nitric acid, which was the most effective solvent in the earlier tests. Addition of 1 drop of 48 percent hydrofluoric acid produced no change, but on dilution of the concentrated acid with water, all four solutions dissolved rapidly to give completely clear solutions. To determine whether this effect was due to the fluoride ion or the water, the test was repeated, heating the residues on the bare hot plate for 1 hour. On boiling

with 30 ml of concentrated nitric acid, very milky suspensions were obtained with the chloride and sulfate residues, less turbid with the nitrate and least turbid with the perchlorate. On addition of an equal volume of water to each flask, the sulfate residue cleared completely and almost immediately while the other residues showed little change. Addition of 1 drop of 48 percent hydrofluoric acid to the three turbid suspensions in dilute nitric acid caused immediate and complete dissolution of the turbidity. This demonstrates the powerful complexing action of fluoride in dissolving refractory oxides of thorium (and many other metals), but water is still necessary to dilute the concentrated acid. The sulfate system provided its own complexing agent to dissolve the hydroxo compounds after addition of water.

Although the above tests were performed with macro quantities of thorium for convenience of visual observation, the principles demonstrated are clearly applicable to much smaller, invisible quantities. Similar experiments were performed with carrier-free plutonium-239 nitrate in 10 percent nitric acid to demonstrate that extremely small quantities of quadrivalent ions would act the same way. Identical 1-ml aliquots of the plutonium-239 tracer were evaporated to dryness in 250-ml Erlenmeyer flasks with 10 ml of concentrated nitric, hydrochloric, and perchloric acids, and 100 mg of sodium hydrogen sulfate, respectively. After baking for 1 hour on a bare electric hot plate, all four residues were boiled vigorously for 2 minutes with 3 ml of concentrated nitric acid, fused with aluminum nitrate and extracted with 30 percent Aliquat-336 in xylene under conditions known to extract plutonium quantitatively [8]. After extraction, the residual aluminum nitrate aqueous phase was analyzed for plutonium. Only 0.2 to 0.4 percent of the plutonium taken initially remained unextracted in the aqueous phase, all of which can be attributed to phase separation. However, even after rinsing three times with water to remove any traces of soluble plutonium remaining from incomplete transfer of the original solution, the empty flasks in which the evaporation to dryness had been carried out contained 1.3, 0.4, 2.3, and 0.006 percent of the initial plutonium activity from the nitric, hydrochloric, and perchloric acids, and the sodium hydrogen sulfate, respectively.

The experiment was repeated except that the baked residues were boiled for 2 minutes with 4 ml of 72 percent perchloric acid before the extraction, and sulfuric acid was used in place of the sodium hydrogen sulfate. The results were virtually identical. Only 0.5 percent of the original plutonium remained unextracted in the aqueous aluminum nitrate phase, and 1.7, 1.5, 0.3 and 0.005 percent of the plutonium remained stuck to the bottom of the respective flasks. The efficiency of even the residual sulfate from the evaporation of sulfuric acid in keeping trace

quantities of plutonium off the container is remarkable. Although the quantities of carrier-free tracer lost on the bottom of the flask under the present conditions is not very large relative to the total recovery of the plutonium present, they will be extremely significant with respect to contamination of the next sample to be processed in the same container if not cleaned up. The flasks can be cleaned completely and reliably by making a pyrosulfate fusion such that no detectable plutonium can be removed in a subsequent fusion and analysis.

Most of the plutonium that was dissolved out of the flask with nitric and perchloric acids was in a form capable of being extracted, but this might not always be the case, particularly with less energetic treatment. For example, to convert a plutonium-239 nitrate solution in 10 percent nitric acid to the chloride form for extraction into triisooctylamine from hydrochloric acid solution, a 1-ml aliquot was evaporated to dryness and inadvertently heated on an electric hot plate for about 5 minutes. The residue was boiled for 2 or 3 minutes with concentrated hydrochloric acid in an attempt to redissolve the plutonium before extraction with 50 ml of 10 percent triisooctylamine from 60 ml of $10M$ hydrochloric acid. The quantity of plutonium remaining unextracted in the aqueous phase was 93.3 percent of that taken initially.

The experiment was repeated except that the plutonium nitrate was converted to the chloride form by evaporation with 5 ml of concentrated hydrochloric acid to about 1 ml in an uncovered 30-ml beaker without letting the solution go dry even in local spots on the bottom. After extraction, 9.3 percent of the plutonium still remained in the aqueous phase, probably due to slight drying and heating on the sides of the uncovered beaker.

The experiment was repeated again, but the plutonium nitrate was converted to the chloride form by boiling with concentrated hydrochloric acid in a covered 30-ml beaker without allowing any evaporation to occur. After extraction under identically the same conditions used above, only 0.52 percent of the original plutonium remained unextracted in the aqueous phase. A repeat experiment under the same conditions gave 0.77 percent in the aqueous phase, both losses being about what would be expected from incomplete phase separation in the time allotted.

It is clear that evaporation of solutions of tervalent and particularly quadrivalent ions in volatile non-complexing acids to dryness is very risky, particularly if the residues are heated very hot or very long. Hydrochloric acid is not as effective as the higher boiling nitric or perchloric acids in redissolving the residues except for those cases in which strong chloride complexes are formed as in the case of ferric iron.

For example, evaporation of solutions of the large tervalent and quadrivalent alpha-emitting elements to dryness prior to electrodeposition for alpha spectrometry on the mistaken assumption that the residue will redissolve completely in hydrochloric acid gives decreased yields and contaminated beakers that require pyrosulfate fusions to clean completely. Addition of even 100 mg of sodium hydrogen sulfate before evaporation to dryness eliminates the problem.

V. Neutralization with Alkali

Another very common operation in analytical chemistry that is performed with surprising casualness and indifference to the consequences is that of neutralizing a solution containing heavy metals to some preselected pH by the addition of an alkali. Generally, the analyst feels that because the final equilibrium pH is below that necessary to produce the beginning of permanent precipitation that no perturbation has in fact been incurred. Obviously, with the small quantities of elements present in trace analysis, there will be no turbidity or other visual evidence to suggest otherwise. Yet, this is undoubtedly one of the most common sources of erraticism, poor separations, and incomplete recovery to be encountered in routine analysis where such operations are performed. The pH required for incipient precipitation of elements forming insoluble hydroxides is dependent on the $K_{s.p.}$, the charge and concentration of the metal ion, the ionic strength and many other factors. However, in many cases, reaction rates are a more important and limiting consideration than the final equilibrium conditions. As alkali is added, the pH in the local vicinity of the individual drops generally is sufficiently high to precipitate part or all of the element present in that region, depending on the strength of the alkali added. Whether or not the precipitated hydroxide redissolves after the solution is stirred and the excess alkali is neutralized to the pH of the main body of the solution depends on the time allowed and how closely the final pH is allowed to approach that at which permanent precipitation occurs under the particular conditions used.

For example, in the determination of the large tervalent and quadrivalent alpha-emitting radionuclides of thorium through californium by alpha spectrometry, the pH of the solution is generally adjusted with ammonium hydroxide to the acid side of a methyl red endpoint (ca. pH 4) prior to electrodeposition. When electrodepositing standards of carrier-free tracers, excellent yields, greater than 98 percent, can be obtained easily and routinely using many current procedures. However, when the

same procedure is applied to the same radionuclides after their chemical separation from soil, the yield on electrodeposition usually drops by 10 to 25 percent or more.

Recent information obtained in this Laboratory demonstrates conclusively that both the yield and tolerance to other elements can be increased markedly by adjusting the pH to the acid side of thymol blue indicator (pH 1.2 to 2.8) rather than methyl red (pH 4.8 to 6.0). Apparently, when the radionuclide being electrodeposited is present in only carrier-free quantities, its precipitation is so slow even at pH's above 6 that subsequent redissolution is virtually complete in a reasonable length of time even at pH's only slightly below 4. However, if even microgram quantities of cerium, lanthanum, iron, *etc.* from the sample survive the chemical separations, the added carrier causes precipitation of the radionuclide to be more complete and the subsequent dissolution at pH 4 considerably less, as should be expected of elements forming such insoluble hydroxides. When thymol blue is used, much less alkali is added, less precipitation of either radionuclide or inert carrier occurs, and more acid is present after neutralization to the acid side of the indicator range to redissolve the small quantities that might have precipitated. Obviously, if the radionuclide is already precipitated in the solution at the beginning of electrodeposition, it cannot be electrodeposited at the cathode. One should always be very cautious in adjusting the pH of a solution containing heavy metals with strong alkali closer than one or two pH units to the pH at which precipitation occurs unless suitable complexing agents are present to prevent significant local precipitation around the drops. A much safer way, particularly if tervalent and/or quadrivalent elements are present in the absence of complexing agents, is to make the final pH adjustment with a buffer solution of pH only slightly higher than the final one desired.

A very different and unexpected type of problem was encountered in a fluorometric determination of thorium [10]. In the original procedure no longer used, a constant quantity of sodium hydroxide was neutralized with sulfuric acid to produce a high and constant salt concentration from variable quantities of sulfuric acid present. To keep the procedure as simple as possible, the diethylentriaminepentaacetic acid (DTPA) and triethanolamine (TEA) being used to prevent precipitation of thorium throughout the entire alkaline range were incorporated in the sodium hydroxide. After adjustment of the pH to about 5 with dilute sulfuric acid, a pH 11 buffer and the fluorometric reagent morin were added, and the fluorescence was measured. The fluorescence produced from 5-μg thorium standards was very erratic and in most trials was reduced completely

to the level of the blank. The trouble was traced to precipitation of part or all of the thorium at the high alkalinity of the strong sodium hydroxide solution despite the presence of TEA, which did not then redissolve on subsequent acidification because of the presence of DTPA. This was a very surprising discovery because of the stability and water solubility of the Th-DTPA complex. If the complexing agents are omitted while the solution is strongly alkaline, thorium will be precipitated completely but will also redissolve rapidly and completely on reacidification. The complexing agents can then be added to the slightly acidic solution and the pH raised to the mildly alkaline conditions required for the fluorometric determination by adding a buffer solution, and the full fluorescence expected from 5-μg standards can be obtained and reproduced with high precision. However, the problem was solved more simply and conveniently by adding a small quantity of sodium sulfate and evaporating the excess sulfuric acid to dryness. The sodium hydrogen sulfate cake dissolves immediately and completely in water, after which the full fluorescence is obtained with equally high reproducibility.

This explanation was developed from a simple experiment. If 2 or 3 mg of thorium in 25 ml of water is treated with sodium hydroxide, the precipitate of thorium hydroxide will redissolve rapidly and completely on addition of a single drop of 72 percent perchloric acid beyond a methyl red endpoint. If a small quantity of ethylenediaminetetraacetic acid (EDTA) is present, no precipitate is formed on addition of a slight excess of alkali. However, if 1 ml of 10 percent disodium EDTA is added after the formation of thorium hydroxide, the precipitate does not dissolve easily or completely even on addition of many more drops of 72 percent perchloric acid than are required to neutralize the alkali and to exceed the total buffer capacity of the EDTA. The cause of this anomaly is not known, but the experiment demonstrates that hydrolytic species will not always redissolve in the presence of foreign materials as easily as they do in pure solution, even if freshly prepared.

VI. Contamination

Contamination is perhaps the most persistent and severe problem with which the analyst has to contend in trace analysis, and requires continuous and unrelenting care for its elimination and/or control. The many difficult problems involved in purification of water, acids and reagents, control of laboratory environment, and availability and choice of containers for storage of solutions and chemical reactions for the parts-per-million

and lower range have been discussed repeatedly elsewhere. Although these problems are admittedly severe and many of the current solutions are not entirely satisfactory, there are many other chemical problems that are potentially more severe and less reproducible for which the analyst himself is responsible, and which can and must be controlled through proper information and attention to detail.

It has always seemed somewhat incongruous to the present author to watch a professional chemist busily scrubbing with soap suds and brush until the beaker is spotlessly clean. Such treatment is fine for getting the greasy fingerprints off the outside of the beaker, but it doesn't do very much to eliminate the inorganic impurities on the inside where it matters. If the beaker was used to hold a solution of an ore on which an ammonium hydroxide or sodium carbonate separation was made, hydrochloric acid containing hydrogen peroxide or other reducing agent will inevitably be required to remove the manganese dioxide from the sides of the container. If zirconium, niobium, tantalum, *etc.* might also have been present, the further addition of hydrofluoric acid would also be desirable and prudent. In other words, unless the analyst plans to use a new container for each analysis, the time to begin controlling contamination is before or immediately after it has been incurred, before its recent use history has been lost by placing it back in the drawer, namely during the cleanup of glassware and other pertinent equipment. Moreover, the cleaning process must not be carried out blindly and by a constant, standard procedure, but must reflect the best chemical remedy for the problem at hand.

During the recent development of a procedure for the simultaneous determination of virtually all alpha-emitting elements in a single sample of soil [8], severe contamination was encountered repeatedly that clearly related to the quantities of the same radionuclide in the previous sample put through the same equipment. Consequently, every empty container was checked after use to determine the source and extent of the contamination from each piece of apparatus, and therefore from the particular chemical operation responsible, and the most efficient way to remove the contaminant. It was found that beakers in which barium sulfate had been precipitated and filtered from a boiling solution to precipitate the large polyvalent ions invariably contained a thin milky deposit of barium sulfate on the sides of the beaker, due to postprecipitation after the filtrate had cooled. This deposit was not removed efficiently or completely on washing with a solution of hydrochloric and hydrofluoric acids, but was dissolved in the subsequent sample releasing the activity it contained. Treating the beaker with any solvent for barium sulfate such as fuming sulfuric or perchloric acids or hot alkaline DTPA eliminated the problem completely. Erlenmeyer flasks in which nitric acid solutions of plutonium,

thorium, americium, *etc.* had been evaporated to dryness prior to elec-
trodeposition required a pyrosulfate fusion to dissolve the refractory ox-
ides produced on strong heating. Addition of sodium hydrogen sulfate be-
fore evaporation to dryness decreases the loss materially as described
above, but pyrosulfate fusion is still recommended to guarantee complete
decontamination.

Separatory funnels used in liquid-liquid extractions should be rinsed
with alcohol to remove the organic solvent and then with hydrochloric
acid containing a small quantity of hydrofluoric acid to remove any
hydrolyzed compounds, particularly of zirconium, protactinium, *etc.* The
most severe source of contamination by far was in the cell used for elec-
trodeposition. Because electrodeposition of electropositive elements de-
pends on deposition of the hydroxides at the cathode, during which time
the pH of the entire solution increases to about pH 7.5, small quantities of
insoluble hydroxides inevitably find their way to the walls of the cell.
Casual treatment with mixtures of various acids, including hydrofluoric,
and hydrogen peroxide at room temperature is totally inadequate to
achieve complete decontamination. The most effective treatment involves
boiling the cell, anode and "O" ring with concentrated nitric acid, repeat-
ing the process in fresh acid when more than a few hundred disintegra-
tions per minute had been electrodeposited. However, hot concentrated
nitric acid precipitates polonium extensively so other means must be em-
ployed for its removal.

Another source of high and variable contamination is the dropping bot-
tles or reagent solutions that are dispensed by dip-type pipets and used re-
peatedly during a series of analyses. The safest way to avoid a continuing
buildup of contaminant is either to rinse the outside of the pipet every
time it is used before it is allowed to reenter the reagent bottle, or to pour
a small quantity of the original reagent into a small beaker or graduate
cyclinder and discard what is not used. Wasting small judicious quantities
of reagents is infinitely less expensive than redoing the analysis to say
nothing of the effort expended in identifying the problem initially. Since
identifying all the sources of contamination in the plutonium-soil
procedure over 4 years ago, and implementing the present program of ap-
propriate chemical cleaning of all glassware and prevention of contamina-
tion of reagent solutions, not a single case of contamination has been ob-
served.

Another problem having an effect similar to contamination in that it is
variable, severe and cannot be corrected for is failure to obtain absolutely
complete decomposition of organic matter, including organic compounds
deliberately used in the analysis. In a fluorometric procedure for berylli-

um using morin [9], acetylacetone is used to extract the beryllium, and the extract is then wet-ashed with nitric and perchloric acids before the fluorometric measurement. When complaints were received about high and variable blanks being obtained, investigation showed that the entire problem was due to the analysts' removing the cover glass so that the perchloric acid could escape rather than leaving the cover in place to cause significant refluxing of the perchloric acid and extend the digestion time as had been intended but not specifically mentioned in the published article. Consequently, the acetylacetone was incompletely decomposed, and the decomposition products remaining included a compound exhibiting a blue fluorescence which contributed substantially to that being measured. Leaving the cover glass in place until most of the perchloric acid had been volatilized rectified the entire problem.

One of the strangest and most unimaginable problems was encountered in the development of a procedure for the determination of lead-210 [11]. Lead and bismuth were extracted into a chloroform solution of diethylammonium diethyldithiocarbamate (DDTC) from a strong acid solution. After wet-ashing the extract, both elements were extracted into dithizone from an alkaline citrate-cyanide solution, and the lead was then stripped out of the organic phase with a pH 2.7 buffer, separating it from bismuth. Although the dithizone separation of lead from bismuth worked extremely well when tested alone, the separation failed completely when applied to the wet-ashed DDTC extract. The lead could not be stripped completely from the dithizone extract with the acid buffer, certainly not the way the lead dithizone complex is known to act. The trouble was traced to incomplete destruction of the dithiocarbamate entity, despite repeated severe treatment with nitric, sulfuric and perchloric acids, and the lead was being retained in the chloroform extract as the dithiocarbamate complex, which is extractable from strong acid.

How a simple molecule like diethyldithiocarbamic acid, containing both a thiono and a powerful reducing thiol group and forming only a 4-membered carbon-sulfur hydrogen-bonded heterocyclic ring, can survive the vigorous wet-ashing conditions used is very difficult to imagine. However, if DDTC is evaporated to fumes with concentrated nitric and perchloric acids and water is added, a clear, colorless and odorless solution is obtained that becomes turbid and develops a strong odor of hydrogen sulfide on standing overnight. The solution still has definite ability to form strong chloroform-soluble complexes with both lead and bismuth from strongly acid solutions that prevents complete stripping of lead in the subsequent dithizone extraction. The ability to extract lead from strongly acid solutions is not shared by many organic compounds

and suggests that some of the diethyldithiocarbamate itself does in fact survive the oxidative attack.

After oxidation with nitric and perchloric acids, the residual organic matter is not charred significantly even by boiling concentrated sulfuric acid but is easily charred on evaporation to dryness. The resulting char can then be oxidized smoothly and completely with nitric and perchloric acids, leaving nothing capable of extracting lead under any conditions. Sodium hydrogen sulfate is added as an acid buffer to prevent hydrolysis and thermal decomposition of lead and bismuth sulfates during heating to dryness and to prevent precipitation of very insoluble anhydrous sulfates of iron and other metals that might be present. When these conditions of wet-ashing the DDTC extract were used in the procedure, all difficulties with stripping lead from the dithizone extract disappeared.

These few examples are intended to show the many kinds of complications that can arise inadvertently that completely change the course of the intended chemical reactions with a consequent decrease in accuracy, precision and reliability of the determination. The analyst must know the characteristics and limitations of his procedure if good results are to be obtained consistently. Although emphasis has been placed on the tervalent and quadrivalent elements, the same principles apply to the lower valent elements in somewhat lower degree.

VII. References

[1] Sill, C. W. and Williams, R. L., *Anal. Chem.* **41**, 1624 (1969).
[2] Bernabee, R. P., Martin, D. B., and Percival, D. R., U.S. Atomic Energy Commission, Idaho Falls, Idaho, private communication, 1974.
[3] Feldman, C., *Anal. Chem.* **46**, 99 (1974).
[4] Bernabee, R. P. and Sill, C. W., *Determination of Polonium-210 in Environmental Samples,* U.S. Atomic Energy Commission, Idaho Falls, Idaho, unpublished document, 1974.
[5] Sill, C. W., *Anal. Chem.* **38**, 1458 (1966).
[6] Sill, C. W., *Anal. Chem.* **46**, 1426 (1974).
[7] Hillebrand, W. R., Lundell, G. E. F., Bright, H. A., and Hoffman, J. I., *Applied Inorganic Analysis,* Second Edition, p. 841, John Wiley and Sons, New York, N.Y., (1953).
[8] Sill, C. W., *Anal. Chem.* **46**, 1725 (1974).
[9] Sill, C. W. and Willis, C. P., *Anal. Chem.* **31**, 598 (1959).
[10] Sill, C. W. and Willis, C. P., *Anal. Chem.* **34**, 954 (1962).
[11] Sill, C. W. and Willis, C. P., *Anal. Chem.* **37**, 1661 (1965).