# THE SYSTEMATIC DETECTION OF THE RARER CHEM-ICAL ELEMENTS[1]

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## PLAN OF THE INVESTIGATION

The aim of these researches has been to work out in detail a systematic, universally applicable scheme of qualitative analysis which shall include as nearly as practicable all the metal-forming elements, and which shall make possible their detection when present in small quantity, even in association with large quantities of any other elements.

The great importance, both from a technological and a purely scientific standpoint, which has become attached in recent years to many of the "rare elements"—so called often only by reason of their traditional and somewhat arbitrary exclusion from the usual schemes of qualitative analysis—has made it highly desirable that a reliable system of procedure for their detection be available. Any chemist who, without previous experience in this field, has occasion to test for small quantities of these elements will infer upon consulting the existing literature, and become convinced when he begins to experiment, that his problem is beset with difficulties and will require much time for its solution. Since no satisfactory systematic scheme of analysis exists, it has been necessary for the analyst to apply as best he could the isolated separations and tests recorded in text-books and journals. Such general schemes of qualitative analysis including the rare elements as do exist do not seem to have been subjected to any adequate investigation with reference to

the effectiveness of the separations or the reliability and delicacy of the tests; moreover, in a field of work where the closest adherence to the proper conditions is essential to success, the directions given are of a most general character. These schemes, therefore, when tested in the laboratory, are found to be seriously defective, and to have little practical value, except for the detection of fairly large quantities of some of the rare elements. A vast amount of valuable work has, to be sure, been published upon the separation of the rare elements of separate groups, such as the rare-earths, the platinum-metals, and the rarer alkali-metals; but this work has been done mainly from the standpoint of quantitative analysis and with reference to the limited number of elements which are found associated in certain important minerals or ores. These quantitative and qualitative investigations have furnished many of the data necessary for the working out of a complete system of qualitative analysis, such as that which forms the object of this investigation.

One consideration that has been kept in mind throughout the investigation is the desirability of employing such processes as will lead to the detection, not necessarily of the minimum detectable quantity of each element, but of some quantity which may be regarded as a norm for all elements, so that the scheme of analysis as a whole may have some definite degree of precision. Accordingly the effort has been made to develop such procedures as will detect one milligram of any element in the presence of 500 mg. of any other; and the results in fact attained enable from 0.5 to 2 mg. of the various elements to be so detected.

Another point of view followed throughout the work is the adoption of such methods as will permit an estimate to be made of the quantities of the various elements present. For a satisfactory scheme of qualitative analysis carefully executed can be made to furnish this important information, thus often making unnecessary far more laborious quantitative analyses. Owing to the fact that qualitative analysis is commonly taught to beginners in a superficial way, without the same emphasis on accurate manipulation as is usual in courses on quantitative analysis,

many analysts fail to realize the practical possibilities of qualitative analysis in this direction. In this scheme of analysis, therefore, tests, such as oversensitive color reactions, flame colorations, and bead tests, which do not enable the amount of the various elements to be approximately estimated have been avoided; and each element is obtained in the solid form as a precipitate or residue so far as possible.

This research has been in progress for over twenty-five years, and has been carried on largely by numerous research assistants and advanced students, to whose valuable aid we wish it were possible to give here adequate recognition. Portions of the work have already been published in preliminary form (1); and the investigation is now approaching such a state of completion that systematic detailed publication of the results will soon be begun in a current chemical journal, and this will be followed shortly by a connected presentation of the whole system of analysis in the form of a monograph. In this paper an attempt will be made to present to the general chemical reader only an outline of the system of analysis, with especial emphasis on its research aspects and with brief discussion of the reasons which have led to the adoption of its main features.

## PREPARATION OF THE SOLUTION AND THE INCIDENTAL ISOLATION OF CERTAIN GROUPS OF ELEMENTS

A primary feature of any system of analysis for all the metal-forming elements must be a general procedure for the preparation of a solution of the material to be analyzed. This fact has been frequently ignored in presenting schemes of analysis; it being assumed that all the elements to be tested for have somehow or other been brought into solution in some type of solvent. The character of the process employed determines, however, the way in which some of the elements group themselves, and is bound to influence greatly the subsequent scheme of analysis.

The procedure here presented has been worked out with the aim of developing a systematic method which is rapid in its application to materials commonly met with, which is so general

and complete as to effect the solution of nearly all substances, which provides against the loss of volatile elements, and which lends itself to sharp and convenient group separations in the subsequent analysis.

Any complete procedure for preparing the solution naturally includes treatment of the material with solvents of the following types: (1) with a strongly acid solvent, so as to dissolve basic oxides and salts of weak acids; (2) with a powerful oxidizing solvent, to dissolve metals and sulfides; (3) with hydrofluoric acid, to volatilize silica and decompose silicates not acted on by the ordinary acids. In selecting the solvents and determining the order in which they are applied account must be taken especially of the facts (a) that several elements volatilize out of boiling solutions, especially when in the form of halides; (b) that certain other elements will not remain in solution in, any dilute acid other than hydrofluoric acid, and must therefore be isolated early in the process; and (c) that sulfuric acid, if added as a solvent or produced by the oxidation of sulfides, causes precipitation of several elements, especially of barium, strontium, and lead. These conditions permit, however, of several combinations in the selection and order of application of the solvents.

The procedure here adopted is outlined in table 1, which should be referred to in connection with the following discussion, in which the main features of the process and the reasons for them are presented.

The first operation is the treatment of the substance with concentrated hydrobromic acid. Hydrobromic and hydrochloric acids have the great advantages over nitric acid that they have a much more powerful acid solvent action on basic oxides and basic salts, like those of iron, aluminum, antimony, tin, and titanium; this being probably due to their tendency to form complex or slightly ionized halides. As the initial solvent they have the further advantage over nitric acid that, when hot and concentrated, they decompose most sulfides with liberation of the sulfur in the form of hydrogen sulfide, instead of converting it into sulfuric acid and thereby causing precipitation of in-

TABLE 1

PREPARATION OF THE SOLUTION, AND ISOLATION OF THE SELENIUM, TUNGSTEN-TANTALUM, AND GOLD GROUPS

Heat the substance with HBr and Br$_2$; then distil the mixture.

**Distillate: selenium group:** Se, As, Ge, as bromides.

**Solution and residue.** Add HNO$_3$ and HClO$_4$, distil, evaporate to fuming, add water, filter.

- **Distillates: osmium group:** Os, Ru, as tetroxides.
- **Solution**
  - **Residue:** SiO$_2$, tungsten-tantalum-group oxides, AgBr, undecomposed material. *Digest with HF, add HClO$_4$, evaporate to fuming.*
    - Solution and residue.

    *Unite, evaporate to fuming, add 12n. HCO$_2$H, boil, filter.*

    - **Residue:** Tungsten-tantalum-group oxides, gold-group as metals, AgBr, undecomposed material. *Digest with HF, dilute, filter.*
      - **Solution:** *Evaporate with H$_2$SO$_4$ add NH$_4$OH and (NH$_4$)$_2$S, filter.*
        - **Solution: tungsten group:** Sb, Sn, W, Mo, Te, V.
        - **Precipitate: tantalum group:** Ta, Cb, Ti, Zr.
      - **Residue:** Gold-group as metals, AgBr, PbSO$_4$...., undecomposed material. *Treat with HCl and HNO$_3$, evaporate, add dilute HCl, filter.*
        - **Solution: gold group:** Au, Pd, Pt, Hg, as chlorides.
        - **Residue:** AgCl, PbSO$_4$, undecomposed material. *Extract with NH$_4$OH and NH$_4$C$_2$H$_3$O$_2$, filter.*
          - **Solution:** Ag, Pb.
          - **Residue: undecomposed material.**
            - **Non-Metallic:** BaSO$_4$, SrSO$_4$; Al$_2$O$_3$, FeOCr$_2$O$_3$, SnO$_2$, TiO$_2$, ZrO$_2$SiO$_2$; some silicates; phosphates of rare earths; ThF$_4$; C, SiC, MoS$_2$ ... *Fuse with Na$_2$CO$_3$ and KNO$_3$.*
            - **Metallic:** Platinum-elements, alloys of Fe, Ni, Cr. *Fuse with Na$_2$O$_2$.*
  - **Solution.** *Analyze for all other elements.*

soluble sulfates.   Finally, they dissolve, because of their reducing action, a few substances, such as manganese and lead dioxides and lead chromate, which are not attacked by nitric acid.   They have the disadvantage, on the other hand, that the elements, trivalent arsenic, selenium, and germanium volatilize largely or completely when solutions of them in the halogen acids are boiled or evaporated.   This difficulty can, however, be remedied by carrying out the treatment in a distilling flask, collecting the distillate, and testing it for these elements, as is done in the process here presented.

Hydrobromic acid, rather than hydrochloric acid, is employed, for the reason that the former acid causes arsenic, whether present in the trivalent or quinquivalent form, and selenium to distil over almost completely, while with the latter acid quinquivalent arsenic volatilizes only very slightly, and selenium partially, but very incompletely.   Hydrobromic acid therefore yields a distillate containing a sharply defined group of elements, called here the *selenium group*, comprising the three elements selenium, arsenic, and germanium.   Moreover, these elements are thereby once for all removed from the main solution, which avoids some complications, especially in the case of arsenic.

If the material does not disssolve on warming it with the hydrobromic acid, the mixture is made strongly oxidizing by the addition of bromine.   The bromine is added before the mixture is distilled, so that any arsenic, selenium, or germanium present in the part of the material that is decomposed only by the bromine may pass over into the distillate and be detected in the analysis of the selenium group.

The next operation is the evaporation of the hydrobromic acid solution with nitric and perchloric acids.   There are two elements, osmium and ruthenium, which, because of the volatility of their tetroxides, escape under these conditions from the boiling solution.   These elements do not volatilize during the distillation with hydrobromic acid, since this acid reduces them to a lower state of oxidation; but after the nitric acid has destroyed the remaining hydrobromic acid and the distillation is resumed, the osmium passes over and is collected and tested for in the distillate.

Finally, when the nitric acid becomes concentrated and the mixture is further heated with addition of perchloric acid, the ruthenium is oxidized and distils over as the tetroxide. The elimination of these two elements at this point does not, however, usually take place, since they are likely to be present in alloys or ores not acted upon by hydrobromic acid and bromine or by nitric and perchloric acids.

The evaporation with nitric and perchloric acid also serves to decompose completely almost all bromides. This is important in several respects. Thus it prevents the loss of some mercury, antimony, and tin in the subsequent evaporation, and it avoids any action on the platinum vessel which is employed in the later treatment with hydrofluoric acid; but, what is more vital, it makes more satisfactory the separation as oxides (when the perchloric acid is diluted) of a large group of elements, some of which are very incompletely precipitated when halides are present. This group, here called the *tungsten-tantalum group*, consists of the elements antimony, tin, tungsten, molybdenum, tellurium, and vanadium (constituting the *tungsten group*), and titanium, zirconium, tantalum, and columbium (constituting the *tantalum group*).

The next major operation, in case there is still an undissolved residue, is the treatment of that residue with hydrofluoric acid for the purpose of decomposing silicates and removing silica by volatilization as silicon fluoride. This method of decomposing silicates is far more satisfactory in qualitative analysis than fusion with sodium carbonate, since it is more rapid, since it does not introduce alkali elements, and since it at once eliminates silica from the solution.

The next problem—one which required extended investigation—was the decomposition of the fluorides. This is commonly effected by heating them with sulfuric acid to the fuming point; but the use of this acid has the serious disadvantage in systematic qualitative analysis that it yields, as a residue slightly soluble in water, the sulfates of lead, barium, strontium, calcium, and chromium. Evaporation with nitric acid, even many times repeated, decomposes very incompletely calcium and rare-earth

fluorides when present in large quantity; and, while it has been found that its decomposing action can be much increased by the addition of silica, the presence of this solid substance makes it impossible to determine at once whether the original substance has been completely dissolved, and makes an additional operation necessary. Since perchloric acid was found to decompose the fluorides much more rapidly and without this complication, it is used in this process of preparing the solution. This acid decomposes moderate quantities of calcium and rare-earth fluorides in a brief fuming, and decomposes completely even a large quantity of any fluoride (except perhaps a little thorium fluoride) when the fuming is continued for ten or fifteen minutes. It converts the soluble fluorides of the tungsten-tantalum group into insoluble oxides, and it converts the other elements into perchlorates or acids which are all readily soluble in hot water.

The next step in the process is isolation of the tungsten-tantalum group, which consists of the elements forming acidic oxides that are very slightly dissolved by perchloric acid (or nitric acid). The separation of five elements of this group, namely, of tantalum, columbium, tungsten, antimony, and tin is sufficiently complete (except in a few combinations with other elements) when the strongly fumed perchloric acid is diluted and heated to boiling. Furthermore, any molybdenum in excess of 2 to 3 mg. and any titanium in excess of about 20 mg. are ordinarily found in the residue; and even all of the titanium and zirconium may be found there when phosphate is also present. Moreover, vanadium may be partly or wholly carried out with tin when they are simultaneously present, and tellurium and bismuth may be precipitated with other elements. Provision must therefore be made for the detection of these elements in the analysis of the tungsten-tantalum group.

The strong perchloric acid solution might be diluted with water, so far as the separation of the tungsten-tantalum group is concerned but, in order to attain certain other results which simplify the late procedures, 12-normal formic acid is added instead, and the mixture is boiled with this reagent. This causes complete precipitation in the metallic state of the four elements,

gold, platinum, palladium, and mercury, constituting the *gold group*. The isolation of these elements at this point might be of questionable advantage were it not that two of them, gold and palladium, are likely to be partially, but not completely, precipitated by the fuming perchloric acid alone. The main reason for the use of formic acid, however, is that it reduces to a lower state of oxidation various elements and thus prevents their precipitation or shortens the subsequent analysis. Thus if water is employed, manganese and vanadium are precipitated as $MnO_2$ and $V_2O_5$ when these elements are present in large quantity; thallium remains in the thallic state and cannot be immediately removed in the form of thallous bromide; and chromium and iron are present as chromic acid and ferric salt so that they may cause the separation of much sulfur in the subsequent treatment. On the other hand, the only disadvantage in the use of formic acid is that it precipitates with the gold group as metals a small proportion of any rhodium and iridium that may be present.

The perchloric acid solution filtered from the residue is analyzed for all metal-forming elements except those of the selenium, tungsten-tantalum, and gold groups, in the way outlined below.

The residue, which may consist of oxides of the tungsten-tantalum group, or of metals of the gold group, or of still unattacked material, or of all of them, is digested with hydrofluoric acid solution to dissolve the tungsten-tantalum group oxides and thus separate them from the gold-group metals and any original material still present. The solution is then subjected to the process of analysis worked out for the tungsten-tantalum group. The first steps in this process are evaporation with sulfuric acid to decompose the fluorides, and digestion with ammonium hydroxide and sulfide to separate the tungsten group (Sb, Sn, W, Mo, V, Te) from the tantalum group (Ta, Cb, Ti, Zr).

The residue from the hydrofluoric acid treatment is next treated with hydrochloric and nitric acids to dissolve the gold-group metals and separate them from any still unattacked material.

Only rarely will any residue now remain after the severe treatments to which the substance has been subjected; and the fusions outlined in the table will seldom need to be resorted to. The more important substances that are known to be likely to be present in the residue are formulated in the lower right-hand section of the table. They are classified as non-metallic and metallic, since a different treatment is appropriate for these two kinds of substances.

Nearly all the non-metallic substances can be brought into a soluble form either by an oxidizing alkaline fusion, in which alkali carbonate and nitrate are employed as flux, or by an acid fusion, with potassium pyrosulfate. Thus the former fusion is effective with alkaline-earth sulfates, with silicates that have resisted the action of hydrofluoric acid, and with substances, like carbon, chromic oxide, or molybdenum sulfide, that are readily oxidized at high temperatures; and the fusion with pyrosulfate, followed by treatment of the melt with hydrochloric acid, brings into solution the oxides of aluminum, titanium, zirconium, and most phosphates that may be present. Stannic oxide is the only important substance that may still remain partially unattacked.

A metallic residue is likely to consist of ores or alloys of the platinum metals or of alloys of iron, nickel, chromium, and silicon. Fusion with sodium peroxide, a strongly alkaline and oxidizing flux, is by far the most rapid method of bringing all these alloys into soluble form, and it is therefore here employed. Even the platinum metals are all quickly converted by this extraordinarily powerful flux into forms soluble either in water or hydrochloric acid, except that platinum itself is partially converted into a yellow oxide which dissolves only very slowly on digestion with the concentrated acid.

### SEPARATION OF THE REMAINING ELEMENTS INTO GROUPS

The plan adopted for separating into analytical groups the elements not already provided for in connection with the preparation of the solution is shown in table 2.

The perchloric acid solution from which the tungsten, tantalum, and gold groups have been separated is immediately treated

TABLE 2

SEPARATION OF THE REMAINING ELEMENTS INTO GROUPS

Perchloric acid solution, from which the selenium, osmium, tungsten, tantalum, and gold groups have been removed. Add $NH_4Br$, filter.

| Precipitate: silver group: Ag, Tl, Pb, as bromides. | Filtrate. Saturate with $H_2S$, filter. | | | | | |
|---|---|---|---|---|---|---|
| | Precipitate: copper group: Pb, Bi, Cu, Cd; rarer elements, Te, Mo, Ir, Rh; as sulfides. | Filtrate. Add $NH_4OH$ and $(NH_4)S$, filter. | | | | |
| | | Precipitate. Dissolve, boil with $NaOH$ and $Na_2O_2$, filter. | | | Filtrate. Add $(NH^4)_2CO^3$ and $C_2H_5OH$, filter | |
| | | Filtrate: aluminum group, Al, Zn, Cr, U, Be, V, In. | Precipitate. Treat with HF, filter. | | Precipitate: alkaline-earth group, Ba, Sr, Ca, Mg. | Filtrate: alkali group, Na, Li, K, Rb, Cs. |
| | | | Filtrate: iron group, Mn, Fe, Ni, Co, Zr, Ti, In. | Precipitate: rare-earth group, Sc, Th, Ce, rare earths. | | |

with ammonium bromide, whereby silver and thallium are completely precipitated and any lead in excess of 15 to 20 mg. is removed, these elements constituting the *silver group*.

The acid concentration is then adjusted, and the mixture is treated with hydrogen sulfide first in a hot moderately acid solution (in a pressure bottle if platinum elements may be present), and then in a cold, more dilute solution. This precipitates completely the *copper-group*, consisting of lead, bismuth, copper, and cadmium, and the elements tellurium, molybdenum, iridium, and rhodium. In the absence of platinum elements the copper group is separated from tellurium and molybdenum simply by treatment with sodium sulfide solution. In the possible presence of platinum elements, it is necessary to employ a more complicated process which need not be here described.

The filtrate from the hydrogen sulfide treatment is digested with ammonium hydroxide and sulfide as in common-element analyses. The elements so precipitated are subsequently resolved into three main subgroups. To this end the precipitate is dissolved in acids, and the solution is boiled with sodium hydroxide and peroxide. There are then found in the solution the aluminum, zinc, chromium, beryllium, vanadium, and uranium; these elements constituting the *aluminum group*. The precipitate is treated with hydrofluoric acid, yielding a residue that contains the scandium, thorium, and rare-earth elements (forming the *rare-earth group*), and a solution that contains the rest of the elements, manganese, iron, nickel, cobalt, zirconium, titanium, and indium (constituting the *iron-group*).

The filtrate from the ammonium sulfide precipitate, after removing from it the vanadium and tungsten it may contain, is treated as in ordinary qualitative analysis; the *alkaline-earth group* (barium, strontium, calcium, and magnesium) being precipitated with ammonium carbonate and alcohol, and the *alkali-group* (lithium, sodium, potassium, rubidium, and cesium) remaining in the filtrate.

## THE ANALYSIS OF THE SEPARATE GROUPS

It would lead far beyond the scope of this paper even to out-line the methods systematically that have been worked out for the analysis of the separate groups; but we may mention a few of the rare-element separations that in their application to quali-tative analysis have some novelty or other special interest.

In the analysis of the distillate containing the selenium group, germanium is separated from arsenic by saturating a hydro-fluoric acid solution with hydrogen sulfide, as recommended by Muller (2), whereby only the arsenic is precipitated.

In analyzing the tungsten group, the rare elements, tungsten, molybdenum, tellurium, and vanadium are separated from anti-mony and tin by igniting the sulfides in a current of hydrogen sulfide and treating the mass with strong hydrochloric acid, whereby the sulfides of the rarer elements are left entirely un-attacked, while those of antimony and tin readily dissolve. Tungsten, after converting the sulfides to oxides, is then separated from molybdenum and the other elements by boiling with 2-normal hydrochloric acid.

In separating the elements of the tantalum group, titanium is dissolved away from the accompanying tantalum and colum-bium hydroxides by boiling with sodium salicylate solution, fol-lowing a modification of the process described by Muller (3). Tantalum is separated from columbium by converting the former into potassium oxyfluotantalate, which is much less soluble than the potassium fluocolumbate. The presence of columbium is then detected by its producing a precipitate of calomel when the filtrate is poured through a zinc column into mercuric chloride solution; this distinguishing it from tantalum and zirconium, which are not reduced by zinc, and from titanium, which, though reduced to the trivalent state, reacts with mercuric chloride only very slowly in the cold.

Iridium and rhodium are separated from the common copper-group elements by precipitating the latter with sodium carbonate in the presence of nitrite, which last converts the iridium and rhodium into double nitrites, thus preventing their precipitation.

The analysis of the rare-earth group has been carried out in a fully satisfactory way to the extent of separating scandium, thorium, and cerium from the other elements and from each other. This is done by extracting the scandium from the fluoride precipitate with ammonium hydrofluoride, and by precipitating from a nitric acid solution of the remaining elements, the thorium and cerium with iodic acid, the cerium being first brought into the quadrivalent state by means of chloric acid, and finally separating them from each other by the same reagent after reducing the cerium.

Many rare-element separations are also involved in the analyses of the aluminum and iron groups; but, as these have been already published, they will not be here mentioned. Indium, not included in the earlier publication, is now provided for.

Finally in the analysis of the alkali group potassium is separated from rubidium and cesium by precipitating these two elements as chloroplumbates through treatment with lead chloride and chlorine; and then rubidium and cesium are separated from each other by employing the different solubilities of their double salts with antimonous chloride.

### THE PRESENT STATUS OF THE RESEARCHES

Finally a brief statement may be made of the extent to which the system of analysis has been completed. The investigations on the preparation of the solution and on the processes of analysis of the selenium, tungsten, tantalum, silver, and rare-earth groups have been finished and written up in form for publication. Satisfactory procedures for the aluminum and iron groups were published some years ago; and it is expected to include these methods with only minor modifications in the complete system of analysis. For the remaining portions of the scheme, namely for the analysis of the gold group and of the hydrogen sulfide precipitate (including the platinum elements), and of the alkali group, seemingly reliable methods have been developed and fairly well tested in the laboratory. These are, however, to be given a final experimental revision.

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