A Study in Group Qualitative Analysis.

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A STUDY IN GROUP QUALITATIVE ANALYSIS

A Dissertation

Submitted to the Graduate Faculty of the Louisiana State University and Agricultural and Mechanical College in partial fulfillment of the requirements for the degree of Doctor of Philosophy in

The Department of Chemistry

by

John T. Diffee
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ABSTRACT

The development of a group qualitative analysis scheme has been investigated. This is a novel form of analysis in which ions are detected as a group rather than individually. This type of analytic technique permits a rapid survey of an unknown, since all tests are conducted without the necessity of prior separations.

Since a rapid, sensitive and selective method was desired, the technique of spot test analysis was utilized. Thirty-seven analytical reagents were screened as potential group reagents. Six were selected for the finalized procedure: benzidine, stannous chloride, phenyl fluorone, morin, glyoxal bis(2-hydroxyanil) and sodium tetraphenylboron. Masking, pH adjustment and selection of proper reaction media were employed to enhance selectivity and sensitivity of the reagents. The final procedure provides for the detection of forty-six ionic species.

A specific and sensitive test for the detection of cadmium ion based on the use of glyoxal bis(2-hydroxyanil) has also been proposed. The reaction was carried out on beads of an anion exchange resin on which the cadmium had been concentrated as the tetraiodo complex. Masking techniques were utilized to make the test specific. The limit of identification is 0.05 μg cadmium ion.
I. INTRODUCTION TO THE HISTORY OF QUALITATIVE ANALYSIS
AND SPOT TEST METHODS

The emergence of qualitative analysis as a science was brought about by the works of many chemists. Interestingly enough many of these people were not interested in analysis per se, but rather discovered analytical reactions in the course of their work or developed analytical procedures as a necessary portion of their work. The bases for the present system of qualitative analysis can be found in the discovery of the individual reagents and the reactions necessary to the development of any scheme of analysis. The comprehensive analyses carried out on waters, the study of ores and minerals by the mineralogists of the eighteenth century, and many other practical applications of analysis greatly hastened this evolution and subsequently brought about the development of a systematic scheme of qualitative analysis.

It is not inconceivable that the idea prevailing today that analytical chemistry is not a true scientific discipline and has only a service function had its beginning during these times. This premise is based upon a knowledge of the utilitarian development of analysis by metallurgists, mineralogists, pharmacists and physicians. In fact, Thomson (74) in 1836 lamented that "the department of analytical chemistry, and even mineralogical investigations in general, have been sneered at by several chemists
in this country, as a branch of chemistry below the notice of men of true science."

The history of the discovery and development of the reagents used as group precipitants, conditioning agents and confirmatory tests in qualitative analysis is scattered throughout the chemical literature. In fact, only recently has there appeared a book on the history of analytical chemistry compiling much of this information (73). This book is the first attempt to record in historical development of analytical chemistry in a systematic way.

The majority of the reactions useful in qualitative analysis, with the exception of those utilizing synthetic organic reagents, was discovered before 1700. It was during this period of iatrochemistry that mineral acids were used to dissolve metals and it became possible to work with these solutions. However, the process of dissolution was surrounded with superstition and mystery, as if in some manner the dissolved substance had disappeared. This concept was responsible for keeping alive the old alchemical ideas on the transformation of substances. Only van Helmont stated definitely that the dissolved substance does not disappear. His work was quite quantitative in nature since he made extensive use of the balance. He realized that metals dissolved in acids can be recovered again by appropriate means. Thus it is at this time in the development of analysis that we see the placement of solution chemistry in its present eminent position (58).
It should be noted that at this period in the development of chemistry as a science (1500-1700) that the important mineral acids were generally known. For example, van Helmont was well acquainted with sulfuric acid; he also described the preparation of nitric acid and hydrochloric acid. He also mentions aqua regia.

The word "analysis" was introduced by Robert Boyle in the sense that we know it today, i.e., for those chemical reactions by which individual substances could be recognized in the presence of one another. Boyle was the first to use the most common of all reactions, i.e., the testing for acidity and alkalinity with paper impregnated with litmus and the juices of violets and cornflowers.

The most striking feature about his studies in chemistry lies in his use of reactions to identify various substances. Boyle's search for analytical reagents was extremely systematic. He is credited with developing the first analytical reagents, using calcium ion to detect sulfuric acid and silver ion to detect hydrochloric acid.

Many of the reactions used by Boyle had been used previously by other workers, but only Boyle seems to have recognized that change of color rather than just color itself might have analytical significance. It is in this principle that we see one of the salient features of modern chemical analysis, that is, the identification of a substance by an alteration in some secondary quality of the substance.
In Boyle's *Memoirs of a Natural History of Mineral Waters*, published in 1685, the juice of gallnuts is used to test for iron and copper. Here he states that the amount of gallnut paper added must be carefully measured as the strength of the color then gives the amount of metal present. This is, in essence, a qualitative statement of Beer's law.

Boyle made an attempt to measure the "limit of detection" or sensitivity of chemical reactions, e.g., the detection of chloride ion with silver ion and the iron-gallnut extract reaction.

In 1685 Boyle described a new reagent which he called "volatile sulphureous spirit". He prepared this reagent by melting flowers of sulfur and gradually added a similar quantity of potassium and distilled the mixture with an aqueous solution of ammonium chloride. This, of course, was hydrogen sulfide. He used it as a reagent for the detection of mercury, tin, lead and copper. Hydrogen sulfide was not used in analytical procedures after this until the end of the eighteenth century. Probably the inconvenience of its preparation, at least as described by Boyle, or perhaps its odoriferous nature prevented it from being more widely used.

It is during this period in the history of qualitative chemical analysis that we see the beginnings of the systematic study of a reagent to expose its general analytical utility with the metal ions. For example,
Tachenius carried out a systematic examination of the effect of gallnut extract on metal salt solutions. He observed the color formed with solutions of many metals. He also observed that iron was not removed from the human body via the urine as had previously been supposed as no color was obtained when urine was treated with gallnut extract. This was the first example of the application of chemical analysis to biochemistry (73).

During the period of iatrochemistry a great deal of work was carried out on the chemical analysis of water. A distinctive feature of European social life in the sixteenth to eighteenth centuries was the popularity of the spas. With this social interest in the baths there grew a gathering curiosity about the medicinal and scientific attributes of the waters themselves. Prior to 1780, thirty-four papers on mineral waters had appeared in the Philosophical Transactions of the Royal Society. Since papers comprising all of science were published in this journal, it is evident that the topic of mineral waters held an important place in the literature of the day. In addition, there was a large literature in book form in existence. Some of the earliest comprehensive reports on water analysis were due to Thurneyser (in 1572) and Libavius (in 1597). The publication in 1779 of Torbern Bergman's De Analysi Aquarum was the beginning of a truly scientific approach to analysis in aqueous solution (7). Bergman's treatment was both thorough and critical, as
evidenced by some of the topics included: observation of physical qualities, precipitation with reagents, methods of collecting volatile constituents, examination of residues and the confirmation of the analysis by synthesis. Thus Bergman's work was a first attempt at a system for qualitative analysis in aqueous solution. It was based upon the separation of different substances into insoluble compounds. Bergman was the first to emphasize the importance of the choice and function of a reagent. He utilized barium ion to detect sulfuric acid, lime water for carbon dioxide, potassium ferrocyanide for iron and copper, silver ion for hydrochloric acid, chloride ion and hydrosulfuric acid, oxalic acid for lime, and ammonium and alkali carbonates for the precipitation of metals and oxides. Bergman's greatest contribution was the idea that a constituent did not necessarily have to be determined in its elemental condition but could be isolated in the form of a known compound.

In 1799 the book An Essay on the Analysis of Mineral Waters by Richard Kirwan appeared. This was an outstanding work, primarily because of its comprehensive list of references and the critical examination of all the work carried out in the field of water analysis since the time of Bergman. Each chemical reagent was considered as to the conditions of its use and the interpretation of the results obtained. Kirwan carried out interference studies and compiled a list of the salts adversely affecting the
determination of a particular species. However, Kirwan was not completely convinced of the usefulness of tests by reagents as opposed to the examination of the residue after evaporation. This reluctance to depend upon tests given by reagents was due to the lack of any standard of purity of the reagents and also the lack of concentration standards of the reagent solutions. In this regard it is interesting to note that Boyle saw the need for controlling the concentration of a reagent. Hoffmann, in 1736, stated that all reagents should be made up with distilled water. However, reagent solutions were commonly made up in rain water, which Marggraf claimed was the purest water obtainable.

The end of the sixteenth century began a period of discovery, colonization, procurement of raw materials, mercantilism and industrialization. During this era, the need for metals, especially iron, increased greatly. This resulted in an increased demand for the basic raw materials, iron ore and coal. The development of the steam engine led to further industrialization with an even greater need for metals. The increased need for metals resulted in more mines being opened and these new ores being examined as possible sources of metals. As a consequence of this new emphasis, the most important contribution of this period was the development of methods for the analysis of minerals. In the course of these studies many new elements were discovered and many new methods of analysis were developed. In addition to
qualitative examinations, quantitative analysis in aqueous solution was attempted for the first time. The people who carried out this work were metallurgists or even miners, and as Sweden possessed the richest ore mines it should not be surprising that chemistry flourished most successfully there. As a consequence of this relationship between industry and science it was during this period that research and technology were first integrated.

The blowpipe occupies a unique position in the history of chemical analysis (14). Although simple in design and easy to use it was an essential for qualitative analysis in earlier times. It is interesting to note that it had been in use by goldsmiths since antiquity and by the seventeenth century was widely used in the glass industry. An interesting comment is found in a book published in 1679 by Johann Kunckel (47) regarding future uses of the blowpipe: "Also many possibilities are concealed in this art; in a chemists' workshop, for example, it might prove to be very useful. For example, one use would be to melt a metal lime in order to see what metal it contains."

In some of the initial work done on the analysis of minerals, qualitative tests were conducted mainly using only the blowpipe. Often based upon an examination of the crystal form and other mineralogical features, it was possible to decide which elements were present. Thus, in the case of a silicate, it was common procedure to determine silicic acid, iron, aluminum, calcium and
magnesium; and only if the results of these analyses did not approximate one hundred per cent were any other elements tested for. In general, only the principal components of a mineral were analyzed for, as suitable methods for detecting amounts less than one per cent did not exist.

Bartholin was probably the first to indicate that the blowpipe could be used for chemical analysis. In his treatise on Iceland spar, published in 1670, he states that this mineral is burned to lime before the blowpipe. Bergman credits the first use of the blowpipe as an instrument of analysis to Anton von Swab, a Swedish metallurgist, in about 1738. However, von Swab, left no written records of his work and the extent of his studies are not definitively known.

J. A. Cramer was undoubtedly the first to record the use of the blowpipe in assay work. In his *Elementis Artis Docimasticae*, which appeared in 1739, he recommended the blowpipe for melting small pieces of metal and for the rapid analysis of minerals and ores. Cramer was also the first to use borax as a flux in blowpipe testing.

When the mineralogist A. F. Cronstedt described a new species of mineral in 1756 and gave it the name of zeolite, his use of the blowpipe was obvious. The word zeolite is a combination of two Greek works meaning "to froth" and "stone". Thus the results of the test of this mineral before the blowpipe dictated its name. Cronstedt, who founded the chemical system of mineralogy, used sodium
carbonate, borax and sodium phosphate as fusion mixtures. The first complete manual on blowpipe analysis was published by Cronstedt in 1785.

The use of the blowpipe was extended from mineralogy into inorganic chemistry by Torbern Bergman, the greatest analyst of the eighteenth century. He improved the apparatus used, noted the difference between the oxidizing and reducing flames and studied a large number of minerals and inorganic compounds. Bergman systematically recorded the reactions of the various groups of minerals with the blowpipe. He also states that a quantitative estimation is not possible with a blowpipe. Here we find the first reference to the difference between qualitative and quantitative analysis.

The blowpipe was given the form it has today by J. G. Gahn, an assistant of Bergman. He introduced the process of reducing metallic oxides with the aid of sodium carbonate on charcoal.

Berzelius was a pupil of Gahn's for ten years and all of Gahn's knowledge of the blowpipe was passed on to his friend. Through Berzelius, blowpipe analysis became an established technique in both mineralogy and inorganic chemistry. Berzelius' work culminated in the publication of his treatise on the blowpipe in 1820. The procedures as given in this book have remained essentially unchanged to the present.

Even during this period of the greatest popularity of
the blowpipe, attention was also being given to reactions in aqueous solution and the use of reagents as analytical tools. It is a historical fact that analysis in the "dry way" and "wet way" were both in use in 1700, but it was not assumed that these two methods should yield similar results. The greatest expansion of the wet method of analysis was due to Bergman, who in 1780 pioneered in the dissolution of minerals. He powdered the mineral to a finely divided state, mixed it with sodium carbonate and ignited it strongly in an iron crucible for several hours, then extracted with hydrochloric acid. Klaproth stated that a chemical analysis was invalid if any of the sample remained undissolved. He achieved complete solution of difficile samples by using more powerful fluxes, for example, potassium hydroxide.

Even when wet methods of analysis had reached a high state of development, the blowpipe often remained the only satisfactory way of deciding between several metals precipitated by the same group reagent. Thus, Thomson in 1836 having precipitated nickel, cobalt, zinc and manganese as sulfides, used the blowpipe for verification. Even Berzelius, considered by many as the greatest analyst of his day, having tested his solution with hydrogen sulfide would confirm his results with the blowpipe.

However, due to their greater convenience, rapidity, and adaptability, reactions in aqueous solution were destined to replace blowpipe analyses. It was probably the
lack of suitability of blowpipe methods for quantitative analysis that led to the universal acceptance of wet methods of analysis.

The development of classical qualitative analysis was undoubtedly due to the keen interest in the chemistry of hydrogen sulfide displayed in the late 1700's and early 1800's. It occupied the attention of the majority of the prominent analysts of the times. Bergman described the properties of hydrogen sulfide noting that it gives precipitates with solutions of silver, mercury, lead, arsenic, zinc, and iron. It is interesting that Bergman did not consider the broader analytical implications of these reactions. The reactions were used only for the detection of hydrogen sulfide and not for the qualitative detection of the metals. The possibility of using \( \text{H}_2\text{S} \) as a quantitative reagent was pointed out by Winterl who noted that lead can be completely precipitated and addition of \( \text{Na}_2\text{SO}_4 \) to this filtrate gave no precipitate.

The difficulty of preparing and conveniently dispensing hydrogen sulfide was circumvented quite early by Hahnemann, who in 1788 used hydrogen sulfide as an aqueous solution prepared by shaking calcium sulfide with a solution of tartaric acid. Prior to this means of preparation, Scheele, in 1777, had stated that the ignition of iron filings with sulfur forms, "sulphurated iron, which yields with acids bad-smelling sulphur-air." The earliest hydrogen sulfide generator was devised by the English
chemist John J. Griffin. This was later modified by Kipp, whose version first appeared in 1864.

The real importance of hydrogen sulfide as a reagent in analytical chemistry is due to Gay-Lussac (26). In 1811, he established that the effect of this reagent is dependent upon the acid strength of the medium, some metals being precipitated from strongly acidic solutions, while others were only precipitated from weakly acidic solutions. He also found that hydrogen sulfide can reduce certain metals in their highest oxidation state, elemental sulfur being precipitated in the process. He also made another interesting point, that is, metals which cannot be precipitated from strongly acidic solutions, are precipitated if potassium acetate is added to the solution, because "by the effect of this the metal is transformed into an acetic acid compound." This is the earliest recorded application of the buffer principle. In basic media, as Gay-Lussac pointed out, the majority of the metals give precipitates with hydrogen sulfide.

The first really general and comprehensive textbook on analytical chemistry was written by C. H. Pfaff (60). Here he lists the metals that form precipitates with hydrogen sulfide in acidic solution. He also notes the sensitivities of these reactions. This book was unique in that it was a critical evaluation of the analytical methods of the day and also gave accurate references to the literature. Pfaff's book contained sections on the preparation and uses
of analytical reagents; apparatus and technique; and the analysis of minerals, salts, metals, mineral waters and gases.

It is interesting to note that Pfaff recommends a new method of water analysis proposed by Murray which consisted of determining the principal constituents in water by the addition of various reagents without previous evaporation of the sample. For example, barium chloride was added to precipitate the sulfate and carbonate ions. This combined precipitate was subjected to an acid treatment and the carbonate determined by difference. Chloride ion was precipitated with silver nitrate, calcium ion with oxalate and magnesium ion with phosphate.

Pfaff also recommended that an unknown solution be examined with reagents that give characteristic reactions with various groups of chemical species: hydrogen sulfide, ammonium sulfide, potassium ferrocyanide, ammonium cyanide, ammonium hydroxide, potassium hydroxide and potassium oxalate being mentioned as group reagents. These reagents are basic substances used in the qualitative analysis scheme for cations today.

Thus, both reagents and reactions were available at this time and all that was required was an arrangement into some systematic order so that a qualitative scheme of analysis could be developed.

One of the first of the systematic group methods was due to Klaproth in 1789. Ammonium hydroxide was used as a
group precipitant and potassium hydroxide was used to separate the amphoteric hydroxides of aluminum and beryllium.

Other attempts at establishing systematic group analysis were made by Rose, Thomson and Berzelius in the period 1830 to 1840. These schemes used basically the same group precipitants as their predecessors but had been extended to include many of the elements being discovered during this period. It is interesting to note that before 1800 there were only twenty-two metallic elements known. In the period from 1800 to 1840, twenty new metallic elements were found. The discovery of this many elements in such a short period of time attests to the intense interest in qualitative analysis prevalent at this time.

After Pfaff's book, the next analytical text of any consequence was the Handbuch der analytischen Chemie written by Heinrich Rose in 1829. In this work, Rose originated the treatment found in current qualitative analysis books of considering each element individually and discussing its analytical reactions. Prior to this, the reagents had been considered as separate entities and the reactions of the individual elements were summarized for each reagent.

Rose presented a general scheme of cation analysis very similar to that in use today. He precipitated silver, mercury, and lead with hydrochloric acid. Hydrogen sulfide was the Group II precipitating reagent and ammonium sulfide was used for the Group III ions of iron, nickel, cobalt,
zinc, manganese and aluminum. The filtrate from this group was treated with ammonium carbonate and the ions of barium, strontium, and calcium were precipitated. In the soluble group, magnesium was precipitated with sodium phosphate and potassium with platinum chloride.

Rose's book was the first to describe the reactions of the individual elements and also the first to present a systematic course of analysis. However, these firsts were apparently more than outweighed by its shortcomings. These deficiencies included an overwhelming mass of information presented and a lack of order in its presentation. It was no doubt the quickness of Fresenius in recognizing these faults that earned for him the reputation for being the developer of systematic qualitative analysis. In the preface of his book Fresenius (24) stated, "I could perceive that in the great wealth of material, presented in the classical work of Rose, beginners are losing their way, as this very fine book is not very clear to them."

Another scheme of some importance was published by Thomson in 1836. Ammonium hydroxide, hydrogen sulfide, ammonium carbonate, potassium sulfate and ammonium oxalate were used as group precipitants. The blowpipe was used for confirmatory tests within the groups.

In 1841, C. R. Fresenius, a young student of twenty-two at Bonn, published his Anleitung zur qualitativen chemischen Analyse. This book was undoubtedly one of the most successful books ever written on analytical chemistry.
The second edition appeared in 1842, the third in 1844, the fourth in 1846, and by 1852 the seventh edition had appeared. The book had reached its sixteenth edition by 1897. There were minor revisions made in each edition, but the original plan of the book was so complete that no major revision was ever required. This work was of such consequence that English, French, Italian, Spanish, Dutch, Hungarian, Chinese and Russian editions were published.

Fresenius originally wrote his book for his own use when he was a student. At this time in the development of chemistry there was no practical laboratory instruction and he was working in the private laboratory of his professor. Since he was working alone without formal laboratory supervision the notes he made came as a natural consequence of these circumstances. His professor encouraged him to publish these notes as he realized their true value.

The original qualitative analysis scheme of Fresenius was essentially the same as is in use today. Only the most important metals were selected for inclusion. It is interesting to speculate upon the effect of the selection of this particular group of elements has had on qualitative analysis. For even today, few chemists have any idea into which group some of the less common metals, such as vanadium or titanium, would be placed.

Fresenius also included a scheme for the detection of anions in his book. These tests today also remain basically unchanged.
It is apparent that Fresenius realized that his schemes could and would be used in a "cook-book fashion", for in the preface to his book he cautioned that any scheme of analysis should be regarded only as a guide, and thought and experience were invaluable in the success of any analysis. Methods had to be varied according to the type of material to be examined. He obviously placed a great deal of importance upon experience because he considered one hundred practical analyses a minimum number to obtain an adequate knowledge of the method. In his words (24), "The first twenty samples should contain only one water-soluble salt, of which only the cation need be identified. Among these samples there should be in addition to soluble salts several samples which require fusion. The next fifteen samples should contain several cations in aqueous solution, followed by a further fifteen samples of solid salt mixtures. The last twenty analyses should be carried out on naturally occurring substances, water, earth, minerals, alloys, etc."

The blowpipe was listed among the equipment recommended by Fresenius and was used in the confirmatory tests for the metals of Groups II and III.

The development of the schemes of qualitative analysis was a significant accomplishment in the evolution of chemistry. This was particularly so, in light of the enormous amount of chemistry involved whose theoretical basis had not been enunciated. One has only to remember
that the theory of electrolytic dissociation was postulated in 1884 by Arrhenius; the modern theory of coordination chemistry had its beginnings with Werner in 1892; the whole problem of equilibrium reactions was studied by Guldberg and Waage between 1864 and 1879; it was in 1892 that Bancroft arranged oxidizing and reducing agents in order of strength based upon their electrode potentials; and Ostwald introduced the concepts of dissociation constants and the solubility product as late as 1894. The first text in which qualitative analysis was treated entirely on the basis of the Arrhenius theory was written by Bottger in 1898.

Because of the toxicity and odoriferous nature of hydrogen sulfide there have been numerous attempts to devise a systematic method of analysis without the use of this reagent. However, in spite of these failings, the use of hydrogen sulfide or sulfide-producing compounds is still overwhelmingly favored in the qualitative cation schemes of today. A recent survey of five hundred colleges revealed that 31.1% used hydrogen sulfide, 64.7% used thioacetamide and only 4% used non-sulfide schemes (40).

There have been approximately three thousand papers and books dealing with the \( \text{H}_2\text{S} \) system. But in spite of this tremendous volume of work the basic scheme of Fresenius remains unaltered. Shortly after the appearance of Fresenius's scheme, Himly proposed that sodium thiosulfate be substituted for hydrogen sulfide (39). This was
the first of many schemes offering H$_2$S substitutes. Other sources of sulfide, such as alkali sulfides, organic sulfides, insoluble metal sulfides, and phosphorus pentasulfide have been suggested. In addition, various organic compounds have been proposed as sources of sulfide: thiourea, thioacetic acid, sodium diethyldithiocarbamate, and ammonium dithiocarbonate among others. All of these were only partially successful but thioacetamide, which was first proposed for analytical purposes by Iwanof in 1934 (42), has proven to be acceptable. The fundamental studies of Barber, Flaschka, and Swift have substantiated its value as a hydrogen sulfide substitute. The possibility of replacing gaseous hydrogen sulfide with thioacetamide in qualitative procedures was initially pointed out by Barber and Grzeskowiak (1) in 1949. In 1951, a complete scheme of qualitative analysis using thioacetamide was published by Lipiec and Pryszczewska (51). The first qualitative analysis text utilizing thioacetamide was that of Barber and Taylor (2).

There have been numerous efforts made to use hydroxides, sulfates, carbonates, phosphates, oxalates and chromates as group precipitates. There are inherent difficulties associated with most of these reagents. For example, phosphate tends to interfere with intragroup separations and inhibits many of the confirmatory tests. Depending upon where they are used in the scheme, hydroxide and carbonate can yield unwieldy sized groups of ten to
twelve metals.

A study of the numerous qualitative analysis schemes that have been published since that of Fresenius enables one to reach the conclusion that the same reagents, procedures and ideas are met time after time in a myriad of modified combinations. It becomes obvious there are only a limited number of stock procedures and reagents with which a system of qualitative analysis can be formed. Success is in large measure due to the skill shown in the selection and arrangement of these stock procedures.

A study of some of the schemes published, leads to the formulation of the following list of requirements necessary for the development of the ideal classical qualitative scheme:

1. group precipitations should be quantitative, i.e., any one ion should be found in only one group.

2. each of the group precipitants should react with approximately the same number of metals, i.e., there should not be a disproportionate share of ions in any one group.

3. group precipitations should not interfere with subsequent confirmatory tests within the group.

4. reagents should be stable and relatively inexpensive.

5. ions susceptible to hydrolysis or precipitation during pH changes should be separated as early in the scheme as possible.

The first completely sulfide-free scheme was proposed in 1867 (90). Division into the major groups was
accomplished with hydrochloric acid, sulfuric acid and metallic zinc in an acidic medium.

Probably the most widely used non-sulfide scheme is the one published in 1953 by West, Vick and LeRosen (86). Some of the advantages claimed for this scheme are: group separations are quantitative, the procedure is rapid, no toxic fumes are generated, results obtained are as good as those with sulfide separations and the scheme is pedagogically sound. Group precipitants used are hydrochloric acid, ammonium benzoate and sodium benzoate, ammonium fluoride, and sodium hydroxide. Although there seems to be a slackening of the feverish activity that characterized qualitative analysis for some time, interest has not died completely. Recently there have been several attempts to develop qualitative schemes in which the groups and subgroups are ordered as they are in the periodic table. One such recent scheme is that of Rich (62) in which the hexacyanocobaltate (III) ion is utilized as a group precipitant and a thiourea hydrolysis acts as a source of sulfide ions. Titanium and uranium are included in this scheme along with the usual metals.

Swift and Schaefer (72) have developed a qualitative scheme in which the elements are divided into three major groupings based upon the basic, amphoteric or acidic properties of the elements. This is a more elaborate undertaking than the conventional qualitative scheme since, in actual fact, it is a combined cation and anion scheme.
It includes titanium and vanadium along with the traditional metals and also provides means of detecting most of the common anions.

In terms of completeness, reference has to be made to the classical work of Noyes and Bray (56) published in 1927. This scheme incorporates procedures for the separation and identification of sixty-five metals. All methods are based on classical inorganic chemical reactions. There are no spot tests or synthetic organic analytical reagents used.

The history of spot test analysis can be dated from the first spot test reaction (45) developed by Plinius (23-79 A.D.) which was used to detect the presence of ferrous sulfate in verdigris. He used a paper impregnated with nut gall, which was blackened when placed in contact with the substance containing iron.

Cassius (45) in 1632 developed a method for the detection of gold based upon the production of a solution of colloidal gold and tin hydroxide by the treatment of auric chloride with stannous chloride. This is the "Purple of Cassius" test.

Tachenius found in 1666 that a drop of a mixture of gold solution with tincture of nut gall, when placed upon paper, produced a metallic spot. He also attached value to certain reactions as tests for different substances. In addition, he stressed the importance of distinguishing precipitates by their colors (45).
One of the earliest published records of the use of spot test methods appeared in a paper by Schiff (68) in 1859. He used filter paper impregnated with silver carbonate to detect uric acid in urine. A drop of the sample produced a brown fleck of free silver. This appears to be the earliest precise description of a spot test, because the great sensitivity of this reaction was determined in the same manner as is presently done, i.e., by testing a series of dilute solutions of uric acid.

The fundamental work for that portion of spot test analysis in which filter paper is used as the reaction medium is found in a study by Schonbein (70) in 1861. He showed that when aqueous solutions rise in strips of filter paper, the water precedes the dissolved material, and the relative height of the capillary rise of solutes can differ enough to make possible the detection of the cosolutes in separate zones. These observations gave impetus to the classic studies of Goppelsroeder (1861-1907), which were compiled in his Kapillaranalyse, published in 1910. He made a very extensive study of the capillary rise of solutions and the capillary spreading of drops of solution in filter paper. He also investigated the analytical use of these effects, particularly in the examination of organic liquids, dissolved compounds, and dyes. His publications also contain references to the capillary spreading of inorganic salts. A large mass of statistical material was collected on the heights and
rates of ascent of organic liquids and solutions of organic liquids and solutions of organic compounds, in strips of filter paper and other fibrous capillary media. He demonstrated that the characteristic data furnished by these systems are dependent on the nature of the solutes, their concentration, the capillary medium, the temperature, and the period of the capillary rise. He coined the term "capillary analysis" for the analytical utilization of the capillary pictures produced by the spreading through filter paper of liquids or solutions.

Bayley (5) described a method of analysis in which a drop of solution was placed upon filter paper, and concentric rings of varying concentrations of substances were formed. He showed that this phenomenon depended upon the concentration and nature of the dissolved material, as well as on the type of paper employed. Using this technique, he described a method for the detection of cadmium in the presence of copper. That there is a limiting distance of travel on the paper for a dissolved substance was noted in 1885 by Lloyd.

Reed (61) noted that the zones corresponding to the separation of the solutes, was due to their different capillary migration velocities. He also recognized the dependence of these phenomena upon the concentration of the solution.

Trey (76) was the first to show that it is possible, in a systematic analysis, to detect two elements in the
presence of one another through adsorption. He found that in an ammoniacal solution, containing copper and cadmium, the cadmium forms the outer ring and may be detected by treatment with ammonium sulfide.

Krulla (46) proposed an interesting method of analysis based upon capillarity. He found that when solutions of salt mixtures containing different ions were allowed to rise in filter paper strips, each component was adsorbed to the same extent as if alone in the solution. The addition of similar ions, however, caused a repression of the capillarity of the ion in question. This fact was used in the following method: to the solution to be tested, different ions were added as long as a distinct decrease in capillarity occurred. Each ion which caused this decrease was, therefore, shown to be present in the test solution. Extensive investigations of the heights to which solutions of salts rose in filter paper were made by Skraup and co-workers (71). They determined a relationship to various chemical and physical factors, such as dissociation and hydrolysis, as well as the temperature of the solution and the ash content of the paper. Salts were placed in two classes with respect to their behavior toward filter paper. The first class contained the alkali and alkaline earth salts, the second consisted of the heavy metal and aluminum salts and also complex salts. While the salts of the first class in aqueous solutions rose almost as high as the solvent and were independent of
concentration with respect to height of ascent and adsorption, those of the second class did not rise as high as the water, and the height decreased with increasing dilution. Cations of a similar nature rose to about the same height.

The history of the study of capillary phenomena is important because of the impetus given to the development of spot test analysis by these investigations.

Due to the extreme importance of the discovery of the analytical utility of organic reagents to the development of spot test methods, some mention is due in this regard.

Many books refer to dimethylglyoxime as the first organic analytical reagent. Dimethylglyoxime was introduced by Tschugaelf in 1905 (77). In fact, the first analytical reagent of which there is a written record, the gallnut extract liquid, is an organic reagent. There were several other organic reagents in use before dimethylglyoxime: oxalic acid, tartaric acid, and starch being worthy of mention.

When organic analytical reagents are referred to, it is usually the synthetic and not the naturally occurring ones that are being considered.

The Griess reagent can be regarded as the first specific organic reagent. It was recommended for the detection of nitrite in 1879 (32). α-Nitroso-β-naphthol was recommended in 1885 by Ilinski and Knorre for the determination of cobalt (41). This was the first synthetic
organic reagent to be used in gravimetric analysis.

The number of organic reagents increased tremendously with the appearance of the first reagents. Diphenylcarbazide (1900), benzidine (1903) and cupferron (1909) were some of the first important reagents to appear.

Since 1918 Feigl and his co-workers have been applying these special techniques and the use of selective and specific reactions to the analysis of cations and anions and to many organic compounds. A specific reaction has been defined as a reaction which, under the experimental conditions employed, is indicative of only one chemical species; while those indicative of a comparatively small number of substances are termed selective reactions (18).

The spot test method has been used in the systematic investigation of mixtures. In 1921, Feigl and Stern (21) utilized spot tests in the confirmation of the ammonia and ammonium sulfide group of cations, i.e., Fe(III), Cr(III), Al(III), Ni(II), Co(II), Mn(II), Zn(II), and U(VI). In a later paper (20), spot tests were used in the detection of the metals of the hydrogen sulfide group.

Hauser (35) in 1921 was the first to suggest the use of spot test methods for systematic analysis. He used the tests described by Feigl and Stern for the analysis of the ions in Group III of the hydrogen sulfide system.

Tananaeff in the 1920's devised many methods for the simultaneous detection of various metals. He published the
first book on spot test methods in 1927.

In 1929, schemes were published by Gutzzeit (33), and by Heller and Krumholz (38). The latter scheme used the familiar groups of the Fresenius system of detection. In all, fifteen cations were detected after division into HCl, $\text{H}_2\text{S}$ and $(\text{NH}_4)_2\text{S}$ groups. Both paper and porcelain spot plates were used as reaction media. The most ambitious work of this fledgling technique was that of Gutzzeit who introduced several new innovations. Adherence to the classical mode of separation was abandoned and division into groups was based solely on solubility principles. The spot tests were then performed on the individual ions within these groups without prior separation. In addition, Gutzzeit was the first to include anions in a detection scheme. Practically all of the common anions were included.

Shortly thereafter, practical use was made of this pioneering work when a scheme (36) was developed for the analysis of the common metals usually found in alloys. By using this technique it was claimed that only one-fiftieth of the quantity of sample required for macroanalyses was needed and the procedure required only one-fourth as much time.

Van Nieuwenburg (79) although reverting to the usual qualitative scheme type of separation did present a complete scheme of detection for all of the common cations and anions. This scheme was developed primarily for
pedagogical purposes.

In more recent times, the most comprehensive use of spot test methods in a systematic scheme was the work of Miller (53). Utilizing the semimicro Noyes and Bray scheme, liberal use was made of spot tests as confirmatory tests. Likewise, Parks (57) using a modified Noyes and Bray system employed the spot test technique in confirmatory tests.

A book has been written (8) which gives methods of detection for cations with spot test methods. Tests are given for the detection of each metal in the presence of one hundred to one thousand times larger quantities of any other metal or combination of metals.

The use of spot tests for detection purposes is admirably suited to the ring oven technique of Weisz (81). Unsurpassed flexibility can be achieved in the chemical separation of complex mixtures using the separatory capabilities of the ring oven itself combined with prior separatory techniques, e.g., solvent extraction. A scheme for the separation and identification of thirty-five ions in a single drop of unknown using a combination of the solvent extraction and ring oven techniques has been developed (85). Successive extractions of the metals into various organic solvents as chlorides, thiocyanates, acetylacetonates, and diethyldithiocarbamates effects separations into four groups. Further separation of each group is then accomplished through use of the ring oven. A fifth group
consists of the aqueous solution of the residual ions. Individual confirmatory tests are applied to the separated ions.

At one time in the development of spot test analysis it was felt that the ultimate goal should be the discovery of a specific reagent for every ionic species. Some specific reagents have been found. But with the growth of spot test analysis came a deeper understanding of the nature of coordination and chelation and the subsequent realization that this would be an unattainable ideal. More importantly, it was realized that by judicious choice of pH, solvent, complexing agent, masking agent, redox potential, oxidation state and reaction media, specific reaction conditions could be attained. Hence the trend today is to seek a conditioned reaction to achieve specificity. At the opposite end of the spectrum, from the concept of a specific reagent for every detectable species, is the idea of a single reagent capable of detecting all cationic species. It is reported that 1-aminoanthraquinone-2-carboxylic acid reacts with "all cations" with the exception of potassium, sodium, lithium and ammonium ion to form red insoluble salts (12). Fisher (22) used dithizone with pH alteration, masking with cyanide and extraction into organic solvents to separate and identify many cations. Another "universal reagent" is composed of a mixture of rubeanic acid and trisodium pentacyanoamminoferrate (III). This mixture forms colored
salts insoluble in acetic acid with twenty-three metal ions (34).

Despite the rapid development of modern instrumental methods of detection and determination there is still need for rapid, sensitive and dependable means of detection using less expensive means. The spot test method is an important means toward this end.

Throughout all of these previously mentioned schemes, it will be noticed that in every case the spot tests were used as individual tests. Therefore, as an extension of this technique of individual test reactions, it was felt that a rapid, survey scheme of detection using spot test methods would fulfill a definite need. In this system of analysis, emphasis would be on detection by groups of ions rather than individual ions. This exploratory or survey scheme would serve as a valuable source of information in a first examination of an unknown. The value of such a scheme might conceivably lie more in the knowledge of what is not present in the material rather than what is present.

Work along these lines was reported (6) in 1957 by Berger and Elvers. The sample was mixed with ammonia-ammonium chloride buffer and Eriochrome Black T indicator. The effects of the addition of KCN, sodium diethyldithiocarbamate and disodium EDTA were observed. The sample was then mixed with sodium acetate-acetic acid buffer and Eriochrome Cyanine R indicator and the effects of KCN, sodium diethyldithiocarbamate, disodium salt of EDTA,
formaldehyde and magnesium salt of EDTA were observed. Twenty metal ions, commonly found in the conventional qualitative scheme, were included in this study.
II. EXPERIMENTAL

A. SAMPLE PREPARATION AND MANIPULATION

One of the truly important aspects of any analytical procedure is sample preparation. This consists of the dissolution of the sample and the conversion of the dissolved sample into a form suitable for appropriate methods of detection and/or determination. It should be noted here, that treatment prior to actual detection of the chemical species involved has considerable importance as to whether the species in question can be detected or not. As an example of this point consider the following. The qualitative analysis of aluminum is desired in a complex silicate. Hydrofluoric acid is used in dissolution of the sample. It is well known that aluminum forms the very stable anionic hexafluoroaluminate complex. Thus, a detection method used for the simple Al(III) ion should not be expected to be suitable for the aluminum in this sample. Indeed, the expedient of adding complexing agents to effectively remove reactive species is widely used in qualitative analysis, especially spot test analysis. The advantage here is the elimination of separations with accompanying loss of material. Since only small amounts of detectable substances are initially present, this is a very desirable analytical innovation.

From the above discussion, the importance of proper sample preparation should be evident. The following
discussion summarizes current thinking (9, 87) on sample
dissolution. Conversion into an appropriate chemical
species, incompatibility of various ions and means of
eliminating various troublesome anions are also considered.

SAMPLE DISSOLUTION:

1. If the sample is soluble in water, it is ready
   for analysis without further treatment. A
   sample of 10 to 100 mg. in 10 ml. of water
   should give a solution sufficiently concen­
   trated for most analyses.

2. If the sample is insoluble in water, it may be
dissolved by attack with acids or fusion
with sodium carbonate or potassium pyro­
sulfate, or by a combination of both these
methods.

REMOVAL OF ORGANIC MATTER:

Due to the complexing ability of various organic
anions and molecules: tartrate, citrate, oxalate, malonate,
various polyhydroxy compounds, EDTA; it is well to remove
all organic matter from the sample. This is effectively
accomplished by destructive oxidation. In general, there
are four methods which may be used.

1. combustion at a red heat. This method excludes
   analysis for mercury, arsenious, antimonous
   and ammonium salts. If chlorides are
   present some iron will be lost. Certain
   acids are expelled and oxidizing agents
   reduced. Complete combustion, without the
   use of oxidizing agents, is the method
   recommended to minimize loss and involving
   the least change of the sample material.

2. oxidation with potassium chlorate and hydro­
   chloric acid. This method does not wholly
   remove organic matter, but so far disinte­
   grates and changes it that the filtrate
   will give the detection tests. All ions
are oxidized to their highest oxidation state.

3. the action of sulfuric and nitric acids. This method leaves behind most of the metals. There is some loss of mercury and arsenic if chlorides are present in considerable quantity. Osmium, ruthenium, and rhenium may be lost by volatilization as the oxides. The sample is first heated with an excess of sulfuric acid, nitric acid is then added in small portions, and the temperature of the mixture is gradually raised.

4. the action of nitric and perchloric acids. Probably the best method of all. Due to the explosive nature of hot, concentrated perchloric acid, the initial oxidation process must be carried out with only nitric acid. In the final stages of oxidation, perchloric acid is added and the complete destruction of organic matter is accomplished. In addition to the rapid and complete oxidation of organic materials, this method has an additional advantage, i.e., the nitrate and perchlorate ions have the least tendency to complex as compared with any other anions. Many volatile weak acids would be driven off by this treatment. All nitric acid may be removed by heating the perchloric acid solution to its boiling point.

Charlot (9) proposes the following procedure whenever interfering anions or strong oxidizing substances are likely to be present. An excess of hydrochloric acid is added and the solution is taken to dryness in a Pyrex beaker on a water bath. The dry residue is moistened with concentrated hydrochloric acid and again evaporated to dryness on the water bath. During this process, silica is precipitated and a number of acids are destroyed or driven off. The acids driven off include: HOCl, HClO₃, HBr, HOBr,
HBrO₃, HF, HI, H₂S, H₂SO₃, H₂S₂O₃, H₂S₂O₈, HNO₂, HNO₃, H₂CO₃, HCN and HSCN. In addition the following oxidants are reduced: MnO₄⁻, Cr₂O₇⁻², SeO₄⁻² and TeO₄⁻².

The following chlorides may be partially or completely lost during this procedure: AsCl₃, HgCl₂, SnCl₄, GeCl₄.

If the test solution contains strong reductants, bromine is removed by warming the solution.

A test for strong reductants consists of the following: use a solution of methylene blue in 0.1 N HCl. One drop of the reagent and one drop of the unknown are placed on a white spot plate. Disappearance of the color indicates the presence of a reducing agent, e.g., Sn(II), Ti(III), Cr(II), V(IV), Fe(II), or U(IV).

The use of ion-exchange resins for the preparation of solutions prior to qualitative analysis has been shown to be quite useful. When either soluble or sparingly soluble salts are mixed as a slurry with a strong cation exchange resin, the cations are retained by the resin. The anions of the salts remain in solution and are separated by filtration. Treatment of the resin with nitric or perchloric acid yields a solution containing all of the cations from the salts. In theory, at least, there is a simple subdivision of the unknown cations and anions into two solutions. A major advantage is that this is accomplished without the introduction of any troublesome ions. When anions of volatile weak acids are present they may be lost during the treatment of the unknown with the
resin. Good results obtained with these insoluble salts: barium sulfate, calcium fluoride, cadmium sulfide and lead chromate, attest to the usefulness of this technique (44, 63).

B. ELIMINATION OF INTERFERING ANIONS

It should be noted that some anions are inherently incompatible. If the past history of the sample is known a knowledge of the anions present would result in the removal of certain incompatible ions from consideration. Thus, the known presence of oxidizing anions excludes the presence of strong reducing anions. In addition, the presence of certain oxidizing or reducing agents mutually exclude other oxidizing or reducing agents. Thus, hypoiodite is not stable in the presence of hypochlorite or hypobromite, since it is oxidized to iodate. Similarly, hypobromite is not stable in the presence of hypochlorite. The pH of the solution is an important consideration in the interactions between anions. The nitrate and chromate ions are quite weak as oxidizing agents in basic solution, but in acid solution they become strong oxidizing agents. Thus these oxidizing anions may coexist with reducing ions in basic solution but not in acid solution. However, some anions have oxidizing ability in both acidic and basic solutions, a common example is the permanganate ion.

In addition to these general treatments for the elimination of interfering anions, there are specific
reactions which may be used to remove particular anions if they are definitely known to be present in the sample.

The following reactions are given as examples for the removal of specific anions and molecules (75, 18, 52, 80, 54). In all cases, reactions were selected such that products were formed, to as great an extent as possible, which did not interfere with subsequent tests. Reactions yielding water, gases, and unreactive molecular species are ideal from this standpoint.

ELIMINATION OF INDIVIDUAL INTERFERING ANIONS:

1. ACETATE

Acetate may be removed from solution by the addition of dilute or concentrated sulfuric acid. If ethyl alcohol is added to a sulfuric acid solution containing acetate and the solution warmed, ethyl acetate is formed.

2. ARSENITE, ARSENATE

Arsenic may be removed from sulfuric acid solution by boiling with barium thiosulfate

\[ 2\text{AsO}_3^- + 3\text{Ba}^{++} + 3\text{S}_2\text{O}_3^- + 6\text{H}^+ \rightarrow \text{As}_2\text{S}_3 + 3\text{BaSO}_4 + 3\text{H}_2\text{O} \]

\[ 2\text{AsO}_4^{3-} + 5\text{Ba}^{++} + 5\text{S}_2\text{O}_3^- + 6\text{H}^+ \rightarrow 2\text{As}_2\text{S}_5 + 5\text{BaSO}_4 + 3\text{H}_2\text{O} \]

All compounds containing arsenic can be reduced, in sulfuric acid solution, by means of metallic zinc to the volatile and extremely poisonous arsine, AsH₃. This reaction takes place readily at ordinary temperatures. The arsenic sulfides are reduced more slowly than the oxides.

\[ \text{AsO}_3^- + 3\text{Zn} + 9\text{H}^+ \rightarrow 3\text{Zn}^{++} + \text{AsH}_3 + 3\text{H}_2\text{O} \]
AsO$_4^{-3}$ + 4Zn + 11H$^+$ $\rightarrow$ 4Zn$^{+2}$ + AsH$_3$ + 4H$_2$O

3. AZIDE

Hydrazoic acid, HN$_3$, is completely removed from dilute mineral acid solution at 37° C.

Nitrous acid also reacts with hydrazoic acid according to the reaction
HN$_3$ + HNO$_2$ $\rightarrow$ N$_2$O + N$_2$ + H$_2$O
This reaction is very rapid.

Solutions of sodium azide and iodine react with vigorous evolution of nitrogen if traces of sulfide or thiosulfate are added.

2N$_3^-$ + I$_2$ $\rightarrow$ 2I$^-$ + 3N$_2$

4. BORATE

Repeated evaporation, on a water bath, of a borate solution with either concentrated sulfuric or hydrochloric acid and methyl or ethyl alcohol, will liberate the corresponding volatile ester.

H$_3$BO$_3$ + 3ROH $\rightarrow$ R$_3$(BO$_3$) + 3H$_2$O

Boron fluoride is sufficiently volatile so that it may be removed by evaporation with hydrofluoric acid alone or by a mixture of sulfuric and hydrofluoric acids.

Borates may also be removed effectively from solution by forming the stable tetrafluoro complex according to the following reaction.

H$_3$BO$_3$ + 4F$^-$ $\rightarrow$ BF$_4^-$ + 3OH$^-$
5. BROMIDE

Bromide is oxidized by concentrated sulfuric acid. Heating will aid the reaction.

\[ 2\text{Br}^- + \text{SO}_4^{2-} + 4\text{H}^+ \rightarrow \text{Br}_2 + \text{SO}_2 + 2\text{H}_2\text{O} \]

Oxidation is also effected with peroxide or persulfate in dilute sulfuric acid solution.

\[ 2\text{Br}^- + \text{S}_2\text{O}_8^{2-} \rightarrow \text{Br}_2 + 2\text{SO}_4^{2-} \]
\[ 2\text{Br}^- + \text{H}_2\text{O}_2 + 2\text{H}^+ \rightarrow \text{Br}_2 + 2\text{H}_2\text{O} \]

The free bromine may be removed from solution by evaporation or by extraction with carbon tetrachloride. The addition of sulfosalicylic acid to a solution containing bromine removes the bromine by the immediate formation of colorless bromosalicylic acid.

Chlorine water, of course, will also oxidize bromide to elemental bromine.

6. BROMATE

Upon warming, a solution of bromate is reduced by an added solution of sodium nitrite according to the equation

\[ \text{BrO}_3^- + 3\text{NO}_2^- \rightarrow \text{Br}^- + 3\text{NO}_3^- \]

7. CARBONATE

Hydrogen ion from either dilute or concentrated acids of even moderate strength liberates carbon dioxide from either the solid carbonate or a carbonate solution.

8. CHLORATE

Reducing agents reduce chlorate to chloride in acid solution, for example:
ClO$_3^-$ + $3$NO$_2^-$ $\rightarrow$ $3$NO$_3^-$ + Cl$^-$

Hydrogen peroxide in the presence of a small amount of nitric acid completely reduces chlorate ion to chloride.

9. CHLORIDE

Hypochlorite in acid solution oxidizes chloride ion

Cl$^-$ + ClO$^-$ + $2$H$^+$ $\rightarrow$ Cl$_2$ + H$_2$O

10. CHROMATE, DICHROMATE

Chromate ion may be quantitatively precipitated from a dilute acetic acid solution with barium ion.

It is conceivable that traces of chromate or dichromate could be removed from solution by the addition of hydrogen peroxide in the presence of dilute sulfuric acid which gives the deep blue color of chromium peroxide extractable by amyl alcohol or diethyl ether.

If a chromate solution is acted upon simultaneously by ethyl alcohol and hydrochloric acid (the reaction takes place upon warming), the alcohol is oxidized to acetaldehyde. The excess alcohol and the acetaldehyde are easily removed by boiling the solution.

Cr$_2$O$_7^{2-}$ + $3$C$_2$H$_5$OH + $8$H$^+$ $\rightarrow$ $2$Cr$^{3+}$ + $3$CH$_3$CHO + $7$H$_2$O

11. CITRATE

Citrate may be destroyed by repeated evaporation with concentrated nitric acid.

12. CYANATE

Cyanates are decomposed by the action of dilute
sulfuric acid.

\[ \text{CNO}^- + 2\text{H}^+ + \text{H}_2\text{O} \rightarrow \text{CO}_2 + \text{NH}_4^+ \]

Cyanates treated with bromine in aqueous solution gives bromide ion, nitrogen gas and carbon dioxide.

13. CYANIDE

Dilute sulfuric acid decomposes solutions of all soluble cyanides, liberating hydrogen cyanide gas. Insoluble cyanides are decomposed by dilute sulfuric acid only upon warming.

The treatment of cyanide ion with a five-fold excess of a strong hydrogen peroxide solution yields bicarbonate ion and ammonia gas upon warming.

14. EDTA (ETHYLENEDIAMINE TETRAACETIC ACID)

Repeated evaporation with concentrated nitric acid will destroy EDTA.

15. FERRICYANIDE

Ferricyanide ion is decomposed by concentrated sulfuric acid upon warming with the formation of ammonium ion and carbon monoxide.

Heating ferricyanide with persulfate ion in an aqueous sulfuric acid solution causes decomposition of ferricyanide. The products produced include hydrogen cyanide, ammonia and cyanogen.

16. FERROCYANIDE

Concentrated sulfuric acid decomposed ferrocyanide solutions completely upon warming.
Fe(CN)₆⁻⁴ + 12H⁺ + 6H₂O → 6CO + 6NH₄⁺ + Fe⁺²

Boiling ferrocyanide solutions causes decomposition with hydrogen cyanide being evolved.

Ferrocyanide is oxidized to ferricyanide by hydrogen peroxide or nitrite in acid solution.

17. FORMATES

With dilute sulfuric acid formates yield volatile formic acid. Ethyl alcohol and concentrated sulfuric acid produce ethyl formate upon warming with formates.

18. FLUORIDE

Fluoride ion forms stable complexes with some metal ions. Among the most stable are those formed with aluminum, beryllium, zirconium and iron (III).

Thorium (IV) ion and calcium ion give very insoluble precipitates with fluoride.

Hydrogen fluoride is volatilized by repeated evaporation to dryness with concentrated hydrochloric acid.

Fluoride may also be volatilized by heating a solution containing concentrated sulfuric acid and a silicate or finely divided silicon dioxide. The resulting gas, silicon tetrafluoride, is readily lost from solution.

4F⁻ + SiO₂ + 4H⁺ → SiF₄ + 2H₂O

19. HYDROGEN PEROXIDE

Extensive use of H₂O₂ has been made in this list of reactions. Therefore, it is conceivable that a test might be needed for the elimination of an excess of H₂O₂. One
such reaction that could prove useful is between hydrazine and peroxide.

\[ 2H_2O_2 + N_2H_4 \rightarrow N_2 + 4H_2O \]

20. HYPOBROMITE

Hypobromite reacts quantitatively with excess ammonia according to the following reaction

\[ 3BrO^- + 2NH_3 \rightarrow 3Br^- + N_2 + 3H_2O \]

Hydrogen peroxide reacts instantaneously with hypobromite to give bromide ion, oxygen and water.

Quantitative yields of Br\(^{-}\) and BrO\(_3\)\(^{-}\) are obtained from alkaline hypobromite solutions at temperatures above 50° C. due to disproportionation.

21. HYPOCHLORITE

Hypochlorites are decomposed by acids (even carbonic), for example:

\[ 4ClO^- + 4H^+ \rightarrow 2Cl_2 + O_2 + 2H_2O \]

or by hydrogen peroxide

\[ ClO^- + H_2O_2 \rightarrow Cl^- + O_2 + H_2O \]

Ammonia reacts with hypochlorite to produce chloride ion, nitrogen gas and water.

22. HYPOIODITE

Traces of hypoiodite are completely destroyed by excess ammonia.

Hypoiodite ion is unknown in solution due to its rapid rate of disproportionation.
23. IODATE

Iodate can be reduced with many reducing agents, the reactions with hydrogen peroxide and oxalate should be especially useful.

\[
2\text{IO}_3^- + 5\text{C}_2\text{O}_4^{2-} + 12\text{H}^+ \rightarrow \text{I}_2 + 10\text{CO}_2 + 6\text{H}_2\text{O}
\]
\[
2\text{IO}_3^- + 5\text{H}_2\text{O}_2 + 2\text{H}^+ \rightarrow \text{I}_2 + 5\text{O}_2 + 6\text{H}_2\text{O}
\]

Since iodine may be either volatilized or extracted, it can be effectively removed from solution.

It should be noted that the presence of excess \(\text{H}_2\text{O}_2\) could result in the formation of iodide ion rather than elemental iodine.

24. IODIDE

Iodide is oxidized by iodate, nitrite and peroxide according to the following equations:

\[
5\text{I}^- + \text{IO}_3^- + 6\text{H}^+ \rightarrow 3\text{I}_2 + 3\text{H}_2\text{O}
\]
\[
2\text{I}^- + 2\text{NO}_2^- + 4\text{H}^+ \rightarrow \text{I}_2 + 2\text{NO} + 2\text{H}_2\text{O}
\]
\[
2\text{I}^- + \text{H}_2\text{O}_2 + 2\text{H}^+ \rightarrow \text{I}_2 + 2\text{H}_2\text{O}
\]

25. MOYLBDDATE

Nitric acid oxidizes the lower oxidation states of molybdenum to Mo(VI) and precipitates \(\text{Mo}_3\cdot\text{H}_2\text{O}\), soluble in an excess of the acid.

Ammonium phosphomolybdate is precipitated from strong nitric acid solutions by phosphoric acid and its salts.

26. NITRATE

Metallic zinc or aluminum in hot, strongly alkaline
solutions reduce nitrate ion to ammonia.
\[
\begin{align*}
\text{NO}_3^- + 4\text{Zn} + 70\text{H}^- & \rightarrow \text{NH}_3 + 4\text{ZnO}_2^{2-} + 2\text{H}_2\text{O} \\
3\text{NO}_3^- + 8\text{Al} + 50\text{H}^- + 2\text{H}_2\text{O} & \rightarrow 3\text{NH}_3 + 8\text{AlO}_2^{-}
\end{align*}
\]
Metallic zinc, in acetic acid solution, reduces nitrates to nitrites or nitrous acid.

27. NITRITE

There are several excellent reactions for the complete removal of nitrite from solution. Both urea and ammonium ion react quantitatively
\[
\begin{align*}
2\text{NO}_2^- + (\text{NH}_2)_2\text{CO} + 2\text{H}^+ & \rightarrow 2\text{N}_2 + \text{CO}_2 + 3\text{H}_2\text{O} \\
\text{NO}_2^- + \text{NH}_4^+ & \rightarrow \text{N}_2 + 2\text{H}_2\text{O}
\end{align*}
\]
The removal of nitrite with sodium azide is complete in acidic solution. Boiling completes the reaction and removes excess hydrazoic acid. The equation is
\[
\begin{align*}
\text{NO}_2^- + \text{N}_3^- + 2\text{H}^+ & \rightarrow \text{N}_2 + \text{N}_2\text{O} + \text{H}_2\text{O}
\end{align*}
\]
Perhaps the best method of all is the reaction of sulfamic acid with nitrites.
\[
\begin{align*}
\text{NO}_2^- + \text{NH}_2\text{SO}_3\text{H} & \rightarrow \text{N}_2 + \text{HSO}_4^- + \text{H}_2\text{O}
\end{align*}
\]
In dilute solutions the reaction is instantaneous.

28. OXALATE

Repeated evaporation with concentrated nitric acid will destroy oxalate ion.

Oxalate forms quite insoluble precipitates with thorium and lanthanum.

Permanganate ion quantitatively converts oxalate to carbon dioxide in a hot acidic solution.
29. PERCHLORATE

Perchlorate may be reduced to chlorine by iodine in an acidic solution.

\[ 2\text{ClO}_4^- + \text{I}_2 \rightarrow 2\text{I}_3^- + \text{Cl}_2 \]

30. PERIODATE

In strong acid solution, periodic acids and their salts are powerful oxidants. Iodate ion is the usual reduction product. Some typical reactions are:

\[ \text{IO}_4^- + \text{C}_2\text{O}_4^{2-} + 2\text{H}^+ \rightarrow \text{IO}_3^- + 2\text{CO}_2 + \text{H}_2\text{O} \]

\[ \text{IO}_4^- + \text{H}_2\text{O}_2 \rightarrow \text{IO}_3^- + \text{O}_2 + \text{H}_2\text{O} \]

31. PERMANGANATE

Various reducing agents in acidic media react quantitatively with permanganate.

\[ 2\text{MnO}_4^- + 5\text{C}_2\text{O}_4^{2-} + 16\text{H}^+ \rightarrow 2\text{Mn}^{2+} + 10\text{CO}_2 + 8\text{H}_2\text{O} \]

\[ 2\text{MnO}_4^- + 5\text{H}_2\text{O}_2 + 6\text{H}^+ \rightarrow 2\text{Mn}^{2+} + 5\text{O}_2 + 8\text{H}_2\text{O} \]

32. PERSULFATE

When a solution of alkali persulfate is boiled, decomposition occurs with sulfate and oxygen being produced.

33. PHOSPHATE

The best means available for the removal of phosphate ion is by precipitation. Magnesium ion in an ammoniacal solution precipitates magnesium ammonium phosphate. The addition of a zirconyl nitrate solution, one molar in hydrochloric acid, will precipitate zirconyl phosphate.
34. PYROPHOSPHATE

Solutions of pyrophosphates change into the orthophosphate slowly at room temperature and more rapidly upon boiling.

Addition of either zinc or cadmium ions will precipitate pyrophosphate from dilute acetic acid solutions.

35. SELENITES, SELENATES

Selenites are easily reduced to elemental selenium by various reagents in hydrochloric acid solution: hydroxylamine hydrochloride, hydrazine hydrochloride and thiourea give good results.

Barium ion will precipitate both selenite and selenate from neutral solution.

Selenates react with thiourea in solution to yield elemental selenium.

36. SILICATES

Treatment of a silicate with hydrofluoric and sulfuric acid will produce volatile silicon tetrafluoride.

37. SULFATE

Barium ion quantitatively precipitates sulfate from a dilute acidic solution.

38. SULFIDE

Hydrogen sulfide can be eliminated from solution by acidification with a nonoxidizing acid and boiling.

Various oxidizing agents convert sulfide to
elemental sulfur or sulfate, for example:

\[
\begin{align*}
S^{-2} & + 4H_2O_2 \rightarrow SO_4^{-2} + 4H_2O \\
3H_2S & + 2NO_3^- + 2H^+ \rightarrow 3S + 2NO + 4H_2O \\
2H_2S & + SO_3^{-2} + 2H^+ \rightarrow 3S + 3H_2O
\end{align*}
\]

39. SULFITE

Hydrogen ion from either dilute or concentrated strong, nonoxidizing acids liberates sulfur dioxide from sulfite solutions upon warming.

Various oxidizing agents convert sulfurous acid or sulfite ion to sulfate ion.

\[
\begin{align*}
SO_3^{-2} & + H_2O_2 \rightarrow SO_4^{-2} + H_2O \\
SO_3^{-2} & + 2NO_2^- + 2H^+ \rightarrow SO_4^{-2} + 2NO + H_2O
\end{align*}
\]

40. TARTRATE

By repeated evaporation with concentrated nitric acid, tartrate ion is completely destroyed.

41. TELLURITE, TELLURATE

Elemental tellurium is precipitated from both tellurites and tellurates by hydrazine hydrochloride in a warm acid solution.

Barium ion in neutral solution precipitates both tellurite and tellurate.

42. THIOCYANATE

With metallic zinc and dilute hydrochloric acid, hydrogen sulfide and hydrogen cyanide are evolved from thiocyanates.
Thiocyanates are decomposed upon warming with nitric acid. Dilute nitric acid produces nitric oxide, sulfate ion and hydrogen cyanide. Concentrated nitric acid evolves nitric oxide, sulfate ion and carbon dioxide.

A warm acetic acid solution of hydrogen peroxide converts thiocyanates into sulfate ion and hydrogen cyanide.

43. THIOSULFATE

Hydrogen ion from either dilute or concentrated strong, nonoxidizing acids yields sulfur dioxide and elemental sulfur upon warming.

Strong oxidizing agents convert thiosulfate ion into sulfate ion, for example:

\[
\begin{align*}
S_2O_3^{2-} + 4H_2O_2 & \rightarrow 2SO_4^{2-} + 2H^+ + 3H_2O \\
S_2O_3^{2-} + 4Cl_2 + 5H_2O & \rightarrow 2SO_4^{2-} + 8Cl^- + 10H^+
\end{align*}
\]

44. TUNGSTATE

Addition of dilute mineral acids to a solution of tungstate yields hydrated tungsten trioxide.

45. VANADATE

Vanadate is completely precipitated, as ammonium vanadate, if solid ammonium chloride is added to a neutral solution.

These tests are intended only as a guide. Their indiscriminate use can result in more harm than good.
C. MASKING

In addition to the reactions given for the elimination of troublesome anions, the technique of masking may be used for the removal of both cations and anions. A reaction system is said to be masked if the normal course of a chemical change that leads to insoluble, colored, or gaseous reaction products is prevented by the presence or addition of certain materials. Masking is a process in which certain reactions of a substance, without physical separation of it or its reaction products, are prevented. The technique of masking is largely empirical. In practice a large concentration of some complexing ligand is generally added to effectively coordinate the interfering ions. Recently, attempts have been made (10, 64) to give a more fundamental approach to this most useful technique. Table I is a comprehensive listing of masking agents.

TABLE I

Masking Agents for the Elements

<table>
<thead>
<tr>
<th>Element</th>
<th>Masking Agents</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ag</td>
<td>CN⁻, NH₃, en, Br⁻, S₂O₃⁻², EDTA, SCN⁻, thiourea, I⁻, Cl⁻, TG</td>
</tr>
<tr>
<td>Al</td>
<td>F⁻, C₂O₄⁻², OAc⁻, cit, tart, EDTA, sulfosal, BAL, NTE, OH⁻, AA</td>
</tr>
<tr>
<td>As</td>
<td>S⁻², S₂O₃⁻², BAL, OH⁻</td>
</tr>
<tr>
<td>Element</td>
<td>Masking Agents</td>
</tr>
<tr>
<td>---------</td>
<td>----------------</td>
</tr>
<tr>
<td>Au</td>
<td>CN&lt;sup&gt;-&lt;/sup&gt;, Br&lt;sup&gt;-&lt;/sup&gt;, S&lt;sub&gt;2&lt;/sub&gt;O&lt;sub&gt;3&lt;/sub&gt;&lt;sup&gt;-2&lt;/sup&gt;, I&lt;sup&gt;-&lt;/sup&gt;, P&lt;sub&gt;2&lt;/sub&gt;O&lt;sub&gt;7&lt;/sub&gt;&lt;sup&gt;-4&lt;/sup&gt;, SO&lt;sub&gt;3&lt;/sub&gt;&lt;sup&gt;-2&lt;/sup&gt;, thiourea</td>
</tr>
<tr>
<td>B</td>
<td>F&lt;sup&gt;-&lt;/sup&gt;, polyhydroxy alcohols, hydroxy acids</td>
</tr>
<tr>
<td>Ba</td>
<td>EDTA, cit, tart, NTA, DHG, SO&lt;sub&gt;4&lt;/sub&gt;&lt;sup&gt;-2&lt;/sup&gt;</td>
</tr>
<tr>
<td>Be</td>
<td>EDTA, F&lt;sup&gt;-&lt;/sup&gt;, cit, tart,</td>
</tr>
<tr>
<td>Bi</td>
<td>EDTA, tart, cit, S&lt;sub&gt;2&lt;/sub&gt;O&lt;sub&gt;3&lt;/sub&gt;&lt;sup&gt;-2&lt;/sup&gt;, I&lt;sup&gt;-&lt;/sup&gt;, Cl&lt;sup&gt;-&lt;/sup&gt;, NTA, DHG, NTE, BAL, TG, thiourea</td>
</tr>
<tr>
<td>Br</td>
<td>Sulfosal</td>
</tr>
<tr>
<td>Ca</td>
<td>EDTA, polyphosphates, F&lt;sup&gt;-&lt;/sup&gt;, P&lt;sub&gt;2&lt;/sub&gt;O&lt;sub&gt;7&lt;/sub&gt;&lt;sup&gt;-4&lt;/sup&gt;, cit, tart, NTA, DHG</td>
</tr>
<tr>
<td>Cd</td>
<td>EDTA, CN&lt;sup&gt;-&lt;/sup&gt;, I&lt;sup&gt;-&lt;/sup&gt;, S&lt;sub&gt;2&lt;/sub&gt;O&lt;sub&gt;3&lt;/sub&gt;&lt;sup&gt;-2&lt;/sup&gt;, cit, tart, SCN&lt;sup&gt;-&lt;/sup&gt;, NH&lt;sub&gt;3&lt;/sub&gt;, P&lt;sub&gt;2&lt;/sub&gt;O&lt;sub&gt;7&lt;/sub&gt;&lt;sup&gt;-4&lt;/sup&gt;, NTA, DHG, TG, DMPS</td>
</tr>
<tr>
<td>Ce</td>
<td>F&lt;sup&gt;-&lt;/sup&gt;, NTA, EDTA, DHG, cit, tart, tiron</td>
</tr>
<tr>
<td>Co</td>
<td>EDTA, SCN&lt;sup&gt;-&lt;/sup&gt;, CN&lt;sup&gt;-&lt;/sup&gt;, NO&lt;sub&gt;2&lt;/sub&gt;&lt;sup&gt;-&lt;/sup&gt;, S&lt;sub&gt;2&lt;/sub&gt;O&lt;sub&gt;3&lt;/sub&gt;&lt;sup&gt;-2&lt;/sup&gt;, cit, tart, NH&lt;sub&gt;3&lt;/sub&gt;, H&lt;sub&gt;2&lt;/sub&gt;O&lt;sub&gt;2&lt;/sub&gt;, NTA, DHG, en, BAL, tren, penten</td>
</tr>
<tr>
<td>Cr</td>
<td>OAc&lt;sup&gt;-&lt;/sup&gt;, S&lt;sub&gt;2&lt;/sub&gt;O&lt;sub&gt;3&lt;/sub&gt;&lt;sup&gt;-2&lt;/sup&gt;, EDTA, cit, tart, NTA, NTE, ascorbic acid</td>
</tr>
</tbody>
</table>
### TABLE I (continued)

<table>
<thead>
<tr>
<th>Element</th>
<th>Masking Agents</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu</td>
<td>EDTA, thiourea, sulfosal, $S_2O_3^{-2}$, $CN^-$, tart, cit, $NH_3$, $SO_3^{-2}$, $I^-$, SCN$^-$, $S^{-2}$, DTC, DHG, BAL, NTA, TG, NTE, tren, penten</td>
</tr>
<tr>
<td>Fe(II)</td>
<td>$CN^-$, $\alpha,\alpha$-dipyridyl, en</td>
</tr>
<tr>
<td>Fe(III)</td>
<td>EDTA, polyphosphates, $PO_4^{-3}$, $P_2O_7^{-4}$, $F^-$, $C_2O_4^{-2}$, $S_2O_3^{-2}$, $CN^-$, cit, tart, sulfosal, SCN$^-$, $SO_3^{-2}$, NTA, DHG, DTC, BAL, PH, $S^{-2}$, TG, NTE, tiron, thiourea, ascorbic acid</td>
</tr>
<tr>
<td>Ge</td>
<td>$C_2O_4^{-2}$, $F^-$</td>
</tr>
<tr>
<td>Hf</td>
<td>$F^-$, $SO_4^{-2}$, DHG, cit, tart, NTA, EDTA, $P_2O_7^{-4}$, $PO_4^{-3}$, $C_2O_4^{-2}$, NTE, $H_2O_2$</td>
</tr>
<tr>
<td>Hg</td>
<td>$I^-$, $SO_3^{-2}$, $CN^-$, SCN$^-$, $S_2O_3^{-2}$, $Cl^-$, thiourea, NTA, EDTA, DHG, cit, tart, NTE, tren, penten, TG, TSC, DMPS</td>
</tr>
<tr>
<td>In</td>
<td>$F^-$, $C_2O_4^{-2}$, TG</td>
</tr>
<tr>
<td>Ir</td>
<td>Thiourea, cit, SCN$^-$, $NH_3$, tart</td>
</tr>
<tr>
<td>Mg</td>
<td>EDTA, polyphosphates, NTA, DHG, cit, $C_2O_4^{-2}$, tart, $OH^-$, $P_2O_7^{-4}$, glycols, $F^-$</td>
</tr>
<tr>
<td>Element</td>
<td>Masking Agents</td>
</tr>
<tr>
<td>---------</td>
<td>----------------</td>
</tr>
<tr>
<td>Mn</td>
<td>$F^-$, $C_2O_4^{2-}$, $PO_4^{3-}$, $P_2O_7^{4-}$, tart, cit, CN$^-$, EDTA, NTA, DHG, BAL, NTE</td>
</tr>
<tr>
<td>Mo</td>
<td>$C_2O_4^{2-}$, $H_2O_2$, SCN$^-$, cit, tart, $F^-$, EDTA, NTA, tiron</td>
</tr>
<tr>
<td>Nb</td>
<td>$H_2O_2$, $F^-$, $OH^-$, cit, tart, $C_2O_4^{2-}$, tiron</td>
</tr>
<tr>
<td>Ni</td>
<td>EDTA, CN$^-$, SCN$^-$, cit, tart, mal, $NH_3$, NTA, tren, penten</td>
</tr>
<tr>
<td>Os</td>
<td>CN$^-$, thiourea, SCN$^-$</td>
</tr>
<tr>
<td>Pb</td>
<td>EDTA, OAc$^-$, $S_2O_3^{2-}$, cit, $F^-$, I$^-$, SCN$^-$, $P_2O_7^{4-}$, tart, NTA, DHG, $SO_4^{2-}$, BAL, TG, DMPS</td>
</tr>
<tr>
<td>Pd</td>
<td>$S_2O_3^{2-}$, I$^-$, CN$^-$, $NH_3$, $NO_2^-$, SCN$^-$, NTA, $SO_3^{2-}$, EDTA, DHG, cit, tart, AA, NTE</td>
</tr>
<tr>
<td>Pt</td>
<td>I$^-$, $NH_3$, en, CN$^-$, $S_2O_3^{2-}$, $NO_2^-$, SCN$^-$, Cl$^-$, NTA, EDTA, DHG, cit, tart</td>
</tr>
<tr>
<td>Rh</td>
<td>Thiourea, cit, tart</td>
</tr>
<tr>
<td>Ru</td>
<td>Thiourea</td>
</tr>
<tr>
<td>Sb</td>
<td>Tart, cit, I$^-$, $S^{2-}$, $F^-$, BAL, $OH^-$</td>
</tr>
<tr>
<td>Element</td>
<td>Masking Agents</td>
</tr>
<tr>
<td>---------</td>
<td>----------------</td>
</tr>
<tr>
<td>Sn</td>
<td>(\text{C}_2\text{O}_4^{-2}), F(^-), I(^-), tart, cit, (\text{S}^{2-}), BAL, OH(^-), NTE, TG, (\text{PO}_4^{3-})</td>
</tr>
<tr>
<td>Sr</td>
<td>EDTA, (\text{SO}_4^{2-}), NTA, DHG, cit, tart</td>
</tr>
<tr>
<td>Ta</td>
<td>F(^-), OH(^-), cit, tart</td>
</tr>
<tr>
<td>Th</td>
<td>F(^-), cit, NTA, EDTA, DHG, tart, NTE, OAc(^-)</td>
</tr>
<tr>
<td>Ti</td>
<td>F(^-), (\text{H}_2\text{O}_2), (\text{SO}_4^{2-}), cit, tart, mal, NTA, sulfososal, tiron, EDTA, NTE, OH(^-), gluconate</td>
</tr>
<tr>
<td>Tl</td>
<td>Cl(^-), CN(^-), EDTA, tart, (\text{C}_2\text{O}_4^{-2}), SCN(^-), NTA, cit, NTE, TG</td>
</tr>
<tr>
<td>U</td>
<td>F(^-), (\text{C}_2\text{O}_4^{-2}), NO(_3^{-}), CO(_3^{-2}), tart, cit, mal, (\text{SO}_3^{-2}), (\text{H}_2\text{O}_2)</td>
</tr>
<tr>
<td>V</td>
<td>CN(^-), F(^-), (\text{SO}_3^{-2}), (\text{H}_2\text{O}_2), EDTA, tiron, NTE</td>
</tr>
<tr>
<td>W</td>
<td>Cit, tart, F(^-), (\text{C}_2\text{O}_4^{-2}), (\text{H}_3\text{PO}_4), tiron, SCN(^-), (\text{H}_2\text{O}_2)</td>
</tr>
<tr>
<td>Zn</td>
<td>SCN(^-), cit, tart, EDTA, glycerol, NH(_3), NTA, DHG, BAL, OH(^-), tren, TG, penten, DMPS, CN(^-)</td>
</tr>
<tr>
<td>Element</td>
<td>Masking Agents</td>
</tr>
<tr>
<td>---------</td>
<td>----------------</td>
</tr>
<tr>
<td>Zr</td>
<td>F(^-), SO(_{4})^{2-}, tart, cit, mal, NTA, EDTA, H(_2)O(_2), P(_2)O(_7)^{-4}, PO(_4)^{-3}, C(_2)O(_4)^{-2}, NTG, DHG</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Ion, Molecule</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Br(_2)</td>
<td>HSO(_3)^- , S(_2)O(_3)^{-2}, NH(_2)NH(_2), AsO(_2)^-</td>
</tr>
<tr>
<td>Cl(^-)</td>
<td>Hg(^+2)</td>
</tr>
<tr>
<td>Cl(_2) (_3)</td>
<td>S(_2)O(_3)^{-2}</td>
</tr>
<tr>
<td>Cl(_4) (_4)</td>
<td>HSO(_3)^- , NH(_2)OH</td>
</tr>
<tr>
<td>CN(^-)</td>
<td>HCHO, transition metals, Hg(^+2)</td>
</tr>
<tr>
<td>Cr(_2)O(_7)^{-2}</td>
<td>Ascorbic acid, HSO(_3)^- , NH(_2)OH, S(_2)O(_3)^{-2}, NH(_4)NH(_2), AsO(_2)^-</td>
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<tr>
<td>F(^-)</td>
<td>B(_2)O(_3)^{-3}, Al(^+3), Be(^+2), Zr(^+4), Fe(^+3), Hg(^+2), Nb(_7), Ta(_7), Hf(_7), Ti(_7)</td>
</tr>
<tr>
<td>Fe(CN)(_6)^{-3}</td>
<td>Ascorbic acid, NH(_2)OH, HSO(_3)^- , S(_2)O(_3)^{-2}</td>
</tr>
<tr>
<td>I(^-)</td>
<td>Hg(^+2)</td>
</tr>
<tr>
<td>IO(_3)^-</td>
<td>HSO(_3)^- , S(_2)O(_3)^{-2}, NH(_2)NH(_2)</td>
</tr>
<tr>
<td>IO(_4)^-</td>
<td>Ascorbic acid, HSO(_3)^- , S(_2)O(_3)^{-2}, NH(_2)NH(_2), AsO(_2)^-</td>
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<tr>
<td>MnO(_4)^-</td>
<td>N(_3)^-, ascorbic acid, NH(_2)NH(_2), HSO(_3)^-, NH(_2)OH, S(_2)O(_3)^{-2}, AsO(_2)^-</td>
</tr>
</tbody>
</table>
TABLE I (continued)

<table>
<thead>
<tr>
<th>Ion, Molecule</th>
<th>Masking Agents</th>
</tr>
</thead>
<tbody>
<tr>
<td>NH$_3$</td>
<td>HCHO</td>
</tr>
<tr>
<td>NO$_2^-$</td>
<td>Sulfanilic acid, Co$^{2+}$, N$_3^-$, HSO$_3^-$, NH$_2$OH, S$_2$O$_3^{2-}$, NH$_2$NH$_2$</td>
</tr>
<tr>
<td>s</td>
<td>CN$^-$, S$^{2-}$, SO$_3^{2-}$</td>
</tr>
<tr>
<td>S$^{2-}$</td>
<td>s</td>
</tr>
<tr>
<td>SO$_3^{2-}$</td>
<td>HCHO, HgCl$_4^{2-}$</td>
</tr>
<tr>
<td>S$_2$O$_8^{2-}$</td>
<td>Ascorbic acid, NH$_2$OH, S$_2$O$_3^{2-}$</td>
</tr>
<tr>
<td>Se anions</td>
<td>S$^{2-}$, SO$_3^{2-}$, DAB, tart, cit, I$^-$, F$^-$, ascorbic acid</td>
</tr>
<tr>
<td>Te anions</td>
<td>I$^-$, F$^-$, cit, tart, S$^{2-}$, SO$_3^{2-}$, ascorbic acid</td>
</tr>
</tbody>
</table>

Abbreviations

- AA = acetylacetone
- BAL = 2,3-dimercapto-1-propanol
- cit = citrate
- DAB = diaminobenzidine
- DHG = N,N-(2-hydroxyethyl) glycine
- DMPS = 2,3-dimercaptopropane sulfonate sodium salt
- DTC = diethyldithiocarbamate
- en = ethylenediamine
Abbreviations (continued)

mal = malonate
NTA = nitrilotriacetate
NTE = 2,2',2''-nitrilotriethanol
OAc = acetate
penten = tetrakis(2-aminoethyl)ethylenediamine
PH = o-phenanthroline
Sulfosal = sulfosalicylate
tart = tartrate
TG = thioglycollic acid
tren = 2,2',2''-triaminotriethylamine
TSC = thiosemicarbazide

Another method being used to gain selectivity and sensitivity in spot test methods is the use of ion-exchange resins to separate and concentrate species being detected (25). These resin spot tests are based on the intense coloration of a few grains of a light-colored ion-exchange resin produced by the uptake from the reaction medium of ions having characteristic colors.

The advantages of resin spot tests are associated with the increased sensitivity achieved, the improved stability of the coloration and the improved selectivity of the analytical tests. Resin spot tests exhibit greatly enhanced sensitivity. This being associated with the increase in the concentration of colored ionic species by adsorption on the fine grains of the resin and with the
subsequent enhancement of the coloration in the resin phase. The coloration is often more stable in the resin phase than in the aqueous phase and often intensifies upon standing. This is due to the ever present exchange capacity of the resin. Colorless or lightly colored resins must be employed to attain adequate sensitivity.

The selective adsorption of the particular ion-exchange resin often makes the test more selective. Thus, any interference by ions of a charge opposite to that of the ionic species adsorbed by the resin is usually removed. In most cases, strongly acidic cationic or strongly basic anionic exchange resins of low cross-linkage are employed.

In general, procedures involving resin spot tests may be classified into four groups (25)

1. simple complex formation
2. chelate formation
3. dye formation
4. interfacial precipitation or crystal growth.

A promising development of resin spot tests is the use of paper coated with an ion-exchange resin as a medium and support for spot tests (66). In addition, the commercial introduction of new types of ion-exchange resins, including chelating resins and redox resins, will offer further possibilities for resin spot tests.
D. THE SCHEME OF ANALYSIS

The *raison d'etre* of any qualitative scheme of analysis is its reliability and speed of usage. Based upon these considerations it was deemed best to use the spot test method in the development of this scheme. Some important advantages of this particular technique are:

1. the amount of sample needed is small.
2. reagent quantities used are small.
3. separations are avoided. Separations, especially when they involve precipitations, are almost always incomplete or they may lead to the loss of elements which are present in small quantities.
4. use of large quantities of flammable or toxic materials is eliminated.
5. the different parts of the analysis are independent, thus it is possible to repeat any test using the original sample solution, without prior treatment.
6. the method is inherently rapid, also, reactions which demonstrate the absence of an entire group of elements are obviously effective means of saving time.
7. since the tests are independent of one another, the method can be improved without disturbing the remainder of the scheme.
8. reactions can be made quite selective by changing reaction media, i.e., from spot plates, filter paper, ion-exchange resin; or by the addition of masking agents or a change in pH.

In addition, a scheme is needed not just to detect ions present in equal amounts but rather the detection of one ion in the presence of others when the concentration ranges over wide ratios. A practical and reasonable goal
would be to detect each metal in the presence of a hundred to a thousand times larger quantity of any other metal or combination of metals. The experimental approach to this goal is made less difficult using spot tests.

It was felt that this scheme would be more useful if it could be divided into six to eight groups, each group consisting of not more than seven ions. This was considered ideal. In actual practice, the scheme consists of six groups. The number of ions in each group range from three to fourteen. The average number of ions per group is eight.

A thorough study of Welcher (82) was made for suitable group reagents. The following items were considered as being desirable in a group reagent:

1. good sensitivity, i.e., the absolute amounts of ions capable of detection are small. Another consideration was the relative magnitude of sensitivity for each ion in a particular group. Ideally there should be approximately equivalent sensitivities for each ion.

2. selectivity: too much overlapping of ions into the various groups was considered unwise. For example, if iron was present in the sample, and iron was included in three separate groups. There would be a positive test for each of these groups, which would obscure information about other ions possibly present in these groups. In other words, the absence of a positive test gives considerable information about the definite absence of many ions.

3. a reagent giving one distinct product or coloration with the metal ion was considered ideal. This is to eliminate doubtful results due to color mixing.
4. reagent stability

5. reagent solubility in water or alcohol

6. no color change with variation in pH. A reagent which gives a color change in the conditioning stage of the test is of doubtful analytical value.

With the above view in mind, almost forty analytical reagents were screened for their suitability as group reagents. Screening reactions were carried out using hydrochloric acid and ammonia, both as gases, when paper was the test medium. The influence of pH upon the reagent was noted. If a reaction took place only in acidic solution, various acids were used to note any differences in sensitivities or test stability. Buffers of varying hydrogen-ion values were also used to find the optimum test pH value. The use of buffers presented problems with many tests. The very materials necessary for preparation of the buffer solutions reacted either by complex formation or precipitation with some of the metal ions being tested. After the effect of pH was determined, the action of some of the common masking agents were studied.

Each reagent screened had to be considered on its individual merits. There were advantages and disadvantages for each. Some reagents reacted with too many ions, others with too few. In some instances the number of ions reacting were of the proper sized group, but other factors decided against that particular reagent. Cases were observed where the reagent was soluble only in alcohol,
acetone or other organic solvent, and the mixing of aqueous test solution and the organic solution caused precipitation of the reagent.

Many problems associated with the colors given by the reagents themselves arose during the screening tests. A saturated solution of diphenylthiocarbazone gave a blue-green color in an acidic aqueous solution and an orange-brown color in an ammoniacal aqueous solution. An even more perplexing reagent was carminic acid which gave a continuum of color depending upon the pH. Thus, starting at a low hydrogen-ion concentration and increasing the basicity of the solution gave a succession of colors ranging from red-orange, orange-red, red, purple-red, red-purple to purple. Tests performed on solutions which were by necessity of high acidity to prevent hydrolysis of metal ions, were questionable using this type of reagent. Only in those cases where a distinctive color was formed from the metal-reagent reaction is unequivocal detection possible.

The group reagents selected for the final scheme give a one-color precipitate or solution. Thus, the scheme in less experienced hands should be more definitive and less dependent upon subjective interpretation. Of course, if a variety of different colored reaction products were given with the same reagents, possibly more information about the nature of the unknown could be obtained.
The complete list of reagents screened is given in Table II.

TABLE II
Compounds Screened for Group Reagents

1. Sodium rhodizonate
2. Thiourea
3. Thioanilide
4. 8-Hydroxyquinoline
5. p-Dimethylaminobenzylidenerhodanine
6. Salicylaldoxime
7. Quinalizarin
8. Diphenylcarbazide
9. Alizarin S
10. Sodium tetraphenylboron
11. Glyoxal bis(2-hydroxyanil)
12. Dithizone (diphenylthiocarbazone)
13. Gallic acid
14. Quinaldic acid
15. Sodium diethyldithiocarbamate
16. Aminopyrine
17. Stannous chloride
18. 1,8-Dihydroxynaphthalene-3,6-disulfonic acid
19. Phenyl fluorone
20. 4,5-Dihydroxynaphthalene-2,7-disulfonic acid
21. Thioacetamide
22. Dithiooxamide
23. Violuric acid
TABLE II (continued)

24. Carminic acid
25. Potassium ferrocyanide
26. Morin
27. Alizarin
28. 6,7-Dihydroxynaphthalene-2-sulfonic acid
29. Tannic acid
30. Pyrogallol
31. Eriochrome black T
32. Zincon
33. 1-(2-Pyridylazo)-2-naphthol
34. 4-(2-Pyridylazo)resorcinol
35. Benzidine
36. Pyrocatechol violet
37. Tetrahydroxy-p-benzoquinone

After screening the reagents listed in Table II, the following group reagents were chosen:

1. benzidine
2. phenyl fluorone
3. morin
4. stannous chloride
5. glyoxal bis(2-hydroxyanil)
6. sodium tetraphenylboron

Preliminary experiments were then carried out with these group reagents in which the best reaction media was selected, the proper pH value judged, the necessary
masking agents chosen, and the manipulative techniques, so essential in spot test work, were learned. In conjunction with these preliminary experiments, a survey was made of the literature to learn the techniques used previously with these reagents.

The finalized procedure for an unknown using the group detection scheme follows. A discussion of the chemistry of each group reaction is given in Section G.

The order in which the groups are analyzed is not critical. Each group stands as a separate entity. However, from a survey of the tables of interference studies, it appears that certain ions are more troublesome than others. In general, these interferences are the obvious ones caused by precipitation of an insoluble compound, complexation, oxidation-reduction phenomena or due to the dark color of the interfering ion. There are few interferences that could not be predicted from a basic knowledge of the chemistry involved. In addition, many of the ions causing interference are those that would be considered uncommon and therefore not ordinarily encountered in the majority of samples.

PROCEDURES FOR GROUP QUALITATIVE ANALYSIS

A. BENZIDINE

Procedure

1. Place a drop of test solution (use 1M HCl for a blank) on a spot plate.
2. Add 1 drop of 10% H₂O₂, mix.
3. Place 1 drop of 2M NaOH on S & S No. 595 filter paper.
4. Place a drop of the mixture from step 2 on top of the NaOH spot on the filter paper.
5. Add a drop of benzidine to this spot.

**Identification Characteristics**
A blue or purple color indicates a positive test for Co(II), Ni(II), Mn(II), Pb(II), Tl(I), Ce(III), Ce(IV), Au(III), Ir(IV), Pt(IV), Ru(III), Ag(I), Fe(CN)₆⁻³, CrO₄⁻².

**Test Solutions**
1. Benzidine, 1% in 3M CH₃COOH
2. NaOH, 2M
3. H₂O₂, 10%
4. HCl, 1M

**Limitations**
1. The interferences encountered in this group are few; nine ions have no interferences. The maximum number of interfering ions was seven with silver: S⁻², S₂O₃⁻², CN⁻, SCN⁻, I⁻, Br⁻, and Cl⁻. All of these precipitation and complexation reactions are well known and could be easily predicted.
2. Sensitivity is not as great for nickel, lead,
thallium, platinum, iridium, ruthenium, osmium and silver as for the other group ions.

3. Nitrite ion is a general interference but can be easily eliminated with the addition of a few crystals of sulfamic acid.

Remarks
1. If the drops of solutions are kept small as they are put on the filter paper, thus preventing unnecessary spreading, the sensitivity of the test will be enhanced.

2. Under the stated test conditions, Cr(III) is oxidized to CrO_4^{2-}, I^- to IO_4^-, and Fe(CN)_6^{4-} to Fe(CN)_6^{3-}, all of which give a positive test.

3. If the concentration of test ion is relatively low, the blue ring formed is quite diffused and is more easily seen as the paper dries.

4. Benzidine is oxidized by cupric ion when the following ions are present: I^-, Br^-, Cl^-, CNO^-, SCN^- and CN^- . The oxidation potential of cupric ions is enhanced by the formation of the corresponding insoluble cuprous salts.

5. Ions giving dark precipitates or colors, e.g., Fe^{3+}, Pd^{2+}, Cu^{2+}, WO_4^{2-}, MoO_4^{2-}, do not interfere since the test ion diffuses outwardly on the paper forming a blue ring with the benzidine.
6. Iodate, persulfate, chlorate and periodate also give positive tests with benzidine.

B. STANNOUS CHLORIDE

Procedure
1. Place a drop of test solution on a white spot plate.
2. Add a drop of SnCl₂ solution, mix.

Identification Characteristics
The following colors are obtained in a positive reaction: Hg(I) (gray-black), Hg(II) (black), Pt(IV) (orange-brown), Pd(II) (black-brown), Au(III) (black), SeO₃⁻² and SeO₄⁻² (red), and TeO₃⁻² (black).

Test Solutions
SnCl₂, 20% in concentrated HCl

Limitations
The most troublesome interfering ions are: S⁻², S₂O₃⁻² and IO₃⁻. All of these ions interfere in three tests with group ions. Vanadate and cyanide interfere in two tests, while six other ions interfere in single tests.

Remarks
The stannous chloride reagent should be freshly prepared as it gradually loses its reducing ability.
C. PHENYL FLUORONE

Procedure
1. Place 1 drop of test solution on S & S No. 595 filter paper (use 1M HCl for the blank).
2. Add 1 drop of phenyl fluorone solution.
3. Expose to NH₃ fumes (from 15M NH₄OH).
4. Add another drop of phenyl fluorone solution to the original spot.
5. Add 1 drop of 1M HCl to each spot.

Identification Characteristics
A positive test is indicated by an orange-red color.
The following ions are positive: Ge(IV), Sb(III), Sn(II), Sn(IV), Ti(IV), Zr(IV), W(VI) and Mo(VI).
The blank test leaves a yellow spot.

Test Solutions
1. Phenyl fluorone, saturated in CH₃OH
2. HCl, 1M
3. NH₄OH, 15M

Limitations
1. There are only a limited number of interfering ions in this group; F⁻ and HPO₄⁻² interfere in two tests, while S⁻², BrO₃⁻ and P₂O₇⁻⁴ interfere in single tests.
2. Pd(II), Ru(III) and Ir(IV) leave a brown spot that would not interfere when the group ions
are relatively concentrated, but could be misleading in more dilute solutions.

Remarks
1. An advantage of using filter paper as a test medium is that solutions having inherent colors would interfere on a spot test while on paper this color will generally diffuse outwardly allowing the test color to be easily distinguished.

2. The interferences due to MnO₄⁻, IO₃⁻ and VO₃⁻ are easily eliminated by the addition of a pinch of ascorbic acid.

D. MORIN

Procedure
1. Place 1 drop of the test solution on a spot plate.
2. Add dropwise sufficient 2M NaHCO₃ to neutralize any excess acidity of the test solution.
3. Add several drops of 3M CH₃COOH
4. Add a small amount of ascorbic acid, mix.
5. Add a drop of morin solution
6. Add 1 drop of p-dioxane
7. Place the spot plate under an ultraviolet light.

Identification Characteristics
A green-yellow fluorescence under ultraviolet light
is a positive test for Al(III), Be(II), Y(III), In(III), Th(IV), Ga(III), Zr(IV) and Sc(III).

Test Solutions
1. Morin, 0.1% in C\textsubscript{2}H\textsubscript{5}OH
2. NaHCO\textsubscript{3}, 2M
3. CH\textsubscript{3}COOH, 3M

Limitations
1. Those ions characterized by good sensitivity have relatively few interferences. In fact the only ion affected to any extent by interferences is Y(III).
2. In general, the following ions are troublesome throughout the entire group: fluoride (6 tests), molybdate (5 tests), oxalate and pyrophosphate (4 tests), phosphate and ethylenediaminetetraacetate (3 tests).
3. Lanthanum gives a weak fluorescence with morin in relatively concentrated solutions. However, due to the lack of sensitivity and the numerous interferences (more than 20 ions), it is not included as a group ion.
4. Ascorbic acid can be used to remove the interferences of Fe(III), Au(III), MnO\textsubscript{4}\textsuperscript{-} and CrO\textsubscript{4}\textsuperscript{2-}.

Remarks
1. Any excess acidity should be neutralized with a
small amount of solid NaHCO₃, otherwise the sensitivity of the test is decreased.

2. All alkaline solutions must be neutralized with acetic acid, since morin itself fluoresces at high pH values.

3. The addition of p-dioxane enhances the fluorescence given by the group ions.

E. GLYOXAL BIS(2-HYDROXYANIL)

Procedure
1. Place 1 drop of test solution on a white spot plate.
2. Add 1 drop of KCN (20%, aqueous), mix.
3. Add 1 drop of 6M NaOH.
4. Add 2 drops of GBHA reagent.
5. Add 1 drop of Mg(NO₃)₂ solution, mix.

Identification Characteristics
A red or red-purple precipitate indicates a positive test for Ca(II), Sr(II), and Ba(II).

Test Solutions
1. Glyoxal bis(2-hydroxyanil), saturated in C₂H₅OH
2. KCN, 20% aqueous
3. NaOH, 3M
4. Mg(NO₃)₂, 1% aqueous

Limitations
1. The following ions were found to be
interferences for all three ions: Be(II), Fe(III), Zr(IV), Cr(III) and HPO$_4^{-2}$. Interfering in two tests were: CO$_3^{-2}$, SiO$_3^{-2}$, EDTA, Sn(IV), Pb(II) and V(IV).

Remarks
1. The addition of Mg(II) ion was found to increase the sensitivity of the group reaction, especially for the Ba(II) ion.
2. It is advisable to carry a blank test through for direct comparison.
3. With very dilute solutions the tests develop slowly, a minute or so should be allowed for its full development.
4. The group tests were attempted using filter paper as the test medium but results were not satisfactory.

F. SODIUM TETRAPHENYLBORON

Procedure
1. Place 1 drop of test solution on a black spot plate.
2. Add 1 drop of Na$_2$S$_2$O$_3$ masking solution, mix.
3. Add 1 drop of acetate buffer solution, mix.
4. Add 1 drop of sodium tetraphenylboron solution.

Identification Characteristic
A white precipitate is indicative of the positive
Test given by $K^+$, $Rb^+$, $Cs^+$, $NH_4^+$ and $Tl^+$. 

**Test Solutions**
1. Sodium tetraphenylboron, saturated aqueous
2. $Na_2S_2O_3$, 10% aqueous
3. Acetate buffer, pH 6

**Limitations**
There were no interferences encountered in this group under the stated test conditions.

**Remarks**
Any excess acidity of the test ion solution should be neutralized with a small amount of solid NaHCO$_3$.

**E. INTERFERENCE STUDIES**
Utilizing the finalized procedure as given, a complete study of interferences was made on each ion included in this scheme. The results of this study are given in Table III. In the majority of cases, the interferences experienced were due to the presence of anions, which would or could have been removed in the dissolution of the sample, removal of organic matter, or other specialized treatments. As mentioned before, in cases where anions are known to be present in the sample that form complexes which are exceedingly stable, e.g., aluminum (III) ion and fluoride ion to give hexafluoroaluminate (III) ion, the fluoride ion should not be called an interference, since in actuality we are not at any time dealing with the
chemical species $\text{Al}^{3+}$ but rather always with $\text{AlF}_6^{-3}$, which exists as a distinct chemical entity and should be considered as such.

Interference studies were carried out using the test procedures outlined in the final scheme of analysis. A drop of the metal ion solution (10 mg. metal ion/ml.) whose interference was to be studied was mixed with a drop of the test ion (1 mg. metal ion/ml.). A drop of this mixture was then conducted through the final scheme. In some cases, due to the lack of sensitivity of a particular ion, solutions of test ions of slightly higher concentrations had to be utilized in the interference studies. Such changes are noted in the tables summarizing the interference studies.

A positive interference is defined (83) as a false test given by an interfering substance in the absence of the test ion. When the interfering substance prevents a true test from taking place when the test ion is actually present, we have a negative interference.

In many cases, negative interferences were caused by dark colors inherent to the particular interfering ion. For example, $\text{Ru(III)}$, $\text{Ir(IV)}$, $\text{Pd(II)}$, and $\text{MnO}_4^-$ presented difficulties in this manner. In actual practice, however, these ions would present no serious problem. The very fact that they are intensely colored in relatively concentrated solutions is indication enough of their probable interference. Accordingly, appropriate steps can be taken
to eliminate their effect.

Another fact that was repeatedly brought to mind was that many ions must be kept in solutions of low pH or they will hydrolyze. In the process of testing for the various ions, due to requirements of selectivity and sensitivity, pH values must be adjusted to the appropriate level. If precipitation occurs when the pH of the test solution is being altered, this attests to the presence of certain ions characterized by this particular property.

The third type of interference commonly met is that of complexation due to the presence of certain species, e.g., $F^-$, $CN^-$, $C_2O_4^{2-}$, and $S_2O_3^{2-}$. It has been pointed out that these species fundamentally alter the original species into a stable entity with its own characteristic chemical reactivity.

The two metals possessing the greatest ability to react with analytical reagents are iron and copper. Interestingly enough, neither are included in this scheme. The only other common ions not included are Mg(II), Cd(II), Zn(II), Bi(III), and As(V). This is not a serious deficiency of the scheme however, since all of these ions can be tested for individually quite easily.
TABLE III-A
INTERFERENCE STUDIES

GROUP REAGENT: Benzidine

REACTING SPECIES: Co(II), Ni(II), Mn(II), Pb(II), Tl(I), Ce(III), Ce(IV), Au(III), Ir(IV), Pt(IV), Os(VIII), Ru(III), Ag(I), Fe(CN)$_6$-$^3$, CrO$_4$-$^2$, MnO$_4$-$^-$.

NON-REACTING SPECIES: Li(I), Na(I), K(I), Rb(I), Cs(I), Cu(II), Be(II), Mg(II), Ca(II), Sr(II), Ba(II), Zn(II), Cd(II), Hg(I), Hg(II), BO$_2^-$, B$_4$O$_7$-$^2$, Al(III), Ga(III), CO$_3^-$-$^2$, SiO$_3^-$-$^2$, Ti(IV), Ge(IV), Zr(IV), Sn(II), Sn(IV), Th(IV), NH$_4^+$, NO$_3^-$, P$_2$O$_7$-$^4$, As(III), As(V), Sb(III), Sb(V), Bi(III), SO$_3^-$-$^2$, SO$_4^-$-$^2$, SeO$_3^-$-$^2$, SeO$_4^-$-$^2$, MoO$_4^-$-$^2$, TeO$_3^-$-$^2$, TeO$_4^-$-$^2$, F$^-$, ClO$_4^-$, BrO$_3^-$, Fe(III), Rh(III), Pd(II), acetate, oxalate, malonate, succinate, tartrate, citrate.

INTERFERENCES:

<table>
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<tr>
<th>Group</th>
<th>Ions</th>
<th>Interfering Ions</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Co(II)</td>
<td>None</td>
</tr>
<tr>
<td>2</td>
<td>Pb(II)</td>
<td>None</td>
</tr>
<tr>
<td>3</td>
<td>Ni(II)</td>
<td>WO$_4^-$-$^2$, UO$_4^+$-$^2$</td>
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<tr>
<td>4</td>
<td>Mn(II)</td>
<td>None</td>
</tr>
<tr>
<td>5</td>
<td>Tl(I)</td>
<td>HPO$_4^-$-$^2$, S$^-$-$^2$, EDTA</td>
</tr>
<tr>
<td>6</td>
<td>Ce(III)</td>
<td>S$^-$-$^2$, S$_2$O$_3^-$-$^2$</td>
</tr>
<tr>
<td>7</td>
<td>Ce(IV)</td>
<td>None</td>
</tr>
<tr>
<td>8</td>
<td>Au(III)</td>
<td>None</td>
</tr>
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<td>Group</td>
<td>Ions</td>
<td>Interfering Ions</td>
</tr>
<tr>
<td>-------</td>
<td>--------</td>
<td>---------------------------</td>
</tr>
<tr>
<td>9.</td>
<td>Ir(IV)</td>
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</tr>
<tr>
<td>10.</td>
<td>Pt(IV)</td>
<td>None</td>
</tr>
<tr>
<td>11.</td>
<td>Ru(III)</td>
<td>None</td>
</tr>
<tr>
<td>12.</td>
<td>Ag(I)</td>
<td>$S^{2-}, S_{2}O_{3}^{2-}, Cl^{-}, Br^{-}, I^{-}, CN^{-}, SCN^{-}$</td>
</tr>
<tr>
<td>13.</td>
<td>CrO$_4$$^{2-}$</td>
<td>None</td>
</tr>
<tr>
<td>14.</td>
<td>Os(VIII)</td>
<td>None</td>
</tr>
</tbody>
</table>

REMARKS:

1. Benzidine is also reported oxidized by iodate, periodate, persulfate and chlorate. However, under the stated test conditions, there was no observed oxidation of benzidine by any of these ions.

2. Some ions, while unreactive toward benzidine themselves, are oxidized by the peroxide to products which are reactive. Thus iodide, chromic and ferrocyanide ions, upon oxidation, all give products which readily oxidize benzidine.

3. Nitrite ion is an interference affecting all group ions. This is due to the formation of a reddish-brown coloration, which effectively masks the benzidine color. This interference can be completely eliminated by the addition
TABLE III-A (continued)

of a few crystals of sulfamic acid.

4. Several ions present difficulties due to colored products formed during the test, e.g., ferric ion forms ferric hydroxide and palladium (II) ion forms a dark brown precipitate and solution, but the test ion usually diffuses outwardly and a positive reaction is readily seen.

5. Excess acidity of the test ion solution should be neutralized with the minimum amount of solid Na$_2$CO$_3$ before attempting the group test.

6. Due to differences in sensitivities of the group ions, varying concentrations of test ion solutions had to be employed in the interference studies. The following ions lacked sensitivity and solutions having concentrations of 5 milligram metal ion per milliliter were used: Ni(II), Pb(II), Tl(I), Ce(III), Os(VIII) and Ag(I). For all other group ions, solutions containing 1 milligram metal ion per milliliter were used.
## TABLE III-B
### INTERFERENCE STUDIES

**GROUP REAGENT:** Stannous Chloride

**REACTING SPECIES:** Hg(I), Hg(II), SeO$_3^{-2}$, SeO$_4^{-2}$, TeO$_3^{-2}$, Pd(II), Pt(IV), Au(III).

**NON-REACTING SPECIES:** Li(I), Na(I), K(I), Rb(I), Cs(I), Cu(II), Ag(I), Be(II), Mg(II), Ca(II), Sr(II), Ba(II), Zn(II), Cd(II), BO$_2^{-}$, B$_4$O$_7^{-2}$, Al(III), Ga(III), Ce(III), Ce(IV), Ti(I), CO$_3^{-2}$, SiO$_3^{-2}$, Ti(IV), Ge(IV), Zr(IV), Sn(II), Sn(IV), Pb(II), Th(IV), NH$_4^{+}$, NO$_3^{-}$, HPO$_4^{-2}$, P$_2$O$_7^{-4}$, As(III), As(V), Sb(III), Sb(V), Bi(III), SO$_3^{-2}$, SO$_4^{-2}$, Cr(III), WO$_4^{-2}$, UO$_2^{+2}$, F$^{-}$, Cl$^{-}$, ClO$_3^{-}$, ClO$_4^{-}$, Mn(II), Br$^{-}$, BrO$_3^{-}$, Fe(III), Co(II), Ni(II), Ru(III), Rh(III), Os(VIII), Ir(IV), SCN$^{-}$, acetate, oxalate, malonate, succinate, tartrate, citrate, EDTA.

### INTERFERENCES:

<table>
<thead>
<tr>
<th>Group</th>
<th>Ions</th>
<th>Interfering Ions</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>Hg(I)</td>
<td>S$^{-2}$, S$_2$O$_3^{-2}$, MoO$_4^{-2}$, IO$_3^{-}$, V$_2$O$_5^{-}$</td>
</tr>
<tr>
<td>2.</td>
<td>Hg(II)</td>
<td>I$^{-}$, IO$_3^{-}$</td>
</tr>
<tr>
<td>3.</td>
<td>SeO$_3^{-2}$</td>
<td>None</td>
</tr>
<tr>
<td>4.</td>
<td>SeO$_4^{-2}$</td>
<td>None</td>
</tr>
<tr>
<td>5.</td>
<td>TeO$_3^{-2}$</td>
<td>MnO$_4^{-}$</td>
</tr>
<tr>
<td>6.</td>
<td>Pd(II)</td>
<td>S$^{-2}$, S$_2$O$_3^{-2}$, I$^{-}$</td>
</tr>
</tbody>
</table>
TABLE III-B (continued)

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<tr>
<th>Group Ions</th>
<th>Interfering Ions</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pd(II) (continued)</td>
<td>IO₃⁻, CN⁻</td>
</tr>
<tr>
<td>7. Pt(IV)</td>
<td>None</td>
</tr>
<tr>
<td>8. Au(III)</td>
<td>NO₂⁻, S⁻², S₂O₃⁻², CN⁻, Fe(CN)₆⁻⁴, Fe(CN)₆⁻³</td>
</tr>
</tbody>
</table>

REMARKS:

1. Tungstate is reduced to a blue, lower oxide by SnCl₂, but due to the relative lack of sensitivity it has not been included as a group ion.

2. The reactions of Hg(I) and Hg(II) are fairly insensitive. In addition, the fine black precipitate forms slowly, especially if dilute. If the precipitate is formed in the presence of colored ions, it may be difficult to identify the elemental mercury.

3. Permanganate, although highly colored, is an interference only in the test for TeO₃⁻². In all cases, it is reduced by SnCl₂ to give clear solutions.

4. Mercury (I), mercury (II), palladium (II) and gold (III) suffer most from interferences in this group. This is easily understood in view of the strong complex-forming ability of all these ions. The most common interferences are
TABLE III-B (continued)

5. Due to the lack of sensitivity of Hg(II), a more concentrated solution had to be used for its interference study. A concentration of 2 milligrams metal ion per milliliter proved satisfactory. All other ions were sufficiently sensitive so that 1 mg/ml solutions were used.

6. Nitrite ion reduces Au(III) to elemental gold.

7. Ferrocyanide and ferricyanide ions decrease the sensitivity of SnCl₂ toward Au(III). Apparently, stannous ferrocyanide and stannous ferricyanide are precipitated.
TABLE III-C
INTERFERENCE STUDIES

GROUP REAGENT: Phenyl fluorone

REACTING SPECIES: Ge(IV), Sb(III), Sn(II), Sn(IV), Ti(IV), Zr(IV), $\text{WO}_4^{-2}$, $\text{MoO}_4^{-2}$.

NON-REACTING SPECIES: Li(I), Na(I), K(I), Rb(I), Cs(I), Cu(II), Ag(I), Au(III), Be(II), Mg(II), Ca(II), Sr(II), Ba(II), Zn(II), Cd(II), Hg(I), Hg(II), $\text{BO}_2^{-}$, $\text{B}_4\text{O}_7^{-2}$, Al(III), Ga(III), Ce(III), Ce(IV), Ti(I), $\text{CO}_3^{-2}$, $\text{SiO}_3^{-2}$, Pb(II), Th(IV), $\text{NH}_4^{+}$, $\text{NO}_2^{-}$, $\text{NO}_3^{-}$, As(III), As(V), Sb(V), Bi(III), $\text{S}_2\text{O}_3^{-2}$, $\text{SO}_3^{-2}$, $\text{SO}_4^{-2}$, Cr(III), CrO$_4^{-2}$, SeO$_3^{-2}$, SeO$_4^{-2}$, TeO$_3^{-2}$, TeO$_4^{-2}$, UO$_2^{+2}$, Cl$^{-}$, ClO$_3^{-}$, ClO$_4^{-}$, Mn(II), Br$^{-}$, I$^{-}$, IO$_3^{-}$, Fe(III), Co(II), Ni(II), Ru(III), Rh(III), Pd(II), Os(VIII), Ir(IV), Pt(IV), CN$^{-}$, Fe(CN)$_6^{−4}$, Fe(CN)$_6^{−3}$, SCN$^{-}$, acetate, oxalate, malonate, succinate, tartrate, citrate, EDTA.

INTERFERENCES:

<table>
<thead>
<tr>
<th>Group</th>
<th>Ions</th>
<th>Interfering Ions</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>Ge(IV)</td>
<td>$\text{S}^{-2}$</td>
</tr>
<tr>
<td>2.</td>
<td>Sb(III)</td>
<td>$\text{BrO}_3^{-}$</td>
</tr>
<tr>
<td>3.</td>
<td>Sn(II)</td>
<td>None</td>
</tr>
<tr>
<td>4.</td>
<td>Sn(IV)</td>
<td>None</td>
</tr>
<tr>
<td>5.</td>
<td>Ti(IV)</td>
<td>$\text{HPO}_4^{-2}$, $\text{P}_2\text{O}_7^{-4}$, F$^{-}$</td>
</tr>
<tr>
<td>6.</td>
<td>Zr(IV)</td>
<td>$\text{HPO}_4^{-2}$, F$^{-}$</td>
</tr>
</tbody>
</table>
TABLE III-C (continued)

<table>
<thead>
<tr>
<th>Group Ions</th>
<th>Interfering Ions</th>
</tr>
</thead>
<tbody>
<tr>
<td>7. WO&lt;sub&gt;4&lt;/sub&gt;&lt;sup&gt;-2&lt;/sup&gt;</td>
<td>None</td>
</tr>
<tr>
<td>8. MoO&lt;sub&gt;4&lt;/sub&gt;&lt;sup&gt;-2&lt;/sup&gt;</td>
<td>None</td>
</tr>
</tbody>
</table>

REMARKS:

1. The group as a whole is relatively free of interferences. Ti(IV) is most seriously affected, HPO<sub>4</sub><sup>-2</sup>, P<sub>2</sub>O<sub>7</sub><sup>-4</sup> and F<sup>-</sup> prevent its reaction. In the case of Zr(IV), HPO<sub>4</sub><sup>-2</sup> and F<sup>-</sup> cause interference.

2. Ascorbic acid can be used for the elimination of the interferences of MnO<sub>4</sub><sup>-</sup> and VO<sub>3</sub><sup>-</sup> throughout the group.

3. Iodate is a negative interference in the test for Sb(III). A few crystals of ascorbic acid eliminates this interference.

4. Ru(III), Pd(II) and Ir(IV) leave a brown spot that would not be a serious interference when the group ions are relatively concentrated, but could be misleading in more dilute solutions.

5. All interference studies, with the exception of tin (IV), were carried out with solution concentrations of 1 mg/ml. For stannic ion, a 2 mg/ml concentration was used.
### TABLE III-D

**INTERFERENCE STUDIES**

**GROUP REAGENT:** Morin

**REACTING SPECIES:** Al(III), Be(II), Ga(III), In(III), Sc(III), Y(III), Th(IV), Zr(IV).

**NON-REACTING SPECIES:** Li(I), Na(I), K(I), Rb(I), Cs(I), Ag(I), Mg(II), Ca(II), Sr(II), Ba(II), Zn(II), Cd(II), $\text{BO}_4^{2-}$, $\text{B}_4\text{O}_7^{2-}$, Ce(III), Tl(I), $\text{CO}_3^{2-}$, $\text{SiO}_3^{2-}$, Ge(IV), Sn(II), Sn(IV), Pb(II), $\text{NH}_4^+$, $\text{NO}_2^-$, $\text{NO}_3^-$, As(III), As(V), Sb(III), Sb(V), Bi(III), $\text{S}^{2-}$, $\text{S}_2\text{O}_3^{2-}$, $\text{SO}_3^{2-}$, $\text{SO}_4^{2-}$, SeO$_3^{2-}$, SeO$_4^{2-}$, TeO$_3^{2-}$, TeO$_4^{2-}$, WO$_4^{2-}$, UO$_2^{2+}$, Cl$^-$, ClO$_3^-$, ClO$_4^-$, Mn(II), Br$^-$, BrO$_3^-$, I$^-$, IO$_3^-$, Fe(III), Co(II), Ni(II), Rh(III), Os(VIII), Ir(IV), Pt(IV), CN$^-$, Fe(CN)$_6^{3-}$, SCN$^-$, acetate, malonate, succinate, tartrate, citrate.

**INTERFERENCES:**

<table>
<thead>
<tr>
<th>Group</th>
<th>Ions</th>
<th>Interfering Ions</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>Al(III)</td>
<td>F$^-$</td>
</tr>
<tr>
<td>2.</td>
<td>Be(II)</td>
<td>F$^-$, $\text{C}_2\text{O}_4^{2-}$, $\text{MoO}_4^{2-}$</td>
</tr>
<tr>
<td>3.</td>
<td>Ga(III)</td>
<td>$\text{MoO}_4^{2-}$, Fe(CN)$_6^{3-}$</td>
</tr>
<tr>
<td>4.</td>
<td>In(III)</td>
<td>$\text{P}_{2}\text{O}_7^{4-}$, Fe(CN)$_6^{3-}$, EDTA</td>
</tr>
<tr>
<td>5.</td>
<td>Sc(III)</td>
<td>$\text{HPO}<em>4^{2-}$, $\text{P}</em>{2}\text{O}_7^{4-}$, F$^-$, $\text{C}_2\text{O}_4^{2-}$, EDTA, VO$_3^-$</td>
</tr>
</tbody>
</table>
TABLE III-D (continued)

<table>
<thead>
<tr>
<th>Group Ions</th>
<th>Interfering Ions</th>
</tr>
</thead>
<tbody>
<tr>
<td>6. Th(IV)</td>
<td>F⁻, MoO₄⁻², C₂O₄⁻²</td>
</tr>
<tr>
<td>7. Zr(IV)</td>
<td>HPO₄⁻², P₂O₇⁻⁴, F⁻, CrO₄⁻², VO₃⁻</td>
</tr>
<tr>
<td>8. Y(III)</td>
<td>F⁻, C₂O₄⁻², EDTA, HPO₄⁻², P₂O₇⁻⁴, MoO₄⁻², Ti(IV), Cu(II), Au(III), Hg(II), Ru(III), Pd(II), VO₃⁻</td>
</tr>
</tbody>
</table>

REMARKS:

1. There are a fair number of interferences in this group. However, the majority of them are easily predicted, being based upon straightforward precipitations and complexations. Fluoride, molybdate, oxalate, pyrophosphate, phosphate and EDTA are most troublesome in this regard.

2. Ions characterized by colored solutions decrease the sensitivities of the group reactions: Au(III), Fe(III), Ru(III), Cr(III), MnO₄⁻, Cu(II), Pd(II) and VO₃⁻.

3. Ascorbic acid will eliminate the interferences of: MnO₄⁻, Fe(III) and CrO₄⁻².

4. Copper (II) and gold (III) decrease the
TABLE III-D (continued)
sensitivity of the morin test but this hindrance can be eliminated by the addition of several drops of 10% KCN. The interference of Hg(II) in the test for yttrium is also removed by cyanide.

5. In the interference studies, a 5 mg/ml solution of In(III) and a 2 mg/ml solution of Sc(III) were used. All other group ions were tested using 1 mg/ml solutions.
TABLE III-E
INTERFERENCE STUDIES

GROUP REAGENT: Glyoxal bis(2-hydroxyanil)

REACTING SPECIES: Ca(II), Sr(II), Ba(II)

NON-REACTING SPECIES: Li(I), Na(I), K(I), Rb(I), Cs(I), Cu(II), Ag(I), Au(III), Mg(II), Zn(II), Cd(II), Hg(I), Hg(II), BO$_2^-$, B$_4$O$_7^{2-}$, Al(III), Ga(III), Ce(III), Ce(IV), Tl(I), Th(IV), NH$_4^+$, NO$_2^-$, NO$_3^-$, As(III), Sb(III), Sb(V), Bi(III), S$_2$O$_3^{2-}$, SO$_4^{2-}$, SeO$_3^{2-}$, SeO$_4^{2-}$, MoO$_4^{2-}$, TeO$_3^{2-}$, TeO$_4^{2-}$, WO$_4^{2-}$, UO$_2^{+2}$, Cl$^-$, ClO$_3^-$, ClO$_4^-$, Mn(II), Br$^-$, BrO$_3^-$, I$^-$, IO$_3^-$, Ni(II), Ru(III), Rh(III), Pd(II), Os(VIII), Ir(IV), Pt(IV), CN$^-$, Fe(CN)$_6^{3-}$, Fe(CN)$_6^{4-}$, SCN$^-$, acetate, oxalate, malonate, succinate, tartrate, citrate.

INTERFERENCES:

<table>
<thead>
<tr>
<th>Group</th>
<th>Interfering Ions</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. Ca(II)</td>
<td>Be(II), Zr(IV), F$^-$, HPO$_4^{2-}$, Cr(III), Fe(III), Rh(III), EDTA</td>
</tr>
<tr>
<td>2. Sr(II)</td>
<td>Be(II), CO$_3^{2-}$, SiO$_3^{2-}$, Ti(IV) Zr(IV), Sn(II), Sn(IV), Pb(II),</td>
</tr>
</tbody>
</table>
### Table III-E (continued)

<table>
<thead>
<tr>
<th>Group Ions</th>
<th>Interfering Ions</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sr(II) (continued)</td>
<td>HPO$_4^{2-}$, VO$^{2+}$, VO$_3^-$, Cr(III), F$^-$, Fe(III), Co(II)</td>
</tr>
<tr>
<td>3. Ba(II)</td>
<td>Be(II), CO$_3^{2-}$, S$^{2-}$, Zr(IV), Sn(IV), Pb(II), HPO$_4^{2-}$, P$_2$O$_7^{4-}$, VO$^{2+}$, VO$_3^-$, As(V), SO$_3^{2-}$, EDTA, Cr(III), CrO$_4^{2-}$, Fe(III), SiO$_3^{2-}$</td>
</tr>
</tbody>
</table>

**Remarks:**

1. Interference studies were conducted using the following test ion concentrations: 1 mg/ml for Ca(II) and Sr(II) and 5 mg/ml for Ba(II).

2. The masking solution used in the test procedure is for the elimination of the following interferences: Cu(II), Ag(I), Au(III), Ru(III), Pd(II), Ni(II), Ir(IV).

3. Ascorbic acid should be used to reduce MnO$_4^-$ if it is present.

4. Ferric ion interferes by forming insoluble ferric hydroxide under the highly alkaline test conditions used.
**TABLE III-F**

**INTERFERENCE STUDIES**

**GROUP REAGENT:** Sodium tetraphenylboron

**REACTING SPECIES:** K(I), Rb(I), Cs(I), NH$_4^+$, Tl$^+$.

**NON-REACTING SPECIES:** Li(I), Na(I), Cu(II), Ag(I), Au(III), Be(II), Mg(II), Ca(II), Sr(II), Ba(II), Zn(II), Cd(II), Hg(I), Hg(II), BO$_2^-$, B$_4$O$_7^{2-}$, Al(III), Ga(III), Ce(III), CO$_3^{2-}$, SiO$_3^{2-}$, Ti(IV), Ge(IV), Zr(IV), Sn(II), Sn(IV), Pb(II), Th(IV), NO$_2^-$, NO$_3^-$, HPO$_4^{2-}$, P$_2$O$_7^{4-}$, As(III), As(V), Ce(IV), Sb(III), Sb(V), Bi(III), S$^{2-}$, S$_2$O$_3^{2-}$, SO$_3^{2-}$, SO$_4^{2-}$, Cr(III), CrO$_4^{2-}$, SeO$_3^{2-}$, SeO$_4^{2-}$, MoO$_4^{2-}$, TeO$_3^{2-}$, TeO$_4^{2-}$, WO$_4^{2-}$, UO$_2^{+2}$, F$^-$, Cl$^-$, ClO$_3^-$, ClO$_4^-$, Mn(II), MnO$_4^-$, Br$^-$, BrO$_3^-$, I$^-$, IO$_3^-$, Fe(III), Co(II), Ni(II), Ru(III), Rh(III), Pd(II), Os(VIII), Ir(IV), Pt(IV), CN$^-$, Fe(CN)$_6^{4-}$, Fe(CN)$_6^{3-}$, SCN$^-$, acetate, oxalate, malonate, succinate, tartrate, citrate, EDTA

**INTERFERENCES:**

<table>
<thead>
<tr>
<th>Group</th>
<th>Ions</th>
<th>Interfering Ions</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>K(I)</td>
<td>None</td>
</tr>
<tr>
<td>2.</td>
<td>Rb(I)</td>
<td>None</td>
</tr>
<tr>
<td>3.</td>
<td>Cs(I)</td>
<td>None</td>
</tr>
<tr>
<td>4.</td>
<td>NH$_4^+$</td>
<td>None</td>
</tr>
<tr>
<td>5.</td>
<td>Tl(I)</td>
<td>None</td>
</tr>
</tbody>
</table>
TABLE III-F (continued)

REMARKS:

1. There were no interferences encountered in this group.
F. SENSITIVITIES OF THE GROUP REACTIONS

A quantitative expression of the sensitivity of a spot test reaction is most important in the comparison of analytical efficiency among various tests. The term "sensitivity" is often ambiguous in its meaning. Sometimes it can mean the smallest absolute quantity of a substance capable of detection by a certain test. At other times, it is the dilution of the test solution without regard to the amount of material being considered.

The terms "limit of identification" and "dilution limit" were suggested by Feigl (16) and Heller (37) respectively, as an unambiguous measure of reaction sensitivity. The numerical value of the identification limit is an expression of the quantity sensitivity, while the dilution limit pertains to the concentration sensitivity of a test. The relationship between the identification limit, the dilution limit and the volume of the test solution is given by the expression:

\[ \text{Dilution limit} = \frac{1}{\text{Identification limit}} \times \frac{\text{Volume of test solution (ml.)} \times 10^6}{\text{Identification limit}} \]

Thus, for a sensitive test, the value of the identification limit is small, while the dilution limit is relatively large.

The sensitivity of a test is not a constant quantity irrespective of the sensitivity term used. It is found to depend upon many factors. The pH, solvents used, order of addition of reagents, and the test medium have been found
to greatly influence the quantity of detectable material. West and Hamilton (84) showed that the identification limit of a given spot test is very much dependent upon the type of filter paper used. Differences in sensitivities were found to be of the order of tenfold, and in some cases, as much as a hundredfold.

The sensitivities of the group ions included in this scheme, stated in terms of their identification limits, are given in Table IV.

TABLE IV
SENSITIVITIES OF TEST SPECIES IN GROUP REACTIONS

1. Benzidine Group

<table>
<thead>
<tr>
<th>Test Ion</th>
<th>Identification Limit (γ)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Co(II)</td>
<td>0.3</td>
</tr>
<tr>
<td>Cr(VI)</td>
<td>0.5</td>
</tr>
<tr>
<td>Ni(II)</td>
<td>3</td>
</tr>
<tr>
<td>Mn(II)</td>
<td>0.5</td>
</tr>
<tr>
<td>Pb(II)</td>
<td>5</td>
</tr>
<tr>
<td>Tl(I)</td>
<td>1</td>
</tr>
<tr>
<td>Ce(III)</td>
<td>0.5</td>
</tr>
<tr>
<td>Ce(IV)</td>
<td>0.8</td>
</tr>
<tr>
<td>Au(III)</td>
<td>1</td>
</tr>
<tr>
<td>Ir(IV)</td>
<td>5</td>
</tr>
<tr>
<td>Pt(IV)</td>
<td>2</td>
</tr>
<tr>
<td>Os(VIII)</td>
<td>2</td>
</tr>
<tr>
<td>Ru(III)</td>
<td>1</td>
</tr>
<tr>
<td>Ag(I)</td>
<td>0.8</td>
</tr>
</tbody>
</table>
TABLE IV (continued)

2. Stannous Chloride Group

<table>
<thead>
<tr>
<th>Test Ion</th>
<th>Identification Limit (γ)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hg(I)</td>
<td>3</td>
</tr>
<tr>
<td>Hg(II)</td>
<td>1</td>
</tr>
<tr>
<td>SeO$_3^{-2}$</td>
<td>0.2</td>
</tr>
<tr>
<td>SeO$_4^{-2}$</td>
<td>0.6</td>
</tr>
<tr>
<td>TeO$_3^{-2}$</td>
<td>0.6</td>
</tr>
<tr>
<td>Pd(II)</td>
<td>0.08</td>
</tr>
<tr>
<td>Pt(IV)</td>
<td>0.04</td>
</tr>
<tr>
<td>Au(III)</td>
<td>3</td>
</tr>
</tbody>
</table>

3. Phenyl Fluorone Group

<table>
<thead>
<tr>
<th>Test Ion</th>
<th>Identification Limit (γ)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ge(IV)</td>
<td>0.6</td>
</tr>
<tr>
<td>MoO$_4^{-2}$</td>
<td>0.3</td>
</tr>
<tr>
<td>Sb(III)</td>
<td>0.2</td>
</tr>
<tr>
<td>Sn(II)</td>
<td>0.2</td>
</tr>
<tr>
<td>Sn(IV)</td>
<td>1</td>
</tr>
<tr>
<td>Ti(IV)</td>
<td>1</td>
</tr>
<tr>
<td>Zr(IV)</td>
<td>0.2</td>
</tr>
<tr>
<td>WO$_4^{-2}$</td>
<td>0.6</td>
</tr>
</tbody>
</table>

4. Morin Group

<table>
<thead>
<tr>
<th>Test Ion</th>
<th>Identification Limit (γ)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al(III)</td>
<td>0.2</td>
</tr>
<tr>
<td>Be(II)</td>
<td>0.1</td>
</tr>
<tr>
<td>Ga(III)</td>
<td>2</td>
</tr>
<tr>
<td>In(III)</td>
<td>3</td>
</tr>
<tr>
<td>Sc(III)</td>
<td>0.2</td>
</tr>
<tr>
<td>Y(III)</td>
<td>1</td>
</tr>
<tr>
<td>Test Ion</td>
<td>Identification Limit ($\gamma$)</td>
</tr>
<tr>
<td>-------------------------------</td>
<td>---------------------------------</td>
</tr>
<tr>
<td>Th(IV)</td>
<td>2</td>
</tr>
<tr>
<td>Zr(IV)</td>
<td>0.1</td>
</tr>
<tr>
<td>5. Glyoxal bis(2-hydroxyanil) Group</td>
<td></td>
</tr>
<tr>
<td>Ca(II)</td>
<td>0.04</td>
</tr>
<tr>
<td>Sr(II)</td>
<td>0.08</td>
</tr>
<tr>
<td>Ba(II)</td>
<td>3</td>
</tr>
<tr>
<td>6. Sodium Tetraphenylboron Group</td>
<td></td>
</tr>
<tr>
<td>K(I)</td>
<td>1</td>
</tr>
<tr>
<td>Rb(I)</td>
<td>3</td>
</tr>
<tr>
<td>Cs(I)</td>
<td>5</td>
</tr>
<tr>
<td>NH$_4^+$</td>
<td>1</td>
</tr>
<tr>
<td>Tl(I)</td>
<td>5</td>
</tr>
</tbody>
</table>
G. CHEMISTRY OF THE GROUP REACTIONS

1. BENZIDINE

The analytical usefulness of benzidine is based upon three characteristics of the benzidine molecule:

a. It is susceptible to oxidation.

b. It has the ability to form complexes with metal salts.

c. It forms salts with various anions which are quite insoluble.

Oxidizing agents of sufficient strength can oxidize benzidine to "benzidine blue". Lead peroxide, chromate, vanadate, periodate, persulfate, chlorate and permanganate can oxidize benzidine directly. Certain other ions, e.g., Mn(II), Co(II), Ce(III), may be detected in the presence of a base by means of an auto-oxidation process.

Schlenk (69) is primarily responsible for the elucidation of the formation of "benzidine blue". Oxidation of benzidine initially produces a meriquinoid compound, p-quinoneimide, which then combines with an equivalent of benzidine and two equivalents of a monobasic acid, usually acetic, to form "benzidine blue".

Feigl (17) postulates that the great sensitivity of the reaction between manganese (II) and benzidine is not wholly due to the manganese dioxide produced by autooxidation. He considers the participation of benzidine itself in the autooxidation to be an important factor. The mechanism advanced is that during the autooxidation process,
half an oxygen molecule combines with the manganous hydroxide and the nacent oxygen that remains oxidizes a molecule of benzidine. Thus, the autoxidation of manganous hydroxide induces the oxidation of benzidine, which results in an over-all enhancement of the reaction.

To prove this hypothesis, Feigl (15) showed that cerium can react with benzidine similarly to manganese since Ce(OH)$_3$ is autoxidized to CeO(OH)$_2$.

Higher oxides of metals, e.g., lead peroxide and osmium tetraoxide, also oxidize benzidine. This type of oxidation is not as sensitive as the autoxidation process. For example, the benzidine spot test will detect only 1 μg lead, in contrast to 0.15 μg manganese or 0.18 μg cerium, which form autoxidizable oxides. The reactions of insoluble higher metal oxides with benzidine are localized reactions occurring at the interface of the metal oxide precipitate with the benzidine solution. These are topochemical reactions.

There is an interesting innovation in the extension of the benzidine reaction to include several species that would not normally be strong enough to affect oxidation. The addition of complexing or precipitating agents are utilized to enhance the oxidation. Thus, the stabilization of the cuprous state by cyanide ion makes cupric ion a more powerful oxidizing agent. Likewise, ferricyanide ion in neutral solution is quite a strong oxidizing agent, especially if zinc, mercury or lead salts
are present to precipitate ferrocyanide and keep the potential low.

Large anions have a tendency to form their least soluble salts with large cations. Thus benzidine forms precipitates with sulfate, molybdate, phosphate, tungstate, selenate, ferrocyanide and ferricyanide.

2. STANNOUS CHLORIDE

The chemistry of the stannous chloride group is quite straightforward, being based on the reducing ability of tin (II). The ions of the platinum metals, gold, mercury, selenium and tellurium are reduced to the metal by stannous ion. Tungstate is reduced by stannous chloride in strongly acidic solution to the blue, lower tungsten oxide.

In view of the relatively small reduction potential of the tin (IV)-tin (II) couple, tin (II) compounds are fairly strong reducing agents. The simple aquo stannous ion is readily hydrolyzed and exists only in the presence of a large concentration of a strong, noncomplexing acid, e.g., perchloric. The presence of a large concentration of hydrochloric acid results in the formation of the chloro complexes. Typical values for these couples are

\[ \text{Sn}^{4+} + 2e^- \rightarrow \text{Sn}^{2+} \quad E^0 = +0.15 \text{ v.} \]
\[ \text{SnCl}_6^{2-} + 2e^- \rightarrow \text{SnCl}_4^{2-} + 2\text{Cl}^- \quad E^0 = +0.14 \text{ v.} \]
3. PHENYL FLUORONE

Phenyl fluorone is 9-phenyl-2,3,7-trihydroxyfluorone (I).

In acid solution, acid-forming metals react with fluorones. Antimony, germanium, titanium, zirconium, tin, vanadium, and molybdenum are among some of the metals that react. The acid-resistance of the reaction product is especially noteworthy. The majority of the reaction products formed are pink to orange-red precipitates.

Little of a definite nature is known about the composition of the reaction products. In view of the phenolic nature of the dye stuff, the possibility of cyclic ester formation (II) is a distinct possibility. Another possible mode of bonding is through the adjacent oxygen atoms of the phenolic and carbonyl oxygens to produce an adsorption compound (color lake). Cluley (11) in studying the reaction between phenyl fluorone and germanium for the spectrophotometric determination of that metal, found that a bis complex is formed. Perrin speculates that an octahedral bis complex of the type Ge(OH)$_2$L$_2$ with bonding to the o-diphenolic oxygens of the fluorone results (59).
It has been suggested that due to the acid-resistant nature of the reaction product that the metals combining with the fluorone are in the form of isopolyacids (17).

Gillis and co-workers (27, 28) have studied various derivatives of phenyl fluorone; where the \(-C_6H_4OH(o,m,p)\), \(-CH_3\), \(-C_6H_3(OH)_2(m,p)\) groups were substituted for the phenyl radical. Other derivatives studied include the 3-nitrophenyl-, 4-nitrophenyl-, and 4-dimethylaminophenyl-2,3,7-trihydroxyfluorones. These derivatives have been used as sensitive colorimetric reagents for zirconium, tin (IV) and tantalum, respectively (65, 48, 55).

4. MORIN

Morin is 3,5,7,2',4'-pentahydroxy-flavanol (I).

Alcoholic morin solutions react with aluminum ion in neutral or acetic acid solution to give an intense
green fluorescence in ultraviolet light. The fluorescence is due to the formation of a colloidally dispersed inner complex aluminum salt of morin (67), or to an adsorption compound of morin with the metal hydroxide. The probable structure of the inner-complex salt is thought to be

![Chemical Structure](image)

The structure for this type of complex is substantiated by the knowledge that thorium forms its most stable complexes with polyanionic, oxygen containing ligands, usually with the formation of bidentate chelates. In addition, almost all of the organic reagents complexing with zirconium (usually as ZrO\(^{2+}\)) do so by forming five or six-membered chelate rings in which the metal is bonded through two oxygen atoms.

It was Goppelsroeder (31) in 1868, who discovered the fluorescence reaction between morin and aluminum ion. Likewise, beryllium, indium, gallium, scandium, yttrium, thorium, and zirconium, among others, also give fluorescing compounds with morin.

The reaction of morin with the various metal ions is quite dependent upon pH. In acid solution morin reacts
with thorium, scandium, aluminum, gallium and indium, whereas in strongly alkaline solutions it is almost specific for beryllium. The only metal ion whose reaction with morin is independent of pH is zirconium.

The highly polar nature of morin explains why some of its metal complexes can be extracted into various oxygen containing solvents such as amyl alcohol and cyclohexanol.

Ions in which the electronic distributions approximate those of the pseudo or inert-gas type atoms preferentially react with oxygen-containing anionic ligands, such as morin (59). Aluminum, beryllium, gallium, indium, scandium, yttrium, lanthanum, zirconium and thorium form ions of this type.

5. GLYOXAL BIS(2-HYDROXYANIL)

Glyoxal bis(2-hydroxyanil) was prepared and its ability to form metal complexes was discussed by Bayer (4). The molecular structure of the reagent is shown in (I). Bayer, after studying the nature of the complexes formed, postulated the formula shown in (II).

![Molecular Structures](image)

(I)  (II)

The singly most important reaction of this reagent
is its reaction with calcium to give a red precipitate. This reaction was reported by Goldstein and Stark-Mayer in 1958 (30). The logical extension of this reaction to a quantitative spectrophotometric method has been reported by several workers (78, 43, 88, 23).

The calcium complex (59) presumably involves bonding to the metal through the oxygen and nitrogen atoms which are disposed tetrahedrally around it. Magnesium does not interfere because it prefers octahedral coordination. The reaction with glyoxal bis(2-hydroxyanil) utilizes the tendency of calcium towards partial covalent-bond formation. Tetradeutate chelation involves bonding to the tertiary nitrogen atoms, a reaction favoring calcium more than strontium or barium.

A serious drawback to the calcium-glyoxal bis(2-hydroxyanil) reaction, especially the quantitative colorimetric method is the fading of the red color. From a study of this problem, Lindstrom and Milligan postulated that the reagent undergoes a base-catalyzed hydrolysis, with the glyoxal produced rearranging into the glycolate anion. This glycolate removes calcium either by precipitation or complex-formation (50).

In a further effort to obtain a stable color with calcium, various methyl and nitro derivatives of glyoxal bis(2-hydroxyanil) were prepared (49). It was found that the introduction of nitro groups in either the 4 or 5-position yielded compounds with no value as an analytical
reagent. Substitution of methyl groups in the 4 position gave a reagent with increased sensitivity toward calcium. Substitution in the 5 positions with methyl groups did not enhance sensitivity but did yield a more stable reagent which gave a calcium complex of greater stability.

6. SODIUM TETRAPHENYLBORON

Wittig (89) first prepared lithium tetraphenylboron in 1949. In this same paper, he states that potassium ion forms a very insoluble salt with the tetraphenylborate ion. Wittig also reported that sodium ion fails to yield a precipitate but insoluble crystalline salts were formed with Rb⁺, Cs⁺, NH₄⁺, and other heavy metals.

In addition to the precipitates formed with the metal ions, sodium tetraphenylboron yields precipitates with various nitrogen containing compounds, for example, amines and alkaloids. The analytical reactions of sodium tetraphenylboron have been treated in several reviews (3, 29).

Sodium tetraphenylboron is a salt-forming organic precipitant. Although less selective than complex-forming agents, the salt-formers are an extremely important class of organic reagent since they permit detection and determination of the alkali metals, the alkaline earths, various large complex cations and anions, plus certain anions, e.g., nitrate, which normally form soluble compounds.
III. A SPECIFIC SPOT TEST FOR CADMIUM UTILIZING
GLYOXAL-BIS(2-HYDROXYANIL)

A. GENERAL DISCUSSION

Although it is a relatively common metal, cadmium has remained one of the most difficult to detect. The problems associated with its detection are apparent when it is realized that the precipitation of yellow cadmium sulfide with all of its associated complications is still considered one of the best means of detecting this element. The precipitation of the cadmium iodide complex using the iron (II) complex with $\alpha,\alpha'$-dipyridyl (19) is probably the most generally useful test reaction available up to the present. The red precipitate is so intensely colored that excellent sensitivity is obtained. Although the test is selective for anionic iodo complexes, the metals that form such complexes are those that would ordinarily be associated with cadmium and are, therefore, critical. It might be mentioned that metals such as lead, silver and thallium which are precipitated by iodide also give positive interferences due to the absorption of the reagent on the respective precipitates. Specificity can only be approached by removing the chloride group of metals and then masking other potential interfering metals as ammine complexes. Various organic reagents such as diphenylcarbazide, di-p-nitrophenylcarbazide,
di-naphthylcarbazone and diphenylthiocarbazone have been employed with only moderate success. The most successful of such reagents has been p-nitrodiazoaminoazobenzene which forms a violet to blue lake in the presence of cadmium. Most interfering metals can be complexed by the addition of tartrate (13).

Preliminary studies of glyoxal-bis(2-hydroxyanil) disclosed its potential value as a reagent for cadmium. Excellent sensitivities were obtained, and pH control did not appear critical. A number of metals react with the reagent, but preliminary investigations indicated the likelihood that most of these could be masked through use of various complexing agents.

Under the highly alkaline conditions of the test, it was evident that tartrate would have to be present to prevent the general formation of hydroxides. In addition, the reactions of lead and thallium with the reagent were also masked with tartrate. The interference due to silver was eliminated with thiosulfate, as were reactions of copper and gold. Fluoride was used to further condition the test by masking the reactions of iron, uranium, calcium, strontium and barium.

The use of a solution of the above complexing agents gave a selective test with only cobalt, nickel and cadmium reacting. The test was made specific for cadmium by utilizing anion exchange resin beads and concentrating the metal ion on the resin as the tetraiodo complex.
B. EXPERIMENTAL

1. REAGENTS AND CHEMICALS

Unless otherwise specified, all solutions were made with AR grade chemicals and distilled water.

a. Glyoxal bis(2-hydroxyanil) solution: one percent in ethyl alcohol.


c. Masking mixture: a solution containing equal volumes of the following was prepared:

(1). sodium thiosulfate, twenty percent aqueous

(2). sodium tartrate, twenty percent aqueous

(3). sodium fluoride, saturated aqueous

d. Potassium iodide: fifty percent aqueous.

e. Metal ion solutions: stock solutions containing 10 mg/ml were prepared using appropriate salts.

f. Dowex 2-X8 anion exchange resin (50-100 mesh in Cl⁻ form). A suitable quantity of resin was packed in a small column and washed with 1N HCl to remove trace metal contaminants. The purified resin was then washed with distilled water and air dried.

2. PROCEDURE

The following procedure is proposed:

A drop of metal ion solution is placed in the depression of a white spot plate. Two drops of the masking mixture and two drops of the potassium iodide solution are added. About 20 ion exchange beads are added, and the mixture is stirred and allowed to equilibrate for a minute
(the equilibration time can be varied depending upon the amount of cadmium present). The supernatant solution is then drawn from the spot plate depression and discarded. A medicine dropper, drawn to a fine point, serves nicely for this operation since care must be taken that the beads are not also drawn off. The beads are then washed three times with distilled water, the washings being drawn off and discarded as previously described. Two drops of distilled water, a drop of glyoxal bis(2-hydroxyanil) solution and a drop of piperidine are added. A positive cadmium test is indicated by a blue color forming on the resin beads. The time of color formation and the intensity of the stain are dependent upon the amount of cadmium present. It is also to be noted that the color is not stable on the resin. Fading takes place generally within a period of several minutes.

Table V gives a list of all the ions studied in the course of this work. Of all the ions listed, only the cadmium ion gave a positive test.

3. NOTES

Those metal ion solutions which had to be prepared in highly acidic media to prevent hydrolysis were neutralized with 6 M Na₂CO₃ before proceeding with the spot test.

Various bases were investigated as to their usefulness for adjusting the pH of the reaction mixture, e.g., ammonium hydroxide, sodium hydroxide, pyridine,
morpholine, diethylamine and piperidine. Piperidine was chosen because of its enhancement of the sensitivity of the reaction. An attempt was made to combine the glyoxal-bis(2-hydroxyanil) and the piperidine into a single solution, but the mixture was found to be unstable.

Preliminary tests indicated that tartrate would have to be added to prevent hydroxide formation under the alkaline conditions of the reaction. Additional observations indicated that other masking agents would be needed to further condition the test. For example, the formation of silver oxide and interference from Cu(II) and Au(III) are masked with thiosulfate, while reactions of Fe(III), U(VI), Ca(II), Sr(II), and Ba(II) are eliminated with fluoride.

The basis for the use of the anion exchange resin is the formation of the cadmium iodo complex with its subsequent adsorption on the resin. This provides an excellent method of separation from cobalt and nickel which also react with the reagent to give a red-brown and blue color, respectively.

4. INTERFERENCE STUDIES

To determine the extent of possible interferences from the various ions listed in Table V upon the detection of cadmium, the procedure given above was modified as follows: A drop of the metal ion solution (10 mg/ml) whose interference was to be studied was placed in the
depression of a white spot plate together with a drop of cadmium solution (1 mg/ml). The remainder of the procedure was the same as that originally given.

A control test was run in parallel with the interference studies. The control was identical to the interference test, except that a drop of distilled water was used instead of the cadmium solution.

There were no interferences, either positive or negative, from any of the ions tested, nor did colored ions interfere.

The sensitivity of the cadmium test is given by:

Limit of identification of Cd(II): 0.05 μg
Dilution limit: 1:1,000,000
TABLE V
IONS STUDIED FOR POSSIBLE INTERFERING EFFECTS

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VITA

John T. Diffee was born August 10, 1927 in Memphis, Tennessee. He attended elementary and secondary schools in Memphis, graduating in 1945 from Catholic High School. He entered the United States Marine Corps after graduation from high school and saw service in China. In 1951, he received a B.S. in Chemistry from Memphis State University.

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Title of Thesis:  Systematic Methods of Spot Test Analysis

Approved:

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Date of Examination:

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