tube. Fine copper wires soldered to the platinum wires lead to binding-posts as indicated. The upper wire is brought smoothly up to the capillary, and tied there with thread in order that it may not be caught by the wire basket placed over the pipette to stop the glass in case of explosion. This basket, as shown in the sketch, is of very heavy wire of about $\frac{1}{4}$-inch mesh lined with heavy 12-mesh wire screen. One side is slit so as to sit astride the capillary of the pipette, and the rough surfaces are bound with tin so that they may not catch on the wires. The bottom of the basket is cut out enough to allow manipulation of the stop-cock of the explosion pipette, while the basket is in place. The method of connecting this pipette to the burette and of transferring the gas is the same as for the other pipettes.

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[CONTRIBUTIONS FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF CINCINNATI. NO. 65.[1]]

A METHOD FOR THE DETECTION OF THE MORE COMMON ACIDS.

BY STANLEY R. BENEDICT AND J. F. SNELL.

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THE following systematic scheme for the detection of the acid radicals (anions) was suggested by the reasonably successful attempts of Bailey and Cady,[2] and of Abegg and Herz,[3] to reduce the analysis for anions to a system resembling that commonly used in the detection of the cations.[4]

This method, though differing radically in its present form from that of Bailey and Cady, grew out of the use of the latter with classes in the University of Cincinnati, and provides for the detection of the same anions with the addition of the nitrite and sulphide ions.

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[1] Read before the Cincinnati Section of the American Chemical Society, November 9, 1904.

[2] Bailey and Cady: "A Laboratory Manual of Qualitative Analysis," 4th ed., 1901.

[3] Abegg and Herz: *Zeit. anorg. Chem.*, **23**, 236; "Chemisches Praktikum," 1900, pp. 113-114.

[4] W. A. Noyes, in the fifth edition of his "Qualitative Analysis," 1901, describes a method based on that of Abegg and Herz, but materially modified and expanded.

The distinguishing features of the method may be summarized as follows: (1) As in the methods of Bailey and Cady, and Abegg and Herz, the majority of the anions are detected and successively removed from one portion of solution. The older and more common procedure of testing for each anion in a separate portion of the solution has the disadvantages of using more substance and of requiring a more exhaustive knowledge of possible "interferences" than can reasonably be expected of a beginner. (2) The groups are made as small as possible. Indeed, wherever practicable we have provided for the removal of the anions singly or in pairs. This renders the separation within the groups very simple, and, we believe, facilitates the analysis materially. (3) The time-consuming operations of distillation and evaporation have been avoided as far as practicable. (4) Preliminary tests for the absence of certain groups of anions (not identical with the groups of the system) are introduced with the object of shortening the subsequent analysis by the omission of the tests for the ions thus proved absent.

The solution is prepared as usual by boiling with concentrated sodium carbonate solution. The boiling must be continued long enough to expel all the ammonia present. If the solution, after boiling with sodium carbonate, is blue, due to the presence of copper, it should be treated with hydrogen sulphide.

For convenience of reference the solution thus freed from cations will be designated "Solution A."

The analysis is carried out as follows:

About half of Solution A is reserved for individual tests for the anions of Group IX. Minor portions of 2-3 cc. are used for the two preliminary tests which follow, and the remaining ("major") portion is used for the precipitation of Group I.

Preliminary Test for Halogen and Nitrite Ions.—Neutralize a small portion (2-3 cc.) of Solution A with dilute sulphuric acid, add to the liquid nearly an equal volume of concentrated sulphuric acid and a small quantity of manganese dioxide, warm and test the escaping vapors with potassium iodide starch paper. If no coloration appears, bromide, chloride, iodide, chlorate and nitrite ions are absent, and the tests for them may be omitted below.

Preliminary Test for Cyanide, Arsenite and Iodide Ions.—To 1 or 2 cc. of N/25 mercuric chloride solution add a little sodium hydroxide solution. A yellow precipitate of mercuric oxide is produced. Now add 1 or 2 cc. of Solution A. If cyanide, arsenite, or iodide ions are present the precipitate will at once dissolve, forming a complex salt. If the precipitate does not dissolve, the tests for arsenite, iodide and cyanide may be omitted below.

GROUP I.—$Fe(CN)_6''''$, SCN', $Fe(CN)_6'''$, CN', I', Br', *and* Cl'.

Acidify the main portion of Solution A with dilute nitric acid (odor of sulphur dioxide at this point indicates sulphite ion; see Group V). Add silver nitrate in slight excess, filter and reserve the filtrate for lower groups. If the preliminary test has indicated the presence of halogens, divide the precipitate, after washing, into two portions.

Treatment of Portion I for the Identification of the Ferrocyanide, Ferricyanide, Sulphocyanate and Cyanide Ions.—Digest the precipitate in the cold with a mixture of three volumes of 2N sodium chloride and one volume of 5N hydrochloric acid. By this means the ferrocyanide, ferricyanide, sulphocyanate and cyanide ions are again brought into solution. Filter off and discard the precipitate of silver chloride.

$Fe(CN)_6''''$.—To the filtrate add ferric chloride in excess. A dark blue precipitate of ferric ferrocyanide shows the presence of *ferrocyanide* ion. Filter and test the filtrate for complete precipitation with a little more ferric chloride.

SCN'.—A blood-red color in the filtrate shows the presence of *sulphocyanate* ion.

$Fe(CN)_6'''$.—To the filtrate add sulphurous acid and a little more ferric chloride and warm the test-tube. A dark blue precipitate indicates the *ferricyanide* ion. The precipitate is again ferric ferrocyanide, the ferricyanide ion having been reduced to ferrocyanide ion by the sulphurous acid.

CN'.—If the preliminary test has not proved the absence of the cyanide ion, filter off the precipitate of ferric ferrocyanide, make the filtrate alkaline with sodium hydroxide and add a portion to a suspension of mercurous oxide prepared by adding a slight excess of sodium hydroxide to N/25 mercurous nitrate solution. If *cyanide* ion is present the precipitate will partly dissolve, while that which remains undissolved will become light gray in color. (One portion of the mercurous oxide is oxidized and dissolved, the other is reduced to metallic mercury.)[1]

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[1] Benedict: *Am. Chem. J.*, **32**, 481 (1904).

Treatment of Portion II for the identification of the iodide, bromide and chloride ions.—This may be omitted if the preliminary test has shown absence of halogens). Transfer this portion of the precipitate to a small beaker, add a few fragments of zinc, cover with water, add a few drops of sulphuric acid and warm until the entire precipitate has become black or brown in color, owing to the reduction of the silver salts to metallic silver. Filter and neutralize the filtrate with sodium carbonate. Filter off and discard the precipitate of zinc hydroxide and carbonate. To the filtrate add N/10 potassium iodate and proceed to A or B below.

A. If sulphocyanate ion is present. I'.—To a minor portion of the solution add sodium acetate and acidify with acetic acid. Liberation of iodine indicates the *iodide* ion. The liberated iodine may be detected either by coloration of the solution or by shaking out with carbon disulphide.

Br'.—Acidify the major portion of the solution with acetic acid and boil until colorless. Add a little more potassium iodate, and if coloration appears, boil again until colorless. Repeat until further addition of potassium iodate fails to produce coloration, but avoid more than a slight excess of potassium iodate. Having expelled all the iodine by boiling, add to the solution nearly one-half its volume of dilute nitric acid. Coloration (due to liberated iodine and bromine) shows the presence of *bromide* ion, which may be confirmed by shaking a portion of the solution with carbon disulphide.

Cl'.—Boil the main portion of the solution until colorless, add 1 or 2 cc. of potassium iodide solution and boil again until colorless. Now add an equal volume of concentrated nitric acid and two or three drops of silver nitrate solution. A white precipitate, insoluble on warming, shows the presence of the *chloride* ion.

B. If sulphocyanate ion is absent.—Acidify the solution (containing the potassium iodate) with acetic acid. Coloration shows the presence of the *iodide ion*, which may be confirmed by shaking a small portion of the solution with carbon disulphide. The main portion is freed from iodide and tested for bromide and chloride, as directed above under A.[1]

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[1] Benedict and Snell: This JOURNAL, **25**, 809 (1903).

GROUP II.—ClO_3'.

(If the preliminary test for halogens has given a negative result, the test for the chlorate ion may be omitted.)

To a minor portion of the filtrate from Group I (which should contain a slight excess of silver nitrate) add a small piece of zinc and warm. A white precipitate of silver chloride shows the presence of the *chlorate* ion.

GROUP III.—AsO_3'''.

To the major portion of the filtrate from Group I add sodium chloride to remove the excess of silver. Filter and discard the precipitate. The major portion of the filtrate is reserved for Group IV, while a minor portion is used for the test for arsenite ion as follows: Make slightly alkaline with sodium carbonate, add barium chloride in excess, filter and reject the precipitate. Acidify the filtrate with concentrated hydrochloric acid and pass in hydrogen sulphide. A yellow precipitate shows the presence of the *arsenite* ion. (This test may be omitted, if arsenic was proved absent in the analysis for cations.)

Note.—The arsenate ion is completely precipitated by barium, while the solubility product of barium arsenite is so high that enough arsenite ion is left in solution to give the reaction with hydrogen sulphide.

GROUP IV.—SO_4''.

To the major portion of the solution from which the silver ions have been removed (see Group III) add more nitric acid and then a few drops of barium chloride solution. A white precipitate indicates the *sulphate* ion. If a precipitate is obtained, add a slight excess of barium chloride and filter.

GROUP V.—SO_3''.

The presence of the sulphite ion will usually have been indicated by the odor of sulphur dioxide obtained on acidification for Group I. To the filtrate from Group IV add more barium chloride and boil for two or three minutes. The nitric acid oxidizes the *sulphite* ion to sulphate ion, which is then precipitated by the barium ion. The boiling should be continued until all the sulphite present has been removed.

Note.—The arsenite ion, if present, is oxidized to arsenate by this treatment. Hence, unless the absence of the arsenite ion has been proved, a test for arsenate ion in Group VII does not prove the presence of that ion in the original solution.

GROUP VI.—C_2O_4'' *and* CrO_4''.

Add more barium to the filtrate from Group V, neutralize with sodium carbonate and acidify with acetic acid. Allow to stand for a few minutes. A yellow precipitate indicates the *chromate* ion, a white precipitate the *oxalate* ion.

Note.—The chromate ion can not be present if the original solution was colorless of if chromium was not found in the analysis for cations.

Filter, to the filtrate add calcium chloride and concentrate the liquid to one-half its volume or less. A fine white precipitate confirms the presence of the *oxalate* ion, the solubility product of calcium oxalate being lower than that of barium oxalate. Filter again and use the filtrate for Group VII.

GROUP VII.—AsO_4''' *and* PO_4'''.

To the filtrate from Group VI add solid ammonium chloride, agitate until dissolved, make alkaline with ammonium hydroxide and add more calcium chloride. A white precipitate indicates arsenate or phosphate ion or both. Filter and reserve the filtrate for Group VIII.[1]

AsO_4'''.—(This test may be omitted if no arsenic was found in the analysis for cations.) Dissolve the precipitate in dilute hydrochloric acid, add sulphurous acid and boil to reduce the arsenate ion to arsenite, expel excess of sulphurous acid by boiling, add concentrated hydrochloric acid and thoroughly saturate with hydrogen sulphide. A yellow precipitate indicates the *arsenate* ion, unless arsenite ion has been found. If arsenite ion has been found, a special test for arsenate must be made in the solution from which the cations have been removed (see Group IX).

PO_4'''.—(This test may be omitted if it has already been made in the course of the analysis for cations.) Completely remove the arsenic by means of hydrogen sulphide, filter and boil out all excess of hydrogen sulphide. Add a little of this solution to an excess of a solution of ammonium molybdate, strongly acidified with nitric acid. Warm very gently and leave standing for five

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[1] A fact overlooked by Abegg and Herz and apparently not generally known is that neither metaborate nor tartrate ions are precipitated by calcium in neutral or alkaline solution containing a considerable quantity of ammonium salt.

minutes. Formation of a yellow precipitate shows the presence of the *phosphate* ion.

Group VIII.—BO_2' *and* $C_4H_4O_6''$.

Acidulate the filtrate from Group VII with dilute hydrochloric acid, concentrate by evaporation, and divide into two portions to be tested for borate and tartrate respectively.

BO_2'.—Portion I: Add an equal volume of concentrated sulphuric acid, cool, add two volumes of methyl alcohol and place in a thick-walled test-tube or specimen tube provided with a two-holed stopper carrying (1) a glass tube connected with the gas supply and reaching nearly to the bottom of the test-tube so that illuminating gas can be passed through the liquid; (2) a glass tube drawn to a jet and surrounded by a glass tube of greater diameter, constituting a miniature Bunsen burner. Pass illuminating gas through the tube and light it at the jet. A green flame shows the presence of the *borate* ion.

$C_4H_4O_6''$.—Portion II: Make just alkaline with ammonium hydroxide, add a little barium chloride and then a little sodium hydroxide. This will cause the formation of a white precipitate. Now make further additions of sodium hydroxide until either the precipitate has been dissolved or the solution diluted to five times its original volume. If the precipitate dissolves and is reprecipitated upon heating, the *tartrate* ion is present.

Note.—On the addition of the first portion of sodium hydroxide a precipitate is always obtained, whether the tartrate ion is present or not. In case the tartrate ion is absent this precipitate consists of barium hydroxide and carbonate, the latter due to impurity in the sodium hydroxide. These precipitates will not dissolve in excess of sodium hydroxide. If the tartrate ion is present, the precipitate consists of barium tartrate only, which readily goes into solution in an excess of the hydroxide.

Group IX.—S'', NO_2', NO_3', $C_2H_3O_2'$, SiO_3'' (AsO_4''').

The tests for the anions of this group are made upon minor portions of "Solution A."

S'' *and* NO_2'.—Acidify a portion with acetic acid and warm slightly. Note the odor and test the escaping gases with lead acetate paper and with potassium iodide starch paper. The test for the nitrite ion may be confirmed by acidifying another portion of Solution A with acetic acid and adding ferrous sulphate. A brown coloration shows the presence of *nitrite* ion.

Note.—If, in removing the cations, copper was precipitated from the sodium carbonate solution by means of hydrogen sulphide, the sulphide ion will evidently be found at this point, but can not have been present in the original solution since it contained the cupric ion.

NO_3'.—Acidify a portion of Solution A with dilute sulphuric acid. In the absence of the nitrite, chlorate, iodide, bromide, chloride, ferrocyanide, ferricyanide and sulphocyanate ions, the "brown ring" test may be made upon this acidified solution as follows: Add an equal volume of concentrated sulphuric acid, cool and pour in gently a solution of ferrous sulphate, so that the two liquids do not mix. A brown ring shows the *nitrate* ion. If the nitrite ion is present, the acidified solution should be boiled until the nitrous acid is completely expelled. It may then be used for the "brown ring" test. The other ions above enumerated as interfering with this test may be removed by treatment of the solution with zinc and boiling (necessary only if chlorate ion be present) followed by the addition of silver sulphate in slight excess. Filter and use the filtrate for the test.

The following well-known test may also be used in the absence of, or after the elimination, as above, of the nitrate and chlorate ions. Add a few drops of the solution to a mixture of equal parts of phenol and concentrated hydrochloric acid and heat to boiling. Add a decided excess of sodium hydroxide. An intense green color, becoming dark blue on dilution of the solution, shows the presence of the nitrate ion.

$C_2H_3O_2'$.—Acidulate a portion of Solution A with dilute sulphuric acid, boil to expel oxides of nitrogen, if present, then make slightly alkaline with sodium carbonate. Add silver nitrate in slight excess to remove anions of other weak acids and filter. Add sodium chloride to remove excess of silver ions and filter. Saturate the filtrate with hydrogen sulphide. In another test-tube acidulate 2 to 3 cc. cobalt nitrate solution with two or three drops of normal acetic acid solution and saturate with hydrogen sulphide (the slight quantity of black precipitate formed may be filtered off or disregarded). Now add a portion of the test solution (prepared as above) to the cobalt solution. An *immediate heavy* precipitate of cobaltous sulphide proves the presence of the *acetate* ion.[1]

In the absence of the cyanide, chromate, chlorate and iodide ions the well-known test for acetate with concentrated sulphuric acid and alcohol (formation of ethyl acetate) may also be used.

SiO_3''.—Acidify a portion of the solution with hydrochloric acid, evaporate to dryness, gently heat the residue, then treat with dilute hydrochloric acid and afterwards with hot water. An insoluble residue indicates the *silicate* ion. Confirm by the usual bead tests, *viz.*, skeleton in metaphosphate, transparency in sodium carbonate bead, or by treatment with hydrofluoric acid.

$As.O_4'''$.—(To be used in case the arsenite ion has been found.) If arsenite ion has been found in Group III, the appearance of arsenate ion in Group VII does not prove the presence of that ion in the original solution (see note on Group V). To test for the arsenate ion in such an instance, to a portion of Solution A add magnesia mixture as long as a precipitate forms, filter out and wash the precipitate, dissolve it in concentrated hydrochloric acid, add a little sulphurous acid and boil until the excess is completely expelled, Pass in hydrogen sulphide. A yellow precipitate of arsenious sulphide indicates the arsenate ion.

GROUP X.—CO_3''.

Acidify the original solution or substance with dilute hydrochloric acid and test the escaping gas with a film of lime-water.

SOME NEW FORMS OF LECTURE AND LABORATORY APPARATUS.

BY G. B. FRANKFORTER AND FRANCIS C. FRARY.

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THE following pieces of apparatus will, we believe, be of some little interest to those who are teachers of chemistry. These forms of apparatus have been used both on the lecture table and in the laboratory, and have given such satisfactory results that we venture to give them a brief notice.

One of the essentials in both lecture and laboratory apparatus is simplicity in construction and manipulation. If a piece of apparatus will give good results in the hands of the average student,

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[1] Benedict : *Am. Chem. J.*, **32**, 481 (1904).