

INORGANIC MICRO ANALYSIS.

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Emich (1) traces Mikroanalysis back to a beginning in 1866, at which time some use was made of the microscope in analysis of small amounts of material. Various works on the use of the microscope in analysis have been published, among the best of which is that of Chanot and Mason (2).

One of the first to introduce separation methods was Behrens (3) who thereby introduced a greater degree of assurance into tests for the individual ions. Schoorl (4) extended this separation work by dividing the ions into characteristic groups.

In Quantitative Organic Microanalysis Pregl's (5) work is probably the most outstanding.

Of late inorganic qualitative analysis has taken another turn. Spot tests, depending on reactions between organic compounds and inorganic ions have been and are being investigated with the idea of developing specific tests for the individual ions in presence of one another. For some ions such tests have already been perfected. One of the foremost workers in this line has been Gutzeit (6), but probably a better known work is that of Feigl (7). Nieuwenburg (8) has also contributed some good work in this field. Emich (9) makes use of some of Feigl's drop reactions in his Laboratory Manual.

Numerous discussions (10), (11), (12), (13), (18), of micro analysis are available in the literature. These discussions comprise reviews, applications, economic factors in the teaching of, and in the application of micro analysis, improvements in old methods and new discoveries, and the growth of the micro system itself.

Qualitative Inorganic Micro Analysis has been given in this University for two years as a second year subject. This year the freshman class was given a certain amount of elementary practice in micro chemistry leading up to second year work.

The method now used in the second year is based on the work of Engelder and Schiller (14). The system as described by them was investigated by Watson and certain difficulties overcome by modification in the procedure (15).

It has always been the desire to get away from the use of hydrogen sulphide (H_2S) in the laboratory. In the macro system Brockman (16) developed a method which dispensed with its use. In the June issue of Journal of Chemical Education for 1934 there appeared a system developed by Gerstenzang (17) which dispensed with the use of H_2S in micro analysis.

With the idea that the system might prove useful here in the University, I undertook a semi-quantitative investigation of it, under the direction of Professor W.O. Walker, to determine the sensitivity of the tests.

Solutions of the cations were made up in 500 c.c. bottles so that each c.c. contained 20 mg. of the cation. Smaller dropping bottles were provided so that 1 mg. quantities were easily available. Test reagents were made up according to Treadwell-Hall (19) as specified in the instructions. In all procedures the instructions were followed closely in the first attempts. If difficulties were found in procedure, quantities were varied in an attempt to clear up or overcome the difficulty.

PART I.

In the following work it is to be understood that the procedure as described by Gerstenzang was followed in each individual experiment, unless otherwise stated, when the varied procedure will be described. This will save repetition of details.

Expt.1.

A solution containing 1 mg. of each of the cations of group I was made up and diluted to 0.5 c.c. Just sufficient dilute HCl was added to precipitate the group as the chlorides. An equal volume of water was added (0.5 c.c.); the mixture was then stirred and centrifuged. One more drop of dilute HCl was then added to ensure complete precipitation. The precipitate was washed twice with 5 drops of cold water.

- (a) The test for Pb^{++} ion appeared after standing a few minutes.
- (b) The test for Hg_2^{++} ion was satisfactory.
- (c) The test for Ag^+ ion was satisfactory.

The only delay in the above experiment was in the test for Pb^{++} ion. This experiment did not follow the procedure as outlined and the difference will appear in later tests, when results on following Gerstenzang's procedure will be described. The sensitivity shown here

was of the order of 2 mg. per c.c. and is really better than that for Hg_2^{++} and Ag^+ ions.

Expt. 2.

A solution of the ions of Group II was made up containing 1 mg. per c.c. each of Hg^{++} , Bi^{+++} , Mn^{++} , Fe^{+++} and Pb^{++} ions.

- (a) When this solution was treated for precipitation of Group I, the test for Pb^{++} ion did not appear.
- (b) The procedure for the precipitation and analysis of Group II was followed through and Groups II-a and II-b were separated.
- (c) The test for Pb^{++} ion was negative.
- (d) The test for Bi^{+++} ion was satisfactory.
- (e) The test for Fe^{+++} ion was positive.
- (f) The test for Mn^{++} ion was positive.
- (g) The test for Hg_2^{++} ion was negative.

Expt. 3.

A solution of Group II ions containing 2 mg. per c.c. of each ion was made up. A white precipitate formed which disappeared on addition of a few drops of dilute HCl . No precipitate of PbCl_2 remained. The test for Pb^{++} ion in the second group failed.

Expt.4.

Solution contained 1 mg. of Pb^{++} ion per c.c.
Addition of 10 drops of dilute HCl left no
precipitate of $PbCl_2$.

Expt.5.

Solution contained 2 mg. of Pb^{++} ion per c.c.

(a) Addition of 10 drops of dilute HCl gave a
white precipitate which persisted on the addition
of 10 drops of water. The mixture was stirred
and centrifuged and the supernatant liquid was
drawn off. The precipitate was washed with
2 x 5 drops of cold water. Precipitate was
dissolved.

Expt.6.

Solution contained 1 mg. of Pb^{++} ion per c.c.

(a) Following Gerstenzang's procedure, the
addition of 10 drops of water dissolved up the
precipitate.

(b) The solution was treated for the precipitation
of Groups II, III and IV. The treatment with the
 $KOH-K_2CO_3-Br_2$ solution gave a precipitate which
dissolved up on warming.

Expt. 7.

Solution contained 2 mg. of Pb^{++} ion per c.c. Treated as in experiment 6, with the same results.

Expt. 8.

Solution contained 4 mg. of Pb^{++} ion per c.c.

(a) Obtained the $PbCl_2$ precipitate in analysis for first group. The precipitate was washed with 2 x 5 drops of cold water, which dissolved up the $PbCl_2$. The washings were added to the centrifugate from the Group I separation and the white precipitate appeared again. The separation and washing were repeated with the same results.

(b) The solution was carried on to the precipitation of Group II. As in experiments 6 and 7, the alkali precipitate disappeared on warming.

Expt. 9.

Solution contained 8 mg. of Pb^{++} ion per c.c.

(a) Solution treated as in previous experiment. The white precipitate persists on washing with cold water. The washings were added to the centrifugate containing Group II and a further precipitate of $PbCl_2$ came down. This is due to solubility of $PbCl_2$ in the cold water, used for washing the Group I precipitate.

Expt. 9.
(continued)

(b) The $PbCl_2$ was then dissolved up in 2 c.c. of warm water. The addition of $K_2Cr_2O_7$ gave a heavy yellow precipitate of lead chromate without standing or cooling.

(c) The centrifugate was treated as directed. The precipitate from the $KOH-K_2CO_3-Br_2$ treatment disappeared when the mixture was warmed. When the mixture was boiled down to about one-half the volume a whitish precipitate appeared which does not correspond to the PbO_2 which should appear at this stage. This white flocculent precipitate was treated as for the separation of Groups II-a and II-b. A residue was obtained which, however, did not give the test for Pb^{++} ion in Group II-a.

Expt.10.

Solution contained 6 mg. of Pb^{++} ion per c.c.

- (a) The test for Pb^{++} ion in Group I was positive.
- (b) The test for Pb^{++} ion in Group II-a was negative.

Expt.11.

Solution contained 5 mg. of Pb^{++} ion per c.c.

- (a) The test for Pb^{++} in Group I was positive.
- (b) The test for Pb^{++} in Group II-a was negative.

Expt. 12.

Solution contained 4 mg. of Pb^{++} ion per c.c.

(a) The test for Pb^{++} was negative in Group I and in Group II-a also.

In all the above experiments the chloride precipitate was washed with 2 x 5 drops of cold water, which is quite evidently too much.

Expt. 13.

Solution contained 4 mg. of Pb^{++} ion per c.c.

(a) Added four drops of dilute HCl, then stirred and centrifuged the mixture. Another drop of dilute HCl was then added to make sure precipitation was complete. Then the mixture was diluted with five drops of water, stirred and centrifuged. The precipitate was now washed with 2 x 3 drops of cold water. The test for Pb^{++} ion in Group I was positive.

Expt. 14.

Solution contained 4 mg. of Pb^{++} ion per c.c.

Gerstenzang's procedure was followed in this experiment and the $PbCl_2$ precipitate was washed with 2 x 3 drops of cold water. There was not sufficient $PbCl_2$ left to give a positive test for Pb^{++} in Group I.

Expt. 15.

Solution contained 2 mg. of Pb^{++} ion per c.c.

(a) Following the procedure of experiment 13, three drops of dilute HCl and three drops of water were added and the mixture stirred and centrifuged. The residue was then washed with 2 x 1 drop of water. There was enough precipitate left in this case to give a positive test for Pb^{++} ion in Group I.

Expt.16.

Solution contained 1 mg. each of Ag^+ and Hg_2^{++} ion and 5 mg. of Pb^{++} ion per c.c.

(a) The solution was treated as directed and the precipitate was washed with 2 x 5 drops of cold water.

(b) The test for Pb^{++} ion was rather faint.

(c) The tests for Hg_2^{++} and Ag^+ ion were quite positive.

Expt.17.

Solution contained 1 mg. each of Ag^+ and Hg_2^{++} ion and 2 mg. of Pb^{++} ion per c.c.

(a) The solution was treated with five drops of dilute HCl and five drops of water, following the procedure of experiment 13. The resulting precipitate was then washed with 2 x 1 drop of water.

Expt.17.
(continued)

- (b) The test for Pb^{++} ion was positive.
- (c) The tests for Hg_2^{++} and Ag^+ ion were both positive.

It appears that following Gerstenzang's procedure, the sensitivity of the tests in Group I is, 5 mg. per c.c. for Pb^{++} ion and 1 mg. per c.c. or possibly ~~less~~ ^{better} for the Ag^+ and Hg_2^{++} ions. By careful manipulation and by using the technique of experiment 13, the sensitivity of the test for Pb^{++} ion in the first group may be increased to 2 mg. per c.c. The sensitivity of the other tests will probably be correspondingly increased. The increased sensitivity, if any, of the tests for these two ions was not gone into. A sensitivity of 1 mg. per c.c. was considered sufficient for the purpose in view.

The next series of experiments is to determine the concentration of Pb^{++} ion which must be present in one cubic centimeter of the original unknown to give a positive test for Pb^{++} ion in Group II-a.

The reason we get Pb^{++} ion in the second group is because of its relatively large solubility in cold water. This is one reason why the volume of reacting solutions should be kept as small as possible. Then again, when the precipitate containing Group I is washed, we get a further loss of $PbCl_2$ which is carried over into the second group.

Expt.18.

Solution contained 2 mg. of Pb^{++} ion per cc.

The $KOH - K_2CO_3 - Br_2$ treatment failed to precipitate Group II.

Expt.19.

Solution contained 4 mg. of Pb^{++} ion per cc.

The same result was obtained as in Experiment 18.

Expt.20.

Solution contained 6 mg. of Pb^{++} ion per cc.

A white flocculent precipitate was obtained from the $KOH - K_2CO_3 - Br_2$ treatment. This does not correspond to the yellow precipitate of PbO_2 which we should get.

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Note: Noyes and Bray (20) make a separation of a group containing Pb^{++} and Bi^{+++} from an acid solution in the

following manner: NaOH is added to the solution to alkalinity. If a large precipitate appears the solution is diluted to from two to three times its volume by the addition of water. This precipitate will contain the Pb^{++} and Bi^{+++} ions (Cd and Cu). This precipitate is now removed and $NaHCO_3$ is added to the centrifugate. If any additional precipitate comes down it is washed and added to the hydroxide precipitate. They recommend that you avoid excess NaOH and the $NaHCO_3$ solution is added after filtering (or centrifuging) since, under these conditions scarcely any of the slightly soluble $PbCO_3$ is converted into the soluble $NaHPbO_3$.

Expt. 21.

Solution contained 6 mg. of Pb^{++} ion per cc. For precipitation of Group II the scheme of Noyes and Bray, outlined in the preceding note, was followed. When the Group II precipitate was obtained Gerstenzang's procedure for the separation of Groups II-a and II-b was then followed. A positive test for Pb^{++} ion was obtained in Group II-a.

Expt.22.

Solution contained 2 mg. of Pb^{++} ion per cc.
The solution was treated as in Experiment 21.
A positive test for Pb^{++} ion was obtained after letting the KOH- excess H_2O_2 solution stand for a few minutes.

Expt.23.

Solution contained 1 mg. of Pb^{++} ion per cc.
The solution was treated as in Experiment 21.
The test for Pb^{++} ion was negative.

Expt.24.

Solution contained 2 mg. each of Bi^{+++} , Fe^{+++} , Mn^{++} and Hg^{++} ion and 4 mg. of Pb^{++} ion per cc.

- (a) The manganese was added in the form of the soluble $MnCl_2$. The addition of this soluble chloride precipitates the Pb^{++} as $PbCl_2$.
- (b) The solution was again treated as in Experiment 21.
- (c) The test for Pb^{++} ion was positive.
- (d) The test for Bi^{+++} ion was positive.
- (e) The test for Fe^{+++} ion appeared very sensitive.
- (f) The material containing the Mn^{++} and the Hg^{++} ions was lost.

It would appear that this procedure of Noyes and Bray could be used at this juncture for the precipitation of Groups II, III and IV, thereby doing away with the bromine oxidation treatment and considerable boiling down.

Expt. 25.

Solution contained 2 mg. of Pb^{++} ion per cc.

Gerstenzang's system was followed through using five drops of Br_2 in place of the saturated Br_2 water. The solution was boiled carefully for two minutes without a precipitate appearing.

Expt. 26.

Solution contained 4 mg. of Pb^{++} ion, 2 mg. each of Hg^{++} and Bi^{+++} ion and 1 mg. each of Mn^{++} and Fe^{++} ion per cc.

(a) The entire precipitate of $PbCl_2$ in Group I was carried over into Group II.

(b) For the precipitation of Group II, liquid Br_2 was used together with fresh concentrated solutions of K_2CO_3 and KOH which were made up by the author. The result of the KOH- K_2CO_3 - Br_2 treatment was a heavy, dark precipitate which was washed with 2 x 5 drops of hot water.

(c) On following the remainder of Gerstenzang's procedure, the tests for the ions of Group II-a were all positive. The test for Mn in Group II-b was positive and that for Hg^{++} was negative.

From the above results it seems all the previous difficulties were due to faulty solutions. The KOH and K_2CO_3 solutions being used were from stock solutions used in the second year laboratories.

Expt.27.

Solution contained 2 mg. of Pb^{++} ion, 4 mg. each of Hg^{++} and Bi^{+++} ion, and 1 mg. each of Mn^{+} and Fe^{+++} ion per cc.

(a) The $MnCl_2$ precipitated the Pb^{++} ion as $PbCl_2$. On addition of 4 drops of dilute HCl this precipitate disappeared.

(b) The prescribed procedure was worked through. The tests were positive for all the ions except the Hg^{++} ion.

Expt.28.

Solution contained 4 mg. each of Bi^{+++} and Hg^{++} ion per cc.

(a) Test for Bi^{+++} was positive.

(b) The test for Hg^{++} was negative.

Expt. 29.

Solution contained 2 mg. each of Pb^{++} and Bi^{+++} ion, 1 mg. each of Mn^{++} and Fe^{+++} ion and 4 mg. Hg^{++} ion per cc.

(a) In the treatment for the separation of Groups II and III eight drops of liquid Br_2 were used as the oxidizing agent. The mixture at this stage was centrifuged and the centrifugate was put in test tube "B". The precipitate was then washed with 2 x 5 drops of hot water and the washings were added to the contents of test tube "B". A precipitate settled out in this tube on standing but no attempt was made to determine what the precipitate was.

(b) Positive tests were obtained for the Pb^{++} , Bi^{+++} and Fe^{+++} ions.

(c) The test for Hg^{++} in Group II-b was again negative; the test for Mn^{++} ion positive.

Expt. 30.

Solution contained 10 mg. of Hg^{++} ion per cc. This experiment was the first of a series to discover where the Hg^{++} was being lost in the procedure.

(a) Hg^{++} was precipitated in Group II as yellow HgO .

(b) The yellowish centrifugate was preserved in test tube "B".

(c) The yellow residue was washed with 2 x 10 drops of hot water and the washings were kept in test tube "C".

(d) The residue was treated for the separation of Groups II and III and a good precipitate of white $\text{Hg}(\text{NH}_2)\text{Cl}$ was obtained.

(Note: $\text{Hg}(\text{NH}_2)\text{Cl}$ is soluble in hot NH_4Cl solution. In the procedure for the separation of Groups II and III, 15 mg. of NH_4Cl was added to keep Mg ion of Group III in solution).

The centrifugate was kept in test tube "D".

The washings were kept in test tube "E".

(e) On treatment for the separation of Groups II-a and II-b a slight precipitate was obtained corresponding to IIa. This is probably due to impurities.

(f) On precipitation of Group II-b a greyish precipitate was obtained. The precipitate at this point should be yellow HgO .

The centrifugate was placed in test tube "F".

The washings were placed in test tube "G".

(g) The greyish precipitate was dissolved up in 8 drops of dilute HCl and 5 drops of 3 % H_2O_2 . This solution was evaporated almost to dryness and then tested for Hg^{++} by means of SnCl_2 . The test was positive.

(h) All the centrifugates and wash waters preserved in the lettered test tubes were now treated by passing H_2S gas through them.

(i) Black precipitates were obtained in test tubes "D" and "E".

(j) Test tube "D" contains the centrifugate from the separation of Group II from Group III. It is a solution containing a little warm NH_4Cl in which $Hg(NH_2)Cl$ is soluble.

Test tube "E" contains the washings of the Group II precipitate.

(k) These black precipitates were found to be soluble in Na_2S solution and in aqua regia. This corresponds to the solubility of HgS , and since Hg^{++} ion was the only one placed in the solution, this is fairly conclusive proof as to where the Hg^{++} is being lost.

Expt. 31.

Solution contained 2 mg. of Hg^{++} ion per cc.

This solution was treated exactly as the one used in Experiment 30. All centrifugates and washings were again kept in the lettered test tubes.

(a) The solutions corresponding to those contained in test tubes "D" and "E" in Experiment 30 again gave black precipitates of HgS when H_2S was bubbled through them.

(b) The test for Hg^{++} ion in Group II-b was very faint. The precipitate representing Group II-b was again a greyish colour instead of the yellowish colour signifying HgO .

(c) It is evident that the presence of more than 2 mg. of Hg^{++} ion is necessary to get a good positive test for Hg^{++} in this group.

Expt. 32.

Solution contained 4 mg. of Hg^{++} ion, 2 mg. Bi^{+++} ion and 1 mg. each of Fe^{++} and Mn^{++} ion per c.c.

This was diluted to 2 c.c., which would be the volume of solution remaining from the separation of Group I.

(a) Used liquid Br_2 as the oxidizing agent for the precipitation of Group II.

The centrifugate was kept in test-tube "B".

Washings were kept in test-tube "C" (2 x 10 drops of hot water).

(b) The residue was now treated for the separation of Groups II and III.

The centrifugate was kept in test-tube "D".

The washings were kept in test-tube "E".

Expt. 32 (continued)

(c) Next Groups II-a and II-b were separated.

The centrifugate was kept in test-tube "F".

The washings were kept in test-tube "G".

The residue contains Group II-a.

(d) The residue was tested for the elements of Group II-a. There was no Pb^{++} ion in the solution but the centrifugate from the lead test was kept in test-tube "H". The residue was washed and the washings were kept in test-tube "I".

(e) The tests for Bi^{+++} and Fe^{+++} ions were positive.

(f) Group II-b was precipitated and the centrifugate was tested for Hg^{++} ion, giving a negative test. The wash water was also free of Hg^{++} ion.

(g) The test for Mn^{+++} ion was positive.

The test for Hg^{++} ion was very faint.

(h) H_2S gives a black precipitate in test-tubes B, C, E and H, which, however, may not be an indication of the loss of Hg^{++} ion alone, since the sulphides of ferric iron and manganic manganese are also black.

Expt. 33.

Solution contained 4 mg. Hg^{++} ion and 1 mg. each of Bi^{+++} , Fe^{++} and Mn^{++} ion per c.c.

(a) $MnCl_2$ precipitates the Bi^{+++} which is dissolved up by the addition of a little dilute HCl .

(b) Group II was precipitated and the combined centrifugate and wash water was kept in test-tube "B".

(c) The procedure for the separation of Groups II and III was followed out and the centrifugate and washings were kept in test-tube "C".

(d) The residue from "C" was treated for the separation of Groups II-a and II-b.

The centrifugate was kept in test-tube "D".

The washings were kept in test-tube "E".

(e) Pb^{++} was absent from the solution, but the centrifugate from the Pb^{++} ion test was kept in test-tube "F".

(f) The tests for Bi^{+++} and Fe^{++} ions were positive.

(g) Group II-b was precipitated and the centrifugate and washings were kept in test-tube "C".

(h) The test for Mn^{++} was positive but the test for Hg^{++} failed to appear.

(i) A slight precipitate which had settled out in test-tube "B" was removed and added to the contents of test-tube "C". This solution was centrifuged and the precipitate was treated in the separation of Groups II-a and II-b.

(j) The centrifugate when worked through for Hg^{++} gave a negative result.

(k) A yellow precipitate which had settled out in test-tube "F" proved not to be HgO .

Expt. 34.

Solution contained 4 mg. of Hg^{++} ion per c.c.

This experiment was to check again with Experiment No. 30 as to where the Hg^{++} was being lost.

(a) Groups II and III were precipitated.

The centrifugate was kept in test-tube "B".

The washings were kept in test-tube "C".

(b) Group II was separated from Group III.

The centrifugate was kept in test-tube "D".

The washings were kept in test-tube "E".

(c) The residue was now separated into Groups II-a and II-b.

The centrifugate was kept in test-tube "F".

This contains Group II-a.

(d) The contents of test-tube "F" when treated in the prescribed manner and tested for Hg^{++} ion gave a faint, cloudy grey precipitate with SnCl_2 . Evidently the limit of sensitivity for this test is about 4 mg. per c.c.

(e) All the test-tubes containing centrifugates and washings were treated with H_2S . None of them gave any black precipitate.

(f) The solution in test-tube "F" which had been tested for Hg^{++} gave a heavy black precipitate when H_2S was passed through it.

Expt. 35.

Solution contained 4 mg. of Hg^{++} ion and 1 mg. each of Bi^{+++} , Fe^{++} and Mn^{++} ion per c.c.

(a) All the tests except that for Hg^{++} ion were definitely positive.

(Note: a freshly prepared solution of saturated bromine water was used in this experiment. Evidently the stock solution in use before was not fresh enough. The freshly prepared solution worked as well as the liquid bromine.)

Expt. 36.

Solution contained 2 mg. of Hg^{++} ion per c.c.

Experiment 35 was repeated without any success.

4 mg. of Hg^{++} ion seems to be the limit of sensitivity for this test.

Conclusions:

With regard to Groups I, II-a and II-b, the following appear to be the sensitivity of the tests to

one milligram:

(a) For Ag^+ and Hg_2^{++} ion in the first group a sensitivity of 1 mg. per c.c.

(b) A concentration of Pb^{++} ion of 2 mg. per c.c. of original material will give a negative test for Pb^{++} ion in Group I following Gerstenzang's procedure, but is sufficient for its identification in Group II-a.

(c) One milligram each of Bi^{+++} , Fe^{++} and Mn^+ will give positive tests for these ions in Groups II-a and II-b.

(d) The concentration of Hg^{++} ion must be at least 4 mg. per c.c. to give a positive identification in Group II-b.

Analysis of Group III.

Expt. 37.

Solution contained 4 mg. each of Ca^+ , Ba^+ , Sr^{++} and Mg^+ ion per c.c.

(a) The test for Ba^{++} was positive.

(b) The test for Sr^{++} was positive.

(c) The precipitation of Ca^{++} and Mg^{++} as the carbonates introduced some difficulties at this stage of the procedure. The precipitate was so voluminous that it could not be dissolved up in 5 drops of dilute acetic acid as prescribed.

Expt. 38.

Solution contained 2 mg. of each of the ions per c.c.

- (a) The tests for Ba⁺ and Sr⁺⁺ were definitely positive.
- (b) The carbonate precipitate was again very large, ten drops of dilute acetic acid being insufficient for its solution.

Expt. 39.

Solution contained 1 mg. each of Ca⁺, Ba⁺⁺, Sr⁺⁺ and Mg⁺⁺ ion per c.c.

- (a) The same difficulty was experienced as in Experiments 37 and 38. The addition of 45 drops of dilute acetic acid failed to dissolve up the carbonate precipitate.
- (b) The mixture was centrifuged and the centrifugate was tested for Ca with (NH₄)₂C₂O₄ (ammonium oxalate). A faint white precipitate was observed but it was too small to identify as calcium oxalate.
- (c) The addition of more dilute acetic acid to the carbonate residue failed to dissolve it appreciably.
- (d) Addition of a few drops of H₂O₂ to the acid mixture gave a blue colouration but failed to aid in the solution of the precipitate. The addition of (NH₄)₂C₂O₄ to a little of the centrifugate failed to give a precipitate.

Expt.39 (continued)

(e) The remainder of the centrifugate was treated for the precipitation of Mg^{++} but no precipitate appeared.

Expt.40.

Solution contained 1 mg. each of Ba^{++} and Sr^{++} ion and 0.1 mg. each of Ca^{++} and Mg^{++} ion per c.c.

(a) The tests for Ba^{++} and Sr^{++} were positive.

(b) The centrifugate from the Sr^{++} precipitation was taken and Na_2CO_3 solution was added dropwise to alkalinity. The alkaline solution was then boiled gently until a gelatinous, translucent, yellow precipitate appeared. On centrifuging the precipitate appeared white, the solution giving it its yellowish colour.

(c) Five drops of dilute acetic acid was not sufficient for the complete solution of the precipitate.

(d) Addition of $(NH_4)_2C_2O_4$ to the centrifugate from (c) gave another heavy gelatinous precipitate.

The precipitates at this point were difficult to handle, so they were abandoned in favour of another attempt.

Expt. 41.

Solution contained 1 mg. of each cation per c.c.

(a) An attempt was made to wash the initial precipitate, which contained all the ions of the group, with alcohol, to get rid of any moisture. The alcohol, however, interfered with the separation of Sr^{++} so this attempt was discarded.

Expt.42.

Experiment No.41 was repeated leaving the treatment with alcohol until the precipitation of the Ca^{++} and Mg^{++} ions.

(a) The alcohol failed to remove any of the moisture from the precipitate. An attempt was made to drive off the water by heating, but it was unsuccessful. Some of the water was driven off but enough was left to keep the precipitate in a gelatinous state. Any attempts to dissolve it in acetic acid were unsuccessful.

(b) The mixture of acetic acid and precipitate was centrifuged and the acetic acid was removed. The addition of $(\text{NH}_4)_2\text{C}_2\text{O}_4$ gave a white precipitate of calcium oxalate.

(c) The centrifugate from the calcium test gave a negative test for Mg^{++} ion.

Expt. 43.

Solution contained 1 mg. of each cation per c.c.

(a) The tests for Ba^{++} and Sr^{++} ions were both very positive.

(b) The precipitate of Ca^{++} and Mg^{++} ions was still very voluminous. It could not be dissolved up in 5 drops of dilute acetic acid and was not completely dissolved by 3 c.c.

Expt. 44.

Solution contained 1 mg. of each ion per c.c.

(a) The washed phosphate precipitate was dissolved up in a solution of dilute acetic acid made up from twelve drops of water and five drops of glacial acetic acid. The best procedure is to add the five drops of acid to the precipitate and then add from eight to twelve drops of water until the precipitate is dissolved. Gerstenzang does not define his dilute acetic acid nor does Treadwell-Hall specify the concentration.

(b) The precipitate of Ca^{++} and Mg^{++} ions was dissolved up by treating the precipitate with one drop of glacial acetic acid and then adding five drops of water.

Expt.44 (continued)

(c) The subsequent tests for Ca^{++} and Mg^{++} ion were positive.

Experiment No. 44 cleared up the difficulty concerning this group. The whole difficulty was in getting the right concentration of acetic acid for the solution of the phosphate and carbonate precipitates.

The sensitivity of the tests as far as they were examined was one mg. of cation per c.c. of original solution. However, judging from the results obtained the sensitivity for some of the ions would be somewhat greater.

ANALYSIS OF GROUP IV.

Expt. 45.

Solution contained 1 mg. each of Cu^{++} , Ni^{++} , Co^{++} and Cd^{++} ion per c.c.

- (a) The test for Cu^{++} ion was negative.
- (b) The test for Ni^{++} ion was positive.
- (c) The test for Co^{++} ion was negative.
- (d) The test for Cd^{++} ion was negative.

Expt. 46.

Solution contained 4 mg. each of Cu^{++} , Ni^{++} , Co^{++} and Cd^{++} ion per c.c.

- (a) The test for Cu^{++} ion was positive.
- (b) The test for Ni^{++} ion was positive.
- (c) The test for Co^{++} ion was negative.
- (d) On application of the ferricyanide test for Cd^{++} ion a heavy, brownish-red precipitate appeared. It may be that the Co^{++} ion came over with the Cd^{++} and masked the test.

Expt. 47.

Solution contained 1 mg. each of Cu^{++} and Ni^{++} ion and 4 mg. each of Co^{++} and Cd^{++} ion.

- (a) The test for Cu^{++} ion failed.
- (b) The test for Ni^{++} ion was positive.
- (c) The test for Co^{++} ion was positive.
- (d) The precipitate supposed to be cadmium pyrophosphate had a pinkish colour which persisted in washing.
- (e) The ferricyanide test for Cd^{++} ion again gave a heavy reddish brown precipitate which was difficult to centrifuge.

Expt. 48.

Solution contained 2 mg. Cu^{++} ion, 1 mg. Ni^{++} ion, 2 mg. Co^{++} ion, and 4 mg. Cd^{++} ion per c.c. of solution.

- (a) The test for Cu^{++} ion was positive.
- (b) The test for Ni^{++} ion was positive.
- (c) On testing for Co^{++} ion, five drops of acetic acid and two drops of a-nitroso-3-naphthol failed to give a positive test. Adding the test re-agent first gave a slight precipitate which, however, disappeared on the addition of the acetic acid.
- (d) The ferricyanide treatment for Cd^{++} ion again gave the heavy reddish brown precipitate.

Expt. 49.

Solution contained 1 mg. Cu^{++} ion, 3 mg. Co^{++} ion and 1 mg. Cd^{++} ion per c.c.

(a) The test for Cu^{++} ion was negative.

(b) The remainder of the solution was lost due to an accident.

Expt. 50.

Solution contained 1 mg. each of Cu^{++} and Cd^{++} ion and 4 mg. Co^{++} ion per c.c.

The last $\text{KOH} - \text{Br}_2$ treatment for the precipitation of Group IV was made at room temperature to see how it would affect the subsequent tests.

(a) The test for Cu^{++} ion was negative.

The solution was a transparent brown-orange colour. On warming the solution it turned blue.

(b) On neutralizing the centrifugate from the Cu^{++} separation with NH_4OH a heavy brown precipitate was obtained which was not identified.

(c) The test for Co^{++} ion was negative.

(d) The procedure for the identification of Cd^{++} ion again gave the heavy dark precipitate.

Expt.51.

Solution contained 4 mg. of Co^{++} ion.

(a) Before treating the solution for the separation of Groups III and IV it was divided into two parts. To the first part NH_4OH was added, first giving a white precipitate. This precipitate persisted on the addition of the NaHPO_4 .

(b) To the second part the NaHPO_4 was added first. A white precipitate came down which, however, dissolved up on the addition of the NH_4OH . On standing a short while a white precipitate again appeared, which resembled that in the first part of the solution. This behaviour is explained in Treadwell-Hall (19) Volume I, page 179.

(c) Using glacial acetic acid a positive test for Co^{++} was obtained.

Expt.52.

Solution contained 4 mg. of Cd^{++} ion per c.c.

(a) The addition of acetic acid and $\text{Na}_4\text{P}_2\text{O}_7$ failed to give a precipitate of cadmium pyrophosphate.

Expt. 53.

Solution contained 2 mg. of Cu^{++} and Co^{++} ion and 1 mg. of Ni^{++} ion per c.c.

- (a) The test for Cu^{++} ion was positive (maximum sensitivity).
- (b) The test for Ni^{++} ion was positive.
- (c) The test for Co^{++} ion was positive.
- (d) The addition of the acetic acid and $\text{Na}_4\text{P}_2\text{O}_7$ to the centrifugate from the Co^{++} test gave a pink precipitate. This precipitate was dissolved up in dilute HNO_3 and $\text{K}_3\text{Fe}(\text{CN})_6$ was added to the solution. The heavy reddish-brown precipitate which had been appearing at this stage all along came down here. Evidently the cobalt pyrophosphate is not soluble in concentrated acetic acid so the test for Cd^{++} ion is masked by the precipitation of $\text{CO}_2(\text{Fe}(\text{CN})_6)_2$.

Expt. 54.

Solution contained 1 mg. each of Cu^{++} , Ni^{++} and CO^{++} ion.

- (a) The test for Cu^{++} was negative.
- (b) The test for Ni^{++} was positive. The sensitivity of this test is probably better than 1 mg. per c.c.

Expt. 54. (continued)

- (c) The test for Co^{++} was positive. The sensitivity of this test too is probably greater than 1 mg. per c.c.

Expt. 55.

The solution contained 4 mg. each of Ni^{++} and Co^{++} ion per c.c.

(a) The procedure was worked through to the separation of Cd^{++} . Next, ten drops of $\text{Na}_4\text{P}_2\text{O}_7$ solution were added without first adding the acetic acid. On warming a precipitate appeared which was a little darker than the one which had been coming down here in the foregoing experiment.

(b) The centrifugate was removed and to it was added the concentrated acetic acid. This procedure gave some of the usual pink precipitate.

(c) Concentrated acetic acid was added to the precipitate of (a). Very little, if any, of the precipitate was dissolved up. The supernatant liquid took on a bluish colouration.

(d) Varying quantities of various concentrations of acetic acid failed to dissolve up the precipitate. 2 c.c. of concentrated acetic acid had no effect on the precipitate. Concentrations from very dilute to a 50 % solution behaved in the same manner.

Expt. 56.

The solution contained 4 mg. of Co^{++} ion per c.c.

(a) The general procedure was worked through to the precipitation of Cd^{++} ion. At this stage the solution was divided into two parts: to one half was added Na_2HPO_4 and to the other half was added $\text{Na}_4\text{P}_2\text{O}_7$. This was done to find out if the material which was taken for $\text{Na}_4\text{P}_2\text{O}_7$ was really that compound and not the original Na_2HPO_4 from which it was made.

(b) The Na_2HPO_4 failed to give a precipitate in the acetic acid solution.

(c) The $\text{Na}_4\text{P}_2\text{O}_7$ gave a heavy pink precipitate which corresponded with the precipitate at this stage in the previous experiments.

(d) The addition of $\text{Na}_4\text{P}_2\text{O}_7$ to the solution from (b) gave the pink precipitate.

Expt. 57.

The solution contained 4 mg. of Cd^{++} ion per c.c.

(a) The procedure was followed through to the precipitation of the Cd^{++} ion as the pyrophosphate. The solution was divided into two parts and to each part was added one half the amount of the reagents required.

Expt.57 (continued)

(b) There failed to appear a precipitate of any kind.

(c) Boiling the solution down to about one-half its volume failed to bring about any precipitation.

Expt.58.

Solution contained 10 mg. Cd^{++} ion per c.c.

(a) The solution was halved as in experiment 57 (a). To the first part was added 0.5 c.c. of concentrated acetic acid and 5 drops of $\text{Na}_4\text{P}_2\text{O}_7$ solution. When the mixture was first warmed no precipitate appeared. On standing for a few minutes a precipitate did commence to settle out.

(b) The mixture was centrifuged and the supernatant liquid removed and the precipitate washed. The ferricyanide test for Cd^{++} ion was quite positive.

(c) The remaining half of the original material also gave a positive test for Cd^{++} ion.

Expt. 59.

Solution contained 5 mg. of Cd^{++} ion per c.c.

(a) The test was done in two halves as before. To the first half was added 0.5 c.c. acetic acid and 5 drops of $\text{Na}_4\text{P}_2\text{O}_7$ solution. Warming the solution and letting it stand failed to give any precipitate.

(b) The other half of the original solution was added to the already treated solution, together with 0.5 c.c. of acetic acid. Still no precipitate appeared on warming the solution and allowing it to stand.

(c) The addition of more $\text{Na}_4\text{P}_2\text{O}_7$ also failed to give any precipitate.

Expt. 60.

Solution contained 2 mg. Co^{++} ion and 10 mg. of Cd^{++} ion per c.c.

(a) The ferricyanide test for Cd^{++} ion gave the usual reddish brown precipitate. Examination under the microscope failed to distinguish the two compounds. It appears certain that the cobalt compounds mask the colour of the cadmium compounds of pyrophosphate and ferricyanide.

Expt. 61.

Solution contained 6 mg. of Cd^{++} ion, 1 mg. of Cu^{++} ion and 1 mg. of Co^{++} ion per c.c.

(a) The use of half or full quantities of the reagents for the identification of Cu^{++} ion fails to give a precipitate.

(b) The test for Co^{++} ion was positive.

(With regard to this test for Co^{++} ion, sometimes the addition of the a-nitroso-B-naphthol does not give enough precipitate to be easily centrifuged. However, if you observe closely a drop of the test reagent as it goes into a solution containing Co^{++} ion, you can distinguish the precipitate in the form of a very faint cloudiness which spreads out from the drop. This does not appear in a solution which contains no Co^{++} ion.). Sometimes on standing the precipitate will become more noticeable. The sensitivity of this test appears to be somewhat better than 1 mg. per c.c.

Expt. 62.

Two solutions, one of which contains a definite amount of Cd^{++} ion and the other an equal amount of Co^{++} ion.

(a) The addition of $\text{Na}_4\text{P}_2\text{O}_7$ to the solution containing Co^{++} ion precipitates the pink cobalt pyrophosphate. This precipitate is soluble in an excess of $\text{Na}_4\text{P}_2\text{O}_7$ solution. The addition of the concentrated acetic acid, however, causes the cobalt pyrophosphate to re-precipitate.

(b) The procedure in (a) was repeated with the solution containing the Cd^{++} ion. The results were the same except that it took a little greater excess of $\text{Na}_4\text{P}_2\text{O}_7$ solution to redissolve the cadmium pyrophosphate precipitate.

(c) If the reaction is carried on in acetic acid solution it is impossible to make a separation by using excess of $\text{Na}_4\text{P}_2\text{O}_7$ solution.

Expt. 63.

Solution contained 5 mg. of Co^{++} ion per c.c.

(a) The solution was made acid by the addition of concentrated acetic acid. Ten drops of $\text{Na}_4\text{P}_2\text{O}_7$ solution precipitated the Co^{++} ion. Thirty more drops of the reagent failed to re-dissolve the pyrophosphate precipitate.

Expt. 64.

Solution contained 5 mg. of Cd^{++} ion per c.c.

(a) The procedure in Experiment No. 63 was repeated. The results for Cd^{++} were the same as those for Co^{++} ion.

Expt. 65.

Solution contained equal amounts of Cd^{++} and Co^{++} ion.

(a) The test solution was made ammoniacal and was then treated to precipitate the cadmium pyrophosphate. The usual pink precipitate appeared.

(b) This precipitate was washed, dissolved up in a few drops of dilute HNO_3 and the solution was then diluted to 2 c.c.

(c) The addition of $\text{K}_3\text{Fe}(\text{CN})_6$ gave the reddish brown precipitate. The precipitate was centrifuged and washed and 10 drops of concentrated HCl were added. ($\text{Cd}_2(\text{Fe}(\text{CN})_6)_2$ is soluble in HCl while the corresponding cobalt compound is not). The mixture was stirred thoroughly and then centrifuged. The centrifugate was drawn off and neutralized with NH_4OH . The addition of $\text{K}_3\text{Fe}(\text{CN})_6$ solution failed to give a yellow precipitate.

Expt. 66.

Solution contained equal amounts of Co^{++} and Cd^{++} ions.

(a) The procedure of Experiment 65 (a) and (b) was repeated.

(b) The $\text{K}_3\text{Fe}(\text{CN})_6$ solution was added and the reddish brown precipitate appeared. After centrifuging and washing, the precipitate was treated with 10 drops of dilute HCl . The mixture was stirred thoroughly and then centrifuged. The centrifugate was drawn off and then neutralized with concentrated NH_4OH . It was then made acid with dilute HNO_3 and several drops of $\text{K}_3\text{Fe}(\text{CN})_6$ solution were added. Again there was no indication of a yellow precipitate.

Expt. 67.

Solution contained only Co^{++} ion.

Experiment No. 66 was repeated, except that in place of the 10 drops of dilute HCl used in 66 (b) the precipitate was treated with 10 drops of concentrated HCl and 10 drops of water. The result, however, was the same.

Expt. 68.

Solution contained 6 mg. of Cd^{++} ion per c.c.

(a) The precipitate of cadmium pyrophosphate did not settle out at once. With concentrations of 6 mg. or less of Cd^{++} ion per c.c. the solution must be allowed to stand a few minutes to insure the precipitation of the cadmium pyrophosphate.

(b) The test for Cd^{++} ion was positive.

(c) The precipitate of cadmium ferricyanide was centrifuged and washed. It was then dissolved up in 10 drops of dilute HCl and the resulting solution was diluted with 10 drops of water. This solution was neutralized with NH_4OH and then acidified with dilute HNO_3 . The addition of several drops of $\text{K}_3\text{Fe}(\text{CN})_6$ solution gave a greyish-green precipitate insoluble in HNO_3 but soluble in HCl. This precipitate is quite possibly $\text{Cd}_2\text{Fe}(\text{CN})_{12}$.

Expt. 69.

Solution contained 4 mg. of Co^{++} and 5 mg. of Cd^{++} ion per c.c.

(a) The same procedure was followed as was used in Experiment No.66. The final addition of the $\text{K}_3\text{Fe}(\text{CN})_6$ solution gave a greyish precipitate which was soluble in HCl.

(b) $\text{Co}_3\text{Fe}(\text{CN})_6 \cdot 7\text{H}_2\text{O}$ is a greyish-green colour but is insoluble in HCl. There was no data to be found as to the colour or solubility of the corresponding cadmium salt.

Expt. 70.

Solution contained 1 mg. of Co^{++} and 2 mg. of Cd^{++} ion per c.c.

(a) The procedure of Experiment No. 66 was repeated. At the neutralization of the HCl solution with NH_4OH a yellowish precipitate appeared, which was insoluble in HNO_3 . The addition of a little $\text{K}_3\text{Fe}(\text{CN})_6$ turned the precipitate a greyish colour. This precipitate was soluble in HCl and gave a yellowish coloured solution.

Expt. 71.

Solution contained 1 mg. of Co^{++} ion per c.c.

(a) This test was run simultaneously with a blank. The blank did not give any precipitates or reactions all the way through.

(b) The procedure of Experiment No. 66 was followed. The final addition of the $\text{K}_3\text{Fe}(\text{CN})_6$ gave a minute amount of a dark precipitate which was insoluble in HCl. The slight precipitate may have come from a little impurity in the pipettes.

Expt. 71 (continued)

It would appear that this test for Cd^{++} ion may be all right. Its usefulness will be definitely ascertained in the analysis of the following unknown solutions.

Expt. 72.

Solution was No.1 unknown containing ions of Group IV.

- (a) The test for Cu^{++} ion was negative.
- (b) The test for Ni^{++} ion was positive.
- (c) The test for Co^{++} ion was negative.
- (d) The test for Cd^{++} ion was negative.

Expt. 73.

Solution was No.2 unknown containing ions of Group IV.

- (a) The test for Cu^{++} ion was negative.
- (b) The test for Ni^{++} ion was negative.
- (c) The test for Co^{++} ion was positive.
- (d) The test for Cd^{++} ion was negative.

Expt. 74.

Solution was No.3 unknown containing ions of Group IV.

- (a) The test for Cu^{++} ion was negative.
- (b) The test for Ni^{++} ion was positive.
- (c) The test for Ni^{++} ion was positive.
- (d) The test for Cd^{++} ion was negative.

Expt. 75.

Solution was No.4 unknown containing ions of Group IV.

- (a) The test for Cu^{++} ion was negative.
- (b) The test for Ni^{++} ion was negative.
- (c) The test for Co^{++} ion was positive.
- (d) The test for Cd^{++} ion was negative.

Expt. 76.

Solution was No.5 unknown containing ions of Group IV.

- (a) The test for Cu^{++} ion was negative.
- (b) The test for Ni^{++} ion was positive.
- (c) The test for Co^{++} ion was positive.
- (d) The test for Cd^{++} ion was negative.

Expt. 77.

Solution was No.6 unknown containing ions of Group IV.

- (a) The tests for all the ions were negative.

Cadmium ion was present in all the above but the tests for it failed in every case. It may be possible to get one of the spot tests for Cd^{++} ion to work in this procedure. A spot test for Cu^{++} ion

Expt. 77 (continued)

would probably be of value too, since the sensitivity of Gerstenzang's test is not any better than 2 mg. per c.c. of original material.

ANALYSIS OF GROUP V.

Expt. 78.

Solution contained 4 mg. each of Sb^{+++} , Sn^{++} and Al^{+++} ion per c.c.

(a) The solution was treated for the precipitation of Groups I, II, III and IV. The centrifugate contains Group V.

(b) This solution was treated as directed for the analysis of Group V.

(c) The test for Al^{+++} ion was negative.

The addition of the $(NH_4)_2CO_3$ solution gave a flaky white precipitate. Next was added 3 drops of NH_4OH , 10 drops H_2O and 2 drops of aluminum solution. The bright red precipitate indicating the presence of Al^{+++} ion failed to disappear.

(d) The test for Sb^{+++} ion was lost.

(e) The test for Sn^{++} ion was positive.

Expt. 79.

Solution contained 4 mg. each of Al^{+++} and Sb^{+++} ion and 2 mg. of Sn^{++} ion.

(a) The procedure of Experiment No. 78 was again followed.

(b) The test for Al^{+++} was negative.

(c) The test for Sb^{+++} was positive.

(d) The test for Sn^{++} was positive.

Expt. 80.

Solution contained 1 mg. each of Sb^{+++} and Sn^{++} ion per c.c.

Experiment cancelled.

Expt. 81.

Solution contained 1 mg. each of Sb^{+++} and Sn^{++} ion per c.c.

(a) The procedure of Experiment No. 78 was again followed.

(b) The test for Sb^{+++} ion was positive.

(c) The test for Sn^{++} ion was positive.

Expt. 82.

Solution contained 5 mg. of Al^{+++} ion per c.c.

(a) The test for Al^{+++} does not appear to be very satisfactory.

Expt. 83.

Solution contained 1 mg. of Al^{+++} ion per c.c.

(a) A fresh solution of aluminum was made up for this and subsequent tests.

(b) The test for Al^{+++} ion was positive.

Expt. 84.

Solution contained 1 mg. each of Al^{+++} , Sb^{+++} and Sn^{++} ion per c.c.

(a) The usual procedure of Experiment No. 78 was followed.

(b) Positive tests for each of the ions were obtained.

ANALYSIS OF GROUP VI.

Expt. 85.

Solution contained 1 mg. each of Zn^{++} , Cr^{+++} and As^{+++} ion per c.c.

(a) This solution was treated for the precipitation of Groups I - V as directed.

(b) The test for Zn^{++} ion was positive.

(c) The test for Cr^{+++} ion was positive.

(d) The test for As^{+++} ion was positive.

The Gutzeit test for As^{+++} ion is more sensitive and is recommended by Gerstenzang himself.

ANALYSIS OF GROUP VII.

Expt. 86.

Solution contained 1 mg. each of Na^+ , K^+ and NH_4^+ ion per c.c.

(a) These tests were carried out on portions of the original solution.

(b) The test for Na ion was positive.

(c) The test for K ion was positive.

(d) The test for NH_4 ion was positive.

Expt. 86 (continued)

These tests of Gerstenzang's are all flame tests and present the usual uncertainties of flame tests. Watson (15) describes spot reactions for testing for Na^+ and K^+ ions which are probably more sensitive and more easily identified than flame tests.

From the preceding experiments, the sensitivity of the individual tests for the various ions are as follows; this sensitivity is expressed in mg. per c.c. of original material:

Group I.

Hg^{++} ion - 1 mg.

Ag^+ ion - 1 mg.

Pb^{++} ion - 5 mg. following Gerstenzang's procedure.

If the quantities of precipitating agent and dilution medium are cut down, the sensitivity is increased to 2 mg. per c.c.

Group II.

Pb⁺⁺ ion - 2 mg.

Bi⁺⁺⁺ ion - 1 mg.

Fe⁺⁺⁺ ion - 1 mg.

Mn⁺⁺ ion - 1 mg.

Hg⁺⁺ ion - 4 mg.

A lot of the Hg⁺⁺ ion is lost in the procedure, as shown in Experiments 30 and 31. Also, if Sn⁺⁺ is present as SnCl₂, the Hg⁺⁺ becomes reduced and appears as the Hg⁺ ion in the first group.

Group III.

Ca⁺⁺ ion - 1 mg.

Sr⁺⁺ ion - 1 mg.

Ba⁺⁺ ion - 1 mg.

Mg⁺⁺ ion - 1 mg.

Group IV.

Cu⁺⁺ ion - 2 mg.

Ni⁺⁺ ion - 1 mg.

Co⁺⁺ ion - 1 mg.

Cd⁺⁺ ion - The test for Cd⁺⁺ ion is impossible in the presence of Co⁺⁺ ion. Perhaps a spot test can be substituted for the present test for Cd⁺⁺ ion.

Group V.

Al^{+++} ion - not a very satisfactory test.

Sb^{+++} ion - 1 mg.

Sn^{++} ion - 1 mg.

Group VI.

Zn^{++} ion - 1 mg.

Cr^{+++} ion - 1 mg.

As^{+++} ion - 1 mg.

The Gutzeit test for As^{+++} ion is to be preferred to that of Gerstenzang.

Group VII.

NH_4^+ ion - 1 mg.

Na^+ ion - 1 mg.

K^+ ion - 1 mg.

Sensitive spot tests may be substituted for the usual flame tests for these ions.

The next series of experiments were complete analysis of made up solutions. These solutions contained the minimum quantity of the different ions whose identification was uncertain or difficult, together with small quantities of various others of the ions. During these experiments spot tests were found and substituted for Gerstenzang's method of identifying certain of the cations.

Expt. 87.

Solution contained the following cations:

Group I - 1 mg. Hg_2^{++} and 5 mg. Pb^{++} ion.

" II - 1 mg. Bi^{+++} and 4 mg. Hg^{++} ion.

" III - 1 mg. Ca^{++} and 1 mg. Mg^{++} ion.

" IV - 2 mg. Cu^{++} and 1 mg. each of Co^{++} and Cd^{++} ion.

" V - 1 mg. each of Al^{+++} , Sb^{+++} and Sn^{++} ion.

" VI - 1 mg. each of Zn^{++} and 2 mg. As^{+++} ion.

(a) The addition of the Sn^{++} ion as $SnCl_2$ precipitated

Group I.

(b) The test for Pb^{++} ion in Group I was quite positive.

The identification was made in about 2 c.c. of solution.

(c) The test for Hg_2^{++} ion was positive. The volume of solution was about 0.4 c.c.

(d) The test for Pb^{++} ion in Group II-a was positive.

The volume of solution was about 3 c.c.

Expt. 87 (continued)

- (e) The test for Bi^{+++} ion was positive, the volume of the solution being about 0.75 c.c.
- (f) The test for Hg^{++} ion in Group II-b was negative. Not only is considerable of the Hg^{++} ion lost in the procedure leading up to the test (Experiments 30 and 31) but quite likely the addition of the SnCl_2 reduced the Hg^{++} ion and it appeared in the first group as Hg_2^{++} .
- (g) The test for Ca^{++} was positive, taking place in about 4 c.c. of solution.
- (h) The test for Mg^{++} ion involving its precipitation as $\text{Mg NH}_4 \text{ PO}_4$ was positive. The 8-hydroxyquinoline test is also very satisfactory for the identification of this ion. The volume of solution in this case was about 5.5 c.c.
- The best concentration of acetic acid for dissolving up the carbonates of Mg^{++} and Ca^{++} is 1 part glacial acetic acid to 5 parts of water (Experiment 44).
- (i) The test for Cu^{++} ion in Group IV was negative. A spot test for this ion would be desirable.
- (j) The test for Co^{++} ion was positive and takes place in about 0.5 c.c. of solution.

Expt. 87 (continued)

- (k) The following spot test for Cd^{++} ion was used at this stage and gave a positive result. The concentration of Cd^{++} ion was about 1/4 of a mg. per c.c. at this stage:

A drop of the hydrochloric acid solution of the cations of Group IV was placed on a piece of spot paper and to it was added a drop of concentrated NaOH solution and a drop of thioisamine (allyl thio urea) solution. On warming the spot gently a yellow colour appeared which showed the presence of Cd^{++} ion. This is the test for Cd^{++} ion used by Watson (15).

- (l) The test for Al^{+++} ion was negative. This aluminon test does not seem to work very satisfactorily at all. The presence of silicic acid will give the same result as the presence of aluminum.
- (m) The test for Sb^{+++} was positive. The volume of solution is about 0.5 c.c.
- (n) The test for Sn^{++} ion was positive. This test also takes place in about 0.5 c.c. of solution.
- (o) The test for Zn^{++} was positive in 4 c.c. of solution.
- (p) The test for As^{+++} was positive. The sensitive Gutzeit test was used in this case.

Expt. 88.

Solution was made up as follows:

Group I - 1 mg. Ag^+ and 2 mg. Pb^{++} ion.

Group II - 4 mg. Hg^{++} ion.

Group III - 1 mg. each of Sr^{++} , Ba^{++} , Ca^{++} and
 Mg^{++} ion.

Group IV - 2 mg. Cu^{++} and 1 mg. each of Ni^{++}
and Cd^{++} ion.

Group V - 1 mg. each of Al^{+++} and Sn^{++} ion.

Group VI - 4 mg. As^{+++} ion.

- (a) The test for Pb^{++} ion was positive. The spot test for Pb^{++} using tetra-methyl-diamino-diphenyl methane reagent failed to give any result.
- (b) The test for Hg_2^{++} ion in Group I was positive.
(See Experiment 87, part (f)).
- (c) The test for Ag^+ ion was positive.
- (d) The test for Pb^{++} ion in Group II-a was negative. You evidently must have at least 2 mg. of Pb^{++} ion carried over into Group II-a to give a positive test. A very slight precipitate appeared on standing, but not enough to warrant its use as a confirmation test.
- (e) The test for Hg^{++} ion in Group II-b gave a very faintly positive result.

Expt. 88 (continued)

- (f) The tests for all the ions of Group III were positive. The 8-hydroxyquinoline test for Mg^{++} ion is the better one.
- (g) A test for Cu^{++} ion at this stage would be as follows: place 1 drop of the HCl solution on a spot plate and add a drop of $\text{K}_2\text{Fe}(\text{CN})_6$ solution. A red precipitate denotes the presence of Cu^{++} ion.

The above procedure for Cu^{++} ion gave a positive test here.
- (h) The test for Cd^{++} ion, using thioisamine reagent, was positive.
- (i) The usual test for Cu^{++} ion gave a negative result.
- (j) The test for Ni^{++} ion was positive.
- (k) The prescribed test for Cd^{++} ion as usual failed to work satisfactorily.
- (l) The test for Al^{+++} ion failed.
- (m) The test for Sb^{+++} ion was positive.
- (n) The test for Sn^{++} ion was positive.
- (o) The material was halved on coming to the test for As^{+++} ion. The Gutzeit test was applied to one-half, giving a positive test for As^{+++} ion. The remaining half was treated by Gerstenzang's method. It was hard to tell whether the copper foil had a metallic coating or not. The Gutzeit test is more definite.

Expt. 89.

A solution was made up containing the following cations:

- Group I - 1 mg. Pb^{++} ion.
- Group II - 1 mg. Hg^{++} ion.
- Group III - 1 mg. each of Ca^{++} and Mg^{++} ion.
- Group IV - 1 mg. each of Co^{++} and Ni^{++} ion.
- Group V - 1 mg. Al^{+++} ion.
- Group VI - 1 mg. As^{+++} ion.

(a) The addition of dilute HCl to the test solution gave a very little white precipitate, -scarcely enough to serve as a confirmatory test for Pb^{++} ion.

In two test experiments the following was found: -

- (1) It requires 2 mg. of Pb^{++} ion in 1 c.c. of original material to give a precipitate in the first group.
- (2) A solution was made up of 1.5 c.c. water and 0.5 c.c. dilute HCl. The addition of 1 mg. Pb^{++} (as $Pb(NO_3)_2$) gave a white precipitate, which, however, dissolved up in a minute or so.

Expt. 89 (continued)

- (b) Concerning the test for Hg^{++} , if Sn^{++} is present as Sn Cl_2 or there happens to be any other reducing agent present in the unknown, then the Hg^{++} will be reduced and will appear as Hg_2^{++} in the first group.

If SnCl_2 is not present, a test for Hg^{++} ion would be to take a drop or so of the HCl centrifugate from the separation of the first group and add a drop of SnCl_2 solution. A white precipitate would indicate the presence of mercuric mercury.

If Sn^{++} is present as SnCl_2 , then we cannot tell whether the mercury in the first group was present as mercurous mercury or whether it was reduced from the mercuric ion.

- (c) The test for Pb^{++} in Group II-a was negative.
- (d) The test for Fe^{+++} was positive, though none of the ion had been placed in the original solution.
- (e) The test for Hg^{++} ion in Group II-b was negative.
- (f) The test for Ca^{++} in Group III was positive.
- (g) The test for Mg^{++} in Group III was negative. This is not usual, however, as the 8-hydroxyquinoline test for this ion is exceptionally sensitive.

Expt. 89 (continued)

- (h) The $K_4Fe(CN)_6$ test for Cu^{++} ion showed none present. The other ions of this group, if present, may form their respective ferrocyanides but the colour of the resulting precipitate will tell if Cu^{++} ion is present, as the other ferrocyanides are lighter in colour, the copper ferrocyanide being a dark red.

The K Br benzidine test for Cu^{++} ion gave a negative result also. This test is as follows:

To one drop of the solution add 1 drop of saturated K Br solution and one drop of an 0.1 % solution of benzidine in alcohol. Add NaOH to neutrality and a blue colouration appears if Cu^{++} ion is present.

- (i) The test for Ni^{++} ion was positive.
(j) The test for Co^{++} ion was faintly positive.

Another test for Co^{++} ion which might be used here is as follows: To one drop of the ammoniacal solution on a spot plate add 1 drop of concentrated acetic acid, 2 drops of alcohol and a few crystals of NH_4CNS . A blue colouration shows the presence of Co^{++} ion. A greenish precipitate indicates Co^{++} ion with Cu^{++} ion also present.

Expt. 89 (continued)

- (k) The thioisamine test for Cd^{++} ion works in the presence of all the other ions in the group. Cu^{++} ion does not interfere. If Ni^{++} and Co^{++} are present, the yellow stain appears around the edge of the spot. Around the outside of the yellow ring there appears a darker ring, probably due to the presence of Ni^{++} ion.
- (l) The test for Al^{+++} ion in Group V gave a precipitate with a faintly pinkish tinge. The test, however, was not good enough to be called a confirmatory test.
- A test based on Hammett and Sottery (20), but using micro quantities, gave a very definite red precipitate. There is, however, no really good test for Al^{+++} ion so far.
- (m) The test for As^{+++} ion in Group VI was negative. The Gutzeit test is the more reliable test for this ion.

Expt. 90.

This experiment was to determine whether the reduction of Hg^{++} ion to Hg^{+} ion by means of SnCl_2 could be used as a test for Hg^{++} ion in Group II-b. It was observed that if Hg^{++} ion was present and Sn^{++} ion was added as SnCl_2 , then the mercury appeared as the mercurous ion in Group I.

A solution was made up containing 2 mg. each of Ag^+ , Pb^{++} and Hg_2^{++} ion.

- (a) The above solution was treated for the precipitation of Group I. The mixture was centrifuged and the precipitate was washed, the washings being added to the centrifugate.
- (b) To a few drops of this centrifugate was added two drops of SnCl_2 solution. A white precipitate appeared.
- (c) The procedure from (b) was repeated using a solution containing Pb^{++} ion only. The addition of SnCl_2 solution failed to give a precipitate.
- (d) Repeated the above with a solution containing Ag^+ ion only, and again the addition of SnCl_2 failed to give a precipitate.

The precipitate in Experiment 90 (b) was evidently due to the presence of Hg_2^{++} ion, so this ion would interfere with the test for mercuric mercury.

Expt. 91.

A solution was made up of 10 drops of diluted HCl, 10 drops of water and 3 drops of SnCl₂ solution. All the ions were added one at a time, leaving the Hg⁺⁺ ion until the last. No precipitate appeared during the addition of all the ions, but as soon as the Hg⁺⁺ ion was added, a white precipitate came down.

Provided mercury is not present in the first group and Sn⁺⁺ is not present as SnCl₂⁺ in the unknown, Hg⁺⁺ can be identified in the filtrate from Group I by the addition of a drop of SnCl₂ solution to a drop of this filtrate.

Expt. 92.

A solution was taken whose contents were unknown.

- (a) The analysis of Group I showed mercury which had, however, been reduced from the mercuric state.
- (b) The analysis of Group II-a and b failed to show any of the ions of these groups present.
- (c) The analysis of Group III showed a positive test for Mg⁺⁺ ion only.
- (d) The analysis of Group IV gave the following results:
 - (1) The test for Cu⁺⁺ ion by means of K₄Fe(CN)₆ and also by the use of K Br and benzidine was positive.
 - (2) The test for Cd⁺⁺ ion using thioisamine was positive.
 - (3) The test for Ni⁺⁺ was positive.

Expt. 92 (continued)

- (e) The analysis of Group V gave a positive test for Al^{+++} , Sb^{+++} and Sn^{++} ion.
- (f) The analysis of Group VI gave negative test results for all the tests.
- (g) The analysis of Group VII gave positive tests for all the ions.
- (h) The only errors in the above were the positive tests for aluminum and antimony. Neither of these ions had been placed in the solution.

Expt. 93.

An unknown solution was made up and divided into two parts. One part was analyzed by the method in use in the second year laboratory, which method makes use of H_2S . The other part was analyzed by the method which has been under examination. The time taken for a complete analysis in each case was kept and the two methods were compared.

The analysis using H_2S was accomplished about one-half hour quicker than the competitive method. The time for the H_2S method was about three and one-half hours. In each case four errors were made.

The two methods might be said to compare favourably. The newer method is perhaps more desirable from the standpoint of its dispensing with the use of H_2S . Both

methods appear fairly accurate and reliable, with the H_2S method having a slight preference with regard to accuracy. As regards the sensitivity of the tests, most of them remain the same as given previously, with the following changes:

Hg^{++} under certain conditions can be identified at a concentration of 1 mg. per c.c. of original material.

Cu^{++} ion can be identified when present in a concentration of 1 mg. per c.c. of original material.

Cd^{++} ion can be identified at a like concentration.

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