[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE CITY COLLEGE OF NEW YORK]

Organic Reagents[1] in Qualitative Analysis. II. The Analysis of the Common Metals of the Ammonium Sulfide Group

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A method of analysis of the common metals of the ammonium sulfide group has been developed which avoids some of the difficulties usually encountered, especially the loss of considerable amounts of zinc.[2] In brief, the group is first separated as usual and then dissolved in aqua regia. Iron is removed with cupferron and the remaining metals divided into two groups by precipitating Co^{++}, Ni^{++} and Zn^{++} with hydrogen sulfide in an acetic acid–acetate solution, Al^{+++}, Cr^{+++} and Mn^{++} remaining in solution.

The precipitate is extracted with hot dilute hydrochloric acid, zinc sulfide easily dissolving, cobalt and nickel sulfides only partially but in sufficient amounts to permit identification. The nickel is precipitated with dimethylglyoxime, a brown filtrate indicating cobalt. Zinc is detected in the presence of the cobalt complex with 8-hydroxyquinoline.

From the solution containing Al^{+++}, Cr^{+++} and Mn^{++}, $Al(OH)_3$ and $Cr(OH)_3$ are precipitated in acid medium with hexamethylenetetramine. The precipitate is dissolved in acetic acid and divided into two parts. In one half the Al^{+++} is detected with 8-hydroxyquinoline. The Cr^{+++} in the other half is oxidized with persulfate and Ag^{+} to dichromate and tested for with either hydrogen peroxide or diphenylcarbazide.

The filtrate containing the Mn^{++} is treated with sodium hydroxide and sodium peroxide to precipitate manganese dioxide. This is identified by the sodium carbonate–potassium chlorate bead test or with $NaBiO_3$ in nitric acid solution.

Experimental

1. Reaction of the Metallic Ions with Hydrogen Sulfide in an Acetic Acid–Acetate Solution.—(A) To 100 mg. separately of each of the metallic ions in 50 ml. of 0.3 *N* hydrochloric acid, 3 g. of sodium acetate (anhy.) was dissolved and hydrogen sulfide passed through the solution in an open beaker until no more precipitation took place; Ni^{++}, Co^{++} and Zn^{++} are completely precipitated; Fe^{++} and Fe^{+++} incompletely, while Al^{+++}, Cr^{+++} and Mn^{++} remain in solution.

(B) A solution consisting of 100 mg. of each of the metallic ions, except iron, under the same conditions as in (A) gave a precipitate free of Al^{+++}, Cr^{+++} and Mn^{++}. The filtrate gave negative tests for Ni^{++}, Co^{++} and Zn^{++}.

(C) To a solution similar to (B), but also containing 100 mg. Fe^{+++}, a 6% cupferron solution was added to precipitate the Fe^{+++}. To the filtrate 5 ml. of 3 *N* nitric acid was added, and the solution boiled for two minutes to oxidize any excess cupferron, which otherwise would interfere with the later precipitation of nickel sulfide. The solution was cooled, 3 g. of sodium acetate (anhy.) dissolved and hydrogen sulfide passed through the solution until there was no more precipitation. Analysis showed the absence of Al^{+++}, Cr^{+++} and Mn^{++} in the precipitate and Ni^{++}, Co^{++} and Zn^{++} in the filtrate.

(D) Similar experiments showed (1) that 1 mg. of Fe^{+++} could be separated from 500 mg. of any other of the metallic ions or combination of them; (2) that after the separation of Fe^{+++}, 1 mg. of Ni^{++}, Co^{++} and Zn^{++} could be separated from 500 mg. of Al^{+++}, Cr^{+++} or Mn^{++} or any combination of them; (3) that 1 mg. of Al^{+++}, Cr^{+++} and Mn^{++} could be separated from 500 mg. of Ni^{++}, Co^{++} or Zn^{++} or any combination of them; and, finally, (4) that in the presence of 500 mg. of Fe^{+++} 1 mg. of each of the other metallic ions could be separated and detected.

2. Solubility of Zinc, Nickel and Cobalt Sulfides in Dilute Hydrochloric Acid.—(A) Separate solutions of 500 mg. Zn^{++} (containing 100 mg. of Ni^{++} or Co^{++} to permit easy filtration of the sulfides) were precipitated as sulfide, filtered and washed. Over the precipitates on the filter were poured 25 ml. portions of hydrochloric acid solutions varying from 0.3 to 2 *N*, cold and hot, and allowed to drain through. The hot 1.5 *N* hydrochloric acid dissolved the zinc sulfide most effectively.

(B) Mixtures of 500 mg. of Ni^{++} or Co^{++}, or of 250 mg. each of Ni^{++} and Co^{++}, and 1 mg. of Zn^{++}, on precipitation as sulfides and extraction with 25 ml. of hot 1.5 *N* hydrochloric acid gave solutions in which the Zn^{++} could be detected (see fourth group of experiments).

(C) The solubilities of nickel and cobalt sulfides separately under the same conditions as in (B) were estimated by evaporating the extracts of varying amounts of Ni^{++} and Co^{++} as sulfides to 10 ml., reprecipitating as sulfides in graduated tubes and comparing the size of the precipitates with a standard containing 10 mg. of the same metallic ion in a similar tube and precipitated as sulfide in the same way. Starting with 15, 25, 50, 100, 200, 300, 400 and 500 mg. of each metallic ion, 2.8, 4.5, 7.2, 9.3, 12.1, 13.9 and 15 mg. of Ni^{++} and 3.8, 6.2, 9.2, 11.3, 14.5, 16.2, 17.8 and 19.8 mg. of Co^{++}, respectively, were recovered. With 1 mg. of each metallic ion a large percentage was dissolved.

3. The Detection of Ni^{++} and Co^{++} in the Presence of Each Other with Dimethylglyoxime.—(A) To mixtures of 1 mg. of Ni^{++} and 25, 30, 40, 50 and 100 mg. of Co^{++}, re-

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[1] The organic reagents are made by the Eastman Kodak Co., Rochester, N. Y.

[2] Noyes, Bray and Spear, THIS JOURNAL, **30**, 482, 484, 488, 544 (1908); Noyes and Bray, "A System of Qualitative Analysis for the Rare Elements," The Macmillan Co., New York City, 1927, p. 153; Swift and Barton, THIS JOURNAL, **54**, 2219, 4155 (1932).

spectively, enough ammonia (concd.) was added to form their complex ions. Then a 4% (satd.) solution of dimethylglyoxime in acetone was added to determine the amount necessary to precipitate the Ni^{++}. The point of precipitation was detected by noting a change in color from the deep brown of the cobalt complex to a lighter reddish-brown, together with the development of a turbidity. If the solution is shaken vigorously with several ml. of carbon tetrachloride, the nickel precipitate can be separated out in the carbon tetrachloride layer. The volumes of reagent needed were 1, 2, 4, 8 and 20 ml., respectively. The brown color of the filtrate indicated the Co^{++}. When there is relatively a large amount of Ni^{++} and a small amount of Co^{++}, the Ni^{++} precipitates immediately and on filtering, the brown color can be seen in the filtrate.

(B) Solutions of 1 mg. of Ni^{++} and 500 mg. of Co^{++}, and 1 mg. Co^{++} and 500 mg. Ni^{++} were precipitated as sulfides, extracted with the hydrochloric acid solution, the hydrogen sulfide boiled out, made alkaline with ammonia and tested with dimethylglyoxime. The Ni^{++} was detected by precipitation and the Co^{++} by the brown colored filtrate. Similar results were obtained with solutions of 1 mg. each of Ni^{++} and Co^{++} and 500 mg. of Zn^{++}, and 250 mg. each of Ni^{++} and Co^{++}.

4. Reaction of Co^{++}, Zn^{++}, Al^{+++} and Cr^{+++} with 8-Hydroxyquinoline in Dilute Acetic Acid.—In these experiments each solution, 5 ml. in volume, was made acid with 2 *N* acetic acid and an equal volume of a 5% solution of 8-hydroxyquinoline in 2 *N* acetic acid added.

(A) A solution of 100 mg. of Co^{++}, as the dimethylglyoxime complex, gave no precipitate.

(B) A yellow precipitate was obtained separately for Zn^{++} and Al^{+++} with either 100 mg. or 1 mg. of the metallic ion.

(C) Cr^{+++} did not react in the cold, but formed a brown precipitate on boiling with either 100 mg. or 1 mg. of the metallic ion.

5. The Separation of Al^{+++} and Cr^{+++} from Mn^{++} with Hexamethylenetetramine.[3]—Experiment showed that acetate ion, present from the hydrogen sulfide precipitation in acetic acid–acetate solution, prevents the precipitation of chromic hydroxide by hexamethylenetetramine. Addition of 15 ml. of 3 *N* nitric acid and evaporation to moist dryness removes the acetate ion, so that after dilution to 20 ml. the separation can be carried out. Experiment showed that 1 mg. of Al^{+++} and Cr^{+++} was separated from 500 mg. of Mn^{++}; also 1 mg. of Mn^{++} with 500 mg. of Al^{+++} or Cr^{+++} or a mixture of 250 mg. of each was separated.

On the basis of the various group experiments a method of analysis was worked out. Combinations of 1 mg. of one metallic ion in the presence of 500 mg. total of other metallic ions of the group were analyzed with positive results in every case.

6. Method of Analysis

The group is separated as usual, treated with 12 ml. of aqua regia, evaporated to 1 ml., diluted to 20 ml. and any sulfur present is filtered off. Fe^{+++} is precipitated with 6% cupferron solution. To the filtrate 5 ml. of 3 *N* nitric acid is added and boiled for two minutes. The solution is cooled, diluted to 50 ml., 3 g. of sodium acetate (anhy.) dissolved, hydrogen sulfide passed through the solution until no further precipitation occurs and filtered (filtrate A). The residue is washed with 5% ammonium nitrate solution.

Residue.—Twenty-five ml. of boiling 1.5 *N* hydrochloric acid is poured over the residue on the filter, allowed to drain through, evaporated to 10 ml., cooled and filtered if not clear. The solution is made just alkaline with 3 *N* ammonia and Ni^{++} precipitated with a saturated acetone solution of dimethylglyoxime. The filtrate, brown if Co^{++} is present, is evaporated to 5 ml., cooled, filtered, made just acid with 2 *N* acetic acid and an equal volume of 5% solution of 8-hydroxyquinoline in 2 *N* acetic acid added. A yellow precipitate indicates Zn^{++}.

Filtrate A.—Fifteen ml. of 3 *N* nitric acid is added, the solution evaporated to moist dryness, treated with 20 ml. of 10% hexamethylenetetramine solution, boiled for three minutes and filtered (filtrate B). The residue is washed with 5% ammonium nitrate solution.

Residue.—After transferring to a beaker it is dissolved by heating with 20 ml. of 2 *N* acetic acid and the solution divided in halves. One half is cooled and an equal volume of 8-hydroxyquinoline solution added, a yellow precipitate indicating Al^{+++}. To the other half are added 5 ml. of 3 *N* nitric acid, 5 ml. of *N*/4 silver nitrate and 1–3 g. of ammonium persulfate and evaporated to 5 ml. The solution is cooled, filtered if not clear, and tested for Cr^{+++} with either hydrogen peroxide or diphenylcarbazide.

Filtrate B.—It is made alkaline with 6 *N* sodium hydroxide, 1–2 g. of sodium peroxide added in small portions with constant stirring, heated to boiling and filtered. The residue is washed with water and Mn^{++} detected by either the sodium carbonate–potassium chlorate bead test or by dissolving in nitric acid and oxidizing with $NaBiO_3$.

Summary

A method of analysis of the common metals of the ammonium sulfide group has been developed so that it is possible to detect 1 mg. of any one in the presence of 500 mg. of any other or combination of others.

In this method Fe^{+++} is first removed with cupferron and then Ni^{++}, Co^{++} and Zn^{++} are separated by precipitation in an acetate–acetic acid solution by hydrogen sulfide. The sulfide precipitate is extracted with hot 1.5 *N* hydrochloric acid, the extract treated with dimethylglyoxime to precipitate Ni^{++}, a brown filtrate indicating Co^{++}, and Zn^{++} detected with 8-hydroxyquinoline. From the solution containing Al^{+++}, Cr^{+++} and Mn^{++}, aluminum and chromium hydroxides are precipitated by hexamethylenetetramine. After dissolving the hydroxides, the Al^{+++} is identified by 8-hydroxyquinoline and the Cr^{+++} by first oxidizing with

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[3] Lehrman, Kabat and Weisberg, THIS JOURNAL, **55**, 3509 (1933).

$S_2O_8^=$ and Ag^+ to $Cr_2O_7^=$ and then testing with hydrogen peroxide or diphenylcarbazide. The solution containing Mn^{++} is treated with sodium hydroxide and sodium peroxide to precipitate manganese dioxide, which is then identified by the sodium carbonate–potassium chlorate bead test or with sodium bismuthate in nitric acid.

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Thermodynamic Functions of Nitrous Oxide and Carbon Dioxide[1]

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Spectroscopic data have been used to calculate accurate values for the free energies, and in some cases the entropies, heat contents, and specific heats, of nearly all the common diatomic gases. Approximate values have also been obtained for several polyatomic gases, with the neglect of all the anharmonic and interaction terms. The infra-red spectrum of carbon dioxide has now been rather well mapped, and the results have been analyzed quite completely; it should therefore be possible to calculate thermodynamic functions for carbon dioxide with high accuracy. The spectrum of nitrous oxide has received much less attention, but the data amply justify calculation, since the free energy is quite unknown. The simpler case of nitrous oxide will be treated first.

Nitrous Oxide

Plyler and Barker[3] studied the infra-red spectrum of nitrous oxide; their work identifies the three fundamental vibration frequencies and determines roughly the anharmonic and coupling constants. The molecule is definitely linear and unsymmetrical. As was pointed out by Badger and Woo,[4] Plyler and Barker made an error in calculating the moment of inertia, the correct value being 66.1×10^{-40} g. cm.^{2}. Since the rotational stretching terms and the rotation–vibration interactions are not known, the Q-sum for each electronic level factors into one term due to a rigid rotator and one to a group of coupled oscillators. We assume that the lowest electronic state is $^1\Sigma$ and that no others need be considered. The only problem then is to calculate the vibrational factor of the Q-sum.

The vibrational levels are given by

$$E = 1288.7v_1 + 593.0v_2 + 2237.9v_3 - 3.3v_1^2 - 3.1(v_2^2 - l^2/3) - 13.8v_3^2 - 9.8v_1v_2 - 26.7v_1v_3 - 13.3v_2v_3 \text{ cm.}^{-1}$$

where v_1 and v_3 are the quantum numbers of the two single valence vibrations, and v_2 and l are the total and azimuthal quantum numbers of the double deformation vibration; the allowed values of l are $\pm v_2$, $\pm (v_2 - 2)$, etc. Using the notation

$$r = e^{-1288.7F} \qquad s = e^{-593.0F} \qquad t = e^{-2237.9F}$$
$$a = 3.3F \qquad b = 3.1F \qquad c = 13.8F$$
$$d = 9.8F \qquad e = 26.7F \qquad f = 13.3F$$
$$g = 3.1F/3 \qquad F = hc/kT$$

the vibrational factor of the Q-sum becomes

$$Q_{\text{vib.}} = \Sigma_{v_1} \Sigma_{v_2} \Sigma_{v_3} \Sigma_l\, r^{v_1}s^{v_2}t^{v_3} \text{ exp. } (av_1^2 + bv_2^2 + cv_3^2 + dv_1v_2 + ev_1v_3 + fv_2v_3 - gl^2)$$

We now expand the exponential term into a power series and perform the indicated summations. In addition to formulas previously given,[5] we require the first of the following two formulas, which will be useful for other linear molecules also.

$$\Sigma l^2 = (v/3)(v + 1)(v + 2)$$
$$\Sigma l^4 = (v/15)(v + 1)(v + 2)(3v^2 + 6v - 4)$$

where the sums run over alternate integral values of l from $-v$ to $+v$. The significant terms in the result are

$$Q_{\text{vib.}} = RS^2T\{[1 + ar(1 + r)R^2 + 2bs(1 + 2s)S^2 + ct(1 + t)T^2 + 2drRsS + erRtT + 2fsStT - 2gsS^2] + [b^2s(1 + 18s + 33s^2 + 8s^3)S^4 + 2bdrRs(1 + 7s + 4s^2)S^3 + 2bfs(1 + 7s + s^2)S^3tT - 2bgs(1 + 10s + 9s^2)S^4 + d^2r(1 + r)R^2s(1 + 2s)S^2] + [(b^3/3)s(1 + 88s + 718s^2 + 1208s^3 + 473s^4 + 32s^5)S^6]\}$$

where

$$R = 1/(1 - r) \qquad S = 1/(1 - s) \qquad T = 1/(1 - t)$$

In this expression the first bracket contains all the terms from the linear term of the exponential expansion, the second bracket the five largest

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[1] Published by permission of the Director, U. S. Bureau of Mines. (Not subject to copyright.)

[2] Associate physical chemist, Pittsburgh Experiment Station, U. S. Bureau of Mines, Pittsburgh, Pa.

[3] Plyler and Barker, *Phys. Rev.*, **38**, 1827 (1931).

[4] Badger and Woo, THIS JOURNAL, **54**, 3523 (1932).

[5] Kassel, *Phys. Rev.*, **43**, 364 (1933).