

Motor Lubricant (e)	320	46.4
" "	340	79.6
Motor Lubricant (f)	340	31.5
" "	350	67.2

(a) M. P. = 60° C.

(b) Technical (White) Eimer and Amend.

(c) Asphalt Base (Zerolene No. 5).

(d) Paraffin Base (Standard Aviation Oil).

(e) Same as (d), previously heated for 1 hr. with 1 g. of selenium.

(f) Same as (d), previously heated for two 1 hr. periods with 1 g. of selenium each period.

Summary. Hydrogen selenide is obtained by heating powdered selenium with high boiling hydrocarbons. A maximum yield of 96.8 per cent H_2Se (based on the selenium used) was obtained by heating 50 g. of a paraffin base motor oil with 1 g. of selenium for one hour at 380° C.

Heating the same 50-gram portions of a paraffin oil with repeated additions of selenium (1 g. each) reduced the formation of H_2Se to approximately that obtained by the use of paraffin at corresponding temperatures.

In contrast with the results obtained by E. D. Scudder and R. E. Lyons with hydrogen sulfide the yield of hydrogen selenide increases with increased temperatures. Only negligible yields were obtained below 300° C.

ANALYSIS OF GROUP III

RALPH W. HUFFERD, Greencastle

Since reporting a paper under the same title to this group eleven years ago several changes have been introduced into the scheme. In conversation with instructors and students in other laboratories the writer still hears the common complaint that cobalt and zinc are prone to give trouble. It has been our experience that the careful student has trouble with neither of these.

As reported before (1) the main departure from the generally accepted scheme of analysis lies in the very strenuous treatment of the group precipitate at the time of separating it into divisions. Detection of cobalt has been made certain and easy by a modification of the Morrel-Vogel test (2). Since the difficulty with detection of zinc lies in the confirmatory test, unless it has been left in the Iron Division precipitate, it has been found expedient, especially for the beginning student, to employ two confirmatory tests. One of these, the ferrocyanide test, has been modified to meet all conditions.

The scheme has been worked out with both speed and accuracy in mind. Almost all filtrations are carried out by suction. Solutions are

prepared to permit the use of ordinary qualitative filter paper. If the importance of permitting precipitates to settle out and of pouring off the supernatant liquid is sufficiently emphasized all filtrations can be done by suction, thus saving considerable time.

SEPARATION INTO DIVISIONS

The group precipitate is dissolved by addition of 3N hydrochloric acid and boiling. If necessary (cobalt or nickel present) the minimum amount of nitric acid is added. No attempt is made to separate the precipitate from the paper before carrying out this step. A little hot water is added and the solution sucked off from the paper pulp and sulfur.

While the solution is still hot 30 per cent sodium hydroxide is added with stirring until a precipitate forms and persists, or, if no precipitate forms, until the solution is strongly alkaline. If there is a precipitate a further excess of 5-10 cc. of 30 per cent sodium hydroxide is added. About half a gram of sodium carbonate is added and put into solution.

The solution or suspension is then cooled somewhat and 1-3 g. of sodium peroxide added a little at a time with stirring. After 2 minutes boiling 2 volumes of hot water is added and boiling continued for 3 minutes. The precipitate is then filtered off without cooling and thoroughly washed with hot water.

ALUMINIUM DIVISION

The combined filtrates are treated in the customary manner to remove aluminium and to test for chromium. Due to the previous use of concentrated hot alkaline solution care must be taken to differentiate between aluminium hydroxide and silicic acid. The use of alizarin has been quite satisfactory.

If the solution does not contain chromium 5 drops of dichromate solution is added to the filtrate from the aluminium hydroxide. Whether or not it has been necessary to add dichromate, acetic acid is added until the chromate yellow turns to dichromate orange. 5 cc. of saturated hydrogen sulfide water is now added. If zinc is present a flocculent precipitate of zinc sulfide will form at once. Colloidal sulfur will also appear, but more slowly. Three suction filtrations through the same filter are sufficient to remove all of the sulfide along with a little sulfur. The filtrate will be milky. The precipitate should be washed with 10 cc. of hot water.

A hot solution of 2 cc. of 6N hydrochloric acid in 10 cc. of water is then sucked through the filter two or three times and boiled to remove hydrogen sulfide. Excess ammonia is added to the cooled filtrate and followed by a slight excess of acetic acid. The solution is divided into two portions in small test tubes. To one portion 2 drops of potassium dichromate solution is added followed by 5 drops of potassium ferrocyanide solution. A white precipitate is zinc ferrocyanide. To the other portion 2 cc. of hydrogen sulfide solution is added. A white precipitate is zinc sulfide.

IRON DIVISION

Without separation from the paper the precipitate is placed in a casserol and 15 cc. of hot 6N nitric acid is added. This treatment either dissolves the precipitate or so loosens it that the paper can be removed and washed with a little 6N nitric acid, which is then added to the contents of the casserol. The solution is evaporated to 10 cc. or less. After adding 10 cc. of 16N nitric acid and boiling for a minute the casserol is removed from the flame. The solution (if manganese is absent or if peroxide has not been carefully washed out) or suspension is permitted to cool slightly and then 0.5 g. of potassium chlorate is cautiously added in small quantities with stirring. After gentle boiling another half gram of chlorate is added and the boiling repeated. This treatment should normally completely precipitate the manganese as the brown or black oxide.

If there is no precipitate the solution is again evaporated to half volume and 5 cc. 16N nitric acid added and followed by more chlorate. After a moment's boiling 20 cc. of water is added and the precipitate filtered off without cooling.

Iron is removed in the customary manner.

The ammoniacal filtrate from the ferric hydroxide is boiled until the odor of ammonia is weak but noticeable. A portion of it is tested for nickel with dimethylglyoxime.

The remainder is evaporated to a syrupy consistency but not to dryness; transferred to a test tube while still hot; cooled; enough water added to put almost all of the solid into solution; and 3 cc. 10 per cent potassium thiocyanate solution added. 3 cc. of a 1:4 mixture of isoamyl alcohol and ethyl ether is poured in and gently shaken. A blue-green color in the ether layer is proof of the presence of cobalt. A colorless layer is proof of its absence. If the color is indistinct due to the presence of a trace of iron a drop of 12N hydrochloric acid added from the point of a pipette to the surface of the ether layer will produce the distinct blue-green color if cobalt is present.

MODIFICATIONS

If *oxalate* is present there is no modification of the scheme until after the removal of manganese. Since manganese dioxide cannot precipitate until oxalic acid has been destroyed its appearance can be taken as evidence of the destruction of the oxalic acid. If manganese is absent 2 cc. of manganese nitrate solution is added and the oxide thrown out by treatment with nitric acid and chlorate.

The filtrate is made ammoniacal and hydrogen sulfide passed in. The filtrate after this treatment is added to the original filtrate from the Group III precipitate. The precipitate is dissolved in dilute nitric acid and the resulting solution freed from sulfur. It is ready for precipitation of ferric hydroxide as in the ordinary scheme.

If *phosphate* is present after testing for manganese as usual test not more than 1/5 of the filtrate for iron by adding ammonia. A red precipitate indicates iron, but should be filtered off, dissolved in 6N hydrochloric acid and tested with thiocyanate and with ferrocyanide. The

filtrate from the red precipitate should be returned to the remaining 4/5 of the filtrate from manganese dioxide.

Following the customary procedure phosphate is removed by adding ferric nitrate, unless iron is present in considerable amount, and throwing it out as the phosphate and basic acetate.

The phosphate and iron free filtrate is made ammoniacal and treated with hydrogen sulfide. The sulfides of cobalt and nickel are filtered off and the filtrate returned to the filtrate from Group III.

The black precipitate is covered on the paper with 6N hydrochloric acid and a few drops of 6N nitric acid added. After filtering and washing the residue, the filtrate is made ammoniacal and treated as though it were the filtrate from ferric hydroxide in the regular scheme.

DISCUSSION OF RESULTS

The following table indicates the accuracy of the scheme under varying conditions.

Milligrams of the Atom

Zn	Cr	Mn	Fe	Co	Ni	Al
—	—	9	9	1.8	9	—
—	—	3.6	3.6	3.6	18	—
—	—	1.3	13.3	.7	13.3	—
—	—	2	100	1	100	—
5	—	—	250	—	—	—
5	—	250	—	—	—	—
5	—	250	250	—	—	—
5	—	500	500	—	—	—
5	—	500	500	2	3	—
5	8.5	500	500	2	3	—
.5	—	1	—	.5	5	—
.5	17	18	20	10	5	—
2	—	500	500	1	10	10
10	—	100	100	2	100	100
10	100	100	100	10	100	100

LITERATURE CITED

- (1) Proc. Ind. Acad. Sci. 1922 (1923) p. 138.
- (2) F. Morrel, Z. f. Anal. Chem., 16, 251, 1877.