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A Metallographic Investigation of  
Cobalt Ore from the Little Gem Mine

Geology 9 Report

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## I N D E X

Introduction	Page 1
Geology	" 1
Ore Occurrences	Pages 2 to 4.
Mineralography	" 4 to 11.
Sections	Page 4
Reagents	" 4
Etch Tests	" 5
Table Showing Etch Reactions - Little Gem ore	" 8
Table Showing Etch Reactions, - Cobalt, Ont.	" 9
Sections under Polarized Light	" 10
Microchemistry	" 10
Assays	" 12
Conclusions	Pages 12 to 15
Acknowledgments	Page 15
Appendix	Pages 16 to 23
Assay Procedures	Page 16
Section Drawings	" 22

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Introduction.

The Little Gem mining property, consisting of eleven mineral claims with fractions, is located in the Lillooet Mining Division in British Columbia. The mine itself is situated near the top of a ridge which rises to an elevation of 7000 feet and slopes westerly down to Roxy Creek, a tributary of Gun Creek.

In addition to considerable trenching work, the management has driven two tunnels on the property, the upper at elevation 6400, and the lower at elevation 6350. The upper is in high grade ore for the greater part of its length of 200 feet, but the lower had not, at the time of writing, reached the ore bodies. The specimens examined were taken from the upper tunnel.

Geology.

The local rock formation is a biotite quartz diorite medium grained and light greenish in color. Alteration into a speckled reddish rock near the mineral deposits is largely due to weathering and leaching by ground water. The diorite is in the form of a tongue 2000 feet wide by about  $2\frac{1}{2}$  miles long, extending from the larger body of diorite that covers

the Gun Creek valley.

Bordering the diorite on the northwest is a large body of very fine grained dark green serpentine, which appears to be quite massive on the surface. The serpentine resembles an olivine basalt as little alteration has taken place except along the contacts where it is badly sheared and broken and has a more banded effect.

Traversing the diorite are numerous aplitic dikes which seem to follow closely a brown weathered dike of ferruginous carbonate composition. Diabase dikes are numerous but small and cannot be traced for great distances. In only a few places are small sections of greenstone seen included in the diorite.

Except on the northwest, as noted, typical Bridge River formations, consisting chiefly of andesites and lava flows, surround the diorite.

#### Ore Occurrences.

The known ore bodies appear to be lenticular and vary in width from a few inches to several feet. Two veins, which are thought to be part of the same orebody, are being developed at present.

The footwall vein can be traced on the surface for about 50 feet, and dips at about 20 degrees striking easterly westerly. This vein varies in width from a few inches at the lower end to about six feet at the upper end, and was covered almost entirely by an altered diorite cap rock later removed by blasting.

The hanging wall vein lies parallel to the footwall vein and about 17 feet southerly. It appears considerably wider and longer than the footwall vein and, the average width being about 6 feet and the length on the surface about 90 feet. This vein only outcropped visibly in one small section before stripping of the altered diorite capping.

Scattered throughout the lenticular ore bodies are masses of quartz and feldspar. Very little alteration appears to have taken place at the borders of the veins.

A shear, 6 to 12 feet wide, striking easterly-westerly, was traced on the surface for over 2000 feet. Assay across the section run from 0.22 to 0.40 percent cobalt. If the average across the section could be increased to 0.50 percent cobalt this shear would become ore, and would therefore appear to be of considerable importance in future development. Moreover, wherever any small dike cuts the shear, there appear small amounts of arsenopyrite and cobalt bloom, indicating a possibility of values below.

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Material for the paragraphs on "Geology" and "Ore Occurrences" as well as for part of the "Introduction" was gathered, by permission of the author, from Mr. R. R. Taylor's 1939 Summer Essay, "The Little Gem Mine".



Mineralography

Sections:

From representative samples of the ore, six sections were made up using dammar gum and brass molds. Later three bakelite mounted sections were prepared and superpolished by Mr. J. Donnan.

Reagents:

On the advice of Dr. H. V. Warren four special etch reagents were made up following the procedure outlined by Mr. Ellis Thompson.\*

(1) CoNiAsS - A.R.

The solution contained:

Co	-	1.82	grams
Ni	-	1.82	"
As	-	2.25	"
S	-	1.00	"

The Co, Ni, As, and S were placed in a 155 cc. beaker, 20 cc. of aqua regia (A.R.) added and the mixture warmed. To enable the solution of as much sulfur as possible, nitric-chlorate mixture was added and the solution taken to dryness overnight. The dried material was then taken up with 20 cc. of aqua regia, warmed for 1 hour, and filtered through an asbestos filter into a 40 cc. reagent bottle.

(2) Co As S - A.R.

The solution contained:

Co	-	1.82	grams
As	-	2.25	"
S	-	1.00	grams

Solution was effected as in (1).

\* A Qualitative and Quantitative Determination of the Ores of Cobalt, Ont.: Ellis Thompson, Economic Geology, Vol. 25, No. 5, 1930.

## (3) Fe A.R.

Iron was dissolved in 2 cc. of aqua regia until the solution was saturated. The clear solution was then decanted into a reagent bottle.

## (4) Fe As S A.R.

A saturated solution of pure arsenopyrite in 20 cc. of aqua regia was prepared following the general method as outlined in (1). The excess arsenopyrite was filtered off through an asbestos filter.

Etch Tests

A table of etch tests, together with those given in Mr. Ellis Thompson's monograph, is appended. Testing required considerable practice before satisfactory results could be obtained.

A detailed description of the tests section by section would involve needless repetition, as the sections differed from each other only by the presence or absence of inclusions. A general description of the etch tests on the groundmass and on the inclusions will therefore be given. Except where noted, the reagents were left on a standard time of 20 seconds.

Groundmass:(1)  $\text{HNO}_3$ 

## (a) Concentrated

This reagent, left on ten seconds only because of its vigorous action, immediately etched the groundmass black. A prismoidal structure, similar to that of arsenopyrite, was

brought out by the etch.

1:1

A differential brilliant blue and brown tarnish was noted. This tarnish seemed to show two different minerals as, on buffing, a differential etching corresponding to the borders of the blue and brown colors was seen.

Fe + A.R.

A blotchy brown stain was noted occasionally but was not definite enough to be considered a positive test.

Inclusions

HNO<sub>3</sub>

Concentrated:

An immediate black etch resulted. The reagent was left on 10 seconds.

1:1

An immediate black etch.

Special Reagents (1), (2), (3), and (4).

In all the reactions with these reagents, the inclusions immediately etched black.

FeCl<sub>3</sub>

A faint etch, emphasizing the outline of the inclusions, was noted in all cases.

Dr. H. V. Warrén, using a high power Leitz arc-light microscope, checked all the tests made by the author except that he found the inclusions to give a faint test with



3:10 HNO<sub>3</sub>. Dr. Warren also found a number of inclusions not seen by the author which tested negative to 3:10 HNO<sub>3</sub> and FeCl<sub>3</sub> and positive to CoNiAsS. Tests were not complete, however, and as the inclusions were very few in number and very hard to find further tests were not made.

Gold

Using a magnification of 1300 diameters, Dr. Warren found that the gold occurred as particles 1 - 10 microns in size, apparently associated only with the inclusions etched with FeCl<sub>3</sub>.

*Insufficiently known  
B.W.*

Table Showing Etch Reactions

"Little Gem" Cobalt-Gold Ore

<u>Reagent</u>	<u>Groundmass</u>	<u>Inclusions</u>	<u>Remarks</u>
1:1 HNO <sub>3</sub>	Differential Etch	Etch	Blue-Brown stain on Groundmass
3:10 HNO <sub>3</sub>	--	--	<u>Under Polarized Light</u>
Conc. HNO <sub>3</sub>	Dark grey etch - showing "prismoidal" structures	Black etch	<u>Groundmass</u> Strongly anisotropic with polarization colors ranging from purple, brown, or gray, to light blue and blue gray. Regardless of colors whole groundmass extinguishes only once per revolution.
A.R. CoNiAsS	--	Etch	
A.R. CoAsS	--	"	
Ar FeAsS	--	"	<u>Inclusions</u> Extinguish 3 times in revolution.
Ar Fe	Faint Tarnish(?)	"	Colors light blue to straw yellow
HCl(dil)	--	--	
FeCl <sub>3</sub>	--	Faint Etch	
KCN	--	⊖	
HOCl <sub>2</sub>	--	--	
KOH	--	--	

A.R. = Aqua Regia = 3HCl:1HNO<sub>3</sub>

Both groundmass and inclusions gave a hardness of 6.0 to 6.5.

## Sections Under Polarized Light.

### Groundmass

Predominant colors were light blue, and brown of various shades. In some of the parts showing blue, irregular patches of reddish pink were noted. These patches became a different shade of brown from the surrounding groundmass on rotation. The many pairs of colors, e.g., blue-brown; grey-dark grey; light blue-deep purple brown, etc. appeared in definite outlines, but these outlines became invisible under ordinary light.

Twinning was noted in several sections.

### Inclusions

Polarization colors of the inclusions were light blue and straw yellow. So distinctive was the straw yellow color that it was found easier to spot the inclusions under polarized light rather than white light.

### Microchemistry

Small chips from section 1, known to contain no inclusions visible under the microscope, were microchemically tested for cobalt. These tests were repeated four times, using chips from the same specimen, in no case showing any visible inclusions, and in every case positive tests for cobalt were obtained.

Chips from a section showing inclusions were also tested, and slightly more positive results were obtained.

The procedure used in these tests was as follows.

\*

Potassium Mercuric Thiocyanate Test

Reagent: 5%  $K_2Hg(CNS)_4$  in  $H_2O$  .

Product:  $CoHg(CNS)_4$  in indigo blue prisms.

Limit: 0.01%  $Co(NO_3)_2$  solution.

The mineral is powdered and dissolved by taking to dryness several times with 1:1  $HNO_3$  on a glass slide. The dry solution is leached with 1:7  $HNO_3$  and the leach solution transferred to a clean place on the slide. A drop of  $K_2Hg(CNS)_4$  reagent is carefully merged with the leach solution and the mixture partially evaporated. A ppt. of dark blue prisms along the edges of the drop shows cobalt. With dilute solutions (0.05%  $Co(NO_3)_2$  or less, the ppt. separates out as dark blue spherulites. If there is nickel with the cobalt in ratios greater than 1:5, only blue spherulites will form. Nickel may be tested for in the same solution by the presence of light brown spherulites when the drop is partially evaporated.

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\* Microscopic Determination of the Ore Minerals: M.N.Short.  
U.S. Dept. of the Interior, Bulletin 825, 1931.

AssaysHead Samples

This was about a 200 gram sample obtained by crushing and quartering the original thirty pounds of high grade ore.

Cobalt	-	6.8%
Nickel	-	0.5%
Iron	-	22.1%
Arsenic	-	39.0%
Sulfur	-	14.1%
Gold	-	1.46 oz/ton.
Insol.	-	<u>11.4%</u>

93.9%

Sections

Assay sections 1, 2, and 3 were chosen to approximately correspond to their respective polished sections. Assay sections 1', 2', and 4 were actual parts of the respective sections, and would be, therefore, more representative.

Section	Description	Assays					Total
		Co	Ni	Fe	As	S	
1	Shows no inclusions under the microscope Yellowish color cleavage noted.	0.77	-	40.1	45.0	18.5	102.9*
2.	Shows inclusions- dense gray color	8.9	-	29.9	46.6	21.8	101.8*
3.	Apparently same as 1.	0.90	-	36.0	43.5	20.1	99.3
1'	Apparently same as 1 and 3.	4.3	0.08	31.5	45.5	17.3	98.7
2'	Same as 2. (insol. noted in assay)	8.7	.04	26.4	40.5	16.2	91.8
4.	"Tree" structure caused by gangue growth. dense gray color.	9.9	0.2	24.3	46.1	16.9	99.3

\* High results probably found their error in the sulfur assay, as it was not possible to check these.



Fire assays for gold on sections #1, #2, #3, #4 and #6 gave the following results:

<u>Section</u>	<u>Au - oz./ton</u>
1	2.05
2	2.15
3	1.58
4	2.10
6	2.10

### Conclusions

Because of lack of time, it was not possible to carry out these tests in greater detail, or to obtain sufficient data to enable a definite conclusion as to the mineralogical species to be reached. It was thought, however, that the ore consisted chiefly of "Danaite" (the groundmass) and "Loellingite" (the inclusions). The presence of danaite was indicated by the assays only, the etch tests being exactly similar to those for arsenopyrite.

⌘  
According to Dana, the composition of danaite varies as shown :

<u>Locality</u>	<u>Assays: %</u>			
	<u>Co</u>	<u>As</u>	<u>Fe</u>	<u>S</u>
Skutterud	9.01	46.76	26.36	17.34
"	4.75	47.45	30.91	17.78
Franconia	6.45	41.44	32.94	17.84
Copiapo	5.84	44.30	30.21	20.25

⌘ Descriptive Mineralogy: <sup>SIXTH</sup> Smith Edition by E. S. Dana. John Wiley, 1914. Page 99.

These assays check closely with those obtained by the author for the sections of Little Gem ore examined. The low cobalt assays obtained for sections 1 and 3 would seem to indicate that considerable arsenopyrite is present as well as danaite, and that therefore the groundmass is a mixture of these two minerals. This might account for the varied polarization colors and the differential blue and brown etching with 1:1 HNO<sub>3</sub>. Results were not conclusive enough, however, to enable a final statement to be made in this respect.

A connection between the amount of inclusions and the cobalt content is indicated as shown in sections 1, 2 and 3. Apparently the inclusions only become numerous in the sections (2, 2' and 4) of nearly pure danaite, and are not present in the sections (1, 1' and 3) of nearly pure arsenopyrite. It would not be necessary that the inclusions contain much cobalt but only that they be associated with danaite, and indeed, considering the relative amounts of the inclusions, it would not seem possible that their cobalt content, even assuming them 50 percent cobalt, would give the high cobalt assays obtained.

Although the etch tests for loellingite given in Ellis Thompson's monograph do not correspond exactly with those obtained for these inclusions, in consideration of the above paragraph, and the etch tests made, it was fairly definitely decided that the inclusions were loellingite, possibly nickeliferous.

The mineral carrying the nickel was not determined,

but was thought to be the loellingite. There is a possibility, of course, that the nickel occurred replacing part of the cobalt or iron in the danaite.

Gold appears to occur in minute disseminations throughout the sections associated with the loellingite.

Much research still remains to be done before the problem could be considered solved, but the present work shows at any rate that the cobalt carrying minerals, if not danaite, is at least not some of the better known cobalt minerals. Indications point strongly to danaite, associated with arsenopyrite and loellingite.

#### Acknowledgments

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A P P E N D I XAssay ProceduresArsenicDistillation Method

This method is used when the sample contains Antimony. Antimony will titrate with the arsenic and hence give an incorrect assay if the fusion method is used.

Weigh out 0.5 grams of sample in 100 cc. beaker, add 25 cc. water, 10 cc.  $\text{HNO}_3$  and some  $\text{KClO}_3$ . Decompose, add 10 cc. 1:1  $\text{H}_2\text{SO}_4$  and take to fumes, usually overnight, then transfer to a 250 cc. distillation flask with brick grape-nuts.

Add 3 grams ferrous or cuprous chloride, 2 grams of ferric chloride and 90 cc.  $\text{HCl}$ . Receive in a 500 cc. beaker containing about 100 cc. water with tip of condenser just under surface. Distill till the volume is down to about 20 cc. then add 15 cc.  $\text{HCl}$  and take down to 20 cc. again. This should take about 40 minutes. Wash out condenser tube into flask.

Neutralise with  $\text{NH}_4\text{OH}$ , make just acid with  $\text{HCl}$  and cool. Make alkaline with  $\text{NaHCO}_3$  (add carefully to avoid foaming over), add starch indicator and titrate with standard Iodine solution.

Standard Iodine Solution

Dissolve 50 grams  $\text{KI}$  in 75 cc. water in a 500 cc beaker. Add 25.5 grams Iodine, and leave in a warm place till in solution. Take bulk to 2 litres.

Take up .099 AS 0 in 400 cc. beaker with  $\frac{1}{8}$  stick of  $\text{NaOH}$  and water. Make just acid with  $\text{HCl}$  and take bulk to 300 cc. and cool. Make alkaline with  $\text{NaHCO}_3$  as noted before, add starch indicator and titrate till stirring rod is invisible.

Starch Indicator

Mix 2 grams prepared starch with 30 cc. water. Pour into 100 cc. boiling water and boil for about 4 minutes. This solution should be alkaline, hence add some  $\text{KOH}$  to the solution before using.



Fusion Method

This method can only be used when the sample contains no antimony.

Weigh out 0.5 grams of the sample, and decompose as in the distillation method. Then dilute with 100 cc. water, add 10 cc. HCl and gas with  $H_2S$  till the super-natant becomes clear. Transfer the precipitate to a 50 cc. beaker, wash the filter paper and the filter with 5% NaOH solution to remove all arsenic sulfide, neutralize the solution with  $H_2SO_4$  and add 5 cc. conc.  $H_2SO_4$ . Add 1 gram  $KHSO_4$  and take to fumes on an electric element. When the sample is fuming strongly add a small pinch of tartaric acid, and heat till the solution becomes colorless. Cool and add 20 cc. water and warm till all the fused mass is in solution. Then neutralise with  $NH_4OH$  and proceed exactly as in Distillation Method.

Sulphide Ores, Mattes and Materials containing Copper.

Add 5 - 10 cc.  $HNO_3$  and .5 to 1 grams of  $KClO_3$  and evaporate to dryness. Add 3 - 5 cc. HCl and again evaporate to dryness, then add 20 cc. HCl and gas, and treat as before. This method of decomposition can also be used in the distillation method of course.

Notes.

The addition of tartaric acid reduces the arsenic and turns the solution black.

The fusion method, while only useful for certain types of ores, gives much more consistent and accurate results than the distillation method.

Only a small amount of tartaric acid should be used or else the solution will tend to boil over.

CobaltElectrolytic Method

Weigh out  $\frac{1}{2}$  gm. sample into 150 cc. beaker, add 3 cc. water and 6 cc.  $HNO_3$  and digest. Then add 8 cc. HCl and a few drops  $H_2F_2$  (if the sample contains much silica) and digest till all action ceases. Then add 10 cc 1:1  $H_2SO_4$  and take to fumes. When sample has fumed 10 minutes remove from hot plate, cool and add 2 cc. 1:1  $H_2SO_4$ , 1 cc. HCl and 30 cc. water, and digest for 1 half hours. Then dilute to 80 cc., heat to about  $80^\circ C.$  and gas with  $H_2S$  till supernatant liquid becomes clear. Filter off ppt. into 400 cc. beaker, wash ppt. 6 times with



hot water and discard ppt. unless it is desired to analyse it for As, etc. Boil filtrate for 10 minutes to remove all  $H_2S$ , then add 20 cc.  $H_2O_2$  and evaporate soln. to about 70 cc. Cool soln. and transfer to an electrolytic beaker (150 cc.), neutralise with  $NH_4OH$  and add one third total volume in excess. Electrolyse at 1.2<sup>4</sup>- 1.5 amps. for 1 hour. Deposit on cathode is Cobalt if no Nickel is present. If nickel is present it must be analysed for in the cathode deposit, and the weight of nickel subtracted from the total weight to find the weight of Cobalt.

#### Analysis for Nickel

Dissolve cathode deposit in warm 1 to 3  $HNO_3$  and wash cathode into the beaker. Dilute to 150 cc., neutralize with  $NH_4OH$  and add 2 cc. in excess. Dilute to 250 cc. warm till first bubble appears, remove from hot plate add 20 cc 1% dimethylglyoxime in alcohol soln. Set in warm place for 1 hour. Filter thru tared Gooch crucible, wash 5 times with hot water, dry and weigh. Multiply difference by 0.2302 to find weight of nickel and subtract from cathode weight to find weight of cobalt.

#### Notes

Soln. from  $H_2S$  pptn. contains, Fe, Co, Ni, etc., ppt. contains As, Sb, Pb, Ag, etc. as sulfides.

A few (2 - 3)cc. of  $H_2SO_4$  added to the soln after fuming helps the solution of the solid material and also speeds up the  $H_2S$  pptn.

In electrolysis, the cathodes should not touch the beaker sides.

For a complete nickel analysis, the solution after electrolysis should be treated as follows: Make acid with HCl, add tartaric acid crystals, (to avoid the pptn. of Fe as hydroxide when neutralised with  $NH_4OH$ ), neutralise with  $NH_4OH$ , add 5 cc. in excess, make up to 250 cc. warm add dmg. as before, and filter off ppt. (if any). If ppt. is dirty in color wash crucible carefully with one to three HCl and wash ppt with hot water, treat soln with tartaric acid, and carry on as before. The weight of nickel found in this manner is added to that found by the analysis of the cathode deposit for the total amount of nickel present in the sample.

Insoluble

Weigh  $\frac{1}{2}$  gm ore into 150 cc. beaker, add 15 cc. HCl, cover till violent ceases, add 10 cc. HNO<sub>3</sub> and heat till brown fumes disappear. (The acids may be added in the reverse order, if desired.) Place on low plate, rinse off cover and take to dryness. Cool, add 10 cc. HCl and again take to dryness, on a low plate. Bake for  $\frac{1}{2}$  hour at 120° C. Cool, add 10 cc. HCl, 15 cc. water and 2 gms. NH<sub>4</sub>Cl. Cover and boil till clear. Filter thru rapid filter and wash 6 times with boiling water. Ignite in a clay cup till the residue is white in color and weigh.

Notes

If the residue is white and does not show gray color on ignition, the assay may be considered an accurate Silica assay.

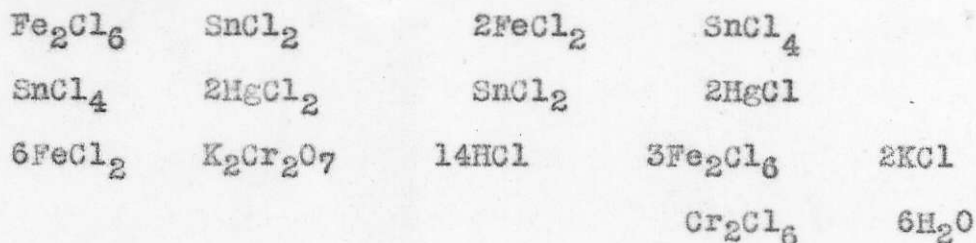
IronDichromate MethodOxides

Weigh out into 100 cc. beaker, add 10 cc. water and 10 cc. HCl. Warm soln. till clear, add 10 cc. chlorate mixture, then add 10 cc. 1:1 H<sub>2</sub>SO<sub>4</sub> and fume nearly to dryness.

Sulfides

Dissolve in 3 cc. water and 10 cc. HNO<sub>3</sub> and warm till red fumes come off. Add 10 cc. HCl and proceed<sup>3</sup> as above.

In either case, cool, add 25 cc. water, 5 cc. HCl and boil. While hot add SnCl<sub>2</sub> drop by drop till yellow color (Fe<sub>2</sub>Cl<sub>6</sub>) goes and add one drop in excess. Cool (to room temp) and add mercuric chloride, about 20 cc, to neutralise the excess SnCl<sub>2</sub> and titrate with potassium dichromate using K<sub>4</sub>Fe(CN)<sub>6</sub> as indicator.

Reactions and standardization of soln.

$$6 \times 55.84 = 294.2$$

$$\therefore \frac{335.05}{294.2} = \frac{.005}{x} \quad \therefore x = .00439 \text{ gms/cc}$$

Therefore, use 4.39 gms of potassium dichromate per litre of soln.

### Standardization

Weigh up 0.7 grams of ferrous ammonium sulfate, acidify with HCl, add 1 drop  $\text{SnCl}_2$ , excess mercuric chloride and titrate. Iron in 0.7 gms. of Ferrous ammonium sulfate divided by the no. of cc. of soln. used gives the standard of the soln. in gms per cc.

$\text{SnCl}_2$  60 gms. in 600 cc. of strong HCl and make up to 1 litre.

$\text{Hg}_2\text{Cl}_2$  60 to 100 gms per litre of water.

### Notes.

$\text{SnCl}_2$  must be added drop by drop as an excess will cause metallic Hg to be pptd. on addition of mercuric chloride.

$\text{SnCl}_2$  must be added hot.

$\text{K}_4\text{Fe}(\text{SN})$  in water is made to a pale yellow color for the indicator soln.

### Sulfur

Weigh .5 gms of sample into 150 cc. beaker, add 40 cc. water and 30 cc. nitric chlorate mixture and take to dryness on a low plate. Bake for 10 minutes on hot plate, cool, add 5 cc.  $\text{H}_2\text{O}$ , 1 cc. HCl and digest. Add excess  $\text{Na}_2\text{CO}_3$  free from sulfate (0.6 gms for calcine; 2 gms for ore). \* Boil for ten minutes, dilute to 75cc. and boil again. Remove from hot plate, add 2 drops phenol and filter thru #1 Whatman, wash 4 times in hot water. Redissolve ppt. in 1:1 HCl, add excess  $\text{Na}_2\text{CO}_3$  and treat as from \*, refilter and wash 4 times then combine filtrates. Neutralise filtrate with HCl, add 2 - 3 cc. in excess, and boil soln, which must be acid, till all  $\text{CO}_2$  is removed. Add hot  $\text{BaCl}_2$  and continue boiling till  $\text{BaSO}_4$  ppt settles out. If both sample and  $\text{BaCl}_2$  are boiling the sulfate

should settle out immediately. Filter thru a #2 Whatman and wash 4 times with hot water. Ignite and weigh as  $\text{BaSO}_4$ . The weight obtained multiplied by .1373 gives the weight of Sulfur in the sample.

Notes

The filtrate from the pptn. with  $\text{Na}_2\text{CO}_3$  must be acid, and should be tested for acidity with Litmus paper. If the filtrate is not acid all the  $\text{CO}_2$  will not be removed, and on addition of the  $\text{BaCl}_2$  the soln. is liable to foam over and  $\text{BaCO}_3$  may be formed.

Ignition must be carried out slowly to avoid the reduction of the  $\text{BaSO}_4$  to sulfide or sulfite by the carbon.