

NOTES ON SOME SULPHARSENITES
AND SULPHANTIMONITES FROM COLORADO.

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In the summer of 1872, Professor Richards obtained specimens of the silver-bearing minerals of some of the Colorado mines.

They were called, by the miners, brittle silver or gray copper, but, as they had never been analysed, nothing definite was known as to their composition.

In March 1873 I was requested to test these specimens sufficiently to ascertain whether they belonged under Stephanite or Tetrahedrite and whether the minerals from the different mines were of the same composition.

A qualitative analysis showed that all contained copper and contained it in varying proportions.

These indications together with the results of the blowpipe tests divided the specimens into two groups.

Those from the Illinois and Walker mines containing much copper and little silver, and both arsenic and antimony, while those from the Hercules and Terrible

mines contained a very large amount of silver with comparatively little copper, and antimony with traces only of arsenic.

The Illinois Lode, Central City, Colorado, yields both gold and silver by the dry assay although neither appear in the results given of the analysis by the wet way.

Lustre, metallic. Color, dark gray. Streak, brown. Not easily fused.

Iron pyrites was abundantly distributed throughout the mass, and although the coarse powder was carefully examined under the microscope, some pyrite and much quartz evidently escaped separation.

This would give a slightly different ratio between (Ag-Cu-Fe) and (As-Sb-S) from that which the exact analysis would give -

The ratio of Tetrahedrite is 1:2⁴ while the ratio of the percentages as given is about 1:2.

The mineral would therefore seem to be a true Tetrahedrite.

The specimen from the Walker mine Montezuma, Colorado, was massive, in quartz rock, without galena.

Lustric, metallic. Color, dark brown. Streak, red. Fusible.

The percentages, given below, of the Wolbar are the results of a single analysis, but suffice to indicate that the mineral is a Tetrahedrite.

	Illinois	Walker	
PiO ₂	15.04	0	
Pb	0	2.64	
Ag	undetermined	5.91	
Au		—	
Cu	41.32	36.07	
Fe	6.24	,80	
Zn	6.00	0	
S	24.03	26.41	
St	1.62		<u>71.83</u>
As	6.31	undetermined	
	<u>100.56</u>		<u> </u>

There were four specimens from Hercules mine and five from Terrible mine both at Georgetown, Colorado.

The gangue rock from both mines seemed to be a tolerably fine granite containing very little mica.

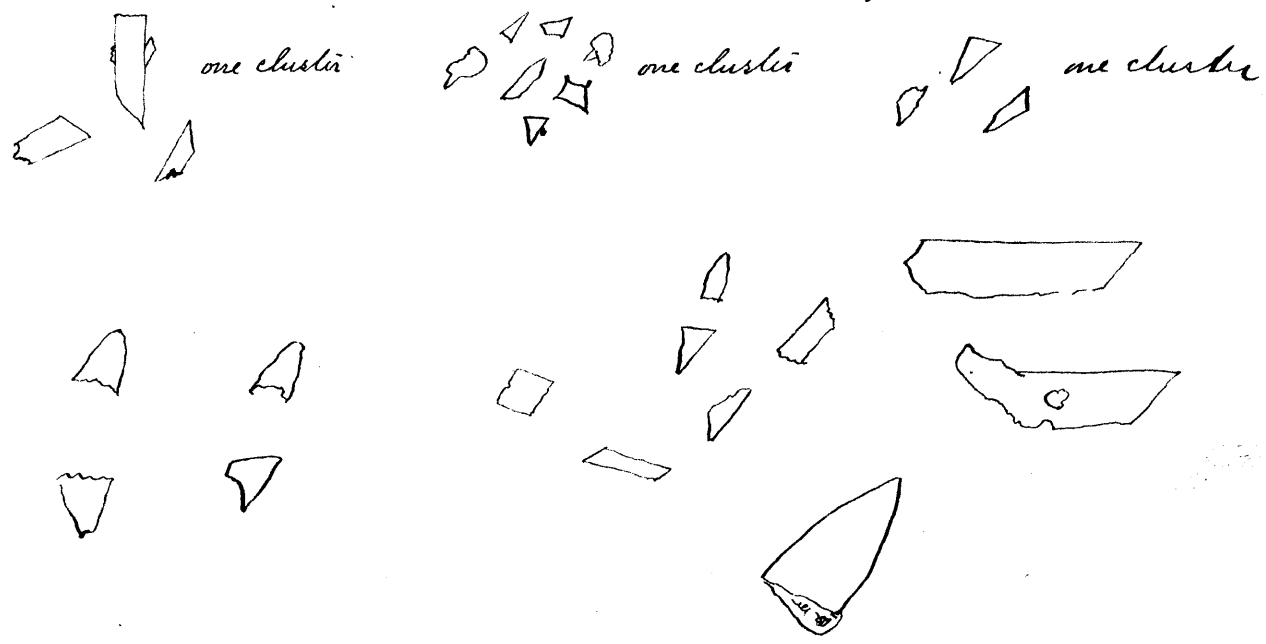
The silver ore occurred, intermingled with finely crystallized galena and zinc blende, in a vein or fissure lined on both sides with splendid crystals of quartz. It seemed, in some instances, to have been deposited after the galena and blende for it filled up the crevices in them and occupied the spaces between the quartz crystals.

In one case it seemed almost a vein between the galena and blende.

Lustre, metallic. Color, steel gray. Striae, black. Very brittle. The specimens were mainly massive although in two something like crystalline form was noticed with striae along the length of the prisms.

On attempting to get them out separately for measurement; they broke into several pieces which, under a magnifying glass seemed to present a micaceous,

laminated structure. Thin scales were placed under a microscope and the forms obtained by examination of the different specimens are roughly depicted below



There was definiteness of form sufficient to indicate a crystalline structure and a similarity of shape indicated that the crystalline form would be the same -

The specimens from Terrible mine numbered 3, 4, and 5, with Hercules 2 and 4, were more silvery in lustre and less massive in structure, rather more brittle, yet as the galena and blende were also in more perfect crystals the outward appearance did not show a difference sufficiently marked to suggest a difference of composition.

The ore was in so small quantity and so intimately mingled with the other ores that it was very difficult to get a clear sample; those, from which the results tabulated below were obtained, were chipped off with a penknife and carefully examined with a microscope that all foreign minerals might be separated, still, only two were free from galena.

The object, originally in view in undertaking the investigation, was merely to see if the ore was of a uniform composition, and absolute accuracy is not claimed for any of the analyses but they are reliable enough to base a theory upon.

Some analyses from Dana's Mineralogy are given for comparison.

	Hercules			Terrible			Stylogypite. Polybasite. Stephanite. Tetrachlorin (Freiburgite)			
	No. 1	No. 2	No. 3	No. 1	No. 2	No. 3				
SiO ₂	2.24	2.00	4.86	2.60	1.00	.80				
Pb	1.67	0	5.00	2.19	11.67	0				
Ag	36.67	60.06	44.68	47.00	28.00 ^{22.50}	57.76	8.30	68.55	68.51	31.29
Cu	18.04	10.18	12.48	9.65	29.20	13.35	28.00	3.36	.64	14.81
Fe	1.10	1.19	5.52	.57	1.90	0	7.00	.14	0	5.98
Sb	17.80	undet	undet	undet	undet	undet	30.53	71.53	14.68	Zn .99 24.63
As	traces?	traces?	traces?							
S	22.70	17.42	17.45	18.90	19.00	20.33	24.30	15.55	16.42	21.17
Ratio	1:2 ² / ₃	1:1 ¹ / ₅	1:1 ¹ / ₅	1:2 ¹ / ₂	1:2		1:2 ² / ₃	1:1 ¹ / ₂	1:2	1:2 ¹ / ₄

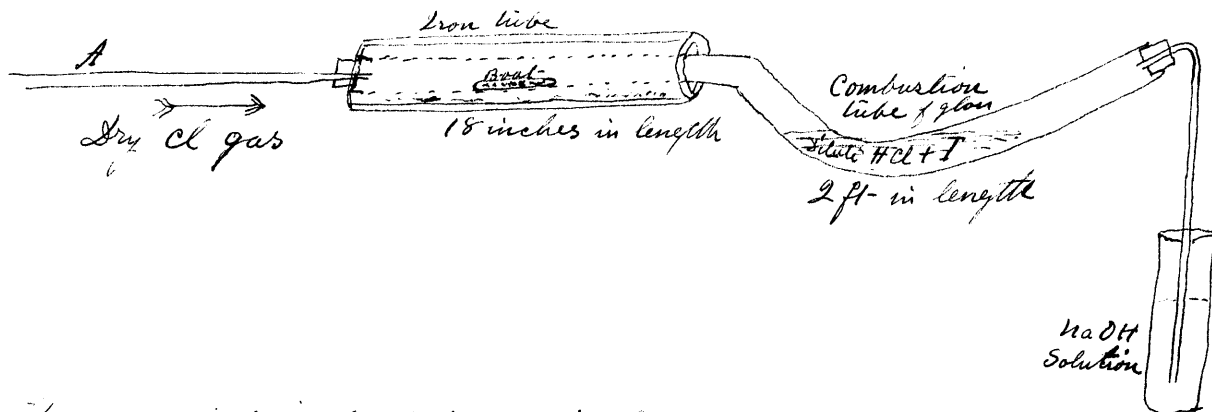
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It will be seen that the percentages do not quite agree with any given analysis. Hercules No 1 and Terrible No 1 are probably Tetrahedrite although containing more silver than any previously analyzed specimen.

These two were darker in color and more compact than the others. Terrible No 2 doubtless belongs with them but the amount of galena which was evidently mingled with the sample throws it out of account.

Terrible No 3 has the ratio of Stephanite, while Hercules No 2 and No 3 are between Polybasite and Stephanite. As the antimony was estimated by difference a more accurate analysis might change the ratios so that they would agree with Stephanite; but, from the amount of copper contained in all the samples, it would seem that they were nearer to Polybasite.

Apparatus suggested by Professor Crafts
for the analysis of Tetrahalides containing possibly
Cu. Ag. Fe. Zn. Hg. Sb. As & also as impurities PbS. ZnS. CuS. & SiO₂



The small straight tube A is long enough to allow of the sliding back of the iron tube quite off from the glass tube.

After the weighed substance is placed in the tube (in a porcelain boat) dry chlorine gas is passed over it without heating as long as there appears to be any action. Then the iron tube is pushed forward over the combustion tube and heated to dull redness by an ordinary combustion furnace.

As to the methods employed, most of the results given in the table were obtained by the Chlorine method, the residue from ~~combustion~~ ^{treatment with chlorine} being first treated, in the boat, with strong hot nitric acid, then well washed with hot water, the residue thus obtained was separated by decantation or by filtration if necessary, treated with ammonia which dissolved the chloride of silver and left only silica which was filtered off dried and weighed. The silver was reprecipitated by nitric acid, weighed as chloride. The copper was precipitated from the first nitric acid solution as subsulphide and the iron determined in the filtrate.

The solutions containing the volatile ^{chlorides} were used in making experiments on the method. The lead was obtained from the evaporation with sulphuric acid for the precipitation of copper as subsulphide.

Duplicate determinations were made as follows. The sulphides were oxidized with nitric acid, evaporated and taken up with nitric acid ^{and water}, filtered, the silver precipitated by dilute chlorhydric ^{acid}, the filtrate evaporated with sulphuric acid with the addition of tartaric and sulphurous acids. The lead was filtered out, the solution heated and then

treated with hyposulphite of soda which precipitates copper arsenic and antimony, ^{as sulphides} the filtrate is oxidized, evaporated to a small bulk the separated sulphur filtered out and the iron and zinc determined as usual - The ~~filtrate~~ precipitate is treated with sulphide of sodium, washed, dried and ignited with sulphur. The solution in sulphide of sodium is acidified with sulphuric chlorhydric acid, the precipitated sulphides of arsenic and antimony filtered out and oxidized and separated and determined by presenius page 399 - p-155 -

In some cases this method is very convenient, not requiring the apparatus of the chlorine method and giving the arsenic and antimony in a more convenient form and I think more accurately

The arsenic and antimony are completely precipitated with the copper if the solution is dilute enough and kept at just the boiling point for a few minutes

In analyzing these minerals I was puzzled to separate the copper in presence of arsenic and antimony, the battery was hardly practicable. I had just been estimating

Copper in some other minerals, not containing arsenic or antimony, as subsulphide according to Fresenius.

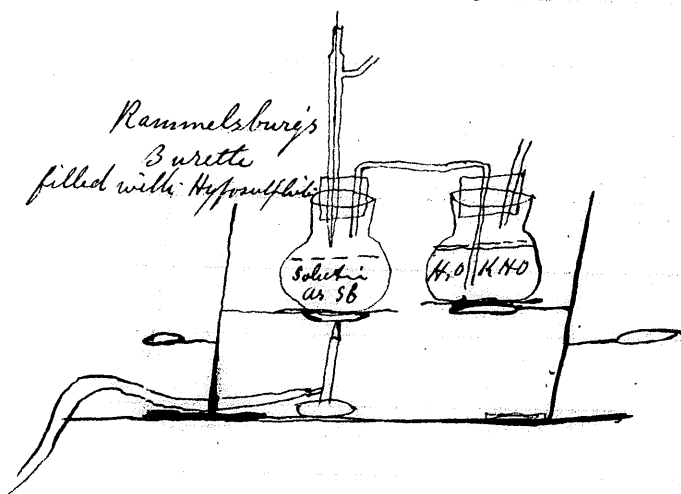
As I found it a quick process I wished to try to use it in the case of the minerals under examination but I could find no reference to the behavior of arsenic or antimony compounds with sodium hyposulphite, and no one could tell me what the reaction would be. I did not know whether I should find the arsenic and antimony in the precipitate with the copper ~~in the precipitate~~ or in the filtrate with the zinc, or in both places.

In order to settle the question known solutions of arsenic and antimony were treated at first separately and afterwards together with a solution of sodium hyposulphite and the conditions of complete precipitation determined as above.

At the time this was an entirely original investigation (march 1873) I have recently (may 1873) noticed an account of the preparation of sulphides of arsenic and antimony for calico printing and for some other technical uses by means of hyposulphite. *Chémie Appliquée Barreswil* 1859
Graham Otto Band.

I have yet seen no mention of it as a method of separation or estimation.

I propose to try to use hyposulphite for determining either arsenic or antimony or both together, and ⁱⁿ that ^{case} separately and estimating the arsenic, volumetrically by an apparatus something like that figured below. The sulphurous acid which is evolved may be received into a flask and after cooling, the contents of both flasks may be titrated with iodine.



There must be no nitric acid and a very slight excess of chlorhydric

I have begun a series of investigations on the behavior of the other metals with hyposulphite with a view to employing hyposulphite in qualitative analysis, in some instances at least, instead of sulphydric acid.

I think it might be used as a preliminary test and save much time - - -

Note: Douglas and Priest since published

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