AN ALKYL SUBSTITUTED TRIPHENYLMETHANE DYE AS A FLOTATION AGENT FOR STIBNITE

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Myron Gilbert Brown
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This is to certify that the

thesis entitled

AN ALKYL SUBSTITUTED TRIPHENYLMETHANE
DYE AS A FLOTATION AGENT FOR STIBNITE

presented by

MYRON GILBERT BROWN

has been accepted towards fulfillment
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C. C. DeWitt
Major professor

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AN ALKYL SUBSTITUTED TRIPHENYLMETHANE DYE AS A FLOTATION AGENT FOR STIBNITE

by

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ACKNOWLEDGEMENT

INTRODUCTION

The most important ore of antimony is stibnite, Sb_2S_3. The best sources of stibnite are in Algeria and Hunan Province, China. (1) There are some sources within the borders of the United States such as in Los Angeles County, California. Most stibnite deposits occur in narrow veins in siliceous rock, (quartz or granite), and when crushed, yield an ore of low antimony concentration. It is advantageous to concentrate these ores cheaply to reduce their bulk before further refining. Froth flotation concentration has been used with some success on various antimony ores. Z-5 and Z-6 xanthate collectors have been shown to yield fair recoveries. (11) There is a tendency for the ground ore to slime. The association of stibnite with dense arsenopyrite makes a good separation extremely difficult. (10)

The present work reports recovery data obtained by the use of a normal-decyl substituted methyl violet dye as a collecting agent. The use of $CuSO_4$ and KCN as conditioning agents at various pH values is studied. Previous work done in this laboratory by Ludt and DeWitt on the flotation of copper silicate indicated that one might hope to obtain a concentration of antimony ore by means of a properly substituted dye. (18) The use of antimony salts as mordants with methyl violet indicates further the possibility of its employment as a collector. (6)

This substituted methyl violet dye was appropriately synthesized. (4) Flotation concentration tests with a California stibnite ore containing 12.7% antimony are reported.

HISTORY

Froth flotation is a comparatively recent method of concentrating ores, especially in the non-ferrous metals industry. Flotation is the means by which a mineral is separated from a gangue by causing the mineral particles to float on the surface of a pulp while the gangue particles sink to the bottom. Flotation had its beginning in about 1860 when William Haynes discovered the difference in wettability of various minerals. Bulk oil flotation was the first type to be employed for mineral separations. This method was based on the fact that minerals with a metallic luster are wet more by an oil than by water: Bulk oil flotation was used as early as 1900. When finely ground sulfide ores are gently placed on a water surface exposed to air the gangue particles will sink but the sulfide particles have a tendency to float. This type of concentration is known as skin flotation. This type of flotation was used mainly about 1910.

Flotation using air as the buoyant medium had its introduction in about 1902 when Froment used air bubbles for the levitation of oiled sulfide particles. This combined use of a small quantity of oil with air bubbles grew rapidly from 1912 to 1925, first in Australia and then in the United States. During this period the flotation process consisted of collecting all metallic ores in a gangue in one single concentrate. The circuits during this period were of the acid type and used an oil or fatty acid as the collector. This type of flotation is known as "bulk flotation".

In the early 20's a need for a more selective type of flotation was seen for the concentration of the various kinds of mixed sulfides. There are about 5 classes of sulfides composed of mixtures of Cu, Pb, Zn, Fe, and Ni. The separation of these sulfides was brought about by three developments:

(1) use of the alkaline circuit

(2) use of specific organic collectors (xanthates)

(3) utilization of cyanides to depress sphalerite and pyrite.

This "differential flotation" became the basis for the concentration of the base metal sulfide ores. (2)

THEORY

In the froth flotation concentration of ores there are several terms used which ought to be defined, namely: (12)

1. frothers - generally organic compounds which are water soluble and will form a stable froth with air.
2. collectors - generally organic compounds which induce a mineral to float at air-water interface and form a stable mineral froth.
3. activators - (conditioners) - generally inorganic compounds which promote flotation with an otherwise inactive collector.
4. depressants or inhibitors - generally organic compounds which prevent the collector frim functioning.

When a mineral is to be concentrated by froth flotation it first must be liberated from its ore by proper grinding. Usually the ore is ground wet to form a pulp which is ready to be introduced into the flotation machines. The amount of grinding to be done must be determined by the economy desired.

A method of producing air bubbles in the bottom of the cell must be furnished by direct introduction of air along with agitation. The right type of collector and modifying agents must be present to form a water repellent coating on the mineral particles desired to be concentrated. The particles are made hydrophobic. The collector used generally consists of a polar and a non-polar part. The polar part reacts with the mineral surface and leaves the non-polar hydrocarbon chain sticking out. This chain is water repellent and will cause the mineral particles to adhere to the air bubbles and cling to them as they rise to the surface of the cell. There must be also present a frothing agent which will lower the surface tension of the water so that the air bubbles coated with mineral particles will be able to break the surface and remain to be collected.

Most of the frothers contain a solubilizing group and a hydrocarbon radical of at least five carbon atoms. A froth is obtained from the opposing tendencies of the polar and non-polar parts. The insolubility of the frothing agent depends on the number of carbon atoms in the non-polar group. Some of the more common frothers used are pine oil, cresylic acid soaps and mixtures of aliphatic alcohols.

In general collectors fall within one of the three following classes:

1. Oils insoluble in water - oleic acid.
2. Organic compounds containing sulfur such as alkyl thio acids and mercaptans.
3. Alkyl sulfuric and sulfonic acids, used in the form of their alkali salts such as soaps and xanthates.

The collector must be either adsorbed or react with the surface of the mineral desired to float and must stick to it securely. There must not be any reaction with the gangue to cause it to take on a hydrophobic layer.

In 1935, over 21 million tons of ore were concentrated using 1,290 tons of synthetic reagents. (12)

The term, modifying agent, would include activators, depressers, pH regulators, etc. Activators are adsorbed as anions or cations or react with mineral surface to make it more susceptible to the collector. Na_2S is used to sulfidize the surface of oxidized heavy metals. $CuSO_4$ is used as an activator in the concentrating of zinc blende and also in the flotation of stibnite with xanthates. The lead ion is also an activating agent in conjunction with aerofloats or thiocarbonilid.

Depressants may change the nature of the mineral surface so that differential flotation can take place. A gangue which may have a tendency to float with a collector may be made, by the use of the proper depressant in the right pH range, to be hydrophilic. Both NaCN and Na_2S are used in alkaline solutions as depressants. The Na_2S can be either an activator or depressant depending on the minerals present in the pulp.

PROCEDURE

Preparation of the Antimony Ore.

About half of the 20 pounds of stibnite ore received from California was crushed in a jaw crusher and then finally in a roll mill so that it would all pass through a #100 sieve. The ore was deslimed by several washings and decantations of the wash water. No ore was used finer than a #325 sieve.

Operation of the Flotation Cell.

Each run was made in a laboratory flotation cell built of lucite to aid observations. 200 ml. of distilled water was added to the unit. This was followed by the addition of the conditioning reagents, HCl or NaOH, and 100 gms. of deslimed ore. The ore was allowed to circulate with the conditioning agents for 10 minutes before filling the cell to within 3/8" of the overflow. The collecting agent (n-decyl methyl violet), tannic acid, and pine oil were added in the order mentioned. The ore was allowed to condition in the absence of air agitation. After the addition of pine oil from a fine dip-wire, compressed air was turned into the flotation cell. The stable foam which formed was swept off into a Buechner funnel over a 5 minute period. The collected concentrate was dewatered by vacuum, dried at 150°F, weighed, and then analyzed according to the method of Treadwell and Hall. (8).

Analysis of the Concentrate.

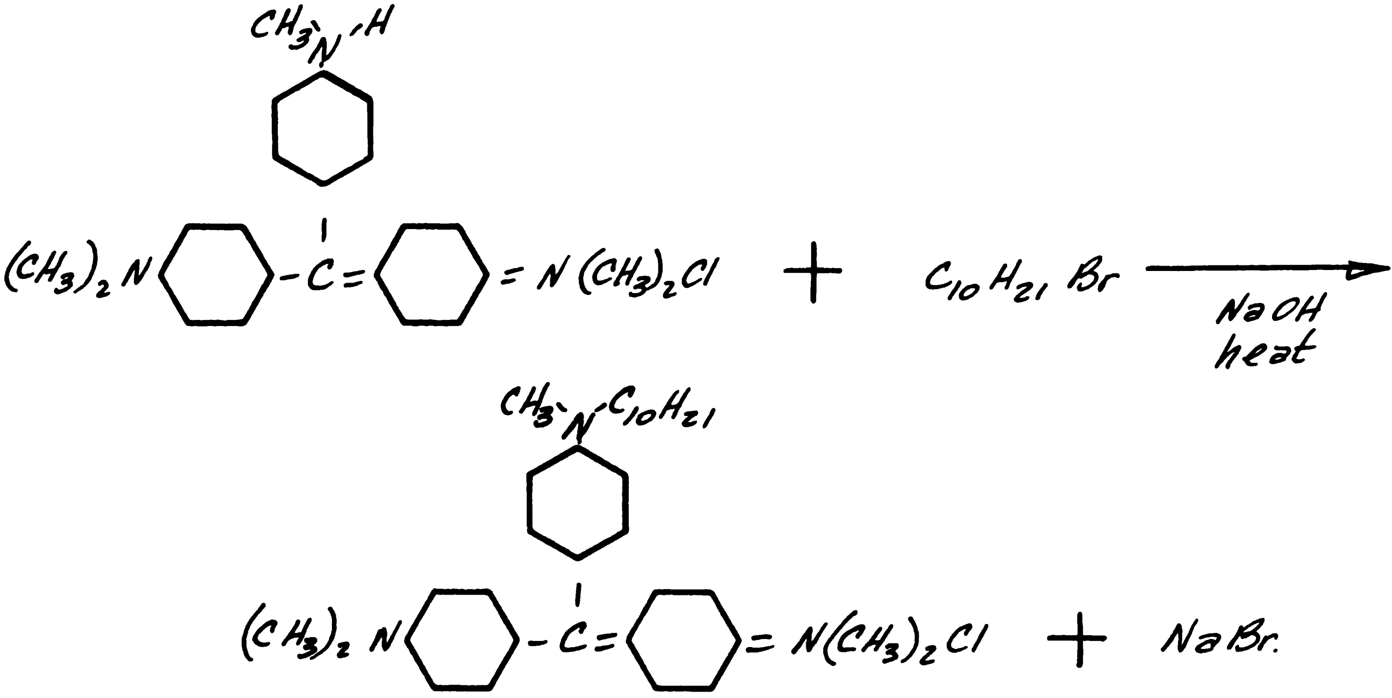
A 0.5 gm. sample of the dried concentrate was dissolved in 10 ml. of cold conc. HCl. After action had ceased 0.3 gm. KCl was added and the remaining H_2S was driven off over a steam bath for 10 minutes. After the solution cooled to room temperature, 3 gms. of tartaric acid in 5 ml. of water was added and then the solution was agitated while adding 10 gm. of Na_2CO_3 in 200 ml. of water. The entire mixture was then titrated with 0.1 N. iodine solution using 2 ml. of a soluble starch solution as indicator. The 0.1 N. iodine solution had been standardized using arsenious trioxide, As_20_3. A pale blue-violet color was obtained at the end point.

The remaining tails and pulp water were drawn off at the bottom of the cell and allowed to settle for about an hour. Upon settling the pH was determined of the fluid by using a Beckman pH Meter. The cell was cleaned out with distilled water between each run.

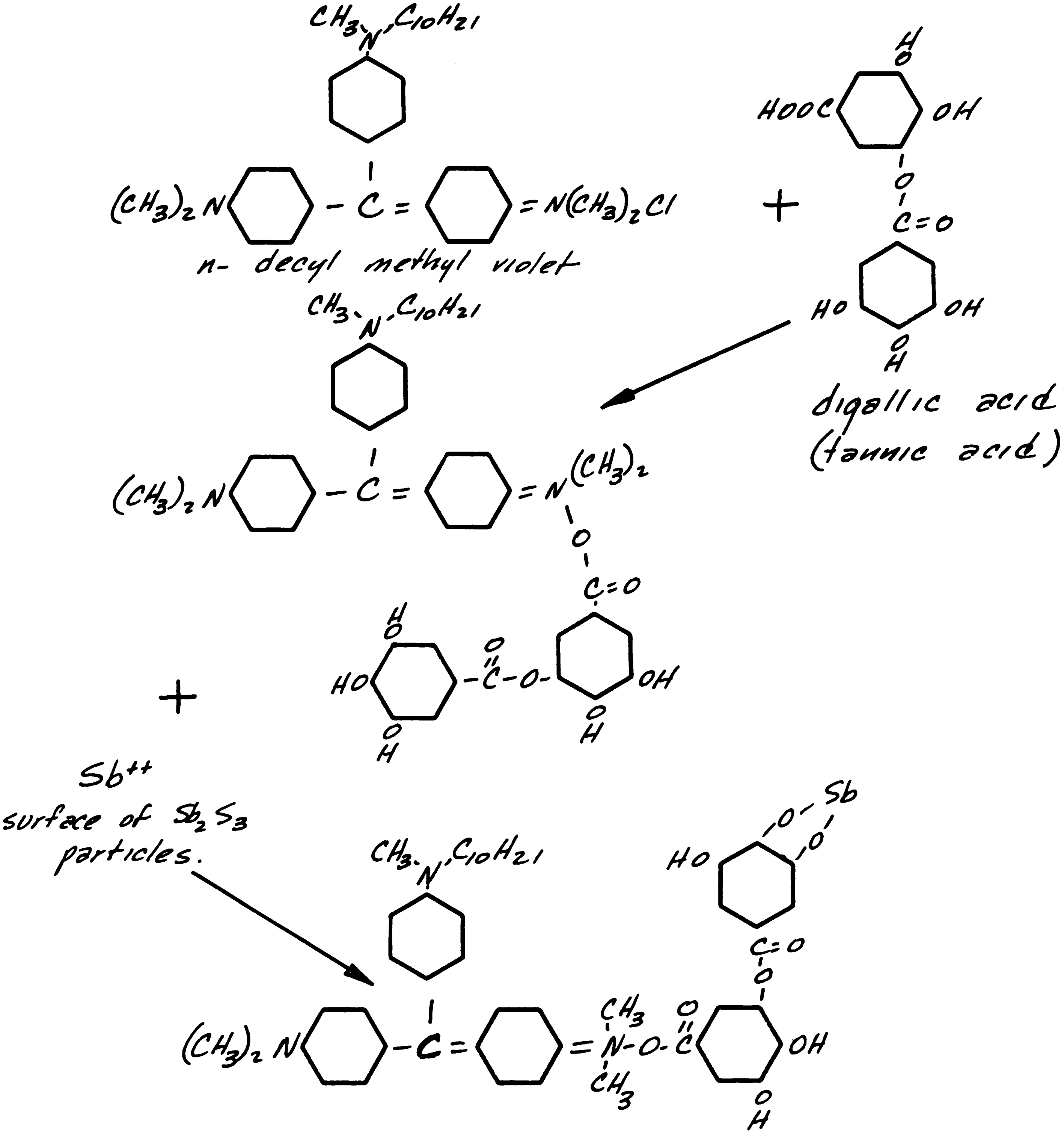
Preparation of the Substituted Methyl Violet

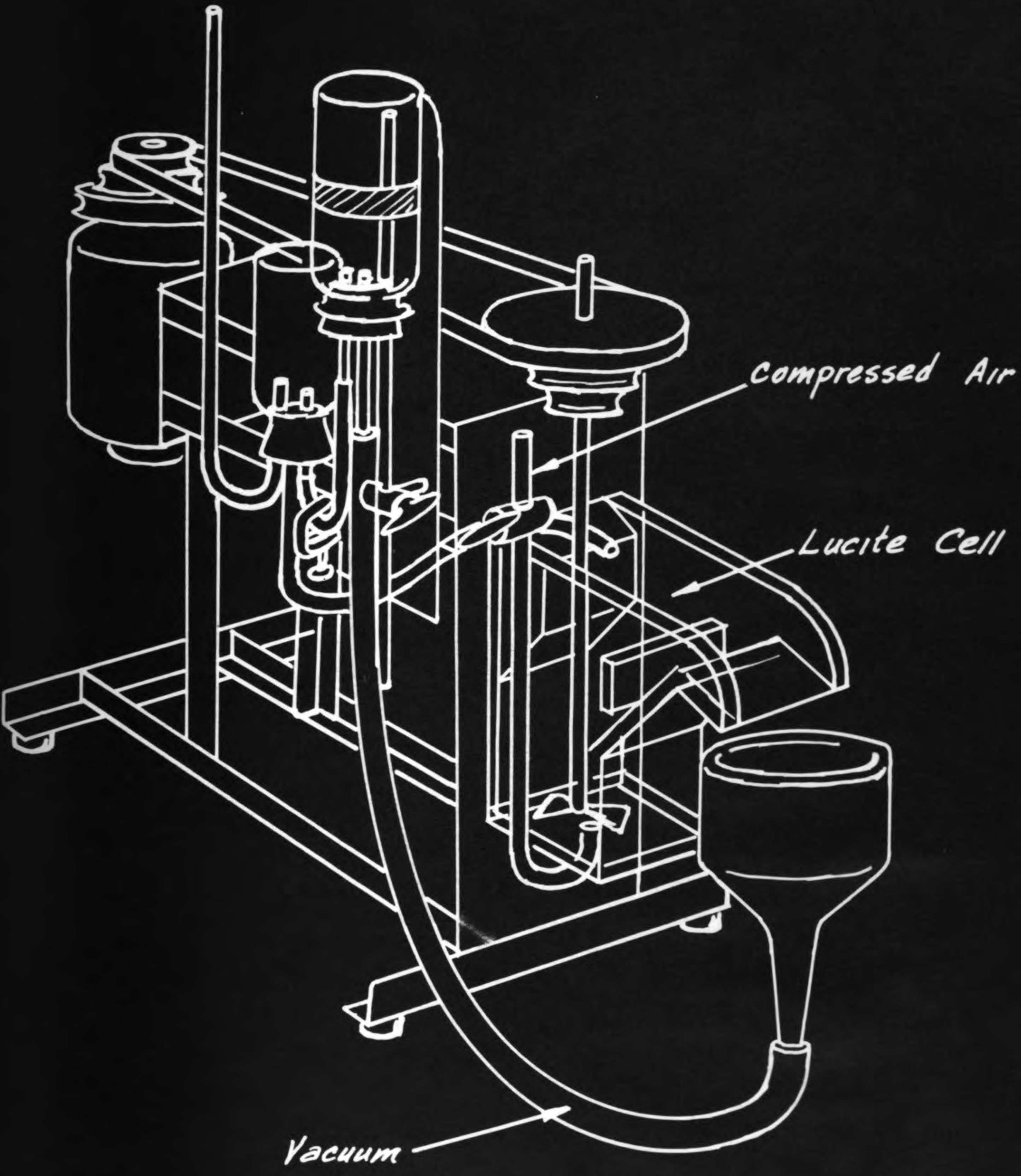
The n-decyl bromide was prepared from n-decyl alcohol, conc. sulfuric acid, and 48% hydrobromic acid in a refluxing apparatus. (4) It was purified by vacuum distillation at 35 mm. pressure. N-decyl bromide was then refluxed with methyl violet B, ethyl alcohol and sodium hydroxide for 6 hours. The solution was then neutralized with HCl, boiled with water, and then filtered. The filtrate was then treated with sodium chloride to salt out the decyl-methyl violet. (9) An alcoholic dye solution, 0.2 gm./100 ml., (30% C_2H_5OH by vol.) was made up for use as a collecting agent.

Reactions:



Reactions showing the formation of the insoluble lake on the stibnite particles.





100 GM. FLOTATION CELL

Test runs:

Collector concentration in all runs = .08 #/ton ore.

Run No.	Reagents #/ton ore	pH	% Sb. in Concentrate	% Recovery
1	Not deslimed		21.3	37.4
2			31.8	67.8
4		7.7	36.8	75.2
5	$CuSO_4$ - 1.0#	9.0	44.6	46.6
9	$CuSO_4$ - 1.0	9.3	44.75	52.1
10	$CuSO_4$ - 1.0	10.85	35.7	59.5
11-	$K_4Fe(CN)_6$ - 1.0	9.4	44.25	66.2
12	$K_4Fe(CN)_6$ - 1.0	10.1	37.5	61.6
13	$CuSO_4$ - 1.0	9.32	33.6	59.7
14	KCN - 1.0	9.16	38.9	67.5
15	$PbAc_2$ - 1.0	10.25	36.4	68.0
16	$CuSO_4$ - 1.0	4.7	50.6	59.8
17	KCN - 10	5.4	48.2	63.5
18	$CuSO_4$ - 1.0	5.5	47.1	68.9

Collector Concentrate in all runs = .16 #/ton ore.

Run No.	Reagents #/ton ore	pH	%Sb. in Concentrate	% Recovery
3			32.1	73.6
6	$CuSO_4$ - 0.5	8.4	35.3	70.6
7	$CuSO_4$ - 0.5	7.2	37.4	72.0
8	$CuSO_4$ - 1.0	10.56	41.9	53.6
20	$CuSO_4$ - 1.0	5.1	46.4	67.6

Collector Concentrate = .24 #/ton ore.

19	$CuSO_4$ - 2.0	4.4	42.2	49.8

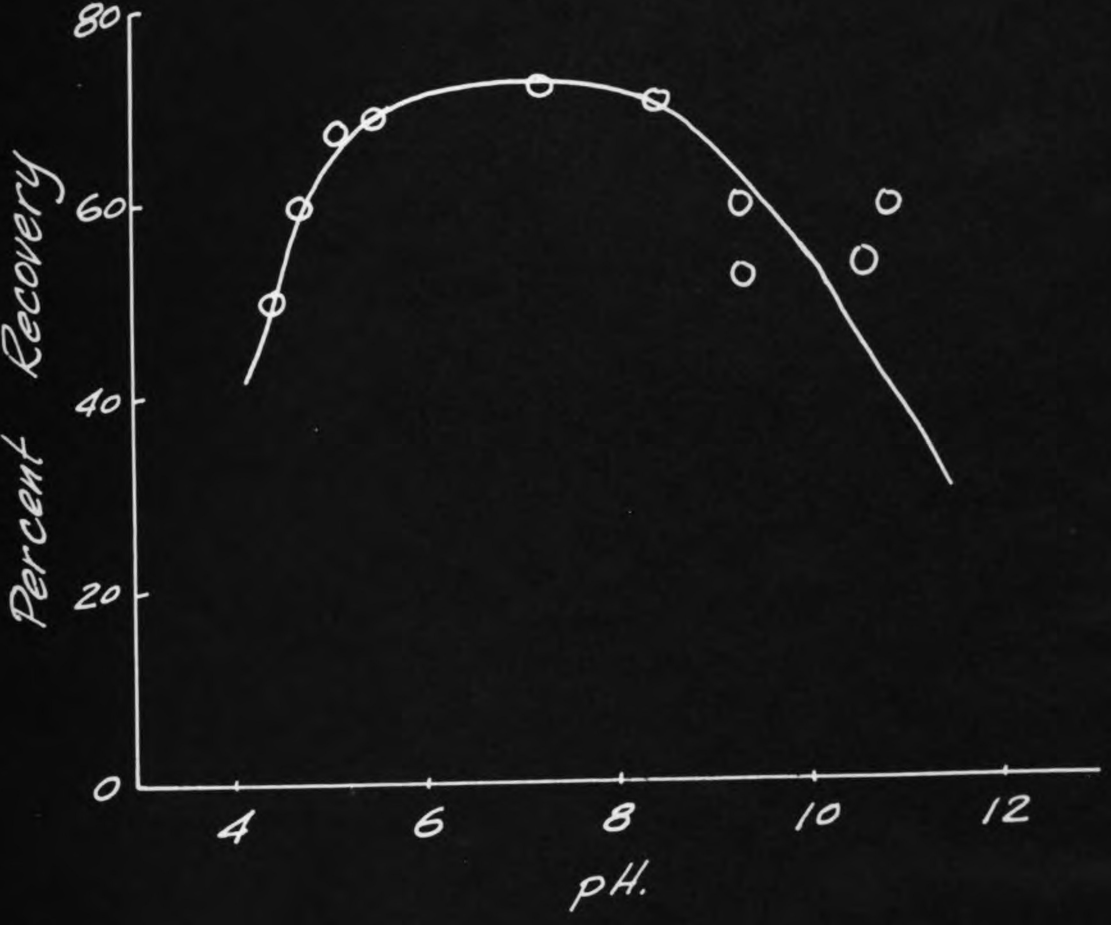
Data from two runs of antimony ores taken from Denver Equipment Company bulletin No. T4-B7

Description of ore	An Antimony ore containing stibnite, a small amount of pyrite, and arsenic in a siliceous gangue.			An ore containing stibnite and antimony oxides in a siliceous gangue.	
Assay of Ore.	Antimony	6.0%		26.0%	
Approximate	Arsenic	0.1			
	Iron	2.0		1.1	
	Insoluble	77.0		59.5	
	Sulfur	3.0		8.7	
Method or Process		Denver "Sub. - A" Unit Cell Denver "Sub. - A" Flotation			
		% Antimony	% Recovery	% Antimony	% Recovery
Concentrates	Unit cell conc.	67.0	69.0	65.5	29.0
and Recovery	Flotation conc.	69.0	26.0	54.0	64.0
Reagents,	$PbNO_3$	2.8		Soda Ash	2.0
lbs. per ton	Z-5 Xanthate	0.3		$PbNO_3$	1.8
	Pine Oil	0.1		Z-6 Xanthate	0.4
				Pine Oil	0.06
Miscellaneous					
Data	pH, 6.5			pH, 8.0	

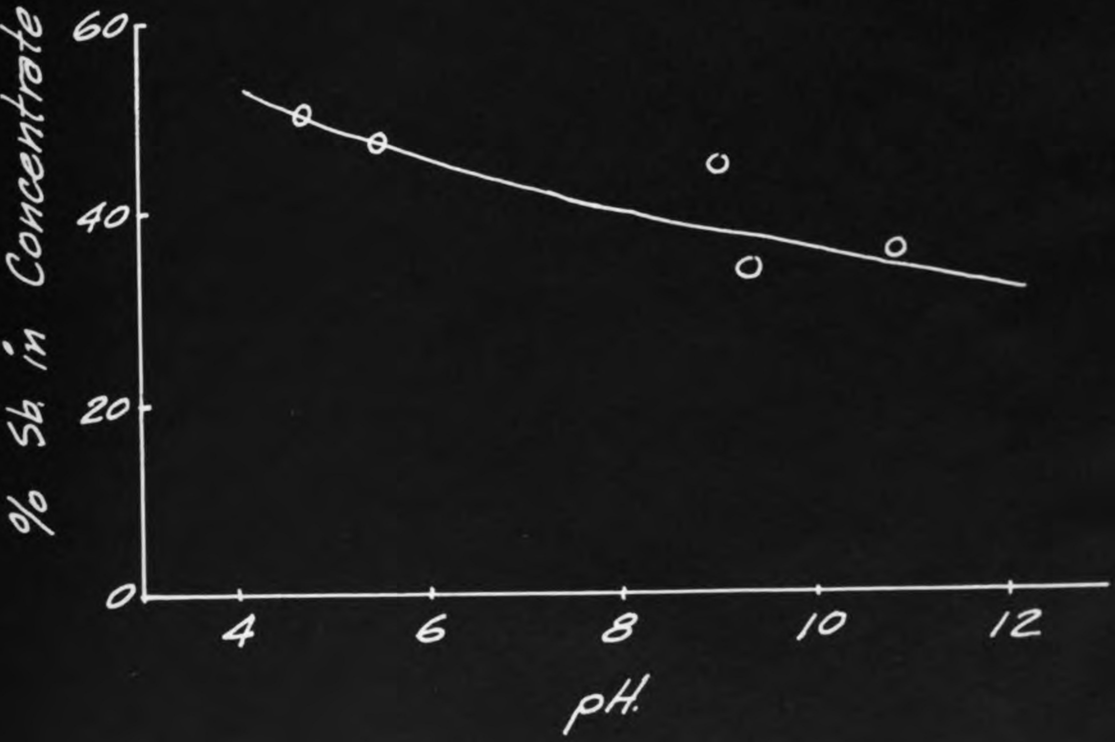
Sieve analysis of the ground stibnite ore:

Fraction	Percent
#100-140	17.0
140-200	34.9
200-270	30.9
270-325	17.2
	100.0

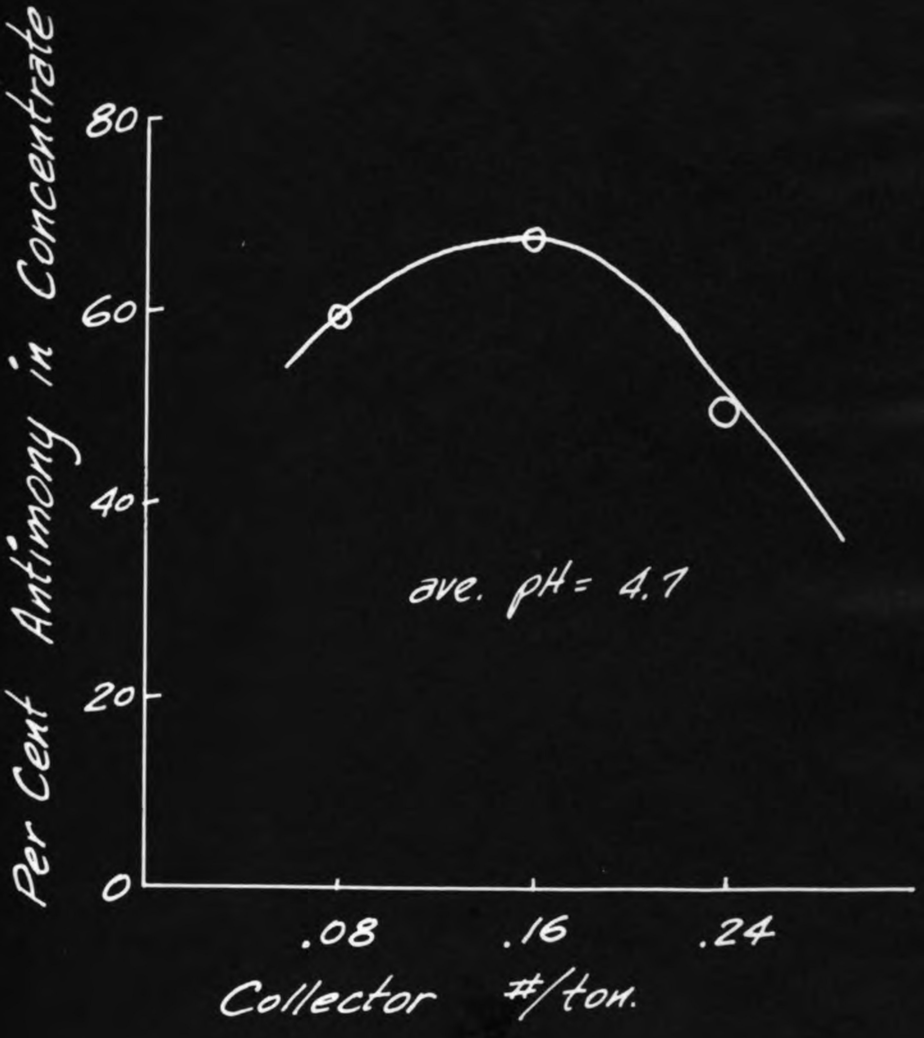
GRAPHS



Percent Recovery
80
60
40
20
0
4
6
8
10
12
pH.



% Sb. in Concentrate
60
40
20
0
4
6
8
10
12
pH.


Per Cent Antimony in Concentrate
80
60
40
20
0
.08
.16
.24
Collector #/ton.
ave. pH = 4.7

DISCUSSION

The writings of Freundlich and Neumann indicate that the adsorption of certain basic dyes on mineral gels occurs with quite a good deal of selectivity. (18) They contend that this adsorption may be chemical in nature, involving the transferral of cations between the dye and the mineral surface. All work at this laboratory grew out of these references. The dyes cited by Neumann and Freundlich actually act as depressants with some minerals. Modification of the dye structure as indicated by Ludt, (18) Thakkar (19) and this report gives strong evidence that when a long aliphatic chain is substituted either in the benzene nucleus or, as in the present report, in the amino side chain the substituted dyes act as good flotation collectors for minerals upon which they adsorb.

Antimony salts have been used as mordants with methyl violet dyes. (6) Upon the addition of an antimony compound to methyl violet which has been partially precipitated with tannic acid an insoluble lake is formed. When applying this fact to stibnite flotation it was hoped that the insoluble lake would form an oriented coating over the stibnite particles leaving the non-polar decyl chain to selectively impart hydrophobic properties to the ore particles. The data tends to indicate that such a coating was formed.

The concentration of 0.2 gm./100 ml. was picked for the collector solution so that one ml. would be equivalent to 0.04 #/ton of ore. One ml. of the activators was equivalent to 0.5 #/ton of ore. The pine oil addition was equal to about 0.1 #/ton of ore. The froth formed after the usual induction period. Too long an induction period indicated that too much pine oil was added.

The desliming of the ore was found to be quite essential. Several runs made without desliming gave poor results. Reference to the data reported indicates much better results with the deslimed ore.

The final concentration of 64% reported by the Denver Equipment Company is for a multi-celled flotation procedure. (11) The maximum recovery reported in this effort is about 73%. This figure of 73% represents the efficiency of the decyl substituted methyl violet in a single flotation separation that could be duplicated. This maximum recovery was found to occur in a pH range of around 6 to 7 using $CuSO_4$ as an activator although the highest concentration of antimony in the concentrate was obtained at a pH of 4 to 5.

For future work with this methyl violet type of collector it would be advisable to make an ore mixtureof less than 12.7% antimony by diluting the California ore with pure ground Ottawa sand or some such siliceous material. It would be interesting to note the effect of other salts as activators, also.

It is hoped that results obtained in this thesis will be helpful in future work with the beneficiation of stibnite ore.

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