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THE PREPARATION OF CERTAIN INORGANIC
AND ORGANIC COMPOUNDS WHICH MAY BE OF USE
IN MINERALOGICAL SEPARATIONS

by

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A

Thesis

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Associate Professor of Chemistry

34481

THE PREPARATION OF CERTAIN INORGANIC AND ORGANIC
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TABLE OF CONTENTS.

	Page
Introduction-----	2
Resumé of the Use of Heavy Liquids For Mineralogical Separations-----	3
Some Properties Of Heavy Liquids That Affect Them For Mineralogical Separations----	5
Specific Gravities Of Some Common Minerals-----	5
Experimental Data-----	7
Preparation Of Compounds-----	12
Experiments With Inorganic Compounds-----	15
Chlor- and Bromacetates-----	18
Summary-----	21
Bibliography-----	22

THE PREPARATION OF CERTAIN INORGANIC AND ORGANIC
COMPOUNDS WHICH MAY BE OF USE IN MINERALOGICAL SEPARATIONS.

Introduction

In the work with minerals, there has been many mechanical means devised whereby the ores could be separated from the gangue and other material. Among those means which are used to-day, especially in the laboratory tests upon minerals, to quickly determine the value of an ore, heavy liquids have become quite popular. This means of mechanical separation is merely to place finely ground ore containing particles of varying density into a liquid of heavier density than the greater portion of the mineral, which will allow the heavier portions to sink and the lighter to float, which is usually gangue. This process is known as the sink-and-float method of separation.

The purpose of this work was to increase, if possible, the specific gravity of some of the heavy liquids already in use, and prepare other compounds which may be soluble, or to devise some new method of preparing such a compound for this purpose, so that a greater concentration of ores could be made. It was thought that this purpose might be accomplished by the solution of heavy compounds in liquids of high density now in use. It may also be accomplished by the study

of other compounds of high density which are very soluble in water, or the preparation of compounds of high density which are liquid at ordinary working temperature. All three of these methods have been used and the results recorded in this paper.

Resumé of the Use of Heavy Liquids
in Mineralogical Separations.

As far back as 1860, liquids were first known to be used for determining the density of ice as recorded by van der Kolk.¹ This liquid consisted of a mixture of chloroform and petroleum. In 1862, acid mercuric nitrate with a specific gravity of 5.3-5.4 was used. Later, ethyl thallic alcohol, a water solution of cadmium boro-tungstate, a solution of barium mercuric iodide, and a water solution of silver nitrate were prepared and all used with some success. In 1886, organic compounds in the form of methylene iodide came into use as heavy liquid for mineralogical separations. This gave a liquid with a density of 3.33 and later its density was increased to 3.7 by adding iodoform.

1. van der Kolk, J.L.C. Schroeder, "Beitrag zur Kartirung der quartaren Sande."
Neues Jahrb. Mineral., Geol., u. Paleont.,
Bd, 1, 1895. pp. 272-276

A saturated solution of arsenic iodide and antimony iodide in a mixture of arsenic bromide and methylene iodide gave a specific gravity of 3.7. A saturated solution of arsenic bromide and stannic iodide gave a specific gravity of 3.73. Fusion mixtures of thallium nitrate and silver nitrate have been used. Among the heaviest of liquids prepared is a fusion mixture of thallium malonate and thallium formate at 50 degrees Centigrade, having a density of 4.5. This was made by Clereci² an Italian who had done a great amount of work on heavy liquids.

In 1924, the United States Bureau of Mines³ started a systematic research of heavy liquids and the following were prepared: acetylene tetrabromide, stannic bromide, thallos ethyl alcoholate, antimony tribromide, thallos nitrate-silver nitrate, thallos acetate, thallos formate, thallos oxalate, thallos malonate, thallos citrate, thallos boro-tungstate. However, of these latter ones, acetylene tetrabromide and the thallos malonate-formate were the only ones that could be successfully used for mineralogical separations.

2. Clereci; " Chemical Abstracts, Volume 1, 1907"

3. Bureau of Mines; "Technical Paper, No. 381"

Some Properties Of Heavy Liquids That
Affect Them For Mineralogical Separations.

There are many properties that condemn some of the heavy liquids against being used for mineralogical separations. For instance in working with zinc compounds, they often become quite viscous at a low temperature and this viscosity becomes greatly changed with a slight rise in temperature. A corrosive action must be guarded against as this affects the ore and also changes the specific gravity of the liquid and usually makes it opaque. Liquids that have a high vapor pressure cannot be depended upon for accuracy in separations as the specific gravity of the liquid changes upon evaporation. Poisonous and irritating compounds often have an affect upon the operator. Hygroscopic compounds are difficult to keep at a constant specific gravity. Solutions that change upon coming in contact with moisture in the ores or those that change in composition through organic solvent action, are not accurate for this work.

Specific Gravities Of Some Common Minerals.

The following is a table of some of the more common minerals given to show the separations that heavy liquids of certain densities could make.

<u>Minerals</u>	<u>Specific Gravity</u>
Feldspars	2.55-2.75
Quartz	2.6 -2.66
Calcite	2.71-2.72
Biotite	2.70-3.10
Dolomite	2.80-2.90
Realgar	3.40-3.30
Rhodocrosite	3.50-4.50
Siderite	3.83-2.88
Spalerite	3.90-4.10
Corrundum	3.95-4.11
Chalcopyrite	4.10-4.30
Rutile	4.15-4.25
Chromite	4.30-4.50
Barite P	4.30-4.60
Pyrrhotite	4.50-4.60
Pyrite	4.50-4.60
Stibnite	4.52-4.62
Ilmenite	4.50-5.00
Magnetite	4.90-5.20
Bornite	4.90-5.40
Chalcocite	6.00-6.10
Arsenopyrite	6.00-6.20

Experimental Data

In the course of the consideration of preparing some chemical compounds which may be of use in mineralogical separations, whereby the gangue and some of the other lighter materials of the ores can be floated and the heavy material allowed to sink, commonly known as the sink-and-float method of separation, attention was first directed to some of the more popular compounds which are used for this purpose. After a study of the properties of some of these compounds it was thought that possibly the specific gravity of these might be increased either by dissolving in them solids of heavier density. It may also be accomplished by chemically adding heavier elements which would form new compounds and the result should be compounds of greater density.

Acetylene tetrabromide being one of the most efficient liquids which is used for mineralogical separations, was taken as a source from which others might be prepared. Acetylene tetrabromide has four bromine atoms attached to the acetylene radical. Bromine has a density of 3.188. Now, if a substance as iodine with a density of 4.948 could be made to

replace one or more of the bromine atoms and a compound of greater density should result, and to be as satisfactory as acetylene tetrabromide it must be a liquid. Should all the bromine atoms be displaced by iodine, acetylene tetraiodide, would be formed, which is a solid of greater density than acetylene tetrabromide.

Acetylene tetrabromide was prepared by passing acetylene gas through liquid bromine and then the free bromine washed out with a dilute solution of sodium hydroxide, and dried by adding calcium chloride.

The possibility was suggested that if acetylene gas was passed into a carbon tetrachloride solution of bromine and iodine in molecular proportions that a compound containing both bromine and iodine atoms would result. This was tried with negative results. Then acetylene gas was passed directly into liquid bromine saturated with iodine, and a combination brought out.

An acetylene generator was prepared and connected to a calcium chloride drying tube and this to an ordinary gas washing bottle in which was prepared a one-hundred cubic centimeter volume of bromine saturated at room temperature with iodine. This use of the calcium chloride tube is to prevent moisture coming over into the liquids and forming hydrobromic and hydroiodic acids

which caused a waste of the bromine and the iodine. The gas was passed into the liquid for about five hours or until there was no further action taking place as determined by the decrease of temperature from that when the gas was first introduced.

The resulting liquid from the above operation was deeply colored from free iodine. At first this free iodine was removed by adding dilute sulphurous acid then washed out with water. This, however, did not leave a clear solution as free sulphur comes out of the sulphurous acid and remains suspended in the heavy liquid. A better method was found and that was to use dilute sodium hydroxide or to leave the liquid in contact with metallic copper shavings. The liquid remaining had the appearance of acetylene tetrabromide except a stronger odor. The specific gravity was found to be 2.916, less than acetylene tetrabromide which is 2.96. The molecular weight was then determined by dissolving a known quantity of the liquid in pure benzene and determining the freezing point. This gave a molecular weight of 330.6 as compared with acetylene tetrabromide which has a molecular weight of 345.7. Upon distillation at atmospheric pressure this liquid began to discolor at about fifty degrees Centigrade

and at sixty degrees, dense violet colored fumes were given off. The residue and distillate both were deeply colored and opaque. With distillation at three centimeters pressure, decomposition started at about ninety degrees and the results were the same as at atmospheric pressure. The boiling point varied in each case.

A chemical analysis of this liquid was made to determine the percentage of iodine and bromine. This was done by precipitating a known quantity of the liquid with silver nitrate and then filtering, weighing and drying in a gooch crucible. A weighed quantity of this dried precipitate was then placed in a porcelain boat and the boat placed in a pyrex combustion tube. Heat from a wing top burner was applied to the outside of the tube while bromine vapor was drawn through the tube by suction, thereby replacing the iodine in the precipitate by bromine. The difference in weight was calculated and from this the percent of iodine and bromine in the original liquid was determined. The results showed that the prepared liquid contained 21.7% iodine and 73.2% bromine. If a compound had been formed here with one iodine atom replacing one of the bromine atoms in acetylene tetrabromide, the compound

should have contained 32.3% iodine and 61.2% bromine, as calculated from the formula. It is quite evident from the above analysis that some compound of lighter specific gravity than acetylene tetrabromide must be present.

The action of the liquid toward light was very much like an alkyl halide. When it was exposed to the light of the laboratory, a noticeable change in color took place during one day. When kept in the dark, the liquid remained colorless.

It was thought that if some substance were added to the bromine and iodine solution to act as a catalytic agent when acetylene gas was added, different results might be obtained. Potassium hydroxide in dilute solution was added but this failed to give any different action than was found without the added alkali.

Since many of the organic chemical compounds of a low specific gravity, as carbon tetrachloride, acetone, methyl iodide and alcohol, have a great solvent action on many of the organic and inorganic compounds, it seemed quite possible that acetylene tetrabromide, might have a similar action on some of the heavier organic and inorganic substances, and produce a liquid with a high specific gravity. Accordingly, methyl iodide and acetylene

tetrabromide were treated with some of the heavier organic and inorganic substances. Many of these substances were not available and had to be prepared by the writer.

When methyl iodide, with a density of 2.28, is saturated with iodoform having a density of 4.08, the specific gravity of the solution was raised to 2.78. Acetylene tetrabromide was treated with an excess of the same substance but the specific gravity was only raised one-tenth of a unit. This showed that acetylene tetrabromide has only a slight solvent action for iodoform.

Preparation of Compounds.

Among the first of these heavy compounds that were prepared was tetraiodethylene. This was prepared by the method used by L. Maquenne⁴ This is done by saturating water with acetylene gas, then making the solution slightly alkaline with potassium hydroxide and subsequently dropping in powdered iodine and shaking till solution takes place and then a white

4. L. Maquenne "English Chemical Abstracts" Vol.64.pp.449.

precipitate comes out. This, Maquenne said, was tetraiodethylene melting at 192 degrees. However, the compound prepared here in this case had a melting point of 78 degrees, that of di-iodacetylene. The pungent and irritating odor and volatility of this preparation is also characteristic of di-iodacetylene. The tetraiodethylene with a melting point of 192 degrees, odorless and non-volatile, was easily prepared from the di-iodacetylene by first dissolving the latter in alcohol and then adding an excess of concentrated sulphuric acid, when the tetraiodethylene is precipitated out in yellow crystals.

These compounds were then dried and their solubility tested in acetylene tetrabromide. Although both of these compounds were quite soluble in acetylene tetrabromide, the specific gravity of the resulting liquid was slightly heavier than the original liquid. In the case of tetraiodethylene, the specific gravity of the solution was 3.02 and with di-iodacetylene it was 3.09. Since the density of the di-iodacetylene was only 2.172, and that of the tetraiodethylene was 2.98, not much increase in specific gravity could be expected even though the solubility was considerable.

These solutions were clear and they

showed no signs of decomposition while working with them.

Hexabromethane was prepared by Meyer and Pemsel⁵ by passing bromine vapor over tetraiodethylene. This compound was prepared in the laboratory in a similar way. At first the crystals of tetraiodethylene became liquified as the bromine fumes attached them leaving a deep iodine colored solution, caused by the replacement of the bromine for the iodine. This free iodine and the excess of bromine was washed out with water, leaving the yellow crystals of hexabromethane. Here the solution of iodine in water was probably much increased by the presence of bromine. This compound showed very little solubility in acetylene tetrabromide as the resulting solution gave a specific gravity of only 3.001. This showed that bromine compounds differed little, if any, in raising the specific gravity of acetylene tetrabromide, than did the iodine compounds. Carbon tetraiodide which contains a very high percent of the heavy element iodine was then prepared and its solubility tested in acetylene tetrabromide. This was prepared by a method given by Robineau and Rollin.⁶

5. Meyer and Pemsel, "Berichte der Deutschen Chemischen Gesellschaft" 1896- Vol. 27, pp. 1411-1412
Robineau and Rollin "Monthly Science" Vol.4. pp. 341

Hypochlorite in a very alkaline solution was treated with iodoform and the resulting carbon tetrachloride extracted with pure benzene. The benzene solution on evaporating deposits ruby red crystals of a density 4.32. This compound showed little solubility in acetylene tetrabromide as was indicated by the density of the resulting solution.

Experiments With Inorganic Compounds.

A number of inorganic compounds of high specific gravity and having a low melting point, yield solutions of high density. These solutions mixed with compounds of the same type usually give an eutectic mixture of lower melting point and high density as is mentioned by Sullivan⁷. Stannic chloride alone gave a specific gravity of 3.64 at 108 degrees Centigrade. Thallous nitrate and mercurous nitrate was found to give a liquid with a specific gravity of 4.70. He also prepared a thallous silver nitrate solution by dissolving the solids in nitric acid and evaporating the mother liquor, obtaining a liquid which at 75 degrees C. had a specific gravity of 4.64. Sullivan also obtained some excellent results by dissolving inorganic compounds in organic compounds. He dissolved antimony

7. Sullivan "Technical Paper", No. 381, Bureau of Mines

tribromide in bromoform and got a range of specific gravities from 2.60 to 3.65. Messmore⁸ gives a method of preparation of thalious malonate-thalious formate whereby a liquid of a specific gravity of 4.6 at 60 degrees can be procured. From these experiments it was thought that by dissolving some heavy inorganic compound in compounds of high density, a solution of higher specific gravity might be obtained, which possibly would be better fitted for sink-and-float tests than many of those that have been used. The density of the solution, of course depends upon the solubility of the eutectic mixture. The solvent may be a liquid either of low or high density.

Most of the metallic iodides were prepared and their solubility tested in acetylene tetrachloride and in methyl iodide. The iodides were prepared as follows:-- Hydrogen iodide was made by passing hydrogen sulphide into a flask containing iodine and potassium iodide in a water solution. Then after filtering out the free sulphur, the clear hydrogen iodide was evaporated to a smaller volume. This acid solution was then added to pure salts of thallium, uranium, thorium, mercury, cadmium, calcium and zinc,

8. Messmore "Specific Gravity Fractionation of
Coke and Coal" pp. 202

and the corresponding iodides produced.

All of the above iodides were added separately to methyl iodide and also to acetylene tetrabromide and no solubility noticed. This was detected by there being no increase in the specific gravity of the liquid. It is well known that the solubility of many compounds is considerably increased by being in contact with some other compound of no greater solubility. This is well brought out by the preparations of solutions of cadmium boro-tungstate,⁹ thallos malonate-formate, thallos silver nitrate, and potassium iodide-mercuric iodide and other double salt compounds which produce very heavy liquids when in contact with each other but alone these compounds are very insoluble. This is due to double salt formation. In the case of the iodides, the stability of these salts are greatly increased which is an important factor in the preparation of liquids for mineralogical separations.

Combinations of any two of the above prepared iodides were added to water and the resulting solution evaporated till the solids crystallized out at 15 degrees Centigrade, and the specific gravity of the resulting solution taken. During evaporation a

9. Messmore "Specific Fractionation of Coal and Coke"

small piece of a glass stirring rod was kept in the solution and only those solutions that kept the glass afloat will be mentioned. The glass rod had a density of approximately 2.56, which indicated that the liquid had a greater density.

Mercuric iodide and thorium iodide, densities 6.257 and 5.63 respectively, gave a liquid with a specific gravity of 3.2 but slightly colored from the decomposition of thorium iodide as this iodide is somewhat unstable. Uranium iodide, density 5.644 and mercuric iodide gave a saturated solution with water, specific gravity 2.83. Mercuric iodide in solution with zinc iodide gave a specific gravity of 2.73. Zinc iodide, density 4.696 and cadmium iodide, density 5.64 gave a solution of specific gravity of 2.64.

Because of the ease at which iodine and bromine compounds decompose with the application of heat, no tests were made to determine the point at which the solids would become liquid when heat was applied to a combination of the solids. Therefore, their solubility in water was the only method tested.

Chlor- and Bromacetates.

Salts of chloracetic acid and of

trichloroacetic acid containing a metal atom in the place of the carboxyl H atom show a very great solubility in water and also organic solvents.

Literature¹⁰ upon the subject of chloracetates show that a number of the mono-di- and tri-chloroacetates have been prepared but nothing was found concerning their use in producing heavy liquids.

In the laboratory, metallic oxides of iron, zinc, copper and mercury and the chlorides of silver and tin were added separately to mono-chloroacetic and also to tri-chloroacetic acids in a water solution, and the resulting solution evaporated slowly to a point where crystallization began and the density of the liquid taken. In these cases tried the chloroacetic acid decomposed giving off strong fumes of acetic acid and in all cases except with the zinc, the salt crystallized out, leaving a liquid of very light density. In the case of zinc, a clear but very viscous liquid remained, having a density of 2.17. Even though in this case an excess of zinc oxide was added to be sure that the acidity was neutralized, this liquid after some evaporation, showed acid reactions. Evidently, the acid decomposed with the water and likely the liquid was a combination of zinc

10. English Chemical Abstracts: 1909--pp. 108

chloride and zinc acetate.

Search in the literature on the action of brom-acetic acid and its action upon metallic salts proved to be without positive results. In an effort to see what results could be gotten from its reactions, the brom-acetic acid was first prepared. This was done by adding red phosphorous to dry glacial acetic acid and slowly dropping bromine into the mixture through a reflux condenser. The reaction was quite violent at first. After all the bromine was added the brom-acetic acid was distilled off under reduced pressure.

The action of this acid on lead oxide, mercuric oxide, copper oxide, and zinc oxide was very similar to the action of tri-chloroacetic acid. In all these cases the salts formed were soluble but they left a liquid of very low specific gravity.

Summary.

A study of certain inorganic and organic compounds has been made with respect to their possible use as reagents in mineralogical separations.

The solution of heavy organic compounds in liquids already used for mineralogical separations, has been noted and in some instances a considerable increase in specific gravity has resulted.

Inorganic compounds in general were found to be insoluble in organic liquids and cannot be used to increase the density of heavier organic liquids used for mineralogical separations.

Solutions of the double salts, mercuric iodide- thorium iodide- mercuric iodide- uranium iodide- zinc iodide- cadmium iodide- gave liquids with such density and properties that they could be successfully used in mineralogical separations.

Many salts of chlor- and bromacetic acid were prepared and their properties in solution noted. The stability of these compounds render them unfit for the purpose in question.

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