VOL. XVIII. [OCTOBER, 1896.] NO. 10.

THE JOURNAL

OF THE

AMERICAN CHEMICAL SOCIETY.

SOME EXTENSIONS OF THE PLASTER OF PARIS METHOD IN BLOWPIPE ANALYSIS.

BY W. W. ANDREWS.

Received August 7, 1896.

IN the years 1883 and 1884 two papers were published by Dr. Eugene Haanel, of Victoria College, Cobourg, Ontario, now of Syracuse University, in the Proceedings of the Royal Society of Canada, in which he described the brilliant results he was able to obtain in the production of the Bunsen iodide films on the blowpipe support then proposed for the first time; namely, thin tablets of plaster of Paris made by casting sheets three-sixteenths of an inch thick on panes of glass and scratching them, before hardening, with ruled lines, so that when set they would readily break into oblongs measuring two and one-half by one and one-quarter inches. The pure white and highly polished surface of these tablets and its great power of condensing heated gases and exhibiting the true colors, their cheapness, thermal and hygroscopic properties of the tablets, the ease with which they may be prepared and carried, and the excellence of the results when the sublimed iodides, bromides, oxides and sulphides are deposited as coatings upon them, make them an ideal form of support in blowpipe work.

A small pit is made at one end of the tablet somewhat larger than a pin's head, and in this the ore to be tested is heated. The oxide coatings are produced by heating the substance *per se*, the bromides by adding to the substance a drop of fuming hydrobromic acid, and the iodides by adding a strong solution of hydriodic acid (made by dissolving five ounces of metallic iodine in seven ounces of water, by passing a steady stream of hydrogen sulphide through the solution while the iodine is slowly added). All who have experimented with this solution will be ready to admit that it yields superb results, but though easily renewable when one is near a hydrogen sulphide generator it is very unstable, takes a long time to prepare and is troublesome to carry.

In 1890 Mr. F. A. Bowman read a paper before the Nova Scotia Natural History Society, in which was described a search for a solid reagent to replace the hydrogen iodide solution. He found that potassium hydrogen sulphide or any alkaline sulphate, which does not yield a coating of its own, mixed with potassium iodide would do very well. He also found that microcosmic salt and potassium iodide gave good results. This mixture is a favorite one with some blowpipe experts. Tin is the only metal in the three series of the periodic table, beginning with copper, silver and gold, which does not yield a characteristic coating with this reagent.

The writer has not been able to find whether there have been any other reagents besides these seriously proposed. Plaster of Paris as a support is mentioned in Moses and Parsons' late work as an alternative to charcoal. This is, as far as known to the writer, the only standard work, in which the colors of the films on the tablets are described.

In the rapid development of other methods in chemical work the blowpipe has fallen largely into disuse, and for many years, besides the work outlined above and that of Col. Ross and some valuable tests for individual elements proposed by Chapman, little or no advance has been made. There are two possible lines of future progress in blowpiping, one in the direction of increased power and simplicity, so as to make the method more valuable for the field work of the mineralogist, geologist and prospector, and the other in the direction of increased range and delicacy until the dry way tests rival the delicacy and distinctiveness of the wet tests, as they surpass them in expeditiousness. It may not be amiss, therefore, to call attention to the instrument of Plattner and Berzelius, which, in its modern form as the hot-blast blowpipe and with the new support and the new reagents and reactions now known to chemistry, is an instrument surpassed by the electric furnace only.

The cleanliness of the method here described, as compared with the charcoal method and the quickness with which sure results can be obtained with very small amounts, should call the blowpipe back to the table of the chemist for preliminary and confirmatory tests, to class work as an accompaniment of the wet methods, and to the lecture table for the purposes of illustration. It is possible to detect five or six metals in presence of each other on one tablet. Many of the coatings are permanent and are all renewable on reheating with addition of a drop of the reagent, so that a set of tablets carefully labelled with a pencil forms a permanent record of a set of experiments. The value of this to the practical chemist and to the student need not be emphasized. It may be noted that blowpiping is so much of an art that new methods are seldom well enough practiced, by those who have become skillful in other methods, to reveal their value.

The extensions of the plaster of Paris method here proposed are: A set of new reagents, which yield some new reactions which are of value in detecting elements in the presence of each other, notably gold and copper in very small amounts in the presence of all elements so far experimented with; arsenic, tin and antimony in presence of each other; sulphur in the presence of selenium and tellurium, and chlorine, bromine and iodine in the presence of each other; a new set of film tests which are found to be of great delicacy (the limits of delicacy are now being measured, it being found that gold, one part in one million, and copper, one part in four millions, are easily detectable); a change in the composition of the tablets which does away with the necessity for using platinum wire in the production of the colored glasses with borax and metaphosphoric acid, these being formed on the tablets with a decided gain in facility and delicacy; and lastly several new methods of handling the tablets themselves.

It is evident that solid reagents will always be the more convenient to carry afield, but, in the laboratory, liquids are to be preferred, since they are more readily applied, and when the assay is heated, the reagent, which has soaked into the tablet, is fed steadily toward the hot portion of the tablet, so that the heated assay is constantly enveloped in the vapor of the reagent. For over two years the writer has used with satisfaction the following reagents, which have been selected from a score of experimental ones. They are stable and almost odorless, can be carried to the field in a solid form and so used if need be, while a few seconds suffice to prepare them in liquid form if it be desired so to use them.

The chief reagent is a saturated solution of iodine in a strong solution of potassium thiocyanate in water. The solution takes place almost instantly and with great absorption of heat. The bottleful now in use has been in use for over two years, a little of one or other of the ingredients being added from time to time as seemed to be required. Exact proportions are not necessary to the efficiency of the reagent. It can be prepared on the field from the solid chemicals at a moment's notice. The brilliancy of the iodide films produced with this solution are not one whit behind those possible with the pure solution of hydriodic acid. Its coatings tend to form in definite bands of color. The spheres of desposition of the iodide and the oxy-iodide are sometimes very well defined. Some striking and important variations are produced by the presence of the potassium thiocyanate, for example, with molybdenum, osmium, iridium, tin, antimony, lead, bismuth, cadmium and mercury.

Dr. Haanel showed in his second paper that by means of hydrobromic acid, copper and iron could be detected at one operation in the presence of each other and in the presence of nickel and cobalt and any other flux-coloring substances. Instead of the fuming acid with its dangerous properties, a mixture in molecular proportions of powdered potassium bromide and metaphosphoric acid, or potassium hydrogen phosphate or sulphate may be used. This, suggested by Bowman's work, suggests further a set of solid reagents, made by using potassium chloride, potassium fluoride and potassium iodide with metaphosphoric acid, and these form a valuable set for special tests. They have the advantage of yielding at once the colored flux and the coatings produced by any volatile matter in the assay.

When heated, the reaction represented by the following general equation takes place: $KX + HPO_3 = KPO_3 + HX$.

These two reagents, the iodine solution and the bromide mixture, suffice for the production of coatings. The following which are used to differentiate them, are dropped upon the oxide or iodide film and colored spots are produced, or the color is discharged to white (technically, *wiped*), or the coating disappears through solution and absorption by the tablet.

Dr. Haanel used ammonium hydroxide and yellow ammonium sulphide for the purpose of testing the solubility of the films and to produce the sulphide spots. Both of these are troublesome to carry, and the latter is objectionable on account of its intolerable odor, its instability and the fact that for its renewal the hydrogen sulphide generator is required. It has been found that a solution of potassium sulphide, strong enough to show a clear amber color, made by dissolving the solid potassium sulphide in water, or by boiling a strong solution of potassium hydroxide with an excess of flowers of sulphur till the solution assumes a blackish color, which on cooling will be amber yellow, fulfils all the required conditions. If through the action of light it is decomposed, all that is necessary for its renewal is to boil the solution and perhaps add a little sulphur. We therefore have a reagent which can be carried as a solid, can be renewed anywhere, is as efficient as the ammonium sulphide solution and is almost odorless.

In the place of ammonium hydroxide a solution of potassium cyanide is used, made a little more stable by the addition of a little ammonium or potassium hydroxide. Besides these the common acids of the laboratory are useful and a solution of potassium thiocyanate.

The potassium thiocyanate solution is used in two ways. It is either dropped on the coating to test its solubility and to note the colors produced after heating, or it is dropped on the tablet before the coating is deposited, and then the hot vapors sweeping over the moist spot, give with some metals characteristic reactions.

Those coatings which are pure white and therefore invisible on the white tablet, are examined on a tablet which has been smoked in a flame, or on one streaked up the middle by means of a glass rod which has been dipped in a solution of boric and metaphosphoric acids mixed with lampblack or bone charcoal. In this way the coatings may be viewed on a white and on a black surface at the same time.

In order that the colored fluxes may be made on the tablets, the latter must be made more resistant to the dissolving effect of the metaphosphoric acid and the alkali in the borax. If one teaspoonful of boric acid be added to each quart of the water used in making the tablets, they will be found to be denser and to have the necessary quality. Borax can be fused on them without gathering any impurities from the plaster and if metaphosphoric acid be substituted for phosphor salt, we have a flux which will spread upon the tablet and exhibit the colors of all degrees of saturation at the same time. This reagent, first proposed by Ross, who described its reactions, is preferable to microcosmic salt, since, as it contains no volatile matter and melts readily to a clear glass, it will show by effervescence the presence of water or carbon dioxide, or other gas in a mineral. With cobalt it yields a fine violet when cold, which becomes blue on the addition of any of the alkali metals, for which therefore it furnishes a ready test. The only objection to this reagent is the tendency of the sticks to deliquesce, but a piece can be kept in a corked test-tube,[1] which can be readily dried over the flame, if dampness should gather. In dry weather it causes no trouble. Its solvent power is very great and the colors are fine. Ross asserts that silica and zirconia are the only oxides which are not soluble in this flux. The whole operation may be completed in the time usually required to form the bead in the platinum wire loop and the volatile oxide films will be found on the tablet above the glass, where they may be tested with potassium sulphide and the other reagents. One operation, therefore, suffices for the determination of the volatile acid elements, the volatile metal or metals, and flux-coloring metal. Metaphosphoric acid well replaces potassium hydrogen sulphate in the operation as

---

[1] In this laboratory each student is supplied with a set of very small dipping tubes and a wooden block into which holes are bored for the reception of a set of test-tubes closed with paraffined corks, to hold the reagents.

described in most text-books for the detection of carbon monoxide, carbon dioxide, iron, chlorine, bromine, iodine, nitrogen tetroxide, chlorine tetroxide, sulphur dioxide, hydrogen sulphide, hydrocyanic acid and acetic acid.

DESCRIPTIVE LIST OF REACTIONS OBTAINABLE ON THE TABLETS.

Copper *per se* yields with difficulty a coating of volatilized metal. With the iodine solution it yields a white iodide coating and an emerald green flame. The iodide treated with a drop of potassium sulphide gives with gentle heat a blackish gray, which is removed by greater heat. Potassium cyanide and nitric acid dissolve the sulphide; hydrochloric and sulphuric acids have no effect till heated and then they remove the spot. Potassium thiocyanate applied to the coating has no effect till heated, when a gray spot is shown. Any part of the coating touched with the tip of the flame shows the emerald green flame (Haanel). Metaphosphoric acid glass is greenish-blue when hot and a fine robin's egg blue when cold. Metaphosphoric acid and potassium bromide yield a splendid reddish violet coating of copper bromide (compare osmium). The bromide plus potassium sulphide shows a brown, which if heated turns blackish and then green, not affected by sulphuric acid, but immediately destroyed by a drop of nitric acid.

Copper plus metaphosphoric acid and potassium chloride yields a yellow brown cupric chloride, which, if treated with a drop of potassium thiocyanate, gives a black ring, which, if heated, becomes a black spot. If, before the assay is heated, a drop of nitric acid be placed one-half inch from the assay and a drop of potassium thiocyanate be placed above that, on heating a fine and very volatile blue-black coating is deposited far up the tablet. This blue-black is not affected by acetic acid, is wiped off by sulphuric acid slowly, and immediately by hydrochloric and nitric acid. The formula of this compound will be determined if some method be found, by which it may be collected in quantity. (See chlorine.)

Silver gives *per se* a pinkish gray coating, which touched by the blowpipe flame (flamed) becomes mottled brown. Reduced globules are often shown. Metaphosphoric acid yields the same coating and a pearl-like glass. The iodine solution yields a pale yellow, paler when cold, and around the assay forms a black, which does not fuse into the tablet (compare lead). Flaming with oxidizing flame yields a mottled brown anywhere on the tablet. This is a very delicate test and as all other coatings are volatile, the flame drives them off and leaves the silver oxide. Potassium sulphide produces a spotted blackish brown, probably potassium silver sulphide, the analogue of ammonium silver oxide, for if treated with a drop of potassium cyanide it immediately disappears, but if it be first heated, the potassium cyanide has no effect. If only one-half of the sulphide spot be touched with the tip of the flame and then the potassium cyanide be applied, the untouched portion will disappear while the other half will remain. Potassium thiocyanate on the iodide wipes it off; when heated the spot turns black, which is not wiped off by potassium cyanide.

Gold is slightly volatile *per se* and more so if a solution of iodine in potassium iodide be used as a reagent, and the result is a fine rose-colored film of the metal. If potassium thiocyanate be present, no volatility is noticed. Gold and the other elements which respond to the new tests will be the subject of another paper.

Zinc *per se* yields a white coating, not very volatile and luminous yellow when hot. Potassium sulphide and potassium thiocyanate produce no visible change on zinc films. The iodide film is a white, which treated in any part with cobalt nitrate solution yields the well-known zincate of cobalt, which is quickly decomposed by a drop of nitric acid (compare tin). This reaction obtained in this way is decisive for zinc, as aluminum and silicon do not volatilize and are therefore not present in the coating. In the metaphosphoric acid glass, zinc causes flashes of light and detonations (Chapman). Metallic zinc sometimes yields *per se* a black sublimate along with the white oxide (compare arsenic.)

Cadmium *per se* yields one of the most beautiful of the oxide films, which consists of a rich brown with black farther away and somewhat iridescent near the assay. Acetic acid does not affect it; potassium cyanide dissolves it at once (compare cadmium sulphide). Potassium sulphide and potassium thiocyanate yield a scarlet when hot, and bright yellow, cold. This cadmium sulphide is not affected by potassium cyanide, is quickly destroyed by nitric acid, less readily by hydrochloric acid, immediately by acetic acid (compare cadmium oxide), and is not affected by sulphuric acid (compare copper).

The iodide coating is white with well-defined borders, which is easily distinguished in the presence of other white coatings by the *per se* and sulphide reactions. In the assay and near it the sulphide reaction will be seen caused by the potassium thiocyanate in the iodine solution (see sulphur). In metaphosphoric acid cadmium acts like zinc and yields at the same time its oxide coating beyond the glass.

Mercury gives *per se* a very volatile film of mercury snow, which, with a feather, may be swept into a globule. It is not affected by the other reagents.

The iodide coating is a splendid combination of scarlet, yellow, and velvety green. This is caused by the mixing of the green mercurous iodide with the scarlet and yellow forms of the mercuric iodide. The reactions of each kind of iodide may be obtained on the one tablet. The green and the scarlet are the stable forms into which the coating changes on standing. A drop of the reagent or some more of the vapor blown across the coating changes all into the scarlet form. With mercurous iodide, sulphuric acid gives a yellow spot (mercurous sulphate). Potassium hydroxide gives a black; so does ammonium hydroxide, (iodomercurosamine, NH_2Hg_2I), and potassium sulphide. With the mercuric iodide, sulphuric acid increases the amount of the scarlet, potassium hydroxide yields a white, as does ammonium hydroxide (iodomercurosamine) and potassium sulphide, yield a white spot, quickly turning black. The sulphide spot, strange to say, is partially dissolved in nitric and hydrochloric acid, while sulphuric acid turns it brownish. Potassium cyanide yields a black and potassium thiocyanate a dark spot, and if heated both are wholly volatilized (compare lead, bismuth, and silver). Water has no effect on this coating (compare lead), nor have hydrochloric, nitric, or sulphuric acids. By the last the coating is not readily wetted.

Gallium has not been experimented with. Indium yields a pale yellow iodide coating and a blue flame.

Thallium *per se* yields a feathery brown with white farther away and a green flame (compare arsenic and tellurium). Potassium sulphide gives a terra cotta brown spot with a black ring. Potassium cyanide and potassium thiocyanate have no effect upon it. The iodide film is an egg yellow with a purple black veil farther away. Potassium sulphide gives a rich brown which potassium cyanide darkens. Hydrochloric acid discharges it slowly and yellow is left (compare bismuth and tellurium). Potassium thiocyanate has no effect on the yellow or the black till heated, when it yields a white (compare bismuth, tellurium, tin, and lead). Potassium cyanide dissolves the black but has no effect on the yellow. Sulphuric acid has no effect. A drop of the reagent on the coating heated shows a spreading black and an orange ring.

Carbon yields a sooty coating, which comes better if sulphuric acid or metaphosphoric acid be used upon the assay. In the case of the carbonates, boric oxide or metaphosphoric acid yield an odorless effervescence (Ross, Chapman). Organic acids blacken the tablet when heated.

Silicon. An interesting reaction given by the silicates, especially the hydrous forms, is being investigated. Chapman dissolves a silicate in boric oxide and then precipitates the silica by adding metaphosphoric acid.

Germanium will give a light yellow iodide film, but none has been on hand to experiment with.

Tin gives a slightly volatile coating, showing a trace of brown when hot. Potassium thiocyanate, if dropped on the oxide and strongly heated gives a pale yellowish green, infusible (compare lead). The slight volatility of tin oxide suggests a scale of volatility, of great use in describing the formation of the films on the tablets. The scale runs in the order of increasing volatility : tin, zinc, cadmium, and mercury. Anything less volatile than tin might be classed as non-volatile.

The iodine solution yields a yellow, reddish brown when hot, the brown fading instantly. Potassium sulphide yields a black with a brown edge, which darkens on heating. Potassium cyanide discharges the color, which turns black on heating, and when strongly heated shows the pale yellowish green (stannous thiocyanate, $Sn(SCN)_2$; compare lead, bismuth, arsenic, mercury and zinc). Water decomposes the film with formation of oxy-iodide.

Cobalt nitrate gives the bluish green, which is not so readily attacked by nitric acid as the zinc green.

Antimony tri- or pentachloride yields with all tin salts a fine purplish blue-black coating, stable in the presence of acids. Potassium thiocyanate decomposes it when heated and forms the pale green.

These tests with iodine, antimony trichloride, and with potassium thiocyanate remove tin from the list of metals determinable with difficulty before the blowpipe. They can be depended on through a wide range of mixtures.

Lead yields *per se* a white and yellow; reddish brown when hot. All lead salts fuse into the tablet with the formation of lead plumbate, one of the constituents of glass. Potassium sulphide produces a brownish black, with reddish brown ring.

The iodine solution gives a film which is chrome yellow, with a band of fainter yellow farther away (oxy-iodide?), and the assay is black. Potassium sulphide yields a spot with the reddish brown edge. Hydrochloric acid destroys the edge at once. Nitric acid wipes the spot off slowly, and sulphuric acid destroys the black and restores the yellow. The very volatile paler yellow on the outer edges is turned to a brighter color by the same treatment (compare mercury). Potassium cyanide produces a slight paleing of the sulphide color. Potassium thiocyanate on the iodide film gives a black ring, which heated becomes a black spot (compare bismuth). Water wipes off the coating (compare mercury, arsenic and silver).

The bromide film made by using potassium bromide and potassium hydrogen sulphate presents some interesting differences. It is white with a trace of yellow, the yellow fusing into the tablet. Potassium sulphide gives a spot, greenish for a moment and then black, on which potassium cyanide and potassium thiocyanate have no effect, but is partly destroyed by hydrochloric acid, more rapidly by nitric acid, and completely by sulphuric acid. Potassium thiocyanate, placed on the sulphide and heated, gives a black ring; with greater heat, a yellow, and still greater heat, a greenish gray ring. Potassium cyanide on the iodide film has no effect till heated; then a white. Potassium thiocyanate has no effect on iodide till heated; then a yellowish spot appears (compare tin). The sulphide heated becomes grayish black, on which nitric acid and the other acids have no effect (compare copper).

It is a good illustration of Carnelley's law of color that in general the bromide film of any metal resembles the iodide film of an element either in a higher series in its own family or in the same series, in another family toward the left in the natural classification. Thus the bismuth bromide film resembles the iodide film of antimony and lead. Lead bromide resembles tin and thallium iodide. Thallium resembles mercury, and mercury resembles silver in the same way.

Nitrogen with metaphosphoric acid in the nitrates yields an effervescence with the fumes, odor and reactions of nitrogen tetroxide farther up the tablet, and in the cyanides, the odor of hydrocyanic acid. Nitrates with carbonaceous matter yield ammonia, which will cause white fumes to rise from a spot on the tablet moistened with hydrochloric acid. Ross reports that any nitrogen compound with boric oxide yields a tough transparent bead, and with metaphosphoric acid, purple in the reducing flame with manganese dioxide.

Vanadium gives with metaphosphoric acid a pale yellow in the oxidizing flame, and in the reducing flame a green. (Ross).

Phosphorus. A great desideratum in blowpipe analysis is a good test for this element and the phosphates.

Arsenic yields *per se* a brownish black with a white film falling farther away with odor of garlic and blue flame (compare thallium and tellurium). The iodide coat is white and pale yellow; the assay wholly volatile. Potassium sulphide, with a drop of hydrochloric acid, forms the yellow sulphide, little affected by acids. If oxalic acid be applied to a sulphide spot and then hydrochloric acid, no effect is noticeable. The yellow will show up still better next day (compare antimony). If a drop of potassium thiocyanate be placed on the tablet about one inch above the assay, and between them a drop of nitric acid and the arsenical vapor be blown over them from the assay, there will generally be formed in the edge of the potassium thiocyanate spot a bright bluish green of unknown composition. All common acids except acetic destroy it. It shows well in the presence of salts of tin and antimony. When it does appear it is decisive for arsenic. This iodide film exhibits a very marked repulsive power for water, probably due to the arsenic oxide which forms with it. Potassium iodide with metaphosphoric acid yields more of the yellow than does the iodine solution.

Antimony *per se* yields a white and yellow band and white fumes. Potassium sulphide yields on this an orange brown, which is quickly destroyed by a drop of nitric acid.

The iodide film is a fine orange yellow far away with yellow nearer the assay and abundant white fumes. Potassium sulphide yields, especially when heated, an orange red with a rich brown and then a black beyond the spot. Hydrochloric acid slightly heated destroys it; nitric acid destroys it instantly; so also does its vapor. Potassium thiocyanate wipes the coating, but heated it yields a fine brown, which is permanent when exposed for months. Potassium cyanide wipes the coat. The orange yellow sulphide spot, produced on the iodide film obtained with potassium iodide and metaphosphoric acid, is not so susceptible to the action of nitric acid and is more rapidly destroyed by hydrochloric acid than the one described above.

If arsenic be present with antimony, there will be shown inside the yellowish orange of the iodide film, a fine peachy pink, which is hard to wet. Stannic chloride yields with antimony in most combinations a purplish blue-black, which is remarkably stable (Haanel). It is now being collected in quantity, with a view to the determination of its formula. It will be seen that with the blue with potassium thiocyanate, the rose pink, and the reactions of the sulphide with hydrochloric, nitric and oxalic acids, the presence of arsenic can be easily demonstrated in the presence of antimony and, as far as experiment has gone, in the presence of any other substances.

Bismuth yields *per se* a yellow ring near the assay and often a brittle globule. Potassium sulphide gives on the white oxide a brownish black which nitric acid destroys and on which hydrochloric acid has little effect till heated, when it removes it completely. Sulphuric acid has no effect. Potassium thiocyanate on the oxide produces a yellow ring, and heated a yellow spot turning black. (It is to be noted that potassium thiocyanate itself when heated or treated with strong acids, shows on the tablet a fine yellow, which further heating renders colorless.)

The iodide film is a splendid combination of chocolate black, crimson and yellow, the assay turning black. Potassium sulphide forms a chocolate black, soluble in nitric acid and not effected by sulphuric acid. The latter acid on the iodide film produces a black and a dull red edge. This is probably the sulphide formed by the reduction of the acid by the decomposition products of the potassium thiocyanate, which fall with the iodides. It has been noticed, however, to happen with no other metal than bismuth. This reaction is very useful in detecting small quantities of bismuth in the presence of other metals giving dark colored films (compare tellurium). Potassium thiocyanate on the iodide wipes it off, forming a yellow ring, but when heated it forms a black spot with a brown ring. Potassium cyanide also wipes the iodide, but when heated forms a dark gray spot. Glacial acetic acid wipes off the yellow and the crimson, but has no effect on the chocolate iodide.

Sulphur. In looking for a better test for sulphur than the ordinary one with soda and a piece of silver, the stability at high temperatures and the two brilliant and characteristic colors of cadmium sulphide attracted attention, and the fact that it is easily formed in the presence of potassium cyanide. To a solution of cadmium bromide, potassium cyanide was added till precipitation took place and then the solution of the precipitate as potassium cadmium cyanide. This, dropped on a fragment of the sulphide and heated, will show on the tablet near the assay a brilliant scarlet when hot, and bright yellow when cold. This is not affected by potassium cyanide (compare cadmium oxide). One great advantage of this is that selenium and tellurium do not yield anything which can be confounded with these colors, selenium giving a grayish brown and tellurium a yellowish brown. Sulphates may be reduced by potassium cyanide, or by glycerol. A sulphide or sulphate fused with potassium cyanide will, if touched with a drop of ferric chloride, show in the tablet the pinkish red of ferric thiocyanate. The sulphur in the tablet causes no trouble.

Selenium and tellurium are further differentiated from sulphur by their characteristic films, which are tests of great delicacy. Twenty-seven varieties of complex sulphides, such as bournonite, tetrahedrite, stannite, etc., and all of the common sulphides and sulphates, were found to respond to this test at once.

Selenium yields *per se* with characteristic odor and flame a fine reddish brown, almost pure red on the outer edges and black on the inner edges near the assay. Potassium cyanide wipes it off, while potassium thiocyanate has no effect, except that, if it be heated, a very stable red compound is formed ($KSeCN$?).

The iodide film forms in color very similar to the *per se* coat, but more volatile. Potassium sulphide yields a yellow. Potassium cyanide wipes the iodide film off instantly, and therefore will reveal the presence of any other element not so affected, whose film might be hidden by the pronounced hues of the selenium film. Potassium thiocyanate has no effect, while it and heat wipe off most other coatings, and therefore will reveal the presence of selenium in obscuring associations, such as lead. Sulphuric acid shows a slight tendency to make this coating darker (compare bismuth).

Tellurium gives *per se* with flame and odor a brownish black with a white film falling nearer the assay (compare arsenic). Sulphuric acid, if gently heated, shows an effervescent pink of tellurium sulphate. Acetic acid wipes off this coat (compare cadmium). So do the potassium cyanide and ammonia fumes. The iodide film is brownish and purplish black, less brown than the *per se* coat. Potassium cyanide wipes it off in the cold. Potassium thiocyanate has no effect on the purple (compare thallium), and slightly dissolves the brown, and if nitric acid be added a yellow appears. Potassium sulphide darkens the coating a little. Sulphuric acid acts as on *per se* film.

Chromium yields an assay which is dark green when hot and a fine green on cooling. This test can be made very delicate. Metaphosphoric acid gives similar colors.

Molybdenum yields *per se*, and especially by flaming, an ultramarine coating. The oxide film, which forms when the iodine solution is used, comes better by flaming of the film and in presence of vapors of sulphuric acid. A potassium thiocyanate spot, over which the vapors from the assay have swept, exhibits a splendid hyacinthine pink. Metaphosphoric and sulphuric acid vapors aid its formation. It is probably molybdenum thiocyanate ($Mo(SCN)_2$). If potassium thiocyanate be added to the assay this color will spread all around the edges of the blue, extending to a distance of two inches from the assay. This very delicate reaction is of special interest, from the fact that it shows that part of the potassium thiocyanate, or at least the radical thiocyanogen travels undecomposed that distance over the tablet and that all these films are formed in the presence of moist potassium thiocyanate or thiocyanogen vapors, which will account for the behavior of some of the films. This pink is decolorized by ammonia, not restored by nitric acid. Sulphuric acid dropped on the tablet will form a blue ring ($MoSO_4$). Metaphosphoric acid yields blue or bluish green glasses according to the degree of saturation (Ross).

Tungsten and uranium in metaphosphoric in the reducing flame yield, the former a blue and the latter a green glass (Ross).

Fluorine. If a fluoride be mixed with phosphoric acid and a piece of glass be laid on the tablet about two cm. away from the assay, a fine etched semicircle will show itself after the heating of the assay. The radius of the semicircle is about three cm. long.

Manganese yields with metaphosphoric acid a glass, which is violet hot and cold, colorless in the reducing flame, and turning green on the addition of an excess of soda (Chapman, Ross).

Chlorine. Chlorides, bromides and iodides of the alkali metals yield *per se* white coatings, which may be distinguished from other white coatings by their flames and by the action of a small quantity of the coating scraped together and mixed with the metaphosphoric acid cobalt glass, which will remain blue on cooling.

A compound of chlorine if mixed with metaphosphoric acid and heated, in the reducing flame (if oxy salt), will cause white fumes to rise from a spot moistened with ammonia situated about two cm. above the assay. If a copper salt be present in the glass or near it, so that copper chloride vapors are formed and these are allowed to sweep over a spot of nitric acid and then over one of potassium thiocyanate, near the assay a yellowish brown coating of cupric chloride will form with an azure blue flame, and beyond the potassium thiocyanate spot a fine blue-black, very volatile (see copper).

A bromide with potassium cyanide added to it and the fused mass laid upon a copper glass and a drop of nitric acid added, a fine red will show itself. Bromides with metaphosphoric acid saturated with copper, upon blowing, yield a fine and very volatile reddish violet coating. If a bismuth salt be exposed to the hot vapors, it will yield a yellow coating. The spot on the tablet moistened with starch paste, not too near the assay, will turn yellow.

Similarly treated iodine compounds yield violet vapors, a violet in the glass appearing with effervescence, and with copper salt they yield a white coating, with bismuth scarlet and chocolate, and with starch a bluish black.

Iron gives an iodide film too delicate in color to show up well, either on the white or the black surface. Its presence can be shown by a red coloration after blowing hydrochloric acid vapors over the tablet, to turn all ferrous compounds into ferric, and then adding a drop of potassium thiocyanate to the coating. It is difficult to obtain plaster of Paris sufficiently pure not to give this reaction for iron. Such reaction can, however, be readily distinguished from that given by an assay. Metaphosphoric acid gives a luminous yellow when hot, which is perfectly colorless when cold. A drop of acid on this to produce ferric compounds, followed by a drop of potassium thiocyanate, will show the red of ferric thiocyanate, which is decolorized by phosphoric acid, but not by hydrochloric acid. Made in this way, this test is not too delicate to show the iron of composition. An assay of iron treated with a drop of sulphuric acid and heated will show on the tablet a film of Venetian red.

Cobalt yields a glass blue hot, and violet cold ; permanently blue if alkali be present. Boron trioxide acts similarly. With the iodine solution a spot around the assay turns pink, then deep blue on heating, and then black.

Nickel with boron trioxide separates as green fragments, which may be gathered by solution of the glass in water, and then the separated nickel (as any nickel compound) will yield in metaphosphoric acid, a reddish brown when hot and amber yellow when cold (Ross).

Palladium gives a dull blue-black film with the iodine solution, which is very characteristic. The assay turns dull black.

Osmium yields *per se* a greenish black. The iodide film is a combination of olive green, dove and slate colors, with red appearing around the lower edges. The edge of the coating nearest the assay shows greenish brown and the assay itself will be closely surrounded with an iridescent black film. Potassium sulphide turns the coating somewhat darker, which heated, becomes a brownish film, which is wiped off by hydrochloric and nitric acids and not affected by sulphuric acid and potassium cyanide. On the iodide films sulphuric acid has no effect; potassium thiocyanate has none till heated and then it turns brown. Hydrochloric and nitric acids remove the film. Potassium thiocyanate dropped on the tablet over an inch from the assay before the coating is deposited, will, when the vapors sweep over it, turn to a fine brick red, destroyed by potassium cyanide and the acids.

Potassium bromide and potassium hydrogen sulphate give a pinkish brown (compare copper). Potassium sulphide produces a gray not affected, which turns darker on being heated, destroyed by acids, and not affected by potassium cyanide.

Iridium yields with the iodide solution an indistinct brownish yellow coating and a potassium thiocyanate spot which in tint resembles the molybdenum spot, but it is covered with dots of darker pink.

Platinum gives an infusible gray film. Ruthenium and rhodium are being investigated.

All these reactions have been obtained from a large number of the compounds of each element except in the cases of osmium, indium and iridium. The writer will be glad to hear of any cases in which they fail and to receive specimens of combinations which cannot be unlocked by this method. One gram weight of any alloy is sufficient. The next work to be undertaken is to exhaustively determine the lowest percentage of any metal which can be determined with certainty in the presence of one, two, or any number of other metals, to describe the characteristic effect that one metal has on the coating yielded by another when they are deposited together and to determine the value of each metal as an interfering element.

COVERED TABLETS.

The tablets are easily cut with a knife and therefore they can be used in various ways. Open tube work can be performed on a tablet, if a groove be cut lengthwise of a tablet and laid upon another, groove down. A small pit for the assay is cut in the lower one about one centimeter from the end. The groove is cut so that its narrowest part is just above the assay pit, and from that point to the lower end it flares into a half funnel form and into this the flame is blown. By regulating the size of the groove at its narrowest part the amount of air which will flow over the assay may be regulated. This method is of great use when very small quantities of precipitates are to be tested. For instance, five-tenths mg. of arsenious oxide gave in one experiment a narrow coating one-half inch long on each tablet. This gives ample opportunity for making confirmatory tests. Various reagents may be placed along the groove to be acted on by the vapors, gold leaf for mercury, potassium cadmium cyanide and lead acetate for hydrogen sulphide fumes, starch, bismuth and antimony solutions for iodine, copper sulphate for chlorine, etc.

If a coating be made, or a small piece of volatile salt be placed in a small pit in the tablet and a thin tablet be placed over it, it is found that if potassium sulphide, or potassium thiocyanate be dropped on the upper tablet and the flame be directed upon the drop, they will pass through the tablet and reactions will take place away from the air. After a few seconds blowing the upper tablet will be found to be floating on a layer of hot gas, which flows between the two smooth surfaces. Tin and arsenic, and other substances easily oxidizing in the air, form their sulphides very readily under these conditions. Potassium thiocyanate forms sulphides. It is in this way possible, by using ammonium hydroxide or hydrochloric acid, to form the sulphides in the presence of moist acid or alkaline vapors.

Other methods of using the tablets will be described later.

In teaching research methods, the plaster of Paris method is one of the finest instruments to use with beginners. In the course of an hour a student will have been able to make from twenty to forty different tests and without any delay in preparing solutions, or in waiting for filtration to take place, he will have produced the oxide, sulphide, chloride, bromide, and iodide of a given metal, and will have noted their colors, manner of deposition, volatility, solubility in several reagents, and the behavior of the assay itself at high temperatures and will have ransacked his vocabulary to find terms to describe the phenomena in his written notes. His skill in manipulation and his powers of observation are kept in liveliest exercise and his independence developed, for it is quite possible to give each student in a large class his own problem. In no other laboratory work do the compelled acts of judgment follow each other as rapidly. There are many problems which may be set requiring reference to standard chemical literature, and many simple and some very difficult equations of reactions to be written.

Not the least valuable consideration from an educational standpoint, is the aesthetic quality of the work. All the coatings are symmetrical in form and beautiful in shading, and many of them in brilliancy of hue and in delicacy of shading, rival the most splendid colors of flowers. This gives added interest to the work and is of great value since adult students are so frequently found to be greatly deficient in the color-sense, as children are not. There has not been opportunity to compare the shades of these films with the descriptions given in the Standard Dictionary. When this has been done, exact training can be given in color language also.

Apology is offered for publishing the results of this research at this stage, when so many unsolved problems stand along its path, but this much is given in order that the practical value of these reactions and methods may be put to the test.

UNIVERSITY OF MT. ALLISON COLLEGE,
SACKVII N. B.

AN ANALYTICAL INVESTIGATION OF THE HYDROLYSIS OF STARCH BY ACIDS.

BY GEO. W. ROLFE AND GEO. DEFREN.

Received July 3, 1896.

FEW problems of commercial analysis have been so complicated and so discouraging as that of the determination of the components of starch conversion products. The well-known schemes of commercial analysis of worts and similar products of the action of diastase are based on the assumption that but two simple compounds are formed from the starch—maltose and dextrin. In the case of glucose syrups and starch sugars, which are the results of acid hydrolysis, it is known that the reaction proceeds farther as dextrose is formed from the maltose and dextrin.

Musculus and Gruber[1] decided that these reactions went on together so that except at the very beginning or final stage of hydrolysis all of these compounds must be present in solution.

The analysis of acid-converted starch products must therefore take into consideration the presence of the third compound, dextrose.

Much doubt, however, has been thrown on the accuracy of such analyses, as during the past twenty years the researches of O'Sullivan, Brown, Heron, Morris, Bondonneau, Herzfeld, Musculus, Bruckner, Fischer, and other distinguished investigators, have shown that not only the simple compounds referred to can be isolated from starch products but also many others of quite distinct optical and chemical properties. Space will not permit a review of this work, which is in many points conflicting. The recent conclusion of Lintner and Düll is that the following compounds result from hydrolysis :[2]

---

[1] *Bull. Soc. Chim.*, 2, 30.

[2] *Ber. d. chem. Ges.*, 28, 1522-1531.