

as follows:—Provide three or four of the weakest concave spectacle lenses produced, but of progressive strength, and chip them down to about the dimensions of a shilling. When of this diameter they will be very thin. Next attach each of these little lenses to a brass stop of the ordinary Waterhouse form, adopting such means as will be suggested to any one possessing a mechanical turn of mind—the best in our estimation consisting in soldering upon the stop a very shallow ring of brass sawn from the end of a tube, the depth being such as to leave it on a level with the edge of the lens. A series of these lenses thus fitted ready for insertion can be carried in a diaphragm pocket-case having divisions to prevent them coming into contact one with the other; and, after the value of each, as respects the additional lengthening of the focus of the combination, has been engraved or scratched on the brass portion of the stop, a photographer who goes to the country with such an adjunct to his lens will find himself enabled to secure effects which without such assistance would be impossible, while, at the same time, the good qualities of the lens as it issued from the hands of its maker are still preserved intact.

What has been said as regards the lengthening of the focus by means of a *concave* lens applies equally to the shortening of it by the expedient of using one of a convex form.

A FEW INSTANCES, SHOWING THE POSSIBILITY OF APPLYING THE
MICROSCOPE TO INORGANIC, QUALITATIVE ANALYSIS. A THESIS.

By FRANK W. VERY.

1873

PREFACE.—The researches narrated in this paper, have been limited by the low power of the microscope used, and by the shortness of the time which could be given to such work. The first cause has obliged us to throw aside many precipitates (often most delicate tests for the substance under consideration), which could perhaps be made available by means of higher magnifying power.

It is the author's opinion, that a method can be devised for carrying on a complete qualitative analysis by means of the microscope,

with the use of appropriate reagents ; but to discover the tests, which are best fitted for the purpose, and which give the most distinctive crystals, under conditions that may be defined, is a labor of years.

Such a method would be of especial use where only a limited quantity of a substance could be obtained, as in the case of rare minerals, a single small crystal would be sufficient for an analysis. Or it might become of use in the examination of the residue left by the evaporation of mineral water.

In its present state, the method does not seem to be as delicate as the ordinary one ; perhaps it can never be made so. The matter which causes a perceptible cloudiness in a large mass of liquid, may be so finely divided, that the microscope would fail to recognize the form of the particles. On the other hand, the microscope will probably have the advantage of rapidity in the prosecution of the work. In many cases it will enable us to recognize one or more elements in the presence of others, which in the ordinary method would have to be removed first.

The few tests which are herein described, can hardly be called very successful. There are doubtless much better ones to be discovered. They will serve, however, as a basis for further investigation, and the general considerations deduced from them will always be of use.

GENERAL DIRECTIONS.—It would be best to use an inverted microscope for these researches, because strong acids could then be applied as reagents without injury to the objective from their fumes. In this case, thin glass slides must be used. These can best be made by cutting a hole in an ordinary slide, over which a piece of thin glass is cemented.

Small test-tubes or phials, two or three inches long, are convenient for holding reagents and the solutions to be tested. A drop of the liquid may be removed from these by means of a glass rod ; or if more of the liquid be needed, a pipette, made of a capillary tube, may be used. In either case, the utensil should be washed at once, and a basin of water should be kept at hand for this purpose, and for washing the slides.

There ought to be several tests for each element, to act as checks, and we can the better afford this since a single test often shows two or three elements at once.

When precipitations are in order, it is a safe rule to have the solutions tolerably dilute, provided the precipitate is sufficiently insoluble. The precise amount of dilution must be determined for each case by experiment. Unless this be done, the crystals come in such confused masses that they are hard to distinguish. Extremely insoluble precipitates are generally very finely divided. Here dilution is absolutely essential, if recognizable crystals are to be obtained. Even very great dilution does not always succeed in bringing this about. In dilute solutions it is often necessary to wait a while for the crystals to form; and, in very many solutions, the formation of crystals is facilitated by agitating the liquid with a stirring rod. As the latter scrapes against the glass slide, the crystals fall in its track in thickly set rows. The crystals produced in this way are generally smaller than they would otherwise be, but are more perfectly formed.

In the production of crystals by evaporation, the liquid must necessarily be concentrated; and the serried, interlacing forms produced in this manner are often difficult to recognize, especially as they are apt to vary considerably. Hence precipitations are generally more desirable than evaporations. However, some substances can be readily recognized from evaporated preparations, particularly if the same conditions of temperature, and so forth, are used in every case; but there is generally an element of uncertainty, because the other substances, which may be in solution, are apt to influence the form of the crystalline aggregation.

Some solutions evaporate well enough spontaneously, but generally a slight degree of heat is necessary. If the heat is applied merely to concentrate the liquid, it need not be noted; otherwise the thermometer should be consulted. Very good results may be obtained, even with deliquescent substances, by evaporating under the receiver of an air-pump, over sulphuric acid; but this is a rather slow operation. To prevent the crystals from interlacing too thickly, the slide may be canted a little, so as to leave a very thin layer of liquid on the upper edge of the drop. Evaporation will here go on very rapidly, and the crystals will be farther apart.

The precipitation of a substance may often be effected by the addition of a liquid, in which it is much less soluble, provided the solution is already sufficiently concentrated. Several examples of this

will be mentioned. The common solvents, water, alcohol and ether, will be the ones most used in this way.

In evaporation, as well as in precipitation, the crystals should be watched from the commencement of their formation, as they are then more distinct, and afterwards become too much intermingled.

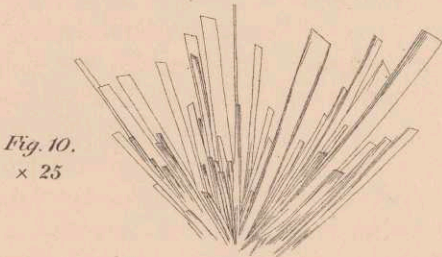
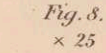
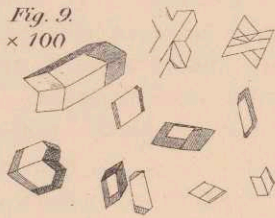
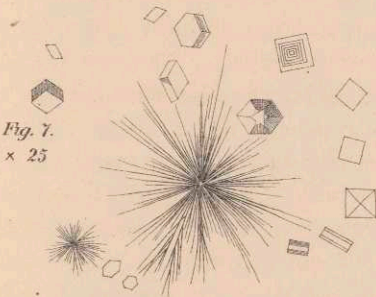
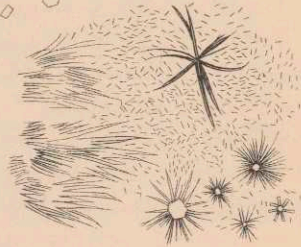
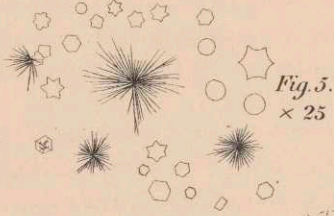
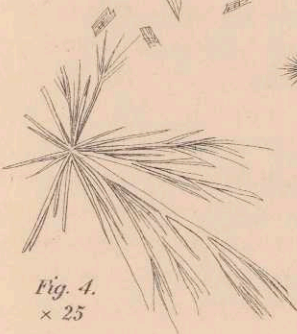
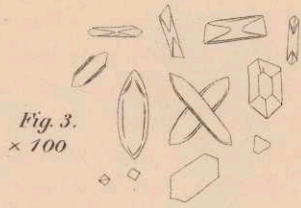
There is undoubtedly a general family resemblance between the various dendritic forms in which the same substance is wont to crystallize under slightly different conditions or on different occasions; but it is very hard to analyze these resemblances, and to state wherein they consist.

The same saline solution, evaporated under the same conditions of temperature, will give crystalline forms which vary remarkably. The multifarious shapes which snow-flakes take, are well known. Perhaps, if we were as well acquainted with other substances, we should find a similar diversity; although water is such a wonderful substance in many other respects, that it would not be surprising if it should surpass all others in the variety of its crystalline forms. It would be interesting to note the variation of a single substance (as Ba Cl_2 , for example), when evaporated under different conditions of temperature, pressure and atmospheric humidity. Perhaps the passage of an electric current would influence the phenomenon.

The deposition of metals upon the passage of an electric current through their solutions, is well observed under the microscope. The crystallizations generally take the form of trees, like those produced when similar experiments are tried on a larger scale, as in the formation of the well known lead and silver trees.

To obtain these metallic crystals, two strips of platinum foil are fastened to the upper surface of the slide with shellac, leaving a distance of three or four millimeters between their free ends. The other ends of the platinum strips communicate with the poles of a battery. The drop of liquid being placed on the slide, so as to connect the platinum terminals, the metallic tree begins to advance slowly from one of these, moving faster, however, as it approaches the opposite electrode; because the resistance to the current becomes less as the distance which it has to travel lessens.

There is a decided difference between the crystallizations of the various metals, yet it would be difficult to recognize them if mixed together; because the differences, though decided, and quite con-



stant, are very slight, and it is hard to recollect the precise degree of complexity of the interlacing feathery fibers.

SPECIAL CASES.—Scheme for detecting Lead, Bismuth, Copper and Cadmium, in presence of each other :

Precipitate the metals as carbonates with sodic carbonate. Wash the precipitate.

I. Dissolve a portion of the mixed carbonates in nitric acid. (N. B. The concentrated reagents are always meant, unless otherwise stated.) If much lead is present, a portion of plumbic nitrate will remain undissolved.

a. To one drop of the liquid add water. The basic nitrate of bismuth will be precipitated in beautiful radiate bunches of plates (Fig. 1, Plate I), which are easily recognized. When the water is added, there is first a very fine precipitate, in the midst of which the radiating bunches appear, and increase in size while the first precipitate disappears.

b. To another drop of the solution add alcohol. Dendritic crosses, formed by three bars intersecting at right-angles, will be formed, (Fig. 2, Plate II). Plumbic nitrate is precipitated in this manner by alcohol.

II. Dissolve a portion of the carbonates in chlorhydric acid. If much lead is present, it will be at once re-precipitated as chloride. In this case, pour off a portion of the supernatant liquid. (See *b.*)

a. To prove the presence of lead, add water to the precipitate, and dissolve by the aid of heat. Plumbic chloride will crystallize on cooling, as represented in Fig. 3, Plate I.

b. Evaporate the solution at a very gentle heat (about 50° C). Cupric chloride will crystallize first in long, branching needles (Fig. 4, Plate I), considerably coarser than those of Cadmium chloride, which is deposited next in bunches of fine radiating needles and hexagons, (Fig. 5, Plate I). Many of the latter have incurved sides, and these seem to be quite distinctive.

Sometimes the convexity is outwards, and then the outline of the crystal often approaches that of a circle. When only perfect hexagons are seen, these cannot be distinguished with certainty from those of bismuth chloride (Fig. 6, Plate I); although the latter, being somewhat deliquescent, require more time for their formation, and are often the centres of radiating, acicular bunches.

In the presence of Bismuth chloride, the existence of Cadmium should be verified by forming its double chloride with potassium, (Fig. 7, Plate I). By evaporating a drop of the solution, simply placed in contact with one of potassic chloride solution without stirring, the crystals of double chloride appear only on the dividing line, as in Fig. 8, Plate I.

III. Dissolve a portion of the precipitated carbonates in acetic acid. The carbonate of copper dissolves quickly with effervescence, and, if in large quantity, is at once deposited again in beautiful, deep blue crystals of the monoclinic system (Fig. 9, Plate I), often forming twins, which fall in heaps in the track of a stirring rod. The other carbonates dissolve quite slowly; and, being very deliquescent, do not crystallize when the solution is evaporated at a gentle heat.

Scheme for distinguishing Barium, Strontium and Calcium, in presence of each other:

Precipitate the group by ammoniac carbonate. Wash and dissolve the precipitate in chlorhydric acid.

I. Let a drop of the solution evaporate spontaneously. The chlorides of Barium, Strontium and Calcium can often be recognized in this way. The chloride of calcium crystallizes in large, radiating prisms with oblique ends, (Fig. 10, Plate I). It is a beautiful sight to see the finer, moss-like forms of strontic chloride (Fig. 11, Plate II), creeping across the field, or the more branching, dendritic crystals of baric chloride, which often come down in four or six-rayed stars, as do these of strontic chloride occasionally. The latter, however, generally forms a 60° cross, while baric chloride has the arms more frequently at an angle of 90° , and more profusely branched. But there is nothing very definite in these, and we have seen the greatest variety in the crystallization of baric chloride of any substance tried.

II. To another drop of the solution add alcohol. Baric chloride comes down in dense heads (Fig. 12, Plate II), reminding one of the ripe heads of dandelions, although the resemblance would not hold good when minutely examined. The first precipitate is sometimes followed by bundles of irregular plates, (Fig. 13, Plate II).

In the absence of calcium, alcohol precipitates chloride of strontium in fine needles, separate, and also in stellate bunches, (Fig. 14, Plate II). These soon dissolve as the alcohol evaporates, and are succeeded by rhombuses.

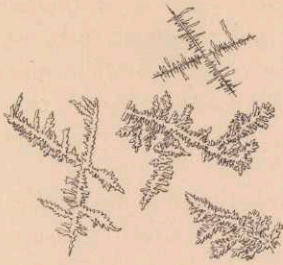


Fig. 11
x 25

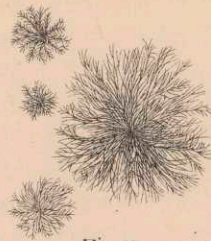


Fig. 12
x 25



Fig. 13.

Fig. 2.
x 25



Fig. 14. x 25



Fig. 16.
x 100



Fig. 15. x 25



Fig. 22. x 25



Fig. 19.
x 100



Fig. 17.
x 100



Fig. 18.
x 25

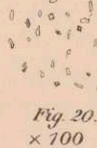


Fig. 20.
x 100

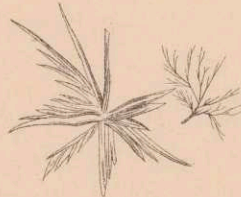


Fig. 21.
x 25



Fig. 23.
x 100

Calcic chloride is not precipitated by alcohol.

III. Dilute a portion of the solution, and add ammoniac oxalate (1-1000 N. S.). It is necessary to wait a short time for this reaction, as the first precipitate is very finely divided, but is gradually succeeded by another one, which is much coarser, particularly in the case of barium. The first finely divided precipitate of baric oxalate will entirely disappear in the course of ten or fifteen minutes, and will be succeeded by branching forms (Fig. 15, Plate II), looking sometimes like a deer's antlers. Strontium is precipitated in pointed crosses (Fig. 16, Plate II), while the oxalate of calcium (Fig. 17, Plate II) is too fine to be recognized with a $\frac{1}{4}$ objective.

Add enough chlorhydric acid to the precipitated oxalates to dissolve them. Then neutralize with dilute ammonia water. The oxalates will be thrown down again, but will have a slightly different aspect, as represented in Figures 18, 19 and 20, Plate II.

IV. An alcoholic solution of picric acid produces a precipitate in the aqueous solution of the chlorides, for the picrates of this group are all insoluble in alcohol. However, the picrates of barium (Fig. 21, Plate II) and of strontium (Fig. 22, Plate II) differ only in size; and the feathery picrate of calcium (Fig. 23, Plate II) does not always come down with sufficient clearness to be distinguished.

V. In the reactions which we have tried thus far, calcium has given the finest precipitates, and the ones most difficult to recognize. All this is reversed when we come to the sulphates. The precipitates of baric and strontic sulphates are too fine to be recognized, while sulphate of calcium forms large, radiating, acicular bunches, something like those in Fig. 14, Plate II, but much thicker. To obtain these, dilute sulphuric acid (1-100 N. S.) is added to the solution of the chlorides. The sulphate of calcium will not come down at once, if the solution contains but little calcium. Upon evaporation, however, the crystals will appear. In the presence of much barium and strontium, it may be necessary to use a more dilute solution, so that the dense cloud produced by the very minutely divided sulphates of these elements, may not obscure the calcic compound.

In conclusion, it may be remarked, that the value of these methods has been tested by the successful analysis of such solutions as would occur in practice.