coloring, and of the manufacture of photographic materials and of modern explosives have to deal primarily with substances in this peculiar state of aggregation; that the clarification of syrups and other liquors and that of water and sewage by precipitation are based on the phenomena of absorption by colloidal substances; that it is with these substances as constituents of living bodies that physiology is mainly concerned; that they constitute the culture-media of the bacteriologist, to the employment of which the development of his science is largely due; and that to the geologist the phenomenon of the sedimentation of mud and slimes, which is closely related to that of the coagulation of colloidal suspensions, is one of much interest.

With these brief indications of the importance of the subject, I must now conclude this very inadequate survey of it. It remains only for me to express to you my thanks for your kind attention.

NOTE ON THE EFFICIENCY OF CENTRIFUGAL PURIFICATION.

By Theodore William Richards.

Received December 14, 1904.

For many years the advantages of centrifugal separation of mother liquor from crystals have been realized by technical chemists in the preparation and drying of sugar and many other substances. Probably also the washing of these substances during rapid rotation has been practiced by many. Certainly both these operations have frequently been used in this laboratory for the preparation of the pure substances necessary in precise work. Nevertheless, there is known to me no quantitative study of the efficiency of these processes; hence a short note concerning a brief series of experiments (made in the first place merely to determine the grade of purity which was probably being attained in a special series of consecutive recrystallizations) may be of service.

In the following tests, sodium nitrate was selected as a typical substance, and to it was added an impurity (nitric acid) whose quantity could easily be estimated. Sodium nitrate was chosen

because a little over half of the dissolved salt may easily be reclaimed by cooling,—an average yield—and the crystals are not of the needle or plate-like forms which commonly retain much mother liquor. Hence they would indicate a minimum, rather than a maximum, advantage in centrifugal action.

For the first series of experiments, 450 grams of this salt were dissolved in 220 grams of boiling water, and to the solution was added 15 grams of nitric acid (sp. gr. 1.40). Thus the original mixture was a solution of the salt with about 2 per cent. of impurity. It remained to determine how effectually the impurity could be removed by centrifugal separation.

The mixture was allowed to crystallize, 240 grams of salt separating out. The resulting mother liquor was about half normal in nitric acid. Upon draining it off by gravitation alone from the crystals, and shaking them together several times, about 3.5 to 4 cc. of this mother liquor were found to be retained by 10 grams of crystals. This volume corresponds to about 0.1 gram of nitric acid. The crystals thus now retained 1 per cent. impurity. With the help of a filter-pump and punctured diaphragm about half of this was removed, leaving still 0.5 per cent. of impurity.

The crystals were now transferred in bulk to the porcelain basket of a centrifugal machine. This basket had a radius of 65 millimeters, and could be rotated 2000 times in a minute. It was found that two minutes whirling or 4000 revolutions removed two-thirds of the residual mother liquor; and after washing with 0.025 liter of water, while rotating, somewhat over two-thirds of the remainder were removed.

The last mentioned portions of 10 grams (the weight of crystals removed for each test) thus contained only 0.005 gram of nitric acid, 0.05 per cent.) or only a twentieth of the amount which was retained when the mother liquor was merely allowed to drain by gravitation.

The crystals remaining were once more washed while whirling with a little water and dissolved in the least possible amount of boiling water and recrystallized. The mother liquor thus resulting was only 1/300 normal in nitric acid, or a hundred and fifty times as dilute as the previous mother liquor. Upon whirling the crystals for two minutes 10 grams of them were found to retain as before about 0.5 cc. of mother liquor, this time corresponding to 0.0001 gram of nitric acid or 0.001 per cent. Another slight

washing while in rotation removed nine-tenths of this acid, leaving only about 0.00001 gram of nitric acid in 10 grams of salt. This impurity of only 0.0001 per cent., or one part in a million, which needed delicate indication and titration in order to be detected at all, would be injurious in only very few cases.

Thus two crystallizations, each followed by centrifugal separation and a little centrifugal washing, had removed 19999/20000 of the impurity, leaving the salt practically pure.

The comparison of this procedure with the simple process of gravitational draining is instructive. Two crystallizations, followed merely by draining, would have removed only about nine-tenths of the impurity, since only about two-thirds of the mother-liquor can be thus decanted. Two more recrystallizations would have removed nine tenths of the residue, and two more, nine-tenths of that. Thus after six recrystallizations the remaining crystals would still have retained 0.002 per cent. of nitric acid or twenty times as much as was left after the *two* centrifugal treatments. Three *more*, or in all nine successive recrystallizations, would have been needed to attain this latter degree of purity; and any one having had experience with this operation can imagine the small residue which would then remain. If as much as half of the substance was recovered each time,[1] 0.2 per cent. or about 2 grams would remain as the total product from a kilogram after nine recrystallizations, whereas the yields after centrifugal treatments, each time washing with 50 cc. of water, would be 500 grams — 44 grams[1] = 456 grams after the first treatment, and one-half of 456 grams — 44 grams = 184 grams after two treatments.

In the first test much of the material was used in the successive analyses, hence a new series of two crystallizations was made. The yield and degree of purity corresponded satisfactorily with the preceding calculations.

In short, in the case of sodium nitrate, with two crystallizations, the salt obtained with the help of centrifugal separations and centrifugal washings is two thousand times as pure as that obtained merely by gravitational drainings; and for the attainment of an equal degree of purity the yield is about a hundred times as good by the centrifugal process, as it is by the draining process. The saving of time and labor is obviously very great.

[1] The solubility of sodium nitrate at 20° is 44 grams in 0.050 liter of water.

Of course these approximate figures, based upon actual experiment concerning a single salt, will not apply exactly in all cases. The size and form of the crystals, the percentage of salt recovered during each crystallization, the solid solution of isomorphous substances, inclusion, adsorption, the time and centrifugal intensity of the draining, and other circumstances, will effect the results. Nevertheless the general principle must apply in all cases. When the crystals are needle-shaped or when the solubility is very great, the gain in efficiency may be even greater, as was shown in an experiment with sodium chromate, $Na_2CrO_4.4H_2O$. This salt, crystallizing in long prisms, was found to gain over twice as much advantage as sodium nitrate from centrifugal treatment.

The analyses of the figures given above shows the great saving of time and efficiency to be gained by centrifugal washing alone. In these tests two-thirds to nine-tenths of the adhering mother liquor were in each case removed with a minimum of labor and very little loss of substance. The washing was conducted by simply allowing a fine stream of cold water blown from a wash bottle to play upon the rapidly rotating substance for a minute or two. This accomplished as much as two or three successive recrystallizations would have done without centrifugal action.

The process of centrifugal washing seemed worthy of a special test. Accordingly, 200 grams of fine crystals of sodium nitrate crystallized from an acid mother liquor were sprayed by degrees with 0.2 liter of water, the outflowing solution being tested from time to time.

The efficiency of the washing progressed with great regularity until about 0.15 liter of water had been used. This amount dissolved about 40 per cent. of salt and the washings of the salt were at this time less than a hundredth as acid as the original mother liquor. Further washing seemed to diminish the acidity but little, probably on account of the mother liquor included in cells in the crystals, hence the limit had been reached, and another crystallization must be made to attain greater purity.

Since 60 per cent. of the salt (120 grams) remained after this treatment, containing only 1 per cent. of the impurity which would have adhered to it without the centrifugal washing, it is clear that this process is a highly advantageous one. It is not, however, the most advantageous, there being two practical disadvantages in its action. One of these is the danger of uneven spraying, and the other the likelihood that even with the most even

distribution of the water some of the interstices between crystals might be untouched. Moreover, time is needed for mixing the impurity with the wash-water. These possibilities were very kindly pointed out to me by Dr. W. A. Noyes, who suggested that it might be more certain and effective to stop the centrifugal machine several times and stir the crystals each time with a small quantity of washing fluid. Accordingly, upon his suggestion, this procedure was tested. Because in the foregoing experiment the superficially clinging mother liquor was hard to distinguish from that included in cells within the crystals, the procedure was somewhat altered in this new trial.

In order to test the efficiency of the washing alone, crystals obtained from a *neutral* solution were thoroughly moistened with a normal acid solution and equal portions were tested by each of the two methods. The method suggested by Noyes proved itself to be the most efficient and trustworthy, in every case greatly exceeding the spraying process in effectiveness. For example, in one experiment 250 grams of fairly large crystals of sodium nitrate were stirred with 0.057 liter of normal nitric acid, enough to dissolve just 50 grams. The 200 grams of crystals remaining were whirled and then carefully stirred into 45 cc. of water—enough to moisten them thoroughly. After another whirling, two-thirds as much more water was stirred in, and after yet another whirling, 25 cc. more. Upon finally separating the mixture by centrifugal action, the residue of 110 grams of crystals was found to contain only a barely perceptible trace of acid. The three wash waters, each collected after thoroughly cleansing the apparatus, were respectively 0.06 normal, 0.006 normal, and 0.0004 normal. Thus the mother liquor had been diluted the first time to one-sixteenth its original strength, the residual liquid had been diluted again to one-tenth of that, and finally the last wash water effected a further diminution to one-fifteenth of the previous washing. Similar tests using the same amount of water continuously always left a larger yield of crystals, because the outflowing solution was not saturated, but never produced so pure a substance. Indeed, in one case the salt continuously washed contained fifty times as much acid as that found in the experiment detailed above, and with careless treatment the residual impurity might be even much greater. Similar confirmatory experiments were made with finely divided sodium chloride with similar results.

Obviously, then, this method of washing by repeated stirring with small quantities of water and subsequent centrifugal treatment is higly efficient. The extent to which it may replace repeated crystallizations must vary so much in individual cases, with the ratio between the superficially and the internally imprisoned impurity, as to make exact calculations difficult; but in most cases it would probably be best to wash twice with small portions of water (enough to give the crystalline mass a pasty consistency) between each recrystallization.

Obviously the reason why centrifugal washing is so efficacious is simply because as much as possible of the preceding impure solution is removed before a new portion of wash water is added, hence a small amount of water will accomplish great dilution of the impurity.

From these remarks, it is clear that any one having a pure substance to prepare in large quantities would do well to find out how he could best combine in his particular case centrifugal washing with repeated crystallization in order to obtain a maximum output with the least labor and waste.

The application of centrifugal separation and washing need not be confined to a preparation on a large scale, however. The organic chemist has often a minute amount of a pure substance whose economical purification may be of the utmost significance to him. The principles in question apply just as well to such cases as to the manufacturer.

For manipulating very small quantities I have found it convenient to use a small centrifugal machine with aluminum containing tubes hinged upon a rapidly rotating axle, of the type so much used by technical analysts to hasten the separation of precipitates. Into the aluminum tubes are placed glass tubes suitable for containing the crystals to be freed from impurity. Several shapes may be used for these glass tubes, but the three forms shown (Figs. 1, 2 and 3) are especially convenient. In order to hold the crystals during the centrifugal separation either the containing tube is narrowed (Fig. 1) or a diaphram or bulb is placed across it (Fig. 2), about one-third of the distance from the bottom. In order that the mother liquor may be removed by suction without disturbing the crystals, a fine glass tube should be in-

Fig. 1.

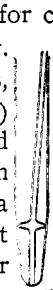

Fig. 2.

serted as far as the bottom of the receptacle. This protruding tube should be bent or inclined to one side so as to interfere as little as possible with the filling. The two opposite arms of the centrifuge should of course be equally weighted. The single tube may be replaced by two tubes, as shown in Fig. 3. This last arrangement is in some respects the most convenient of all.

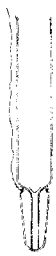

Fig. 3.

Yet another form of apparatus has been frequently used here, in work upon atomic weights. This apparatus may be described for the benefit of those unable to obtain the forms described above, because it is extremely inexpensive, and may be made by any one (see Fig. 4). Fig. 4 is three-sixteenths regular size. It was based on a form used by Professor Landolt long ago, although not resembling this in detail. A very stout large test-tube, intended to hold the crystals, was provided with a fine exit tube at the bottom; this exit tube was passed through the doubly-bored stopper of a smaller test-tube, designed to hold the separated mother liquor. A small platinum cone or bead supported the crystals. Each test-tube was provided with a bucket-like handle of stout wire, of copper or better of platinum, the wire from the smaller tube being firmly fastened to that around the neck of the larger one. To the larger wire-handle was attached a strong leather strap, or very stout closely woven cord, about 75 cm. long, by means of which the apparatus was whirled in the air as rapidly as possible in a circle nearly two meters in diameter. The radial support must be very strong, and not easily cut or frayed, because the strain is great. In our most accurate work, a platinum funnel has replaced the larger glass tube as a support for the crystals. This apparatus must be used only in an empty room, with great caution, since the strap may break, and might give rise to serious injury. On the whole, however, the gain from this extremely efficient apparatus has in our hands exceeded greatly the loss caused by its occasional destruction. Nevertheless, if obtainable, the rapidly revolving basket of porcelain or platinum, or the test-tube centrifuge, with aluminum guard-tubes so firmly mounted as to preclude disruption, is to be preferred on the score of safety.

Fig. 4.

In brief, the contents of the present note may be summarized as

follows: The very great gain in time, labor and material effected by centrifugal draining and washing during the purification of crystals is demonstrated by quantitative experiments, and simple forms of apparatus are suggested which secure these advantages to the organic chemist or to the worker with small quantities of precious material.

THE WATER OF THE YUKON.

BY F. W. CLARKE.

Received December 7, 1904.

ANALYSES of river waters are commonly made with reference to one or another of three distinct purposes, which we may call, respectively, the technical, the geological, and the sanitary. To the geologist, who requires a complete determination of the inorganic contents of a water, the data are interesting in so far as they help to elucidate the problem of "chemical denudation"; that is, to show how much material is removed from the surface of the land, and transported to the sea. On this subject much has been written, but the conclusions have been drawn from incomplete or defective evidence, as I shall show in a future publication. The present note is merely an addition to the list of available analyses, and it relates to a region for which, hitherto, no data existed.

On June 14, 1904, Mr. F. L. Hess, of the U. S. Geological Survey, collected, at my request, a sample of water from the Yukon River. The sample was taken in midstream, above the town of Eagle, a little below north latitude 65°, and nearly on the boundary between Alaska and Canada. It was fairly but not absolutely clear, and contained 0.1565 gram of suspended, inorganic sediment, as weighed after ignition. The soluble, inorganic constituents of the water are given in the subjoined analysis by Mr. George Steiger, and there was also some organic matter undetermined. The CO_3 represents normal carbonates only, in order that the water may be compared with others which are stated in similar terms; the silica and alumina are conventionally reported as present in colloidal form.