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CURRENT NOTES ON CHEMISTRY.—IV.

(*Edited by Charles Platt, Ph.D., F. C. S.*)

ADVANCE IN THE ANALYTICAL CHEMISTRY OF RECENT YEARS.

PROF. ALBERT B. PRESCOTT has outlined some of the most distinctive advances of analytical chemistry in a paper read before the World's Congress of Chemists. First we have "the resolute attempt to find out the composition of matter, as a whole, in any and all of its mixtures of whatever source." Complete analysis, proximate and ultimate, of complex substances has been entered upon, and "undetermined residues" have been made the beginning instead of the end of chemical research. The courage of analytical effort in recent years has been seen especially in the elaboration of methods for the isolation of carbon compounds, both natural and artificial. Proximate organic analysis has been called for by many practical workers, and we are now enriched by the labors of thousands in this field, which was opened largely by Dragendorff and Hoppe-Seyler. We have an increased knowledge of the molecular structure of bodies produced by nature—mineral, vegetable, and animal, as well as those of artificial production. Important advance has also been made in the employment of physical methods of inspection whereby molecular change is avoided. We have but to mention in this connection the multiplication of optical methods, the polarimeter, the refractometer, the spectroscope, recent studies in molecular mass, the freezing and melting points, solutions, adhesion and capillarity.

An exhibition of advance made is furthermore found in the reciprocal benefits of scientific research and of technical skill as seen in the work of experts in biological and pathological analysis, sanitary and forensic analysis, in the industries, and in agriculture and metallurgy.

SODIUM PEROXIDE IN ANALYSIS.

Probably no other recent addition to the reagents of the laboratory has become of such importance as has the peroxide of sodium, $Na_2 O_2$. Its superiority as an oxidizing agent is firmly established, both because of its purity and because of its rapidity of action; and while but a few years ago it was something of a curiosity, it is now an article of commerce used in industrial operations, as well as in the finer applications of the laboratory. So long ago as 1871 Dr. John Clark pointed out, through the *Chemical News*, the strong oxidizing power of a mixture of caustic soda and calcined magnesia, and, a little later, illustrated the value of this action in the analysis of sulphides. As Dr. Clark states in a recent paper in the *Journal of the Chemical Society* (London), the exact cause of the above action was not quite clear at the time, but has since been determined by him to be due to the formation of the peroxides of sodium and magnesium. Hempel shows the superiority of the peroxide for the detection of chromium and manganese, and for rendering titaniferous iron ore soluble, but considers that for the oxidation of sulphur compounds that the addition of sodium carbonate is necessary to reduce the violence of the action. Clark, however, in the article referred to, prefers to use the peroxide without admixture with carbonate, stating that when a sufficiently low temperature is employed there is less tendency to loss by spurting and the action is completed in less time. In the analysis of pyrites, the procedure is as follows: One part, by weight, of the pyrites is mixed with six parts, by weight, of sodium peroxide in a platinum or nickel crucible, placed about two inches above a very low Bunsen flame. Oxidation immediately sets in and the mixture becomes red-hot. A few minutes suffices for the action, and upon its completion the sulphur is easily soluble in water. The solution is acidified and the sulphur precipitated as barium sulphate. In the case of blende part of the zinc dissolves with the sulphur, so that when it is desired to determine the zinc also the mixture is acidified with hydrochloric acid and precipitated with sodium carbonate before filtration. Galena, after treatment with peroxide, yields part of its lead into solution, and it is therefore advisable to acidify slightly with nitric acid and to boil with excess of sodium carbonate, when all the lead will be rendered insoluble, and upon filtration the whole of the sulphur will be found in the filtrate. By fusion with peroxide, arsenic is converted into soluble arsenate, and may then be estimated by any of the ordinary methods.

Dr. Clark uses peroxide of sodium most advantageously in the estimation of chromium and in the analysis of chrome ore. The temperature should not be so high as to liquefy the mixture, but just enough to form a paste, under which condition the contents of the crucible shrink, leaving a space between the mixture and the walls of the crucible. The mass is extracted with water and the solution boiled to decompose any excess of peroxide if the chromium is to be titrated. The insoluble residue dissolves easily in hydrochloric acid, and should be tested for any traces of undecomposed ore. The beauty and ease of this process can only be fully realized by analysts who have had practical experience with refractory chromium compounds. The analysis of ferro-chromium is conducted in the same manner, the metal being first reduced to a fine powder and then mixed with six times its weight of peroxide. This reagent is also applicable with some modifications in procedure to the quantitative estimation of chromium in steel, and in the quantitative separation of manganese from zinc, nickel and cobalt, the solution in this latter case being made in cold water, to avoid decomposition, which gradually sets in. In the separation of zinc and manganese, the latter is thrown down perfectly free from the former by the addition of peroxide to the ammoniacal liquid, or, as is recommended in the separation of manganese and cobalt, that the cobalt should be in the highest state of oxidation, the sodium peroxide may be added to the cold acid solution before rendering it alkaline with ammonia. In the separation of manganese from nickel and cobalt it is advisable to redissolve and to repeat the operation. Another valuable application of sodium peroxide is in the breaking down of tungsten minerals for analysis.

In a paper read before the British Association, at the Nottingham meeting, Dr. S. Rideal and Mr. H. J. Bult propose the use of sodium peroxide as a substitute for alkaline permanganate in water analysis. It is hoped thereby to throw light upon the character of the organic nitrogen in the water by differentiation in comparison with the results obtained using potassium permanganate. With 1 gramme of the peroxide for 1-2 litre of water the total ammonia evolved equaled 0.027 parts per 100,000, while with the permanganate 0.050 parts per 100,000 were obtained. Repeating with the same water gave with the peroxide 0.026 parts, and with the permanganate 0.048 parts per 100,000.

The addition of a further quantity of sodium peroxide and further distillation failed to increase the amount of ammonia produced, hence it is evident that the peroxide does not break down certain of the nitrogenous contents, and it was found possible to obtain a fresh quantity of ammonia after the distillation with peroxide by adding the permanganate. Some of the results obtained were as follows:

Water.	Free NH_3	NH_3 by sodium peroxide.	NH_3 by potassium permanganate after the peroxide.
A,	0.01	trace	0.007
B,	0.001	0.004	0.011
C,	0.012	0.011	0.015
D,	0.021	0.024	0.057

Water.	Free NH_3	NH_3 by permanganate.
A,	0.01	0.008
B,	0.001	0.013
C,	0.012	0.027
D,	0.019	0.078

The sodium peroxide thus liberates a portion of the ammonia, and apparently this is included in that set free by potassium permanganate. There is evidently no ratio between the two, and hence we may have a means of differentiating. Wanklyn's method also indicates a differentiation of the nitrogen, but the problem is too complex to be of service. A water after being partially oxidized by the peroxide yields its nitrogen more quickly than water not so treated, and it is suggested that this is due to the partially oxidized nitrogenous substances being left in such a condition as to be readily broken up by the stronger reagent.

The Bacteriological Examination of Water.

According to C. E. Cassal, F. I. C., in a recent report abstracted in the *Chemical News*, the assertions that the bacteriological examination of water indicates its condition with relation to disease germs and that the analytical method gives the past history of a water rather than its present condition, are entirely devoid of foundation. "The so-called analytical method is the only one whereby a knowledge of the actual conditions of a water can at present be attained, whatever views may be held as to the degree of efficiency possessed by *any* method for arriving at an accurate knowledge of such condition." The bacteriological examination depends upon the successful cultivation of micro-organisms and their spores in a nutrient media, such as "nutrient gelatin" and meat broth, which may be carried out on a minute portion of a sample, and consequently can hardly be representative. The difficulties are in the method itself, in the small sample, in the particular treatment which is artificial and unlike the conditions of the body, and which, only if successful, gives some knowledge of the organisms present. Negative results are practically worthless. A further difficulty is the recognition of disease-producing germs as such when found.

Mr. Cassal is an extremist, but we have many such upon the opposite side, and undoubtedly we shall hear from them.

Nature of Red Phosphorus.

When exposed to the direct sunlight under water common phosphorus becomes covered with a red coating, and the same red modification is formed in abundance by heating in an atmosphere of CO_2, or other inert gas, to a temperature of between 235°–250°. The red variety is insoluble in carbon disulphid, undergoes no change in dry air, and may be heated to 250° without taking fire. The density is, furthermore, always superior to that of white phosphorus, though it is not constant, varying with the conditions of preparation. Commonly red phosphorous is spoken of as amorphous, and it was formerly so considered, but the error of this was shown by MM. Troost and Hautefeuille, who obtained a crystalline variety at 580° having a specific gravity of 2.34 (that obtained at 270° has a sp. gr. of 2.15). Mr. Hittorf had previously obtained a black crystalline variety by heating with lead to a red heat in a tube, without contact with air. After cooling, the lead is dissolved in dilute nitric acid and the crystallized phosphorus left as a residue. J. P. Cooke describes rhombohedral crystals of this substance.

The nature of red phosphorus has recently been under discussion in Germany. J. W. Retgers (*Zeitschrift fur anorganische chemie*) has made microscopic examinations in polarized light, and finds that the smallest and thinnest particles are distinctly transparent, though owing to their high index of refraction most of the light, with the exception of a central red glimmer, is internally reflected. When, however, the internal reflection is diminished by moistening with a highly refractive liquid, such as methylene iodide, the particles transmit a clear, ruby-colored light. In polarized light these show extinction in two mutually perpendicular planes, and they are consequently described by Retgers as crystalline, he considering the refractive power as too great to be accounted for by internal stress in an amorphous body. A few short prisms were observed, but the crystal system has not as yet been determined. Referring to the "metallic" phosphorus obtained by Hittorf, Retgers concludes that it is merely a better crystallized form of the red variety. The black color may be due to impurities, arsenic or lead. W. Muthmann criticises Retgers' article, and points out that red phosphorus is dimorphous, and that in the commercial product we have frequently a mixture of crystalline and amorphous forms. According to Muthmann, when phosphorus is heated in an atmosphere of CO_2 at 230° for 24 hours the product is principally amorphous, but is also crystalline in part. If the experiment is conducted in a glass tube the separation of the two is accomplished, as the amorphous variety sublimes and the crystalline does not. The sublimed portion has the optical properties of an amorphous substance. From the assumed greater purity of the sublimate it is argued that the presence of impurities, as for instance, arsenic, may favor the formation of crystals.

The Origin of Petroleum.

Among the papers presented in Chicago was one by Dr. C. Engler on the artificial production of petroleum, of both chemical and geological interest. Dr. Engler briefly reviews some of the better known of the various theories on this subject, as, for instance, that of Sokoloff, that petroleum was produced during the formation of our planet out of cosmical hydro-carbons, which, in the beginning, dissolved in the soft mass, separated from it later on. Mendeljeff assumes that water entering by fissures and chasms into the interior, comes into contact with melted carbide of iron, and produces by interchange oxide of iron and hydro-carbons of petroleum. The "distillation theory" is dismissed, for chemical and geological reasons—first, because it is difficult to conceive of the substance of plants being split up by distillation into petroleum without leaving a residue of charcoal or coke, while in nature, according to Dr. Engler, we have no connection between doposits of coal and the occurrence of petroleum. Another theory, defended by Whitney, Hunt, Höfer and others, ascribes the origin of petroleum to animal remains. To test this latter theory, Dr. Engler has conducted a series of experiments so successful as to demonstrate clearly its possibility, at least, if not its probability, from a chemical point of view. First, some thousands of salt-water fishes were distilled under strong pressure, with the production of a liquid containing nitrogenous bases such as pyridin, but having no similarity to petroleum. Recalling experiments of Wetherill and Gregory as to the nature of so-called "adipocere," the idea was conceived that possibly in nature the nitrogenated animal substances were destroyed and the fatty residue converted into petroleum. Animal fat (train oil) was submitted to distillation under a pressure of 25 atmospheres at a moderate heat of 300°–4008, and it was found that 70 per cent (or 90 per cent of the theoretical) of the train oil was transformed into petroleum. The same results were obtained from the other fats like butter, hog fat, artificial fats, the free, fatty acids, etc. Not only illuminating oils were obtained, but also the lighter hydro-carbons, gasoline, ligwin, benzine, etc., and in those parts of the crude oil which show a high boiling point were found and separated paraffin wax and lubricating oils. "As a matter of fact," says Dr. Engler, "I have found in the distillate obtained by decomposition of train oil nearly all of the constituents which have been separated from the natural crude petroleum, and even the gases, which, like natural gas, consist essentially of marsh gas." For the chemism of the formation of the hydro-carbons, Dr. Engler refers to a recent paper in the *Berichte der Deutschen Chemischer Gesellschaft.*

RETICULATION OF SPINDLE-CELLED SARCOMA.

BY A. COWLEY MALLY, MUNSLOW, ENGLAND.

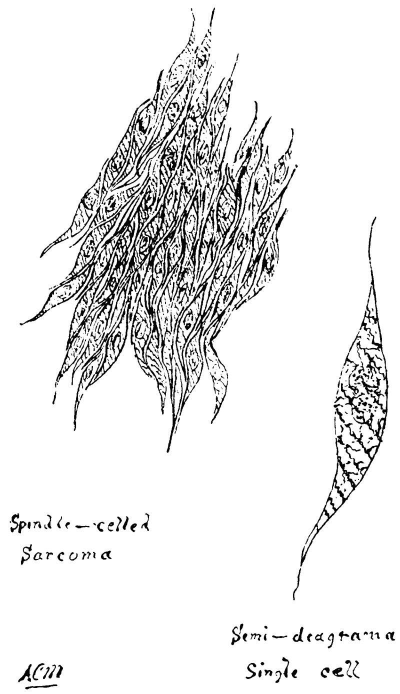
No subject lends itself more freely to errors of interpretation than the description of the microscopical appearances presented by histological and pathological preparations.

Even the delineation, both manual and photographic, of the structure of the Diatomaceæ bear some semblance of uniformity in the descriptions of different observers. Still, to quote Dallinger, "In the present state of the theory and practice of microscopy, it would be extremely unwise to give absolute adhesion to what is now held, by some students of diatom structure of no mean repute and of unrivalled manipulative skill, to be the absolute structure of some of the larger forms."

The same observation applies with still more force to the former investigations, as it is impossible to compare and correllate either the methods of preparation, observation or interpretation of different observers. They all differ, as a rule, in some detail, and in addition there is not only a marked tendency on the part of histologists and pathologists to copy the methods, drawings and results of others, but also a great liability to subjective imitation through suggestion.

Before confining myself to the evidences of reticulation in sarcomal structures, I may mention that the appearance in Polymyxa, so interpreted, is perfectly evident in some individuals and absolutely imperceptible in others. When seen, it is extremely evanescent, and, therefore, can scarcely be looked upon as evidence of the existence of formed material, but rather as the effect of some temporary chemical or physical change in or upon the external surface of the protoplasmic mass. The same or very similar appearances may be observed in Volvox, which are equally erratic, but as they are unquestionably received as the evidence of formed material, the foregoing statement is put forward as only a conditional hypothesis.

The portion of the tumor from which the accompanying sketch is taken was placed in Muller's fluid twelve hours before the sections were cut. These sections were taken from the central portion, where the fluid had evidently no time to act, then slightly stained with carmine, mounted in balsam and in the usual way. On being examined the same evening with a one-sixteenth water immersion and No. 12 compensating eyepiece, it was found that the markings forming portions of the reticulations took a definite direction, that is, obliquely lateral to the long diameter of the cell. This lateral obliquity did not change on revolution of the stage, and therefore cannot be interpreted as the result of oblique illumination. In many of the cells a granular nebular nucleus was observed, connected by slender and almost phantom branches with the oblique lateral markings. At the junction of these branches with the nucleus their point of insertion or outgrowth, as the case may be, seemed to be placed in the hyaline substance surrounding the granules, and unconnected with the granules themselves. This latter observation is not laid down as an established fact, but simply as something more than ordinary conjecture. At the points of junction with the lateral markings there seemed to be definite nodal enlargements increasing in frequency towards the edges of the cell, and the whole section had a peculiar watered-silk appearance, which it was found impossible to represent on paper.



On examination of teased preparations, it was evident that the sections were cut obliquely, as the cells appeared very much elongated; at the same time they showed no reticulation.

Sections from the same portion of the growth were treated with osmic acid and several aniline dyes without effect. I am, however, by no means skeptical as to the results which ought to be obtained in perfectly fresh specimens with chloride of gold. Its manipulation is difficult, owing to the nature of the tissue, changes in temperature, light and color definition, therefore annoyingly variable in its results.

I cannot endorse Chatin's statement, as quoted by Dr. Stokes on p. 374, No. 517 of this journal, that reticulated structure in amœboides and in the blood corpuscles of