

THE ANALYST.

OBITUARY.

FRANCIS SUTTON.

FRANCIS SUTTON, the author of the well-known "Systematic Handbook of Volumetric Analysis," was born in 1831 at Great Plumstead, near Norwich. His father, a farmer, apprenticed him to a Mr. Harper, chemist and druggist, of Bank Plain, Norwich, that he might acquire some knowledge of drugs and chemicals before entering the Veterinary College, London, with a view to becoming a veterinary surgeon. Young Sutton's interest in chemistry, however, showed itself in such a marked manner that he relinquished all further thought of a veterinary career and remained as assistant with Mr. Harper. In 1851 he removed to Newcastle-on-Tyne, where, in partnership with another Norfolk man, he opened a pharmacy in West Clayton Street. In Newcastle he made the acquaintance of other young men of scientific tastes, and took up the study of chemistry with a great deal of ardour. He was encouraged in this by a Dr. Glover, a physician then living in the town, who devoted a good deal of time to medical chemistry and analysis, and who afterwards went to London as Physician to the Royal Free Hospital. Dr. Glover lent him valuable books and employed him in various chemical experiments as an assistant. The doctor also advised him to take up the study of chemistry as a profession. Accordingly, he entered the laboratory of Dr. Richardson, Professor of Chemistry in Durham University, as a student. These studies, however, were brought to an abrupt termination by an urgent request of his former Norwich master, who was in a dying state, that he should return to Norwich and carry on the business of pharmacist in partnership with Mrs. Harper. This he consented to do, and returned to Norwich in November, 1854. While thus engaged, he studied analytical chemistry assiduously, and finally, in 1876, set up in practice as an analytical chemist, breaking away from the business of pharmacy altogether. Some little time before this, he started and became managing partner in a chemical manure works at Runham, Great Yarmouth (Baly, Sutton and Co.), where the manufacture of sulphuric, hydrochloric, and other acids was carried on, as well as that of sulphate of ammonia and other fertilizers. Mr. Sutton was appointed Public Analyst for the County of Norfolk and the County Borough of Great Yarmouth, and was Consulting Chemist and Analyst to the Norfolk Chamber of Agriculture, also Gas Examiner to the City of Norwich. He was a Vice-President

of the Society of Public Analysts, and one of the analytical chemists admitted to the Fellowship of the Institute of Chemistry on its incorporation in 1877. Mr. Sutton was one of the few survivors of the generation of pharmaceutical chemists elected under the Charter and the 1852 Act, and maintained his membership of the Society up to the time of his death. He was early elected to serve on the Council of the Pharmaceutical Society of Great Britain, and held the position for many years. In 1874 he was chosen by the Council as one of its representatives to attend the meeting of the International Pharmaceutical Congress held in St. Petersburg (now Petrograd), and was afterwards elected as corresponding member of the Imperial Pharmaceutical Society of that city and also of the Apotheker Verein, Vienna.

Mr. Sutton's first contributions to scientific literature were two papers on the Determination of Phosphoric Acid by Uranium Solution, which were published in the *Chemical News* (1860, 1, 97, 122). In 1863 he brought out his now well-known work on Volumetric Analysis, which has made his name familiar to analytical and technical chemists all over the English-speaking world. The original edition of this book appeared as an 8vo volume of 282 pages. The following extract from the Preface to this will, I think, be found interesting: "Up to the present time, with the exception of a small and somewhat exclusive book, written by Mr. Scott, of the Trinity Office, Dublin, there has been no English text-book on the subject; the want of this has been felt, and often expressed. I trust I shall not be thought presumptuous in hoping that this treatise will supply that want. The experiments made in connection with the various processes for the purpose of testing their accuracy have extended over several years, and amounted in number to many thousands; the book is therefore based on the right foundation, granting only (and this is of the utmost importance) that the foundation be rightly laid. Very little will be found in it in the way of originality or personal discovery, for I hold to the doctrine advanced by the wisest of men that 'in the multitude of counsellors there is safety,' and consequently have adhered mainly to those processes which have received the approval of general experience. Nevertheless, I trust that whatever is new in system or arrangement may find a generous reception."

Previously, in the same Preface, the author has remarked that "the following pages are devoted, not to a history of all the processes that have been devised and advocated, but exclusively to those which have been tried and found worthy of confidence, for, like all new branches of science, volumetric analysis has had an abundant crop of weeds and rubbish, together with, here and there, sound fruit." Is it too much to ask, in passing, whether this growth of "weeds and rubbish," which Mr. Sutton noticed in 1863, is entirely unknown even in 1917?

From the above extracts it will be seen that Mr. Sutton personally examined and practically vouched for the accuracy of the various volumetric processes described in his book. This arduous, but valuable, work he evidently continued in connection with the preparation of further editions of the work, for we read in the Preface to the Eighth Edition, published in 1900, the following statement: "I must confess that the thorough investigation necessary for new methods or for modifications of those previously known has in many cases been impossible, but an endeavour has been made to insert those only which have been found on experiment to have

some claim to accuracy. The Ninth Edition, published in 1904, was the last that Mr. Sutton was able to produce practically single-handed, and he placed the preparation of the Tenth Edition, published in 1911, entirely in the hands of his second son, W. Lincoln Sutton, and Alfred E. Johnson. A French translation of the Fourth Edition was made by Dr. C. Méhu, and published by Masson, of Paris, in 1885. The book has had a large sale, not only in this country, but also in America and the colonies, and has, in fact, become *the* text-book on the subject in all chemical schools where the English language is used.

One of the penalties of living to an advanced age is that he who attains to it frequently remains as the sole survivor of a group of friends. Mr. Sutton, who lived to celebrate his eighty-sixth birthday, was no exception to this rule, and none of his old professional friends remain to give details of a personal character. In these circumstances the present writer was asked to contribute the obituary notice, a task he would gladly have seen placed in the hands of one who knew Mr. Sutton better. His acquaintance with Mr. Sutton dates back only about twelve years, when, having noticed two important errors in the Ninth Edition of the "Volumetric Analysis," he wrote to the author pointing these out. The result was a letter of thanks expressed in terms of almost boyish enthusiasm. He has only seen Mr. Sutton once, when he spent a week-end with his son Lincoln. Nevertheless, he always looked upon Mr. Sutton as a personal friend, and much regretted he was unable still further to cultivate his friendship. One personal characteristic he may mention was Mr. Sutton's handwriting, which was in that beautiful, round, flowing style that is but seldom seen nowadays.

With increasing age Mr. Sutton had gradually retired from active work in his profession. Since 1900 he has been in partnership with his second son, W. Lincoln Sutton, Public Analyst for the County of Suffolk and the City of Norwich, who has carried on the analytical practice in Norwich and succeeded to his father's appointments, his eldest son, Mr. F. Napier Sutton, being the well-known Alkali Inspector. Mrs. Sutton predeceased her husband by five years, and he leaves six surviving children, three sons and three daughters. Mr. Sutton died on April 16, 1917.

A. E. JOHNSON.



PROCEEDINGS OF THE SOCIETY OF PUBLIC ANALYSTS AND OTHER ANALYTICAL CHEMISTS.

SOME EXPERIENCES IN THE USE OF COPPER SULPHATE IN THE DESTRUCTION OF ALGÆ.

By G. EMBREY, F.I.C.

(*Read at the Meeting, June 6, 1917.*)

IN the year 1870 the author had frequent opportunities for observing the evil effects of the rapid growth of *Algæ* in an artificial lake at Sutton Coldfield, Warwickshire. The growth of weeds during the spring and summer was so rapid that the lake was almost useless for boating or fishing. Attempts were made to destroy the weeds by fixing scythes to the sides of a punt and dragging it through the water, the weeds being removed at intervals by means of rakes; this method was, however, costly and not very effective.

In 1872 a railway line was constructed between Sutton Coldfield and Walsall; an embankment consisting of ferruginous sand passed over the narrow end of the lake, at which the water entered. This sand, washing into the lake during a rainy period, effected in one season what the cutting method had failed to do in seven: the vegetation was almost entirely destroyed and this particular pool cleared of weeds.

In 1873 the author observed the bad odour and colour of the drinking-water in Gloucester. On inquiry he learned that it was due to plants growing in the reservoirs, and he suggested the use of ferrous sulphate. One of the reservoirs was so treated, and in a month the *Algæ* were destroyed. About this time trouble arose at a tannery, the skins being stained red by oxide of iron washed out of the service pipes. This was wrongly attributed to the ferrous sulphate used in the reservoirs, and for this reason experiments were discontinued.

Until 1908 the weeds were removed by rakes worked from punts. At intervals the pools were emptied and the organic mud removed, fifty or sixty men being frequently employed at this work. During the months of July, August, and September the water was badly coloured and gave out so offensive an odour that it was unpleasant to use it even for a warm bath.

In 1901 the United States Department of Agriculture directed the performance of experiments for removing objectionable *Algæ* from water-cress beds by means of copper sulphate. The result was satisfactory, the water-cress plant being in no way injured. In 1904 and 1905 this department issued Bulletins Nos. 64 and 76, the first entitled, "A Method of Destroying or Preventing the Growth of *Algæ* and Certain Pathogenic Bacteria in Water-Supplies;" and the second, "Copper as an Algæcide and Disinfectant in Water-Supplies." Both of these were written by Messrs. G. F. Moore and K. F. Kellerman.

In 1908 the author obtained permission from the Corporation of Gloucester to carry out experiments at their Witcombe Reservoirs, which were at that time choked by a species of *Chara*. These plants are propagated by means of the fertilisation of spores contained in an archegonium. The bursting of the archegonium sets free myriads of minute greenish cells, which gave the water a distinctly green colour, and were also thought to be the cause of the offensive odour.

The pools being periodically stocked with rainbow-trout, it was desirable to use as little copper sulphate as possible. Following the instructions of Messrs. Moore and Kellerman, 1 part of the salt was added to 3,000,000 parts of the water: this removed the odour but not the *Chara*. It was then decided to employ 1 part of the salt to 1,000,000 parts of the water; this destroyed the *Chara* and the fish.

At this period (1908) it was generally thought that *Chara* was the chief cause of both colour and odour, and one observer rather unwisely suggested that it was caused by a new species and named it *Chara fetida*.

The author collected a number of the plants and found them largely covered with *Spongilla fluviatilis* and probably other organisms. These were carefully removed, and the cleansed *Chara* no longer gave out the peculiar odour, while it was very evident in the washings. A portion of the latter was then used to inoculate a nutrient agar-agar medium. This on incubation developed *Proteus vulgaris*—an organism well known to produce a fishy odour. This seemed to account for the trouble, yet I always had some doubts as to its sufficiency.

In 1913 Dr. Houston's valuable work, "Studies on Water-Supply," appeared, and on p. 100 the following occurs: "At the beginning of the year 1913 part of London (Hammersmith, Kensington, and Hampstead) experienced a somewhat serious 'taste visitation,' the Algal growth causing the objectionable taste and smell being chiefly composed of *Tabellaria* with some *Asterionella*."

This gave me a new clue, and as the water from the reservoirs at Witcombe passes through a battery of Bell filters, it was easy to collect the washings and examine for minute organisms. This practice has been continued weekly since the latter end of 1913, and I am now convinced that *Chara* and its parasites only contribute to a small extent in the production of the unpleasant odour.

The most remarkable thing is that, in Dr. Houston's experience, in the London water *Tabellaria* was the predominant organism, and there were only a few *Asterionella*, while at Witcombe the reverse was the case: *Asterionella* was present in abundance, but only a few *Tabellaria*. A considerable number of the former were collected and dried; the mass was then placed in a fat extractor and the oil extracted with petroleum ether. After the removal of the solvent the residue gave out the identical odour which had caused the trouble.

The odour associated with diatoms has generally been ascribed to an essential oil, but this is not so in *Asterionella*. The substance removed by petroleum ether is certainly a fatty oil coloured with diatomin—a body closely allied to chlorophyll.

Works on microscopy make little reference to this diatom, which, considering its wide distribution, is surprising; even such an excellent treatise as Dallenger's edition of Carpenter makes no reference to it. A good description of it is given in

“Microscopy of Drinking-Water,” by George Whipple. The figure given at the end of Dr. Houston’s studies is different from the photographs prepared for this paper.

The frustules each contain three or four rounded openings, and before collecting into stars each moves fairly quickly through the water. It seems probable that the motion is effected by the protrusion of protoplasm through these holes; if this be so, the reason for the presence of a lubricating body becomes apparent. In what manner, then, does the copper sulphate destroy these organisms? Water collected from limestone rocks contains sufficient calcium bicarbonate to bring about the following reaction: The calcium will unite with sulphuric acid to form the sulphate, and the copper will become basic carbonate; this will then give up carbon dioxide and yield a hydroxide which accumulates on the bed of the reservoir. This is the usual explanation, but an observation made by the writer in 1911 shows that under certain conditions the hydroxide will become oxide. As the water was lowered in the pools both cuprous and cupric oxides were observed, red and black bands being visible, the red band below or immediately above the water and the black band some distance above this. This points to a probability that oxide of copper is the real poisoning agent, and if my suggestion be correct that the fatty oil is to serve as a lubricant, the oxidation of this may cause the death of the plant.

EFFECTS OF THE TREATMENT.

1. Slight increase in permanent hardness.
2. Evolution of an offensive odour for two or three days.
3. Increase in the number of bacteria.

The slight increase in permanent hardness is easily accounted for.

The evolution of the offensive odour is probably due to the setting free and oxidation of the fatty oil.

The increase in the number of bacteria appears to be due to the decomposition of the *Algæ*, and quickly ceases, as shown by the following observations:

<i>Date.</i>	<i>Number of Micro-organisms per c.c.</i>
1913. April 12, sulphate of copper added	150
„ April 25	200
„ May 10	110
1914. April 18, sulphate of copper added	140
„ May 2	320
„ May 16	480
„ May 27	350
„ June 17	260
1915. April 23, sulphate of copper added	180
„ May 6	210
„ May 20	150

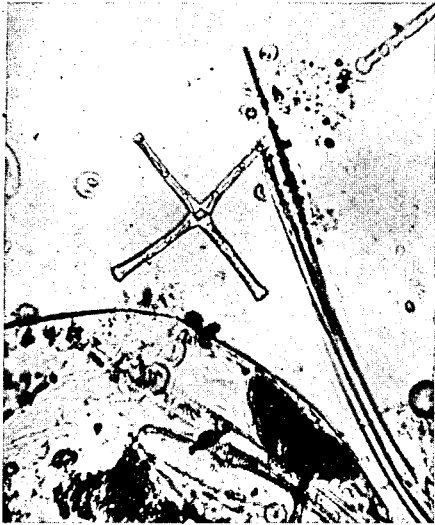


FIG. 1.—ASTERIONELLA FORMOSA WITH FOUR FRUSTULES. (MAGNIFIED 500 DIAMETERS.)

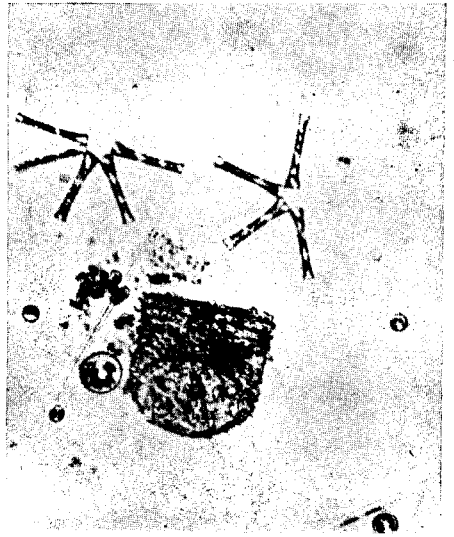


FIG. 2.—ASTERIONELLA FORMOSA: PARTLY FORMED STARS; DIATOMS IN LOWER PORTION.

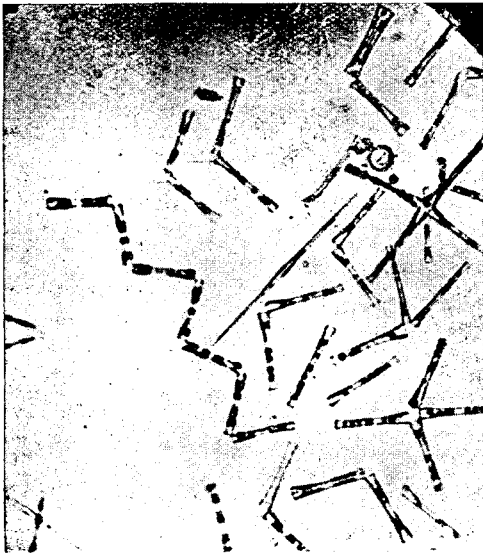


FIG. 3.—MODE IN WHICH FRUSTULES FORM V's AND CHAINS PRIOR TO FORMING STARS.



FIG. 4.—MUD FROM BOTTOM OF RESERVOIR, CONSISTING ALMOST ENTIRELY OF ASTERIONELLA.

<i>Date.</i>								<i>Number of Micro-organisms per c.c.</i>
1916. April 12, sulphate of copper added	125
„ April 19	170
„ May 8	196
„ May 20	148
1917. April 28, sulphate of copper added	170
„ May 12	240
„ May 25	185

After the purification certain organisms increase rapidly. Three of these were very noticeable: *Diffugia*, *Anurea cochlearis*, and *Anurea aculeata*; these probably act as scavengers, and use up the poisoned diatoms.

PRACTICAL APPLICATION.

It would seem advisable to add the sulphate of copper not later than the end of April, so as to destroy desmids and diatoms, and thereby prevent the formation of an organic mass into which the root-like thallus of *Chara* can penetrate; this view is supported by the fact that in these pools *Chara* is now rarely found.

Experience has shown that 1 part of copper sulphate to 3,000,000 parts of water is sufficient, and this amount has no injurious effect on the fish.

It is generally recommended to place the copper sulphate in a canvas bag and trail this at the stern of a boat, but this has not proved so effective as allowing the crystals to fall into the water, and in this way produce greater concentration at the bottom of the reservoir, where most of the diatoms may be found.

It has been the practice at Witcombe to fix a copper tank perforated with holes having a diameter of 4 mm. at the stern end of the punt, and allow the crystals to fall through the holes; in this way they quickly reach the bottom of the pools.

COMPARISON WITH OTHER METHODS.

Of the methods for the prevention of Algal growths the following points may be noted:

1. Covering the reservoirs: This is expensive, and not always effective.
2. Constant cleansing: Expensive, and not effective.
3. Frequent agitation: Fairly effective, but not always convenient.
4. Copper sulphate: Inexpensive, safe when properly controlled; quite effective, increasing in efficiency each year.

The experience at Witcombe has shown that where similar conditions prevail, reservoirs in which a potable water is stored may be kept free from weeds, colourless and odourless, by a simple and inexpensive method.

In conclusion, I would mention that my success has been largely due to the confidence placed in me by a sympathetic and intelligent Municipal Authority, and the ready help of my fellow officials—viz., the Medical Officer of Health and the City Surveyor.

DISCUSSION.

Dr. S. RIDEAL said that his attention had been drawn to this subject about twelve or thirteen years ago by some experiments made in America by Moore and Kellerman, which had for their object the prevention or checking of the growth of *Spirogyra* in water-cress beds. Dr. Baines collaborated with him, and they studied the action of copper sulphate, copper chloride, and metallic copper as "algicides." They soon found that the activity of the copper salts was proportional to the weight of copper in them—i.e., that it was an ionic reaction based on the weight of copper present, copper sulphate and copper chloride being equivalent salts if the weight of copper was the same in each case. It was then found that the action of copper was selective as regards different kinds of organisms; and in studying London tap-water it was found that when different quantities of copper salts were used different organisms survived, so that in that way one could get, in a series of bottles with different proportions of copper, almost pure cultures of the different organisms present. It was found, too, that a piece of metallic copper 1 centimetre square, put into 100 c.c. of water, gave off sufficient of the metal to kill the *B. coli*, streptococci, etc., present, and this seemed to suggest that possibly the use of a copper tank, or the passing of water or sewage effluent through a sufficient length of copper pipe would result in the killing off of all typhoid coli, etc. It also suggested the idea of a copper water-bottle for military use, and such a bottle had actually been made. The use of copper in that way, however, had never been developed, though he thought it would probably prove valuable if the surface of the copper could be kept clean and in a condition to do its work. A friend living in India had observed that the natives who drank with impunity polluted water such as that of the Ganges always used copper vessels for its conveyance, and it might be that the use of copper for the purpose had been adopted as the result of some instinctive knowledge that the water would be thereby purified. In the East, earthenware pots were also used for water, because of their cooling action, and it might be worth while to study what difference there was, if any, between the effects of water stored in copper and earthenware respectively. Europeans in India usually used tinned copper vessels for storing water, and possibly the use of ionic metals in a fine state of division might be among the means of bringing about germicidal action, for it was difficult to see why the same effects which were produced by metallic salts should not be produced by sheets of metal suspended in the reservoir or conduit. Copper had been looked upon as a poison, but Mr. Embrey had shown that it produced no bad effect on fish in the reservoir in question, while the Minority Report of the Departmental Committee on Food Preservatives, on the question of the use of copper in preserved peas, showed that it was not at all agreed that the use of copper in food should be prohibited. Dr. Molson about the same time advocated the wearing of copper discs during cholera epidemics, not as a charm, but as a scientific prophylactic, "on the ground that cholera is absolutely unknown among the workers in copper mines," and said that such discs were used by Baron Fredericks as far back as 1894 in Russia at Nijni Novgorod during a plague of cholera there. The practice of using metallic copper discs against cholera was

common in this country and in France much earlier than this (*British Medical Journal*, 1893).

Professor K. C. BROWNING, referring to the use of copper vessels in India, said that a friend who had made a considerable study of the sacred writings of the East had informed him that in more than one passage reference was made to the fact that water put into a copper vessel was less likely to cause disease. Certainly the use of copper and brass vessels was very common among all classes in the East. As to the question of copper being poisonous, the United States Food and Drugs Board, after exhaustive experiments, came to the conclusion, he believed in 1913, that the presence of copper in food or drink should be entirely prohibited, and it is now an offence against the laws of the United States for copper to be present in any food or drink. It is true that there are people who can ingest small quantities of copper salts for a short time without apparent harm, but this is, of course, no argument in favour of allowing the presence of copper salts in food, especially as some individuals show a marked idiosyncrasy for copper.

In the case of water, this objection would not hold good if the copper is completely precipitated before it reaches the consumer.

Lieut. E. K. RIDEAL said that copper had been long in use as a germicide, not only in the case of water, but for a variety of other purposes which did not seem to bear out the cupric and cuprous oxide theory. For instance, in France very large quantities of copper sulphate were used, in the form of Bordeaux mixture, for the destruction of phylloxera, while for sterilising the surface of seeds copper sulphate was a most efficient agent, 1 part of copper in 700,000,000 being sufficient for the sterilisation of a wheat seedling. When that strength was exceeded the seedling itself appeared to suffer. As a matter of fact, very little was understood about the mechanism of disinfection. Experience had shown that colloidal metals did react with micro-organisms, and, on the other hand, it was known that micro-organisms were really suspensoid colloids protected by emulsoids; the trivalent elements aluminium and iron, and also hydrogen ions, would cause precipitation of such organisms, owing chiefly to the electrostatic charge on the latter. But precipitation did not necessarily mean the death of the organism. Precipitation was also brought about by some divalent metals, such as mercury and copper, and in the case of copper the cupric ion was more effective than the cuprous, firstly because of its higher electrostatic charge, and secondly because the mechanism by which the cupric ion was adsorbed on to the cell wall was different. Copper reacted with cellulose and also with chitin—the cupro-ammonium process for determining cellulose being, of course, well known—while wool, on treatment with cupric ammonium sulphate, yielded amino-acid copper complex with the wool chitin. The activity of the copper ions, however, was much greater towards cellulose than towards chitin, which latter was the main constituent of bacteria, while cellulose predominated in the higher forms of life. It was therefore reasonable to suppose, other things being equal, that copper would be more inimical to organisms in which cellulose predominated than to those in which chitin predominated; and such seemed to be the case, concentrations of from 1 in 1,000 to 1 in 100,000 having, in the American experiments, been found necessary to kill bacteria, while from 1 per million to 1 in 3 million would effect the

removal of *Algæ* and similar higher forms of life. Now, since in the organism, after absorption of the copper, free copper is not present, it seemed to follow that the copper must act in the form of a cupramine base; and, since the reaction with cellulose occurred in presence of ammonia, one might postulate a reaction with the amino-acids in the cell wall of the organism. It would therefore appear that, in tracing the germicidal action of copper on any cell, two different reactions must be followed—namely; first of all, direct absorption, due in certain cases to the electrostatic charge, or in other cases to chemical affinity—*e.g.*, Ehrlich's parisitotropic groupings—or to the absorptive power of the cell membrane itself; and secondly, chemical reaction with the cell constituents, in regard to which it appeared possible that an amino-compound was formed in the case of both copper and chlorine. Chloramines, which were coming more and more into use as germicides, were more active than chlorine itself, since the amino-compound reacted with greater avidity with the cellulose or chitin. Chlorine, too, gave good results as an "algicide," and possessed the advantage that anaerobic conditions were not so easily set up, while there would be no bad-smelling chloramines such as were produced from animal matter, since the vegetable amino-compounds were relatively unstable as compared with those yielded by animal matter.

Mr. W. T. BURGESS remarked that, as was well known, organisms like *Algæ* and diatoms flourished in water containing relatively large quantities of nitrates, so that it would be interesting to know the proportion of nitrates in the water of the reservoir in question at different times of the year. He should also like to ask whether, when the *Chara* was present in large quantities, any considerable reduction was noticed in the hardness of the water. Some varieties of *Chara* had the power of, not exactly secreting, but at any rate causing the crystallisation of relatively large quantities of carbonate of lime on their structure.

Mr. J. H. JOHNSTON said that he understood that some varieties of *Algæ* were capable of becoming acclimatised to small doses of copper sulphate, so that, to be effective, the dose had to be continuously increased. He had no personal experience of this, and understood that it only occurred late in the season.

Mr. A. CHASTON CHAPMAN said that Mr. Embrey's observation as to the increase in the number of bacteria at first, followed by a decrease, was paralleled by an experience which he had had in connection with certain breweries, in which the amount of yeast produced had been very small, the yeast being deteriorated, and the outcrop scarcely more than was put in. That was found to occur in copper-lined fermenting tuns, and particularly in those tuns in which the workmen had scoured the copper very thoroughly. In some experiments which he was thereby led to make on the growth of yeast in wort containing minute and gradually increasing quantities of copper, he had found that the effect of the copper at first was to stimulate the growth of the yeast, it being only when a certain point was reached that the toxic effect became marked, the yeast ultimately being killed. The selective action of copper extended so far that he believed he was right in saying that copper was actually a necessary constituent in certain bodies (*e.g.*, molluscs and crustaceans), while everyone would remember Professor Church's obtaining, from the feathers of certain species of parrots, the compound which he called turacin, con-

taining about 6 per cent. of copper. Predictions as to the effects of copper on any organism should always be avoided, but it was undoubtedly shown by Mr. Embrey's experiments, and by others on the same subject, that as regards *Algæ* and similar lowly organisms of that description, it was markedly toxic and did its work in an admirable manner.

Lieut. RIDEAL mentioned that the late Henry Crookes, in experiments made with discs of metal in Petri dishes, each containing a specific organism, had found indications of the stimulating action referred to. Round each disc there appeared first a zone showing no growth, then a zone showing stimulated growth, and then a zone showing normal growth. These effects were obtained with several metals, including copper, zinc, and nickel, and with a great variety of organisms.

Mr. BURGESS remarked that experiments had also been made in Petri dishes with various metals used for dental purposes, the result being to show that the most effective from a germicidal point of view was the ordinary copper alloy.

Mr. EMBREY, in reply, said that in the case of these reservoirs it did not seem that metallic copper played any part in the destruction of the *Algæ*, since it was hardly conceivable that reduction to the metallic state could have taken place, while the bands of cupric and cuprous oxide were perfectly distinct; but in face of what had been said, it was clear that one could not safely generalise as to this. It would be remembered, too, that Mr. Burgess some time ago had called attention to the fact that the growth of *Algæ* in condensers could be prevented by the introduction of a coil of copper wire; but he had found that after a time the copper coils, although still effective in preventing the growths, were completely covered with oxide. He had asked the opinion of several friends as to the smell of the oil obtained from *Asterionella*, and they all agreed that it suggested rancidity, showing that it was a fatty and not an essential oil; and it might perhaps be conjectured that it was the oxidation of the oil that killed the organism. With regard to nitrates, these were never found in this water. He had not tried what effect the *Chara* might have had on the hardness of the water, and it was now too late, for the *Chara* had all disappeared.



NOTE ON ORANGE-PIP OIL.

BY DOROTHY G. HEWER, B.Sc. LOND.

(Read at the Meeting, June 6, 1917.)

IN the process of producing marmalade, the pips of the oranges are separated by centrifugal means, and in large factories the weight of pips produced in one season is considerable. As far as the author is aware, attempts to utilise the oil for any commercial purpose have only been made on isolated occasions. There seems to be no reason why the pips should not be dried immediately after separation, and the oil removed either by hydraulic pressure or by means of volatile solvents.

A sample of the pips, described as "bitter orange pips," which was examined in the laboratory, were found to consist of—

Kernel	69 parts, by weight.
Shell	31 " "

The pips yielded, on extraction with petroleum ether, 37·5 per cent. of a golden-yellow oil, which is equivalent to 54·95 per cent. of the weight of the kernels.

The oil is almost odourless, and had, when freshly extracted, only a slightly bitter flavour, but the bitterness increased considerably and rapidly on keeping.

The oil is easily saponifiable, and should prove suitable for soap and glycerol manufacture.

The following analytical figures were obtained :

Saponification value	193·7
Unsaponifiable matter	0·14 per cent.
Iodine value	100·3
Refraction at 40° C. (Zeiss)	57·5
Free fatty acids, as oleic	0·3 per cent.
Specific gravity at 15° C.	0·9208
Titer test	34° C.
Neutralisation value	200·1

Apparently the only published figures on orange-seed oil are due to R. Meyer (*Chem. Zeit.*, 1903, **27**, 958), which Lewkowitsch quotes with the remark that they stand in need of confirmation. The figures given above do not confirm his surprising saponification value of 229.

The author's thanks are due to Messrs. Loders and Nucoline, Ltd., for the specimen of separated pips, and to Mr. E. R. Bolton, in whose laboratory the analysis was conducted.

DISCUSSION.

Mr. E. T. BREWIS said that he had had an opportunity of examining a sample of oil from bitter orange pips, but, unlike the author's sample, it had a strong odour of the essential oil of bitter orange, and it was not so clear. The figures it yielded were substantially similar to those obtained by the author, being as follows:

Specific gravity	·922
Saponification value	194·6
Iodine value	97·8
Refractive index at 25°	1·4700
Solubility in absolute alcohol	partial.

It could scarcely be used for anything but soap-making, having too strong a flavour of the bitter orange oil to make it of any use for edible purposes.

Dr. RIDEAL asked whether this oil had anything to do with orange-blossom oil, or perfume of orange-blossom.

Mr. BREWIS said that this orange-pip oil had the odour of bitter oranges or of marmalade, and was quite different from orange-blossom oil, or neroli. As to the essential oils of orange, there were the oil of sweet orange, obtained from the rind; the oil of bitter orange, also from the rind, but slightly different in flavour; the oil

of orange-blossom, otherwise known as neroli; and petitgrain oil, somewhat similar to neroli, but not quite so soft in odour, from the unripe fruits, leaves, and young shoots. There were three or four varieties of oils of neroli and petitgrain on the market, varying in value according to the purity and softness of the odour.

Mr. E. R. BOLTON said that two portions of the oil were obtained, one of which was quite sweet, while the other was bitter. It was the latter sample which was now exhibited.



THE RAPID ESTIMATION OF THE STRENGTH OF SULPHURIC ACID.

BY H. DROOP RICHMOND, F.I.C., AND J. E. MERREYWETHER.

(*Read at the Meeting, June 6, 1917.*)

WHILE it appears a simple problem, the rapid estimation of the strength of sulphuric acid presents many practical difficulties. The direct titration involves a weighing of a very hygroscopic substance, and a titration with a strong standard alkali, which has an appreciable coefficient of expansion; under these circumstances rapidity is not easy of attainment, and we have found that the factors which make for rapidity do so at the expense of accuracy.

The density cannot be employed as an index of the strength, owing to the abnormal density of strong sulphuric acid, the maximum being attained at 97.5 per cent.; the gradients of acids near this strength are so low and the influence of impurities on the density and the temperature corrections sufficiently large to render the calculation of strength from the density unreliable.

We turned to another physical property—the heat evolved on dilution—and found that this gives good results in a minimum of time.

We, of course, make no claim to any originality for the method, but merely have worked out the practical details. So far as we have been able to ascertain, the method was first employed by C. B. Howard in 1886; he communicated his results to the Finsbury Technical College Chemical Society, but we have been unable to find the exact details he used. H. Howard (*J. Soc. Chem. Ind.*, 1910, 29, 3) has described a method for determining the strength of sulphuric acid from the heat evolved on mixing an oleum of known SO_3 content with water, and we have adopted one detail from his paper, the use of a vacuum-jacketed flask as a calorimeter.

Our method consists in measuring 400 grms. of water at about 18° C. into a vacuum-jacketed flask, provided with a stirrer and thermometer reading to 0.01° C. The temperature soon becomes constant and is read off; 5 c.c. of the sample are measured in, allowing the pipette to drain for fifteen seconds, and the mixture stirred till the temperature is constant. No cooling corrections have been found to be necessary.

The water equivalent of the calorimeter was found to be 14.5 grms., and the volume of sulphuric acid delivered by a 5 c.c. pipette 4.911 c.c., varying from 4.869

to 4.926 c.c.; from the mean of these data, and from the results of Pickering (*J. Chem. Soc.*, 1890, **57**, 64) the following formula was calculated:

$$\% = 100 - 7.6 (3.994 - R).$$

With other calorimeters the formula is:

$$\% = 100 - 7.335 \times \frac{400 + w}{400} (4.139 \times \frac{400}{400 + w} - R).$$

There is some slight doubt as to the correct value for the corrections to infinite dilution to be subtracted from Pickering's figures for a strength corresponding to our final dilution, as the two series given by him do not agree very well, but we have taken the mean.

Using this formula, we have found the following results:

<i>R.</i>	<i>Percentage calculated.</i>	<i>Percentage by Titration.</i>
3.635°	97.3	97.4
3.49°	96.2	96.1
3.22°	94.1	94.2
3.15°	93.6	93.6
3.01°	92.5	92.4

The concordance of duplicate determinations has been excellent and usually within 0.02°; for these we have to thank Mr. E. England, whose first results were 3.69° as against 3.70° and 3.71° by ourselves, and 3.205° as against 3.19° by ourselves.

The formula connecting percentage and rise of temperature is not quite so simple as that given, but the errors introduced by the simplification are less than those of experiment.

The method is very rapid, avoids all weighings, does not expose the acid to air, and entails nothing more than rinsing to clean the apparatus; we have been fortunate in finding a thermometer which requires no correction between 18° and 23° C., but, of course, the thermometers must be carefully standardised and appropriate corrections applied.

This work was carried out in the Analytical Laboratory of Messrs. Boots' Pure Drug Company, to whom we wish to express our thanks.



NOTE ON THE ESTIMATION OF THEOBROMINE.

By NORAH RADFORD (NÉE ELLIOTT), B.Sc., AND G. BREWSTER.

(*Read at the Meeting, June 6, 1917.*)

THE estimation of theobromine by Kunze's method (*Zeitsch. Anal. Chem.*, 1894, **33**, 1) of extraction with chloroform, precipitation with sodium phosphotungstate, separation of the mixed alkaloids with baryta, and formation of the silver salt, depends for the final result either upon the weighing of the insoluble silver theobromine compound or upon an estimation of the silver therein. The method has been modified by Monthulé (*Ann. Chem. anal.*, 1911, **16**, 137), and the estimation by

him is made to depend upon a titration of the excess of silver left in a solution after the silver compound of theobromine has been precipitated by neutralising the ammoniacal solution.

In our hands the estimation of the silver has not been found to be satisfactory, especially when the theobromine is impure or associated with other organic matter. The reason is not hard to find. The result is vitiated by the presence of any substance capable of reducing silver. All our estimations of theobromine by the silver method have been too high (e.g., a sample of crude theobromine which showed 92.08 per cent. theobromine deduced from the nitrogen according to Kjeldahl's method, showed in one experiment 110 per cent. theobromine, and in a second 103 per cent., when the silver estimation was made).

To depend upon the results of a direct Kjeldahl experiment performed upon the sample would be equally unsatisfactory, as any other substances present containing nitrogen would interfere. In particular, the presence of small quantities of caffeine is extremely probable. It therefore occurred to us to separate the silver theobromine compound, and estimate in it the nitrogen instead of the silver, and this method gave excellent results, which show that a very complete quantitative separation of theobromine is effected and justify the adoption of the method.

The mode of procedure is briefly as follows: 0.25 gm. of the sample is taken, dissolved in water and 5 c.c. of 0.880 ammonia. [The solution is boiled, and to the boiling solution is added a hot solution containing 5 grms. of silver nitrate.] Any precipitate which forms will redissolve on the addition of a little more ammonia. The boiling is continued until the volume of the solution is about 10 c.c.; before this stage is reached a gelatinous precipitate, which gradually darkens in colour, will have been thrown out. This precipitate, after thorough washing by decantation till free from silver, is transferred to the filter-paper. The filter-paper and precipitate are then treated according to Kjeldahl's method. Then, if 0.25 gm. of the sample be taken, the percentage of theobromine is given by the following:

$$\left(\text{Vol. of } \frac{N}{10} \text{ HCl absorbed} \times 1.80104.\right)$$

A "blank" is made with the Kjeldahl reagents, and this correction is applied. The following results show the accuracy of the method:

The sample before mentioned, which gave 92.08 per cent. by a direct Kjeldahl, showed 91.1 per cent. when the nitrogen in the silver salt was estimated.

A second sample gave 98.6 per cent. according to the direct Kjeldahl, and 98.0 per cent. from the analysis of the silver compound.

With this second sample the following experiments were made:

0.15 gm. was taken and 0.1 gm. of caffeine added. A direct Kjeldahl estimation made on this mixture showed 99.02 per cent. (Assuming the caffeine to be pure and the theobromine to be 98 per cent., the calculated result is 98.8 per cent.)

A second mixture, of 0.15 gm. of the 98 per cent. theobromine and 0.1 gm. caffeine, was treated with silver nitrate, and the nitrogen in the silver compound estimated as described. The result showed 58.7 per cent. theobromine. (Calculated result, 58.8 per cent.)

Thus, the presence of caffeine, even in considerable quantities, does not appear

to interfere with the theobromine estimation. 0.25 gm. of caffeine was treated in exactly the same way, and a small quantity of a dark-coloured precipitate, which might have been silver, was produced.

The nitrogen was estimated as before, but the 0.2 c.c. of $\frac{N}{10}$ HCl absorbed in the experiment was equal to that in the "blank." It is evident, however, that whilst this precipitate does not vitiate the results obtained by the new method, yet its presence might have a serious effect in the estimations made either according to Kunze or Monthulé.

This work was carried out in the Analytical Laboratory of Messrs. Boots' Pure Drug Company, Limited, to whom we wish to express our thanks.



ABSTRACTS OF PAPERS PUBLISHED IN OTHER JOURNALS.

FOOD AND DRUGS ANALYSIS.

Estimation of Antipyrine. J. Bougault. (*J. Pharm. Chim.*, 1917, 15, 337-339.)—Both the volumetric and gravimetric methods for the iodimetric estimation of antipyrine yield trustworthy results when carried out as follows: *Volumetric Method.*—Ten c.c. of an aqueous 1 per cent. antipyrine solution are treated with 1 gm. of potassium bicarbonate and an excess of $\frac{N}{10}$ iodine solution; after one hour the mixture is acidified with 1 c.c. of acetic acid, 10 c.c. of chloroform are added, and the excess of iodine is titrated with thiosulphate solution. Two atoms of iodine combine with 1 molecule of antipyrine. The method yields 99.6 per cent. of the antipyrine present. *Gravimetric Method.*—A quantity of about 0.5 gm. of the antipyrine is dissolved in 50 c.c. of water, 2 grms. of potassium bicarbonate are added and concentrated iodine solution is added drop by drop; the brown turbidity which is produced by the addition of each drop should disappear before the next drop is added. The addition of the iodine requires about thirty minutes. Colourless crystals of iodoantipyrine begin to form within about ten minutes, and are coloured black as soon as an excess of iodine has been introduced. After one hour the mixture is decolourised by the addition of sodium thiosulphate; the precipitate is collected on a filter, washed with a small quantity of water, dried, and weighed. The filtrate is then extracted with chloroform to recover a quantity of iodoantipyrine which remains in solution. About 99 per cent. of the antipyrine actually present is found by this method. W. P. S.

Simplified Inversion Process for the Determination of Cane-Sugar by Double Polarisation. H. S. Walker. (*J. Ind. and Eng. Chem.*, 1917, 9, 490-492.)—Many advantages are claimed for the method of acid inversion which consists

in adding the acid to the sugar solution at a temperature of 65° to 67° C. and then allowing the solutions to cool spontaneously for a definite time. Fifteen minutes was chosen as a convenient time for the duration of the inversion, the same concentrations of sugar and acid being used as in the Hertzfeld method. The constant $144.66 - .5t$ was used in all cases. The method is worked as follows: 50 or 75 c.c. of the solution used for direct polarisation are placed in a 100 c.c. flask (when 50 c.c. are used 25 c.c. of water are added) and the flask heated in a water bath to 65° C. The flask is removed from the bath and 10 c.c. of a mixture of equal volumes hydrochloric acid (sp. gr. 1.188) and water are added, and the whole allowed to cool down spontaneously in air for fifteen minutes or as much longer as may be convenient. The volume is then made up to 100 c.c. after cooling in water to air temperature, and the solution polarised as usual. In the case of low-grade products which have been clarified with a large excess of basic lead acetate, it is imperative that the excess alkalinity be neutralised before heating, this being best accomplished by the addition of 1 c.c., or more if necessary, of the dilute acid used for inversion. A serious loss occurs if solutions of molasses clarified with excess of basic lead acetate are heated before adding acid, while, if the alkalinity be neutralised prior to heating, all the irregularities seem to disappear. The safe limit of initial temperatures for waste molasses was found to lie between 70° and 63° C. for a fifteen-minute inversion period.

H. F. E. H.

Identification of Emodin-Containing Drugs. W. S. Hubbard. (*J. Ind. and Eng. Chem.*, 1917, **9**, 518-521.)—In the case of liquids, about 10 c.c. are evaporated to a pasty consistency, acidulated with hydrochloric or sulphuric acids, and the residue extracted several times with ether. Pills and solid material are powdered, acidified and extracted with ether. The addition of ammonia or dilute alkali causes the formation of a red colour in the water layer if emodin or other anthraquinone compounds are present. The colour given by phenolphthalein disappears in the course of an hour or so in presence of 5 to 10 per cent. potassium or sodium hydroxide, while that of anthraquinone compounds is permanent (Bornträger reaction: *Zeitsch. anal. chem.*, 1880, **19**, 165).

Aloes can be identified by the fluorescence given with saturated aqueous borax solution, no matter what combination of emodin-containing drugs may be present. Rhubarb gives a deep rose colour with borax, and cascara a brown, while senna sometimes gives a light brown, but usually no colour. Rhubarb can be identified by obtaining a positive reaction with both bleaching powder (red) and iron sulphate (blue) solutions; no other substance so far as known will give *both* reactions. Cascara is identified by the brown colour already mentioned imparted to the water solution by borax, provided the two tests for rhubarb are negative. Cascara can be identified in any combination of the emodin-containing drugs if rhubarb is absent. Senna is the most difficult to detect and is identified by its failure to respond to any except the Bornträger reaction. It is sometimes difficult to get senna to respond even to this test, probably owing to the fact that glucosides of the anthraquinone compounds are present in greater quantity than the compounds themselves. Senna cannot be identified in combination with any of the other drugs. Cascara solution

sometimes gives the fluorescence, which need not be confounded with aloes, since that given by cascara has a brown colour. The colours produced by an aqueous solution of the following chemicals on the ether extractions of these drugs were found to be as follows:

Ammonium Thiocyanate—

Senna : Yellow to brownish colour in water layer.

Rhubarb : Yellowish colour in water layer.

Cascara : Brownish to rose-red colour in water layer.

Aloes : Red in ether and brown in water layer.

Ammonium Molybdate—

Aloes and Cascara : No colour change.

Rhubarb : Mahogany brown in water layer.

Senna : Very light brown to yellowish in water layer.

Uranium Acetate—

Aloes, Cascara, and Senna : No colour change.

Rhubarb : Reddish mahogany colour in water layer (*cf.* ANALYST, 1917, 203)

Ammonium sulphate, persulphate, and oxalate give no colour changes.

H. F. E. H.

Differentiation of Pasteurised Milk from Raw Milk. I. Reductases.
R. E. Lee and M. G. Mellon. (*J. Ind. and Eng. Chem.*, 1917, 9, 360-367.)—
Schardinger's F.M. Reductase test (*J. Ind. and Eng. Chem.*, 1913, 5, 922-927) is carried out by adding 1 c.c. of Schardinger's F.M. reagent (*viz.*, 5 c.c. of saturated alcoholic methylene blue, 5 c.c. of 40 per cent. formaldehyde, and 190 c.c. of water) to 20 c.c. of milk in a test-tube, keeping it at 45 to 50° C. and covering the contents of the tube with a layer of liquid petroleum to prevent the access of air. The formaldehyde hastens the time of reduction, and Lythgoe (*J. Ind. and Eng. Chem.*, 1913, 5, 922-927) states that raw milk will decolourise this reagent in less than twenty minutes, and that pasteurised milk takes longer. The authors find that methylene blue as it occurs in the above reagent is not decolourised by—(a) Normal fresh milk in less than twenty minutes: when decolourisation was effected in ten minutes or less the milk was found to contain a million or more micro-organisms per c.c.; (b) Milk pasteurised at 70° C. for ten minutes, unless about forty-eight hours had elapsed since the milk was pasteurised, or until the bacteria had time to multiply sufficiently; (c) Old milk in which the "preservative" formaldehyde had inhibited the growth of bacteria. Schardinger's reagent F.M. is as a rule decolourised by normal milk allowed to "age" under normal conditions for twenty-four to forty-eight hours. Pasteurisation in all cases was found to increase the time required for decolourisation. As a general rule, it was not possible to trace any proportionality between the time required for the decolourisation of a sample of milk and its bacterial content, though in any given sample a general relation appears to exist between the two up to a certain acidity. It would therefore appear probable that reductase is of bacterial origin, but that not all bacteria in milk produce it.

Formaldehyde probably gradually retards or destroys reductase (*cf.* ANALYST, 1906, 31, 299; 1909, 34, 352).
H. F. E. H.

Rapid Method of Testing the Suitability of Oils for Soap Making. R. Lecoq. (*Bull. Soc. Chim.*, 1917, 21, 101-103.)—A rapid method of testing oils in the soap-works is based upon the following observations: (1) It is possible to make neutral soaps by treating the oil with the exact quantity of alkali indicated by the saponification value. (2) The formation of a paste (*i.e.*, of an emulsion of the fat in a soap solution containing alkali) is essential to saponification. (3) A good emulsion can only be obtained by the use of weak alkali lyes (1.059 to 1.074). (4) To produce a good emulsion the lye should be added to the oil rather than oil to the lye. (5) Weak lyes (1.059 to 1.074) cannot effect complete saponification. (6) The quantity of sodium chloride required for "salting out" neutral soaps varies with the nature of these soaps. (7) Pure soaps "salted out" under the same conditions contain different quantities of water, according to the chemical composition of the soap. The emulsification is best produced by the addition of a special emulsifying soap prepared by saponifying an oil in the presence of alcohol and evaporating the alcohol. Ten grms. of this soap in 50 c.c. of water are used for the emulsification of 100 grms. of the oil, and the mixture is heated on the water-bath in a conical flask covered with a watch-glass with a hole in the centre for an agitator. The quantity of alkali solution for saponification, calculated from the saponification value, is then diluted to 60 c.c., and added in portions of 12 c.c. every thirty minutes, so as not to destroy the emulsion, and, after boiling the liquid for one and a half hours, saponification is complete. In the case of soft (potassium) soaps the mass is diluted to the conventional standard of 50 per cent. of water. In the case of sodium soaps the product is dissolved in 400 c.c. of water, and treated with 125 grms. of salt, the liquid decanted, and the precipitated soap dried with the aid of a pump. The quantity of salt added is somewhat high, but in certain cases the excess is necessary. In saponifying fatty acids the sample is melted, and added in two fractions (three parts and one part) to the whole of the alkali lye which has been heated on the water-bath. An interval of thirty minutes is left between the addition of the fractions, and the soap is then boiled for an hour, and treated as described above.
C. A. M.

Direct Method for the Estimation of Starch. T. von Fellenberg. (*Mitt. Lebensmittelunters. Hyg.*, 1916, 7, 369-383; through *Chem. Zentr.*, 1917, i, 450-451.)—In the method described the starch is dissolved in calcium chloride solution, then precipitated by iodine; the iodine-starch compound is decomposed with alcohol, and the starch is weighed. A quantity of from 0.3 to 1.0 gm. of the fat-free substance in which the starch is to be estimated is moistened with water, 20 c.c. of 50 per cent. calcium chloride solution are added, the mixture is heated in a boiling water-bath for thirty minutes, then boiled for five minutes, cooled, diluted to 100 c.c. and filtered through cotton-wool and asbestos. It is sometimes necessary to submit the filtrate to centrifugal action in order to obtain a perfectly clear liquid. Fifty c.c. of the filtrate are now treated with $\frac{N}{50}$ iodine solution until a flocculent precipitate

forms, the addition of a large excess of iodine being avoided. After twenty-four hours a quantity of asbestos-wool is added, the precipitate and asbestos are collected in a Gooch crucible containing a layer of asbestos, and the mixture in the crucible is washed four times with 5 per cent. calcium chloride solution containing a few drops of iodine solution. The contents of the crucible are then extracted thoroughly with 85 per cent. alcohol and finally with 100 c.c. of 90 per cent. alcohol. If this treatment does not render the precipitate colourless, a quantity of hot alcohol is added to the crucible. After further washing with cold alcohol, 5 per cent. calcium chloride solution, and dry ether, the crucible and its contents are dried, weighed, ignited, and reweighed. The loss in weight gives the quantity of starch present.

W. P. S.

BACTERIOLOGICAL, PHYSIOLOGICAL, ETC.

Phenolphthaleïn Reagent for the Detection of Blood in Urine. E. Justin-Mueller. (*J. Pharm. Chim.*, 1917, **16**, 20.)—A modified Meyer's reagent is recommended, the decoloration of the alkali-phenolphthaleïn being effected by sodium hydrosulphite in place of zinc dust. Two grms. of phenolphthaleïn and 20 grms. of potassium hydroxide are dissolved in 130 c.c. of water and the solution is boiled with the addition of 3 grms. of sodium hydrosulphite until colourless. For the detection of blood in urine, 10 c.c. of the urine are mixed with 10 c.c. of alcohol containing 2 per cent. of acetic acid, and 4 c.c. of the reagent and a few drops of hydrogen peroxide are added; if blood is present, the colourless mixture develops a more or less intense red coloration on the addition of the hydrogen peroxide.

W. P. S.

Detection of Blood in Urine, Fæces, and Pathological Fluids. Thevenon and Rolland. (*J. Pharm. Chim.*, 1917, **16**, 18-19.)—The test depends on the formation of a violet coloration when blood is treated with pyramidone in the presence of hydrogen peroxide. Four c.c. of the unfiltered urine are mixed with an equal volume of 5 per cent. pyramidone solution (in 90 per cent. alcohol), 8 drops of 30 per cent. acetic acid are added, the mixture is shaken, and a few drops of hydrogen peroxide are then introduced. The coloration appears within a short time according to the quantity of blood present; even traces of blood yield a blue-violet coloration within fifteen minutes. After attaining its maximum intensity the colour gradually fades. For the detection of blood in fæces, etc., the material is mixed with water, filtered, and the filtrate tested as described.

W. P. S.

Biochemical Reactions for Distinguishing Pyrocatechol, Quinol, and Resorcinol. J. Wolff. (*Ann. Chim. anal.*, 1917, **22**, 105-107.)—The reagent employed is prepared by macerating *Russula delica*, or other fungus rich in laccase, in its own weight of glycerol, and filtering the mixture through glass-wool. An intense blue coloration is obtained when a 0.1 per cent. pyrocatechol solution is treated with 2 drops of the reagent 5 drops of starch solution containing potassium iodide and 3 drops of dilute acetic acid. Under similar conditions, quinol (hydro-

quinone) does not yield a coloration, but does so when dilute sulphuric acid is used in place of the acetic acid. Resorcinol does not give a coloration in the presence of either acetic acid or sulphuric acid.

W. P. S.

ORGANIC ANALYSIS.

Improvements in the Copper Method for Estimating Amino-Acids. P. A. Kober. (*J. Ind. and Eng. Chem.*, 1917, **9**, 501.)—The improvements on the author's copper method (*ANALYST*, 1913, **38**, 567) consist of (1) a simpler method for dehydrating and weighing copper sulphate for making standard copper solutions, (2) the preparation of a stock suspension of cupric hydroxide which is very sensitive in its reaction with amino-acids and keeps well, and (3) a method for making and keeping saturated solutions of potassium iodide containing starch and acetic acid.

Copper sulphate, when heated to 105° to 110° C. for several hours, is converted into the monohydrate, and this latter salt may be converted into the white anhydrous salt by heating for two or three hours from 245° to 260° C. in an oil-bath in a current of dry air. 1.77 grms. of the monohydrate when dehydrated will give sufficient copper when dissolved in 250 c.c. of water to make a $\frac{1}{25}$ molar solution which, if kept slightly acidified in a stoppered bottle, will keep almost indefinitely.

In the original method cupric hydroxide was made freshly when required, but, by avoiding excess of alkali—*i.e.*, not adding enough completely to precipitate the copper—a suspension of the hydroxide can be obtained which keeps for months and can be easily pipetted. To prepare the copper hydroxide, 22 c.c. of $\frac{M}{2}$ cupric sulphate are diluted with ice-water to 6 litres, and at 0° to 1° C. are precipitated with about 175 c.c. $\frac{N}{1}$ sodium hydroxide free from carbonate, phenolphthalein being used to test the final reaction. After filtering and washing by decantation the precipitate is finally suspended in 250 c.c. of water and used as required.

The appearance of free iodine in the saturated stock potassium iodide solution employed appears to be chiefly due to the presence of traces of nitrites and nitrates which act catalytically, and, by removing these and keeping the solution out of contact with the air, the iodide, starch, and acetic acid will keep well for three months or more. Four hundred grms. of potassium iodide are dissolved in 450 c.c. of distilled water, and with 40 c.c. 1 per cent. soluble starch solution and 10 c.c. glacial acetic acid are placed in a 750 c.c. flask. After adding 2.5 c.c. $\frac{M}{2}$ cupric sulphate and an inch layer of paraffin and mineral oil mixture (1:3), the whole is allowed to stand for thirty minutes, when the iodine is titrated with $\frac{M}{2}$ sodium thio-sulphate to just the neutral point—*i.e.*, when it becomes colourless; after which the flask is fitted with an inlet tube containing strong alkali and boiled for thirty minutes. The alkali is for washing the air that enters the flask on cooling. The paper concludes with some further details as to the preparation of the insoluble "copper complexes" already described (*ANALYST*, *loc. cit.*). H. F. E. H.

Estimation of Alcohol and Water in Ether. R. L. Perkins. (*J. Ind. and Eng. Chem.*, 1917, **9**, 521.)—Mallinckrodt and Alt (*ANALYST*, 1916, **41**, 342) estimated water by absorbing it with potassium carbonate and weighing the latter, and

the alcohol by sp. gr. tables showing ether-alcohol strengths in admixture. The author considers it simpler to solve the problem by merely making two sp. gr. determinations, one on the original sample and another after dehydrating with potassium carbonate. Tables are given in the form of graphs from which the percentage composition of the mixture can be calculated.

H. F. E. H.

Action of Solvents on Coal. A. Wahl. (*Bull. Soc. Chim.*, 1917, 21, 76-88.)—Bedson (*J. Soc. N. England Mining Eng.*, 1899, 82) has shown that pyridine has a pronounced solvent action on certain kinds of coal, whilst from anthracite it extracts little or nothing. Analogous results were obtained by Vignon (*ANALYST*, 1914, 39, 320, 406) by the use of other solvents. In order to determine the nature of the constituent extracted by pyridine, the author dried typical samples of the finely powdered and sifted coals *in vacuo* and extracted them with boiling pyridine. The extracts were evaporated to a small volume and poured into an excess of dilute hydrochloric acid (1:1), heated to about 90° C. This precipitated the dissolved substances as an amorphous brown powder which was washed with boiling water and dried *in vacuo*. In this way the following results were obtained:

<i>Origin of Coal.</i>	<i>Ash.</i>	<i>Volatile Substances.</i>	<i>Carbon (Fixed).</i>	<i>Dry Pyridine Extract.</i>
	<i>Per Cent.</i>	<i>Per Cent.</i>	<i>Per Cent.</i>	<i>Per Cent.</i>
Bethune	1.95	34.40	63.65	19.90
Frankenholz—1	2.40	39.85	57.75	19.3
" 2	1.85	43.07	55.08	18.6
" 3	2.54	40.36	57.10	17.6
Lens—1	4.17	34.47	61.36	24.90
" 2	3.46	13.48	83.06	trace
" 3	2.20	21.27	76.53	0.44
Anthracite (Belgian)	3.43	8.70	87.87	<i>nil</i>
Boghead coal	13.92	47.47	38.61	5.56
Spanish lignite	6.10	43.66	50.24	21.55

The extracted coals contained from 0.83 to 5.03 per cent. less volatile matter than the original coals, with the exception of two of the Lens samples, which contained 0.36 and 0.99 per cent. more after the extraction, probably due to pyridine retained by the material. Speaking generally, therefore, anthracitic coals and those low in gas yields are those which give the smallest proportion of substances soluble in pyridine. There is, however, no definite relationship between the amounts of volatile matter and of pyridine extract. The effect on the coke-forming property of the coal is much more pronounced. Those samples which yield a spongy coke give a less voluminous coke of darker colour after extraction. By mixing an extracted coal with its extract the mixture yields a coke similar to that given by the original coal. The pyridine extract of coal is insoluble in water, acids and alkalis, but is partially soluble in organic solvents, yielding a solution with an intense yellow fluorescence. It is soluble in nitric acid, and the solution when diluted with water

yields a brown precipitate. Pyridine extracts have practically the same composition as the coals from which they were derived. For example, in the case of the sample of Bethune coal the following results were obtained:

	<i>Carbon.</i>	<i>Hydrogen.</i>	<i>Nitrogen.</i>	<i>Sulphur.</i>	<i>Oxygen.</i>
	<i>Per Cent.</i>	<i>Per Cent.</i>	<i>Per Cent.</i>	<i>Per Cent.</i>	<i>Per Cent.</i>
Bethune coal	85.95	5.55	1.18	0.76	6.56
Pyridine extract ..	85.55	6.09	1.41	0.53	6.42

C. A. M.

Detection and Estimation of Sulphur in Petroleum. C. K. Francis and C. W. Crawford. (*J. Ind. and Eng. Chem.*, 1917, **9**, 479-481.)—The silver coin test gives good results with crude oil, but is not delicate enough to detect the small amount of sulphur (0.03 per cent.) sometimes present in the lighter petroleum products. Of the other tests available the methylene blue test is more sensitive than the nitroprusside test, and is conducted as follows: A piece of bright sodium, contained in a hard glass test-tube, is covered with the oil, which is heated over a free flame until it has completely vaporised or charred, using a piece of glass tubing about 18 inches long as reflux condenser with gasolines and burning oils. The cooled residue is treated with water, drop by drop, until violent action ceases, then with 5 c.c., then made slightly acid with HCl, the solution neutralised with hydrochloric acid, using phenolphthaleïn as indicator, and then made distinctly acid by addition of a few drops more. A small crystal of *p*-aminodimethylaniline sulphate is added and followed by a few drops of ferric chloride solution. If the oil contains sulphur, a blue colour is formed which becomes more intense on standing. This latter fact must be borne in mind if the attempt be made to use the method for roughly approximate quantitative work, as also the fact that the intensity of the coloration is dependent on the concentration of acid, either too much or too little decreasing the sensitiveness of the test, about 10 per cent. of concentrated acid giving the best results. For such roughly quantitative work, sodium nitroprusside, applied to the solution of the product of the sodium fusion, is the better reagent, but it is less sensitive.

For the estimation of sulphur in petroleum, Eschka's method is not applicable. The results may be 50 per cent. below the truth. Either fusion with sodium peroxide in a Parr bomb or a modification of Dammer's combustion method (*Zeitsch. angew. Chem.*, **22**, 440) gives accurate results. Apparatus, specially designed by the authors for carrying out their modification of Dammer's method, is figured in the paper, but they themselves say the method requires so much care and vigilance that they prefer the bomb method. According to this method, a mixture of 12 grms. sodium peroxide and 0.5 grm. potassium chlorate is placed in a Parr bomb and about 0.4 grm. of the oil weighed into it. After mixing by stirring with a platinum rod, the bomb is closed and the charge ignited. After cooling, the fusion is dissolved in hot water, acidified with hydrochloric acid, and the sulphur estimated as barium sulphate.

G. C. J.

INORGANIC ANALYSIS.

Estimation of Boric Acid in Special Glasses. P. Nicolardot and J. Boudet. (*Bull. Soc. Chim.*, 1917, **21**, 97-101.)—One grm. of the powdered glass is fused with alkali carbonates in a platinum crucible, the fused mass treated with hot water, and the liquid boiled for five minutes with 5 grms. of ammonium chloride. A current of carbon dioxide is then introduced to precipitate the silica and metallic oxides (ZnO , CaO , Al_2O_3 , MgO), and the liquid is boiled until it no longer smells of ammonia. The precipitate is separated and washed with water containing ammonium chloride, and the filtrate is boiled with 5 grms. of sodium hydroxide to remove ammonia, after which it is concentrated to 100 c.c., and titrated with hydrochloric acid, using methyl orange as indicator, and then boiled for fifteen minutes beneath a reflux condenser to remove carbon dioxide. After cooling, it is neutralised with $\frac{N}{10}$ sodium hydroxide solution, methyl orange being used as indicator, and is then treated with 10 c.c. of glycerol or of a freshly made solution of 0.8 grm. of mannitol in boiling water, and the titration continued with phenolphthaleïn as indicator. The method is thus a modification of that originally devised by Klein (*Bull. Soc. Chim.*, 1878, **29**, 195). The amounts of boric acid thus found in various kinds of glass ranged from 4.72 to 8.58 per cent., and were in close agreement with the results obtained by difference. Magnesia and alumina even in proportions much higher than are present in glass do not interfere either with the estimation or with the distillation of the boric acid as methyl borate in the method of Bertrand and Agulhon.

C. A. M.

Estimation of Chromium in Ferrochromium, Steel, and Slags by the Permanganate Method. P. Koch. (*Chem. Zeit.*, 1917, **41**, 64; through *J. Soc. Chem. Ind.*, 1917, **36**, 552.)—From 0.2 to 0.3 grm. of the finely divided material is weighed into a porcelain crucible, 4 grms. of sodium peroxide added, and the mixture fused by heating carefully with a small flame, or on a sand-bath, so as to avoid too high a temperature. When cold, the product is extracted in a beaker with a litre of boiling water, which is then boiled for a further half-hour to decompose the hydrogen peroxide. The solution is acidified with sulphuric acid to dissolve the ferric oxide, and a measured excess of ferrous sulphate solution is added, when the yellow colour of the chromic acid changes to that of green chromium sulphate, and the excess of ferrous sulphate is titrated with permanganate solution. The end-point, which is indicated by the disappearance of the green colour due to ferrous salt, is best observed by diluting the solution with water to 2 litres. The red colour of the permanganate is masked by the complementary colour of the chromium salt. The titration of all chromium solutions requires to be conducted rapidly. The analysis of chromium alloys by liberation of iodine by chromic acid and titration with thiosulphate gives an erroneously high value for the chromium through the presence of other compounds which liberate iodine. If the fusion with sodium peroxide is made in a nickel crucible the solution must be freed from particles of nickel and nickel oxide by filtration before acidifying. An alternative method, applicable to the estimation of chromium in steels, consists in dissolving 1 grm. of the metal in dilute sulphuric acid,

oxidising with saturated potassium permanganate solution until the red colour of the latter persists on continued boiling, adding 10 to 20 c.c. of manganese sulphate solution, filtering from the separated manganese dioxide, and then adding standard ferrous sulphate solution and titrating with potassium permanganate. With slags containing manganese, 3 to 5 grms. are well mixed with 20 to 40 grms. of sodium peroxide and heated in a crucible of nickel, iron, or copper until disintegration of the slag is complete, the product is extracted with hot water, boiled, and the residue containing manganese dioxide and the oxides of silicon and iron is filtered off. The small quantity of manganese which is held in solution as manganate and permanganate is decomposed as before by boiling the acidified solution with a few c.c. of manganese sulphide, and the solution is filtered and the chromium estimated by adding ferrous sulphate and titrating back with potassium permanganate or $\frac{N}{10}$ potassium chromate or bichromate.

Cobaltic Ammonium Molybdate, Tungstate, and Vanadate. Estimation and Separation of Cobalt. A. Carnot. (*Compt. rend.*, 1917, 164, 897-903.) —Hydrogen peroxide in alkaline solution converts cobalt salts into the sesquioxide, while nickel remains in the condition of protoxide, so that a separate estimation may be made by volumetric methods. In presence of excess of ammonium chloride and ammonia the cobalt forms a cobaltic ammonium salt which may be precipitated by ammonium molybdate. The colour of the solution passes through changes, becoming dark and then gradually purple-red or pink according to concentration; the change takes place fairly quickly if the solution be gently heated, but it should not be allowed to boil, otherwise the salt undergoes a change in composition [from roseo- or purpureo-cobaltic to luteo-cobaltic. For quantitative purposes the last condition should be avoided; either of the other salts after neutralising with hydrochloric acid, gives a coloured precipitate with ammonium molybdate. On neutralisation of the free ammonia the solution becomes yellowish-pink, and one drop of dilute acid should be added in excess. On the addition of a 5 per cent. solution of ammonium molybdate in measured quantity to the cold solution a peach-blossom coloured precipitate is formed which settles rapidly after agitation. The precipitate is readily soluble in presence of the slightest excess of ammonia and in dilute acids, so that neutralisation must be done very carefully. On drying at 110° C. it becomes violet and later lilac-grey, and has the composition $\text{Co}_2\text{O}_3 \cdot 10\text{NH}_3 \cdot 6\text{MoO}_3$. On heating at a higher temperature it blackens with loss of ammonia, and should therefore be collected on a tared filter. A pink precipitate, in all respects similar to the molybdate, is obtained with ammonium or sodium tungstate. Ammonium vanadate forms two kinds of precipitate, one yellowish-pink with $3\text{V}_2\text{O}_5$ and the other dull yellow with $6\text{V}_2\text{O}_5$. Neither the tungstate nor the vanadates are so suitable for analytical purposes as the molybdate. The separation of nickel from cobalt salts is influenced by the fact that nickel gives a green crystalline precipitate in concentrated solution, so that the quantity of substance taken must vary according to whether nickel or cobalt predominates. With excess of cobalt only a few centigrms. are taken. After separation of the metals precipitated by ammonia the cobalt is converted into the purpureo-cobaltic condition by warming with hydrogen

peroxide; the solution is then neutralised and the cobalt precipitated with molybdate. The washed precipitate is free from nickel. The nickel may then be precipitated after the addition of a few drops of ammonia by an alcoholic solution of dimethylglyoxime or *α*-benzylidioxime; the presence of a small excess of molybdate does not interfere. If the nickel be predominant, 0.5 to 1.0 grm. of the substance is taken, and the cobaltic ammonium molybdate is precipitated in very dilute solution. The precipitate is filtered off as soon as possible, before the nickel ammonium molybdate has time to form. It is then redissolved by dilute ammonia solution, the excess of ammonia is neutralised to the faintest trace of acidity, a little fresh molybdate solution is added, and the estimation completed. The united filtrates containing the nickel are freed from ammonia by boiling with soda, and the hydroxide is oxidised by the addition of bromine. If manganese be present, it is eliminated along with the iron by the treatment with hydrogen peroxide and slight excess of ammonia. If the precipitate is considerable the treatment should be repeated. In presence of zinc or cadmium, the cobalt precipitate is formed in the usual way, and then redissolved in ammonia and reprecipitated. In the case of copper, which tends more than other metals to attach itself to the cobalt precipitate, the reprecipitation should be repeated twice.

J. F. B.

Analysis of Cast Nichrome. E. W. Reid. (*J. Ind. and Eng. Chem.*, 1917, 9, 488-490.)—The following methods are recommended: The turnings are dissolved in hydrochloric acid containing a little nitric acid. The solution is evaporated to dryness and the residue ignited, taken up in acid, and the solution filtered. The washed residue is ignited, weighed, treated with hydrofluoric and sulphuric acids, ignited and weighed again to estimate silica, and finally dissolved in hydrochloric acid containing a little nitric acid. An insoluble residue may still remain. This is filtered off, fused with sodium peroxide, and the acid solution of the fusion added to the other filtrates, which are diluted to a definite volume. On portions of this solution nickel, iron, chromium, manganese, and zinc are estimated, the first by the cyanide method. In another portion iron, chromium, and zinc are estimated as follows: The iron and chromium are precipitated with a small excess of ammonia in presence of much ammonium chloride, and zinc estimated in the filtrate by the ferrocyanide method after suitable treatment to eliminate nickel. The hydroxides of iron and chromium are dissolved in acid, reprecipitated with sodium hydroxide, oxidised with bromine water, and the ferric hydroxide is filtered off, dissolved in acid, reprecipitated with ammonia, filtered off, dissolved in sulphuric acid, the solution reduced with zinc, and iron estimated by titration with permanganate. The chromate filtrates are acidified, and 3 or 4 grms. of manganous sulphate and a measured amount of standard ferrous ammonium sulphate solution are added, and the excess of the latter, beyond that necessary to reduce the chromate, is titrated with permanganate.

For the estimation of zinc, the filtrate from the iron-chromium precipitate is evaporated almost to dryness, the residue taken up in nitric acid, the solution evaporated to half bulk, treated with 2 grms. potassium chlorate, boiled, diluted, and filtered. The filtrate is neutralised with ammonia, heated to boiling, and nickel

precipitated with dimethylglyoxime. The nickel precipitate is filtered off, and zinc estimated in the filtrate by the ferrocyanide method.

Manganese is estimated in a separate portion of the solution by evaporating this to dryness, taking up in nitric acid, evaporating to half bulk, precipitating manganese with potassium chlorate, filtering through asbestos, dissolving the precipitate in a beaker in a measured volume of standard ferrous ammonium sulphate solution, and titrating the excess of ferrous iron with permanganate.

G. C. J.

Pemberton Volumetric Method for Estimating Phosphoric Acid. P. McG. Shuey. (*J. Ind. and Eng. Chem.*, 1917, 9, 367-370.)—This method is trustworthy provided that strict attention is paid to details of the procedure (*cf.* ANALYST, 1914, 39, 100). The factors which have the greatest influence on the results are the temperature at which the phosphomolybdate is precipitated and the proportion of sulphuric acid present. Concordant results cannot be obtained when the precipitation is made at temperatures between 40° and 65° C., but no trouble arises if the precipitation is made between 30° and 40° C. For the estimation of phosphoric acid in acid phosphates it is recommended that a control test be carried out at the same time by adding to a weighed quantity of standard phosphate rock the same amount of sulphuric acid as was used in the case of the sample; the sulphuric acid may be added after the substance has been dissolved in nitric acid. In dealing with samples containing organic matter, treatment with sulphuric and nitric acids with the addition of potassium nitrate is suggested, the control being treated in a similar way. The molybdic acid reagent used should not be too old; a solution which contains separated molybdic acid must not be employed.

W. P. S.

Recovery of Ammonium Molybdate from the Filtrates obtained in the Estimation of Phosphoric Acid. H. Kinder. (*Stahl. u. Eisen*, 1916, 36, 1094; through *Chem. Zentr.*, 1917, i., 530.)—The solution containing the molybdic acid residues is treated with sodium phosphate, the yellow precipitate formed is collected, washed with 0.1 per cent. sodium sulphate solution until free from soluble phosphate and iron, and dried. A quantity of 325 grms. of the dry precipitate is then dissolved in 1,100 c.c. of ammonia (sp. gr. 0.96), the solution is treated with 30 grms. of magnesium chloride and 30 grms. of ammonium chloride dissolved in water to make 100 c.c., the ammonium magnesium phosphate is separated by filtration, and each 420 c.c. of the filtrate is mixed with 1,200 c.c. of nitric acid (sp. gr. 1.2); the resulting solution is then ready for use in the precipitation of phosphoric acid.

W. P. S.

APPARATUS, ETC.

British Glass-Making Sands: The Substitution of Some British Sands for Foreign Sands in the Manufacture of High-Grade Glass. C. J. Peddle. (*J. Soc. Glass Technology*, 1917, 1, 27-61.)—Many British sands have been investigated both as to their chemical composition and their suitability for glass-making, and it is found that good colourless glass can be made from some of the sands, particu-

larly after they have been subjected to a proper treatment. The chief requirements of a good sand are that it shall have a high silica content (not less than 99 per cent.), be as free as possible from iron, alumina, lime, and alkalis, and that the grains shall be nearly of one size and be angular. Thorough washing of the sand is essential, and washing and proper elutriation yield a product which is as satisfactory as that obtained by sifting. Treatment with hydrochloric acid does not improve a sand to any marked extent. British sands which have proved to be best for glass-making are those from Muckish Mountain, Aylesbury, Lynn, Huttons Ambo, and Burythorpe; the first-named gives a good glass without washing, and if placed on the market cheaply and in bulk would rival Fontainebleau sand. The other four sands give colourless glass after treatment, and, when manganese dioxide is used as a decoloriser, are good enough for the manufacture of flint glass. In order, however, that British sands can compete with foreign sands, greater attention must be paid by the sand merchant to the production of a uniform article, and different consignments should not vary in chemical or mechanical composition. W. P. S.

Palladium-Gold Crucibles as Platinum Substitutes. *Met. and Chem. Eng.*, 1917, **16**, 533; through *J. Soc. Chem. Ind.*, 1917, **36**, 670.)—An alloy of palladium and gold known as "Palau," which has been prepared as a substitute for platinum, has the surface colour of pure palladium and is similar to, but slightly darker than hammered platinum. Tests at the U.S. Bureau of Standards showed that a crucible formed of the alloy is not so easily de-formed as one of pure platinum, though not so rigid as a crucible made of platinum with about 8 to 10 per cent. rhodium. The sp. gr. of the alloy is 17.22 and the melting-point 1370° C. The E.M.F. against pure platinum is 8.5 millivolts at 960° C. and 7.2 millivolts at 860° C. A crucible of the alloy was heated to 1200° C., in a furnace free from metal vapours for two periods of four hours each, and weighed before and after each heating. The weighings to determine the loss due to heating were followed by treatments for five minutes with boiling hydrochloric acid (HCl to $4\text{H}_2\text{O}$), and the loss in weight due to the acid treatment was determined. The solutions obtained from this crucible contained less than 0.01 mgrm. of iron. The tests indicated that the "Palau" crucible, as far as resistance to loss on heating to 1200° C. is concerned, is superior to platinum containing about 2.4 per cent. iridium. The comparative freedom from iron is an improvement over most platinum ware now in use. The alloy compares favourably with platinum in resistance to hydrochloric, nitric, hydrofluoric, and sulphuric acids, ferric chloride, and sodium hydroxide solutions and fused sodium carbonate. The "Palau" crucible is not as suitable for potassium pyrosulphate fusions as platinum. Both this alloy and platinum are seriously attacked by fused sodium carbonate and nitrate mixture, though in this case the "Palau" crucible is the more resistant.



REVIEW.

Coal-Tar and Ammonia. By **George Lunge**, Ph.D., Professor Emeritus of Technical Chemistry in the Federal Technical University, Zurich. Fifth and Enlarged Edition. Parts I. and II., Coal-Tar; Part III., Ammonia. London: Gurney and Jackson, 1916. Price £3 3s.

Seven years have passed since the last edition of Professor Lunge's treatise on Coal-Tar and Ammonia appeared, and this period has witnessed great extension in the production and use of coal-tar, the commercial realisation of new processes of obtaining ammonia, and—towards its close—the opening up of fresh sources of aromatic hydrocarbons to meet the insatiable demand for their nitrated products as the most potent agents for the destruction of man and his handiwork. Professor Lunge has essayed to cover this seven years' progress in the coal-tar and ammonia industries by a considerable enlargement of his treatise, which is now bound in three volumes comprising in all 1,658 pages. He has excised a little obsolete matter and he has rewritten a few paragraphs, but for the most part his mode of revising his treatise for this new edition has consisted in inserting here and there new paragraphs, the matter of which sometimes is rather inconsistent with that of the older context. The net result of this procedure has been—in the writer's view—the production of an unwieldy treatise, the contents of which lack co-ordination and cohesion as well as conciseness. The work no longer is worthy of Professor Lunge's former great repute as an authoritative guide to the branches of industrial chemistry with which it deals.

Many concrete instances might be cited from each of the three volumes in support of this harsh judgment of the present status of the work as a whole, but it will suffice, before passing on to the analytical problems discussed, to refer to Professor Lunge's treatment of one fundamental question. It is now common knowledge that the character or composition of the volatile products of the carbonisation of coal is determined by the conditions of carbonisation rather than by the precise nature of the coal carbonised. The greater part of the volatile products of the carbonisation of coal are evolved from the particles of coal as they reach, in turn, a comparatively low temperature, and it is the secondary effect of heat on these primary volatile products which determines the character or composition of the gas and tar which are the ultimate products. The extent of this secondary effect depends not simply on the temperature of the retort or containing vessel itself, but on the rate of passage of the volatile products through it and the degree of baffling by heated surfaces to which they are subjected. If we could measure the maximum temperature which each particle of vapour or gas attains before it escapes from the retort or oven, we should be in a good position to predict what the final products yielded by it and its neighbours would be. As matters stand, however, we know merely the temperatures of the retort walls and different zones of the charge of coal, and it is only by increasing or retarding the rate of flow of the vapours and gases primarily evolved, so that their contact with these more or less highly heated objects is more

or less prolonged, that we can influence seriously the temperature which the vapours and gases themselves attain, and can thereby determine the nature of the ultimate products. Given a retort of a particular size maintained at a certain high temperature, the temperature which the volatile products evolved from a contained charge will attain will be affected almost solely by the *quantity* of hydrocarbon matter which there is in the contained charge. If that hydrocarbon matter is, say, four times as much in one instance as in another, either by reason of the charge consisting of four times as much of the same coal, or by reason of its consisting of the same quantity of a coal containing four times as much "volatile matter" or hydrocarbon, it is fairly obvious that the vapours and gases evolved will travel through the retort in the first instance at not less than four times their rate of passage in the second instance. When the difference in the amount of hydrocarbon matter in the charge is obtained by increasing the weight of the charge inserted (the kind of coal being unaltered), it is clear that the free space in the retort for the passage of the evolved vapours and gases is correspondingly reduced, and hence individual particles of these vapours and gas must on this account also make a more rapid passage through and out of the retort. A fully-charged retort therefore gives much less opportunity to the vapours and gases to approximate to the temperature of its walls than does one only one-quarter filled with the same coal. In this lies the rational explanation of the relative freedom from naphthalene and other high temperature products, of the tar and gas produced from fully charged gas retorts or coke ovens.

Professor Lunge, however, when discussing in his second chapter the causes of differences in tars, virtually ignores these fundamental considerations, but gives several pages of less relevant data on the influence on the tar produced of the temperature of the retort, of the shape of the retort, and of the quality of the coal. These data in many instances would be useful provided they were correlated by the author with the general principles underlying carbonisation, but in the present work they stand as so many unconnected items. They are even in several cases wrongly quoted. Thus, on p. 42, Professor Lunge gives figures purporting to be taken from A. Schäfer's text-book ("Einrichtung und Betrieb eines Gaswerkes"). First he quotes average temperatures for the horizontal retorts in certain settings at Mannheim, but he gives as an alternative temperature for the middle retorts a figure which is in reality the mean of the temperatures of the outer and middle retorts. The same mistake occurs in his next quotation for certain inclined retort settings at Mannheim. The third quotation from the same source refers, according to Professor Lunge, to a "coke-furnace," which the reader will probably take to be a translator's mistake for coke-oven. Reference to Herr Schäfer's book, however, shows that the figures given really refer to "Coze" settings of inclined retorts. The want of care with which Professor Lunge's quotations are made is again demonstrated on the next page, where he gives a table showing only the calorific and illuminating powers of gas distilled from gas coal (from Saxony) at different temperatures, and proceeds to say that the table proves that with rise of carbonising temperature calorific values are increased. The table shows (quite correctly) the reverse. It may be surmised that Professor Lunge wished to show that with rise of carbonising temperature the multiple of calorific power by gas-yield increased, but he quotes

neither the gas-yield nor that multiple, and draws an inference which is palpably false.

These instances, from two consecutive pages, of the slipshod work embodied in the latest edition of "Coal-Tar and Ammonia," might be multiplied indefinitely, but they serve to show that it can be used safely as a work of reference only by the specialist who will descry the errors with which it teems. A reader not thoroughly well acquainted with the technical literature of the gas, coal-tar, and ammonia industries may well be seriously misled if he relies on this work for guidance.

The writer is unable to form a much more favourable opinion of the utility of the book to the analytical specialist. In the section on "Testing of Tar on a Small Scale or in the Laboratory," very little guidance is given to the public analyst, who now frequently is called upon to make a simple assay of coal-tar on behalf of his local authority which probably buys large quantities of tar for the surface dressing of roads. Many crude tars, and not a few modern refined tars, give endless trouble in a small-scale distillation unless the heating of the flask or retort is conducted with a view to breaking up incipient frothing and spurting, yet Professor Lunge contents himself with quoting Watson Smith's directions, which were excellent for the coal-tars of their date—viz., 1887—but need supplementing in order to be applicable to the more troublesome high-temperature coal-tars of later years and the carburetted water-gas tars which were then unknown in Europe. The only useful hints of later date are given under the heading Estimation of Water, and are quoted from Payne, who in 1903 described precautions which he had found valuable, and which, in principle, are now generally followed in tar-testing in this country.

Again, nothing useful to the analyst is said as to English methods of taking the viscosity or consistency of tars for road-dressing and for preparing tar-macadam, though, thanks to the pioneer work of—amongst others—Brigadier-General H. P. Maybury, first as County Surveyor of Kent, and later as Engineer and Manager of the Road Board, this country is much in advance of the rest of Europe in the application of tar in road-making and repair. The success of tar treatment of road stone or road surfaces is well known here to depend primarily on the use of tar of appropriate consistency or viscosity, and failures—especially of tar-macadam—may constantly be traced to a fault in this respect. The Engler viscosimeter and similar instruments are really useless for comparing the consistencies of the heavier grades of road tars, and Lunge's immersion tar-tester has obvious defects as a standard instrument. The carefully standardised Hutchinson viscosity gauge, which is now so widely used in this country for controlling the consistency of road tars, does not appear to be properly appreciated by Professor Lunge, as he gives merely a bare reference to the number of Hutchinson's patent. But he even ignores English methods of using and testing road tars to the extent of making no mention of the Road Board Specifications for Tar and Pitch, which are now incorporated in the Engineering Standards Committee's Specifications.

The ignorance of English practice and methods which these examples display would be excusable in a foreign work, written primarily for the technical men of another country and merely translated into English. But Professor Lunge's "Coal-

Tar and Ammonia" purports to be an original standard work, written by him in the English language, and since it is much more bulky and costly than its counterpart in the German language (which he has prepared with the aid of Dr. Köhler), it is not unfair to expect in it some account of modern English standards and methods of testing tar. The expectation will, however, be realised in very few sections of the treatise.

In some respects the volume on Ammonia is less disappointing than the two volumes which deal with Coal-Tar, perhaps because methods and uses differ less in various countries with ammonia than with coal-tar. There is no other work on Ammonia which is quite so authoritative and comprehensive, but there is too much patchwork about the present edition to make even this volume of Professor Lunge's handbook an ideal technical work of reference. Further, so long as the treatise retains its present pretensions and size, there is no sufficient reason why the volume on Ammonia should be so closely attached to the volumes on Coal-Tar as to have a common index and be sold only with them. It is always troublesome to have to take down a second volume for the index of the volume in one's hand, and with a little compression, which would be wholly to the benefit of the treatise, Professor Lunge's "Coal-Tar" could be published in one volume complete with index, and his "Ammonia" in a second volume with separate index—as, indeed, is the case with the German counterpart of the handbook. The form of the present work makes it cumbersome in use and involves an unfair drain on the pocket of the reader who is interested in Coal-Tar or in Ammonia, but not in both.

W. J. A. BUTTERFIELD.



INSTITUTE OF CHEMISTRY.

PASS LIST: JULY (1917) EXAMINATIONS.

THE results of the Examinations of the Institute of Chemistry recently held in London, Dublin, and Johannesburg have now been published.

Four Candidates passed the Intermediate Examination, viz.: E. R. Baines, (Miss) Ella Caird, W. H. Craven, B.Sc. (Lond.), and A. J. Dando.

Four Candidates passed the Final (A.I.C.) Examination, viz.: H. J. Hegan, B.Sc. (Lond.), in Mineral Chemistry; A. J. Hall, B.Sc. (Lond.), and S. J. Rogers, B.Sc. (Lond.), in Organic Chemistry; and H. Jephcott, B.Sc. (Lond.), in the Chemistry (and Microscopy) of Food and Drugs, Fertilisers and Feeding Stuffs, Soils, and Water.

Two Candidates passed the Final Examination for the Fellowship, viz.: H. R. Adam, B.Sc. (Aberd.), in Metallurgical Chemistry; and George Taylor, in the Chemistry of Food and Drugs, etc.
