The Journal of Industrial and Engineering Chemistry

Published by THE AMERICAN CHEMICAL SOCIETY

Volume IV SEPTEMBER, 1912 No. 9

Contributions and communications should be addressed to the Editor, M. C. Whitaker, Columbia University, New York City.

Published monthly. Subscription price to non-members of the American Chemical Society, $6.00 yearly.
Foreign postage. seventy-five cents, Canada, Cuba and Mexico excepted.

Entered as Second-class Matter December 19, 1908, at the Post-Office at Easton, Penna., under the Act of March 3, 1879.

ESCHENBACH PRINTING COMPANY, EASTON, PENNA.

TABLE OF CONTENTS

EDITORIALS:

ORIGINAL PAPERS:

LABORATORY AND PLANT:

ADDRESSES:

CURRENT INDUSTRIAL NEWS:

NOTES AND CORRESPONDENCE:

BOOK REVIEWS:

EDITORIALS

OUR GUESTS.

As this issue of THIS JOURNAL comes from the press, men from all parts of the world, representing every branch of applied chemistry are assembled in New York in a great International Congress. Individuals, great manufacturing corporations, technical societies and progressive governments are coöperating to make this the greatest event in the history of chemistry. Never before has industry been so willing to acknowledge its debt to chemical science, and the forces behind these international movements will establish its position as the fundamental basis for permanent industrial growth.

Other countries have held these congresses, but American chemists are now for the first time occupying the position of official hosts. We are being honored by the presence of many of the most distinguished men in the profession, and their contributions to the deliberations of the Congress will be of inestimable benefit to the industries. International interchange of ideas has now become a recognized necessity to great industrial progress, and we are proud of this opportunity to render a service in such a cause. Manufacturers are throwing open their plants to inspection and excursions are provided to show the agricultural resources, natural wealth, commercial possibilities and scenic beauty of our country.

The chemists of America feel the sincere solicitude of hosts for the comforts and pleasures of their guests on this auspicious occasion. We hope their visit will be both pleasant and profitable and that they may come again. We wish great benefits to come to the profession itself and to the industries and governments represented as a direct result of the meeting of the Eighth International Congress of Applied Chemistry in America.

FUSSY ADMINISTRATION.

President McKinley handed Colonel Roan a message to carry to Garcia. There were no strings tied to that commission. He had chosen a man of intelligence, resource and ability to do a job and he was willing to let him do it in his own way. This very fact proved that the President was a great executive. He knew how to centralize responsibility and how to hand out a message to a messenger, an art which many men in administrative positions have not yet acquired.

Conversation among employers of men sooner or later drops into a type of experience meeting, for discussing and illustrating the inefficiency of subordinates. Employers never assume any responsibility for the failures of employees, nor do they analyze the causes of shortcomings in their subordinates with a view to seeing how much of the trouble is due to the boss. Many of the failures of men to make good on a given job are due not to a misfit with the job nor to a lack of ordinary ability, but to the man's misfortune in choosing a boss, a condition which he can not always control, but one which he must see and remedy before he will have a chance to succeed.

At a conference in the office of a corporation manager recently, it was decided to send one of the young engineers regularly employed by the company to a point some distance from the main line of travel to take some measurements and get certain simple statistical data. The engineer was called into the office; he quickly caught the points and purpose of the trip, as it was explained to him by the manager; glancing at the clock, he said he would catch the next train. This took about five minutes. The fact that he understood instantly what was to be done, knew what train to take and when to take it, entirely escaped the manager who then spent twenty-five valuable minutes in an unsuccessful attempt to figure out railroad connections from a railroad guide. This bright, well educated young man was then successively told to be sure to order his sleeper tickets at once; to draw what money he needed from the paymaster; to telephone home; to avoid drinking the water because one engineer had been taken sick on a trip similar to this; to be sure to take a note-book but that if he forgot it he could buy one there. At last the young man escaped: the manager mopped his brow and referred at length to the great knowledge of detail he was obliged to carry in his mind in order to run his job.

Subordinates are bound to fail under such conditions as these. Initiative and independence are soon killed, and men and women should not be blamed if they sleep securely at their work in the belief that the "old man" will look out for the details and do the "small thinking" as long as they make a show at the general results. From the manager's standpoint such a system of administration is sure to end in failure. If the business grows, he soon finds his mind so overcharged with fussy details that matters of importance bearing on new problems of development have to be neglected or deferred. Instead of leading and directing the business he becomes a camp follower.

The value of simple mechanical work, whether it be in an office, factory or laboratory, is represented by the market price for the services of a man employed to wield a pick and shovel. A stenographer who simply graphitizes the sounds wafted to her across a flat top desk and later bats them out on her machine without any regard to whether or not they make sense, is worth about one dollar per day—perhaps less, but certainly not more. If she is paid more it is because she is expected to have and use some skill and intelligence in addition to the physical labor of punching keys and making records. It is skill, judgment, intelligence and mental faculties which bring the earning premium to men and women who depend upon industry and business for support. These are the faculties for which the employer pays the premium. If the subordinates do not possess them, they should not be paid the premium; if on the other hand they have the faculties, latent or developed, they should be required to use them and in this way render services for value received. The employer can find a greater field for his ability and a greater reward for his labor in the consideration of means for developing the intelligence of his employees rather than assuming that part of their work. The problem is one in education—drawing out, developing—and not one in mental "spoon-feeding" to be solved by the circulation of voluminous printed instructions, or by plastering office and works with signs, mottos and "don'ts."

There can be no general rule laid down for developing the responsibility and reliability of subordinates, but it is reasonable to assume that lack of opportunity to exercise these faculties will have much the same effect on their growth that a life of ease and indolence has on the muscles of an athlete. One work manager gave his power-house men much personal instruction for a period of three years on ways and methods of firing and controlling feed water in order to reduce coal consumption. At last in despair at his failure to get results, he gave up this plan, which he was pleased to call education, and adopted in its place a system of paying a bonus on the amount of coal saved below the best previous minimum. The firemen then began to use their own intelligence—the intelligence they had always possessed but never had occasion to exercise while the boss was doing their thinking for them. They soon found that open spots in the grate surface affected their general results as much when the boss was not in sight as when he happened to be present in the boiler room. They became their own bosses and maintained a constant supervision over their own work because they had an objective point, the successful accomplishment of which required an exercise of their own judgment and intelligence. The coal consumption automatically dropped 20 per cent. in two months.

The employer who "butts in" on the prerogatives of his subordinate is not only rendering himself less efficient in the performance of his own work, but is dissipating his resources by paying others for work for which they are employed but which they are not permitted to do. Such employers do not recognize the point at which *directing* ends and *doing* begins.

Probably the most fussy and inefficient form of administration ever invented is the committee system. Committee administration does not exist in approved business organizations, but it appears to be the preferred system in society, public and academic administration.

Questions of business policy, plans for manufacturing development, technical or educational problems all require discussion, consideration and analysis. The experience and knowledge of a number of men working in coöperation is required to determine these matters of general policy. Such questions are properly and efficiently handled by a representative committee selected with a view to reaching a correct and lasting solution. With the solving of these problems and the fixing of a policy for the future administration of the organization their duty should end. It is when this big, unwieldy committee engages in the consideration of nursery problems or attempts to function as an administrative body, that it becomes ridiculous. It has repeatedly been demonstrated that the administrative efficiency of a committee varies inversely as the square of the number of men on the committee. It is well known that business administration is much more efficient and prompt than public, society or academic administration, and the reason is to be found, to a large extent, in the complete freedom of business administration from a triagonal or pentagonal committee attempting to make a job for itself out of the duties of a reliable man. Suppose we take a specific case: An office boy in a well managed business may ask for an increase in salary because he has reasoned out that he is rendering service which will justify it. He goes to the chief clerk who is his immediate superior and is therefore the logical person to control such matters and through such control is enabled to exercise a discipline which puts a premium on efficiency. The chief clerk knows the value of the boy's services, considers all of his arguments and makes a decision one way or the other. If the request is granted, the paymaster is instructed as to the agreement and when it is effective. Total time consumed, about five minutes. Suppose this same boy is working for a committee-mad organization and makes an application for more salary. He is usually advised to "write a letter" covering all points to be considered. The letter is brought up at the next meeting of the board of directors. In order to "save time," after being duly moved, seconded and discussed, the matter is referred to a committee of three or five, to be appointed by the chair, to consider and report at the next meeting on the question of salary for office boy. The committee on office boy's salary is made up of busy men and they find it difficult to get together; it will be a miracle if they do not come in at the next board meeting and report "progress."

In the meantime the boy has become discouraged and has reduced his services to a value comparable with his salary or has obtained a new job at a better salary on account of the knowledge and experience gained while employed by the committee-ridden organization. Running a training school for employees who leave as soon as they have learned enough to be valuable is a discouraging operation at best; such a system of filtration, in which the values all go to the filtrate, will, in an incredibly short time, leave a residual organization which will blunder along with a maximum of inefficiency.

Speed is an important factor in efficient administration. How is the work of a committee going to be expedited? The chairman may call a meeting but the only result is an echo. Men are busy, too busy to be spending their time fussing over insignificant details. We have seen ten ten-thousand-dollar-a-year men sit for hours discussing, considering and acting upon a quantity of insignificant administrative matter which could have been disposed of by one two-thousand-dollar-a-year man in one hour. Such a man, familiar with all questions of policy peculiar to this organization, would have acted with even better judgment than the committee because of a more intimate, direct, first-hand knowledge of the facts. The results would have been snappy administration and a living example of practical efficiency to the subordinates—a lesson which could not be drawn from the operations of the hundred-thousand-dollar committee. The committee men themselves often see the ridiculous waste and yet become resigned victims of a system of "fussy" administration which literally oozes with delays, procrastination, irresponsible and inefficient methods.

Most societies and institutions have at least a carload of committee reports which have been made at great expense of time and labor but which have not been read or adopted. Some offices have records—records everywhere—but no obtainable information. In other places the whole organization is busy with the administrative "double pass," where instructions are handed from one subordinate to another and everybody is busy with the system of passing orders along but no one has time to do a job.

Professional men, engineers, chemists and educators might do well to recognize administration as a profession by itself and not a side show to some specialized occupation. As a matter of fact, administrative power is the rarest of all talents and is therefore the best paid profession. We entrust our legal, technical and educational problems to men trained and experienced in their respective specialties. The proper administration of policies so established is equal in importance to, and often more difficult to accomplish than the formulation of the policies themselves. One might properly suggest therefore that the question of efficient administration is important enough to justify careful analysis.

In successful business organizations we find centralized responsibility and power in the hands of a man whose business is administration. Policies are prescribed and commissions are assigned for the purpose of having them executed, and the person who undertakes the work is held responsible for the results. Men of ability and judgment are not converted into errand boys and assigned to duty between the board of directors and the job. Technical questions and questions of policy may be considered and decided by committees but these committees are not "woodenized" by don'ts and limitations. Every man in such an organization believes that the easiest way to dispose of work is to do it. He knows that his boss is waiting for results, not excuses. When he is told to do something, he does not rack his brain for reasons and arguments as to why it should not be done, but puts some intelligence and energy into the matter of doing it. Things are accomplished in an hour which, if undertaken at all in an organization saddled with committee administration or a fussy manager, would take six months.

Since the introduction of laboratory methods of instruction into our educational systems, men trained for numerous activities have been taught to study conditions, observe facts and interpret results. Administrators who apply this training to problems arising in the development of men and women in their organization will have less cause to complain of inefficiency. They will have more people who can carry a message. The elimination of fussy systems of administration will go a long way toward successfully dealing with the human element in efficient management.

ORIGINAL PAPERS

EPINEPHRIN[1] FROM THE WHALE.

By Edward R. Weidlein.

Received June 12, 1912.

The object of this investigation[2] is a study of the ductless glands of deep sea mammals, especially of the whale. The whale is a true mammal, and on account of its size affords a splendid advantage for the study of these glands This paper will be confined entirely to the epinephrin content of the suprarenal glands from the whale and some of the results observed while purifying this product. However, before entering into the subject of epinephrin, it will be best to present something on the morphology and histology of the glands.

The adrenals or suprarenals of the whale are two glandular masses situated above but in close relation with the upper extremity of each kidney, occupying about the same position as the corresponding glands in cattle which they resemble more nearly than those of any other mammal. The left capsule is a little larger than the right, semilunar in form, the right being more nearly triangular. The glands are also larger in the female than in the male whale, but vary in size. The following table gives an average size of the glands found in the animals indicated.

	Glands.	Length. Inches.	Breadth. Inches.	Thickness. Inches.	Weight. Grams.
Fin-back whale, female	Left	9.5	6	1.5	684
	Right	9.5	5.5	1.6	566
Fin-back whale, male	Left	8	5.5	1.1	538
	Right	8	5	2	491
Fin-back whale, calf	Left	7.4	4.1	0.9	280
	Right	6.5	3.2	1.5	264
Sheep		1.0	0.5	0.25	1.18
Hog		1.75	0.5	0.25	2.00
Cattle		2.25	1.5	0.50	12.50

These results show the suprarenal glands of the whale to be about 500 times larger than the glands of sheep and 50 times larger than the glands obtained from cattle.

The glands are composed of a cortex and medulla,

---

[1] Epinephrin will be used throughout the paper as the standard name for the active principle from the suprarenal glands, as adopted by the Council of Chemistry and Pharmacy of the American Medical Association, in preference to using a commercial or protected name, such as adrenaline, suprarenin, suprarenalin, adrin, supracapsulin, adnephrin and so on. *J. Am. Med. Assn.*, March 25, 1911, p. 910.

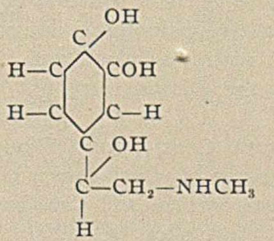
[2] This work was carried out under an Industrial Fellowship established at the University of Kansas by Hon. Walter Roscoe Stubbs, Governor of the State of Kansas, in honor of Dr. Wilfred T. Grenfell, and was known as the Stubbs-Grenfell Fellowship. The Fellowship was extended by a prominent citizen of Pittsburgh.

surrounded by a connective tissue capsule of considerable thickness. The cortex is of a light yellow color, averaging about a quarter of an inch in thickness. It is distinct in lobular division, but does not give as even an appearance as the glands from cattle and sheep. The cortex can readily be separated from the medulla and is oftentimes pulled apart from the medulla. The medulla is of a deep red color varying in thickness, in the right gland from $1-1^3/_4$ inches, in the left from $^3/_4-1$ inch. The medulla undergoes decomposition very rapidly and can be obtained in good condition from the fresh whales only. The capsule surrounding the gland is of a yellowish-white color and is quite thick. The glands are well supplied with blood vessels, lymph vessels and nerves. The yellow-pigment cells in the medulla are very numerous and well marked.

HISTORY.

Since the extraction of the vaso-constrictor excitant substance of the suprarenal glands from the skin secretions or poison glands of the tropical toad, Bufo Aqua, by Abel,[1] it has given added interest to this field of work, as to the sources of epinephrin. While the discovery of the active principle in the suprarenal glands of the whale is not out of the ordinary or something not to be expected, as compared with Abel's important research, yet it has led to some very interesting results.

The active principle of the suprarenal glands has been a subject of very great importance ever since the valuable discovery of Oliver and Shaefer,[2] that an extract from these glands when injected intravenously would cause a marked rise in the blood pressure. However Vulpian,[3] as early as 1856, observed the characteristic emerald-green and rose-red color which ferric chloride and iodine, respectively, give with epinephrin, while working with the juices from the medulla of the suprarenal gland, thus indicating that there was present in the gland a substance of physiological importance. Abel, Von Fürth and others by very careful and extensive research paved the way for the separation of the active principle, which was accomplished by Takamine in 1901 and named by him "adrenaline." Aldrich advanced this important work by determining the formula for the active principle as $(C_9H_{13}NO_3)$. The structural formula generally accepted is orthodihydroxyphenylethanol methylamine:



Comparatively little work had been done on the suprarenal glands until the vaso-constrictor action was made known by Oliver and Shaefer; since that time, however, numerous papers have appeared on the physiology of the glands, together with even more articles on the therapeutic and toxic action of epinephrin. It, therefore, seems preferable to refer only to methods of preparing epinephrin and its physiological results which bear directly on this work. A very complete and excellent bibliography may be obtained by referring to the valuable papers of Abel,[1] Aldrich,[2] Schultz,[3] Vincent,[4] and Shaefer.[5]

The early workers in this field were primarily interested in the therapeutic and toxic action of epinephrin. The preparations used were either water or glycerine solutions from the glands. Of these early workers, Krukenberg[6] and Frankel[7] were instrumental in throwing light on the chemical nature of the active principle, by declaring that it was a pyrocatechin derivative. Fränkel separated what he thought was the active principle and termed it "sphygmogenin." This, however, was later proved to be a mixture. Von Fürth[8] separated the active principle from the glands in the form of an impure iron compound. Later contributions[9] showed that he separated the active principle by extracting the fresh capsules with slightly acidulated water in the presence of a little zinc dust, concentrating the extract in a vacuum, precipitating the impurities by the use of methyl alcohol and lead acetate, recovering the excess of lead by the use of sulphuric acid, again evaporating the liquid to a small bulk, and precipitating the epinephrin with ammonia. The active principle thus separated was called "suprarenine." Abel[10] first separated the active principle by using benzoyl chloride, one of the benzoyl radicles being retained in a modified form of epinephrin: $C_{17}H_{15}NO_4$ was the formula ascribed to this substance. This compound gave certain of the alkaloidal reactions and was formerly known as epinephrin but as it was stated in the foot-note at the beginning, this name has lately been adopted as the standard name for the active principle from the glands. Abel[11] has since separated epinephrin by using absolute alcohol and trichloracetic acid as the solvent, and precipitating the epinephrin from the concentrated solution by the use of ammonia. In order to distinguish this new substance from his former preparation, he called it epinephrin hydrate. This method increased the yield from 0.2–0.3 per cent. of the moist glands.

The first true separation of the active principle, however, was made by Takamine[12] at the beginning of the year 1901. The method used was in part: to steep the glands in acidulated water, concentrate this solu-

---

[1] *J. Am. Med. Assn.*, **56**, 1531–6 (May 27, 1911).

[2] *J. Physiology*, **16** (1894); **18**, 230–79 (1895).

[3] *Compt. rend.*, **93**, 663–5 (1856).

[1] *J. Pharm.*, **75**, 301–25 (1903).

[2] *J. Am. Chem. Soc.*, **27**, 1074–91 (1905).

[3] *Bull.* Nos. **55** and **61**, Hyg. Lab., U. S. Pub. Health & Marine Hosp. Serv., Wash.

[4] *Lancet*, **171**, 348–53 (1906).

[5] *Brit. Med. J.*, **1**, 1277–1346 (May 30 and June 6, 1908).

[6] *Virchow's archiv.*, **101**, 542 (1885).

[7] *Wiener Med. Blat.*, **14**, 16 (1896).

[8] *Z. physiol. Chem.*, **24**, 24, 142; **20**, 15 (1898).

[9] *J. pharm. chim.*, [6] **18**, 362; *Pharm. J.*, **24**, 437 (1907).

[10] *The Johns Hopkins Hospital Bulletin*, July, 1897, No. 76; **12**, 339 (1901).

[11] *Ber.*, **36**, 1839–47 (1903). *Am. J. Pharm.*, **75**, 311 (1903).

[12] *Am. J. Pharm.*, **73**, 523–31 (1901).

tion in a vacuum to a small bulk, precipitate the organic, protein and inorganic matter by the use of strong ethyl alcohol, reconcentrate and precipitate the epinephrin by the use of ammonia. Aldrich,[1] a little later in the same year, also separated the active principle by using a slightly altered form of Takamine's method. Many new methods have since been worked out to increase the yield and at the same time to improve the quality of the product. Among these might be mentioned a modification which Aldrich[2] made in his own method by using lead acetate as a precipitant. This consists of a precipitation with lead acetate, just after steeping the glands in acidulated water, in order to complete the precipitation of the inert matter, which is removed by filtration. The excess of lead is recovered by passing hydrogen sulphide into the filtrate. The epinephrin is recovered from the filtrate in the same manner as described before. Another method of interest is that of Freund[3] which is the electrolytic reduction of impure solutions of epinephrin or its salts. The electrolytic reduction is by the use of a platinum cathode, a carbon anode and a porous cell as a diaphragm. The solution is made acid and the time required from one to two hours.

Epinephrin has been prepared synthetically through the splendid researches of Dakin, Stolz, Jowett, Böttcher and Pauly. Flächer[4] separated Stolz's synthetic preparation into the *d* and *l*-epinephrin, and showed the *l*-epinephrin to be more effective on the blood pressure and to be identical with natural *l*-epinephrin

Various processes have been suggested for standardizing epinephrin, with the result that three reliable methods have been worked out. These are toxicity, pupil experiments, and blood pressure.

Läwen[5] based a quantitative method on the effect of epinephrin upon the blood vessels of frogs. By this method he could obtain quantitative results and also detect the degree of deterioration of a solution. Strips of muscle were also used in determining the strength of an epinephrin solution.

The toxicity method is of little value, since so many of these experiments were made with solutions from the glands and impure preparations of the active principle, that it is difficult to determine just what is a lethal dose. Schultz[6] has improved this method and has determined the lethal dose to be 0.008 mg. per gram mouse, yet it cannot be used for exact quantitative work.

The dilator mechanism of the frog's eye is quite sensitive to epinephrin. Meltzer[7] was the first to call attention to this method for standardizing such solutions. Auer, Wessely, Ehrmann and Schultz have been instrumental in developing this method of assay. Schultz[8] pointed out that the method devised by Meltzer was good only for qualitative results. He called attention to the various factors which influence the reaction of the iris to adrenaline. A modification of this method was also devised so that the length of the long and short axis of the pupil could be expressed in millimeters, thus eliminating the error that would result by trying to make these observations with the naked eye. These necessary precautions do not eliminate all the sources of error, and not only make the method a very tedious one, but also give unreliable results. There is always present considerable individual variation.

Houghton[1] took advantage of the change of blood pressure produced in the carotid artery by injecting into the femoral vein of an anesthetized animal variable quantities of preparations from the suprarenal glands. In a later paper[2] he proved this method to be the most accurate means for assaying epinephrin. Three solutions of epinephrin of known concentrations were given to an assistant for assay. The unknowns contained 40, 85, and 130 per cent., based on a standard of 100 per cent., and the results reported were 40, 83, and 135 per cent.

Cameron,[3] after trying the various methods for standardizing epinephrin, finally decided on the blood pressure method as being the easiest and most reliable. He was the first to standardize the commercial epinephrin solutions. His method depended upon the antagonistic action between nitrites and epinephrin. He found by using nitroglycerine as a standard, that when 0.5 cc. of 1.5 per cent. 1 : 1000 epinephrin solution was injected along with 1 cc. of solution containing 0.6 mg of nitroglycerine the rise in blood pressure due to epinephrin was almost cut down, and the opposing effect of the nitroglycerine was soon shown by a slight fall and then a return to the normal pressure. After many trials the opposing action between the nitrites and epinephrin was found to be as 80–1. Some of these commercial preparations caused a fall of blood pressure instead of a rise. Papers by Hunt[4] and by Sollman[5] have clearly pointed out the practical necessity for testing the various commercial products from the suprarenal glands. They further show the great value of the blood pressure method in making these determinations. In order to more clearly show the accuracy of this method, Abel calculated that 1 gram of the dried gland from the cattle should contain 0.018 gram of epinephrin and should yield 18 cc. of a solution corresponding to 1 : 1000 of the active principle. Hunt found that it yielded 15 cc. of such a solution and called attention to the fact that the glands were not completely exhausted.

Schultz[6] has more clearly pointed out the necessity of knowing the degree of effectiveness of an epinephrin solution. He also emphasized the fact that a pure epinephrin base furnishes a reliable standard in

---

[1] *Am. J. Physiol.*, **5**, 457 (1901).

[2] *J. Am. Chem. Soc.*, **27**, 1077 (1905).

[3] *Chem. News*, Feb. 19, 1909.

[4] *Z. physiol. Chem.*, **58**, 185–8–9–94 (1908).

[5] *Arch. exp. Path. Pharm.*, **51**, 413–31 (1903).

[6] *Bull.* **55**, 36, Hyg. Lab., U. S. Pub. Health & Marine Hosp. Serv., Wash.

[7] *Am. J. Physiol.*, **11**, 28–51 (1904).

[8] *Bull.* **55**, 23, Hyg. Lab., U. S. Pub. Health & Marine Hosp. Serv., Wash.

[1] *J. Pharm.*, **73**, 531–5 (1901).

[2] *J. Am. Med. Assn.*, **38**, 150–3 (1902).

[3] *Proc. Roy. Soc. Edinburgh*, **26**, 157–71 (1906).

[4] *J. Am. Med. Assn.*, **47**, 790–2 (1906).

[5] *Ibid.*, **47**, 792 (1906).

[6] *Bull.* **61**, 7–10, Hyg. Lab., U. S. Pub. Health & Marine Hosp. Serv., Wash.

assaying vaso-constrictor substances. The blood pressure method is used and the efficiency expressed in terms of pure epinephrin base. The relative activity is calculated by the following equation:

$$\frac{a \text{ epinephrin base}}{y \text{ vaso-constrictor excitant}} = \text{relative activity},$$

in which a = grams of base in 1 cc. of solution and y the unknown vaso-constrictor excitant.

In this method of standardization,[1] he clearly points out the advantages of different anesthetics and shows that ether for cats, with only enough curare to render it free from muscle tremors, yields the best results. He has standardized all synthetic preparations against the natural *l*-epinephrin and also all commercial preparations against the pure epinephrin base. Three out of seven different brands of epinephrin were found to compare with the standard. The other solutions varied from 3.71 to 71 per cent. of the required activity. These results are given in the following table:[2]

Laboratory number of solution.	Commercial name.	Precipitate present.	Relative physiological activity expressed in percentage of A.
A[1]	Epinephrin	none	100.00
Bd[2]	Adnephrin	none	50.00
Bm[3]	Adnephrin	none	50.00
Cd	Adrenalin	none	100.00
Cm	Adrenalin	none	100.00
Dd	Adrin	none	50.00
Dm	Adrin	abundant	3.75
Em	Caprenalin	abundant	25.00
Fd	Supracapsulin	none	100.00
Fm	Supracapsulin	trace	100.00
Gd	Suprarenalin	none	66.71
Gm	Suprarenalin	none	66.66
Hd	Suprarenin synthetic	trace	50.00
Hm	Suprarenin synthetic	some	50.00

[1] Solution A made up on morning of experiment from a pure sample of natural base, the optical activity of which is $\frac{26.4^{0}}{\mathrm{D}}=5340^{0}$.

[2] Series "d" bought directly from manufacturer or from their agents.

[3] Series "m" bought on the open market from a reliable druggist.

Epinephrin solutions deteriorate very rapidly, especially when exposed to the air or if kept in partially filled containers. Schultz has also made a careful examination into this phase of the subject and has summarized his preliminary results in the preceding table.

CHANGES IN PHYSIOLOGICAL ACTIVITY UNDERGONE, IN THE COURSE OF TEN DAYS, BY 1–10,000 SOLUTIONS OF COMMERCIAL EPINEPHRIN SOLUTIONS.[3]

Laboratory number of solution.	Commercial name.	Rise of blood-pressure caused by 1 cc. injection of a 1–10,000 solution. Oct. 29 (fresh).[1] Mm.	Rise of blood-pressure caused by 1 cc. injection of a 1–10,000 solution. Oct. 29 (old).[2] Mm.
Bd[3]	Adnephrin	74.2	69.2
Bm[4]	Adnephrin	67.8	58.0
Cd	Adrenalin	106.0	75.0
Cm	Adrenalin	66.6	64.4
Dd	Adrin 1 : 500	0.0	0.0
Dm	Adrin 1 : 1000	0.0	0.0
Em	Caprenalin	0.0	0.0
Fd	Supracapsulin	102.6	101.6
Fm	Supracapsulin	99.0	93.4
Gd	Suprarenalin	97.6	78.6
Gm	Suprarenalin	83.0	79.0
Hd	Suprarenin synthetic	74.2	60.0
Hm	Suprarenin synthetic	73.8	60.2
Hd	Suprarenin synthetic	74.2	24.4
Hm	Suprarenin synthetic	73.8	48.0

[1] Solution made Oct. 29.

[2] Solution made Oct. 19.

[3] Series "d" bought directly from manufacturers or from their agents.

[4] Series "m" bought on the open market from a reliable druggist.

Sollman and Brown[1] have also tested the relative efficiency of epinephrin solutions from different sources after allowing them to stand for a specified time. The values obtained, taking the best sample as 100, were 95, 86, 70, 63 and 0.

Gunn and Harrison[2] studied the factors which caused the deterioration of such solutions. Their results show that the container is responsible for some of the deterioration, as an acid solution of epinephrin is more stable than an alkaline solution since the latter seems to increase the rate of oxidation. They also point out that twice the minimal amount of hydrochloric acid necessary to dissolve the base will give a more stable solution. Solutions in saturated boric acid free from iron were twice as active as similar solutions in ordinary medicinal boric acid. The medicinal boric acid was not purified and it developed considerably more color than the other solution. Solutions kept in bottles only partially filled showed a rapid change in color. Dixon[3] made the physiological tests of these solutions and found that all solutions deteriorated on change of color and those solutions which had become deep red were almost inactive.

Siegel,[4] on testing the effect of oxidation upon an epinephrin solution, comes to the conclusion by using Ehrmann's reaction, the pupil dialation, that epinephrin alone or in the blood-serum is not destroyed by oxidation.

On account of the rapid deterioration of epinephrin solutions, the impure preparations and the uses of different anesthetics in the blood pressure method of assay, varying results have been obtained on the action of epinephrin. The most important diversion of opinion rests on the deterioration of an epinephrin solution and whether the epinephrin rise in the blood pressure is followed by a depression. Schultz[5] does not call attention to the action of epinephrin, but he does speak of an after-depression which invariably follows the initial effect of the drug. He does not say whether this was characteristic of his standard epinephrin, which he took every precaution to prepare (from the results obtained, it must have been perfectly pure), or whether it occurred only with the different commercial preparations.

Van Leersum[6] calls special attention to this after-depression by pointing out that it is a characteristic of epinephrin.

The disagreements in regard to the physiological action of epinephrin, both in the pure state and after-oxidation, together with the difficulty encountered in obtaining pure epinephrin from the glands of the whale, which on standardizing gave so many conflicting results, led the author to investigate other

---

[1] *Bull.* **55,** 24–5, Hyg. Lab., U. S. Pub. Health & Marine Hosp. Serv., Wash.

[2] *Ibid.*, **61,** 25.

[3] *Bull.* **61,** 23, Hyg. Lab., U. S. Pub. Health & Marine Hosp. Serv., Wash.

[1] *J. Am. Med. Assn.*, **47,** 792 (1906).

[2] *Pharm. J.*, **26,** 513–4 (1908).

[3] *Ibid.*

[4] *Pflüger's*, **138,** 617–37 (1911).

[5] *Bull.* **55,** 48, Hyg. Lab., U. S. Pub. Health & Marine Hosp. Serv., Wash.

[6] *Pflüger's*, **142,** 377–95 (1911).

means for separating the epinephrin and to determine if possible the best method for its purification. It is hardly plausible that such a strong vaso-constrictor substance as epinephrin should also possess a strong depressant action.

EXPERIMENTAL.

The material for part of this investigation was obtained by the writer during the summer of the year 1910, while visiting the various whaling stations in Newfoundland and Labrador. A fresh supply of the suprarenal glands of the whale was received from the same locality, late in the year 1911. The glands were removed from the whales within twenty-four hours after death. Obtained thus under these conditions, they were fresh and were easily preserved. Chloroform was used as the preservative and on account of the size of the glands they were cut up into small pieces Five cc. of the chloroform were added to one quart of the material and the jars completely filled, so as to leave the minimum amount of air space above the glands. The majority of the glands preserved remained in good condition, which was partly accomplished by keeping them in a cool place.

The first step in the investigation was to secure the suprarenal glands from cattle, hogs and sheep and separate the active principle from these glands by Abel's and Takamine's method. The epinephrin obtained was compared with respect to its qualitative and quantitative properties and found to agree in every way. Similar tests were made on the whale epinephrin and certain peculiarities were noticed, more especially in regard to the quantitative tests. Instead of obtaining the characteristic rise of the blood pressure at once, there was a fall preceding the rise. The suprarenal glands of the whale contain large quantities of phosphates and in using Takamine's method for extracting the epinephrin from the glands, only phosphates were obtained. Abel's method also removed more phosphates from the glands than it did epinephrin. This was probably due to the old condition of the glands and not unlikely in part to the preservative. Some of the jars of whale glands were preserved and sent to me from Newfoundland. These glands contained as much as 100 cc. of chloroform to the jar. The glands from one of these jars were pressed and the solution made distinctly acid with acetic acid (50 per cent.) and boiled for about one hour on a water bath. This coagulated a part of the inert matter, which was filtered and the clear filtrate was evaporated under pressure to a small bulk The residue obtained was made alkaline with ammonia and epinephrin immediately separated out. This was repurified and gave the first good yield of epinephrin from the glands of the whale. This would indicate that epinephrin is not present in the glands as a free base, since it is not soluble in chloroform, but that it is a constituent of a more complex substance[1] which is probably broken down by the acid used in the process. Experiments are now in progress, to determine, if possible, the form of epinephrin in the glands. This led to further investigation into the methods for separating epinephrin and the following method was finally devised:

A solution containing 500 cc. absolute alcohol, 50 cc. chloroform and 25 cc. of acetic acid, was gradually added, with constant shaking, to 1000 grams of the finely disintegrated preserved glands of the whale. This was allowed to stand over night. The liquid was pressed from the glands, made distinctly acid with an additional 25 cc. of acetic acid (50 per cent.) and brought to a boil on a water bath, to coagulate the protein material. The precipitate was filtered off and 600 cc. of a clear yellowish filtrate obtained. The filtrate was concentrated under diminished pressure to 60 cc. This residue was filtered and made distinctly alkaline with strong aqueous ammonia whereupon a heavy precipitate of epinephrin formed. This was immediately collected on a filter under pressure, washed thoroughly with water, absolute alcohol and ether and dried in a vacuum over sulphuric acid. The yield on the first precipitation was 2.1103 grams.

The residual glands were treated in the same manner a second time, except that the solution contained 500 cc. of 70 per cent. methyl alcohol, 100 cc. chloroform and 25 cc. acetic acid. This second precipitation gave a yield of 0.36 gram of epinephrin.

The epinephrin was repurified by adding 20 cc. of a 25 per cent. solution of acetic acid, containing 1 cc. of sodium sulphite, to 2.0525 grams of the impure epinephrin. This dissolved the base, giving a brown solution. The solution was filtered and to the clear filtrate ammonia (sp. gr. 0.950 was added until the precipitation was complete. The epinephrin formed as a heavy white flocculent precipitate. This was allowed to stand in a cool place for about an hour. The precipitate was collected on a filter under pressure, again thoroughly washed with water, absolute alcohol, ether, and dried in a vacuum over sulphuric acid. This yielded 1.7680 grams. The second precipitation of 0.36 gram of impure epinephrin was recrystallized by the same method and gave a yield of 0.3104 gram of the pure base. This totaled 2.0784 grams of pure, almost white, crystalline epinephrin or a little better than 0.2 of 1 per cent. yield rom the moist glands. The loss in the repurification was 13.8 per cent. This method could hardly be called quantitative, yet every precaution was taken to prevent oxidation and loss through manipulation.

The same method was used for extracting epinephrin from the fresh suprarenal glands of cattle. On the first precipitation 3.2225 grams of impure epinephrin were obtained from 1000 grams of the fresh glands. This contained a large percentage of impurities, mostly phosphates. The phosphates obtained in some cases were 0.1 per cent. of the moist glands. Other impurities were also present, as will be pointed out from the physiological tests.

The whale epinephrin possesses all of the properties of epinephrin, such as giving with ferric chloride the emerald green color which quickly turns rose red on

---

[1] This suggestion was made by Dr. F. W. Bushong, of this laboratory. Some experimental work has been done which gives evidence of the existence of such a compound.

standing in the air, the rose-pink color with iodine, reduction of ammonical silver nitrate solution and Fehling's solution.

Nitrogen determinations by the Kjeldahl method showed the following results:

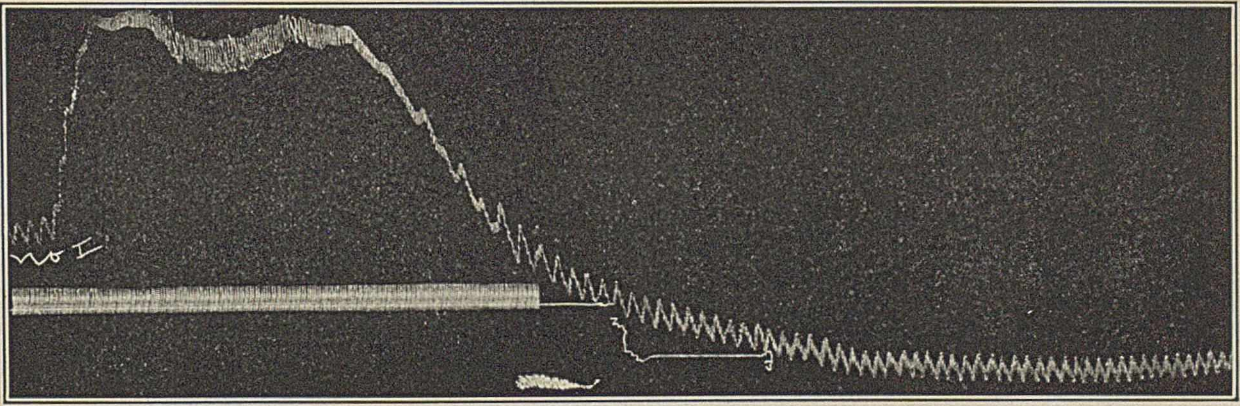
Product analyzed.	Theoretical requirements for formula $C_9H_{13}NO_3$.
N = 7.91	N = 7.65

The polarimetric reading was $[\alpha]_D^{25} = -52.00°$. The melting point was 212° C. This would indicate that the whale epinephrin is the same as the active principle separated from the glands of other mammals.

The exact yield of the epinephrin content of the whale glands is hard to determine, as the extractions were made from the glands after they had stood from six to nine months The best yield obtained was 0.2 of 1 per cent. of the moist glands and these glands were in exceptionally good condition. Most of the determinations show about 0.15 per cent. Abel[1] has described a method which is said to give a yield of 0.3 per cent. from the fresh cattle glands, and it is quite possible to expect a like yield from the fresh glands of the whale. Several tests were made to detect iodine in the glands, but all gave negative results.

As was pointed out in the early part of the paper the different commercial and synthetic preparations of epinephrin may compare very favorably in all the qualitative tests and yet the quantitative results vary widely. This was clearly demonstrated in Schultz's[2] table where only three out of seven brands of epinephrin were found to compare with the standard. The other solutions varied from 3.71 to 7[illegible] per cent of the required activity. Thus, after making sure of the qualitative properties of the whale epinephrin, every precaution was taken to obtain the best quantitative results. The success of these quantitative results was due largely to the valuable coöperation of Mr. Burket. Of the various methods investigated and tried, the blood pressure proved the most satisfactory. The method used was practically the same as that described by Schultz,[3] which indicates the change of the blood pressure in the carotid artery produced by making the injection in the femoral vein of an anesthetized animal, except that cats were used in place of dogs, and no curare was given with the ether anesthesia. The only advantage to be gained by the use of curare is to prevent muscle tremors, but this could hardly be called an advantage, since curare has a depressant action which might interfere with the action of the epinephrin. By very carefully administering the ether at specified times and between each injection, a very uniform condition of anesthesia could be maintained and the animal could just be kept in a state of unconsciousness, which condition seemed to be favorable for the best results.

The epinephrin used for these physiological tests was carefully prepared and the degree of purity was determined by testing solutions which contained impurities and solutions of the recrystallized epinephrin. Several different methods for recrystallizing the base were used. The solutions were not made up until about two hours before the experiments were performed and then they were prepared from the crystalline product. The amount of base necessary to make a 1 : 1000 solution was weighed out on an analytical balance and dissolved in Ringer's solution, containing the calculated amount of hydrochloric acid necessary to dissolve all the epinephrin. This solution was then diluted to the desired strength. The injections were usually 1 cc. of a 1–10,000 parts solution of the base. The syringe and pipettes used were standardized.



CURVE I.

Showing change in blood-pressure produced by an intravenous injection of 1 cc. of 1–10,000 parts solution of commercial epinephrin. Data under Table IV, Lab. No. I. The perpendicular lines in the curve represent the heart action and respiration; the lower line is used as a base line and to determine the time. This curve shows very clearly the characteristic after-depression obtained by the use of impure epinephrin.

The epinephrin thus prepared from the whale was compared with a commercial preparation of epinephrin obtained directly from the manufacturers and with commercial solutions of epinephrin placed upon the market.

The blood pressure experiments were made in connection with some experiments Mr. Burket was making on the influence of epinephrin modified by various salt solutions, such as sodium chloride, potassium chloride, barium chloride, salts of phosphorus and the like, on the blood pressure, in the Physiology Department of

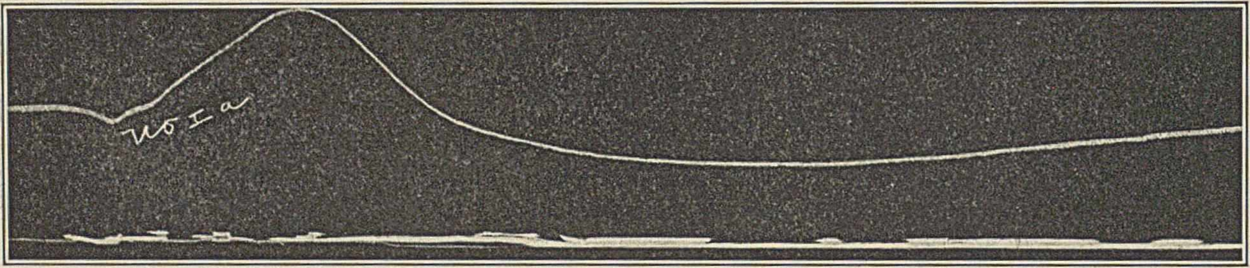
---

[1] *Loc. cit.*

[2] *Ibid.*

[3] *Bull.* **55**, 25, Hyg. Lab., U. S. Pub. Health & Marine Serv., Wash.

this University. The results of his research will appear in the *American Journal of Physiology*.



Curve II.

Showing change in blood pressure produced by an intraven us injection of 1 cc. of 1–50,000 parts solution of commercial epinephrin. Data under Table IV, Lab. No. I*a*. The depression here is in about the same proportion to the rise as is that shown in Curve I.

The blood pressure experiments were made on 17 cats, but the data from only a few of the typical experiments will be given. The greater part of this data will be confined to the active principle from the whale glands, a part that was not taken up in detail by Mr. Burket. Sufficient data will be taken from the commercial preparations to show the difference in action between the pure and impure product of both whale and cattle epinephrin, the effect of oxidation on a solution of the base and to prove the quantitative properties of whale epinephrin.

In all but one of the injections (see Table I) the epinephrin rise was followed by an after-depression which was more apparent with the commercial epinephrin than with the purer product obtained from the glands of the whale and cattle.

Table I.—Blood Pressure Experiment, Feb. 21, 1912.

Male cat, 3.5 kilograms weight. Ether anesthesia. Record of the change of the blood pressure in the carotid artery. Solutions prepared 11.30 A.M. and injected into the femoral veins: 5 milligrams of the base dissolved in 5 cc. of Ringer's solution, acidulated with calculated amount of HCl and diluted to make 1–10,000 parts solution (base). Amount injected, 1 cc.

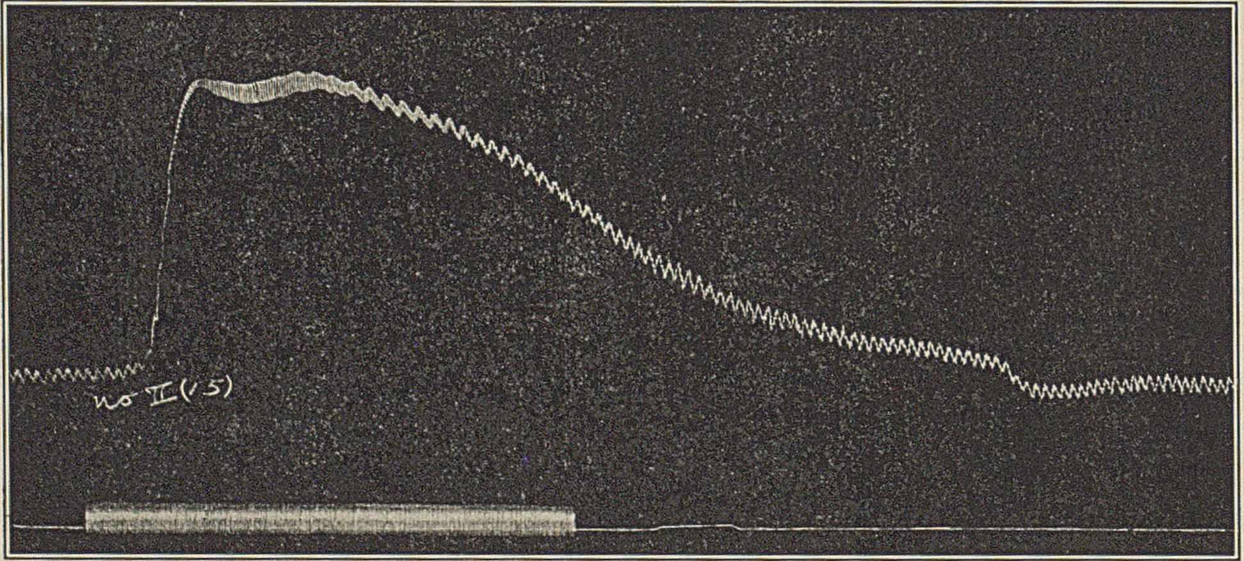
Solution injected.	Lab. No.	Time of injection.	Blood pressure measured by mercury manometer. Before.	After.	Rise.	Duration of rise.		Depression.	Duration of depression.	
		P.M.	Mm.	Mm.	Mm.	Min.	Sec.	Mm.	Min.	Sec.
Epinephrin:										
Commercial[1]	I*a*	2.48	170	248	78	1	10	50	1	30
Whale "A"[2]	II	3.03	160	238	78	1	45	24	..	30
Whale "B"[3]	III	3.08	156	220	64	1	30	32	1	30
Whale "A"	II*a*	3.32	160	234	74	1	..	28	..	10
Commercial	IX	3.54	120	196	76	2	..	30	1	..
Cattle[4]	X	3.57	132	212	80	2	..	none	..	..

[1] Commercial crystalline epinephrin obtained directly from the manufacturers.

[2] Recrystallized.

[3] Impure.

[4] This epinephrin was prepared by the same method used to prepare the whale epinephrin and was repurified the same as Whale "A" epinephrin.

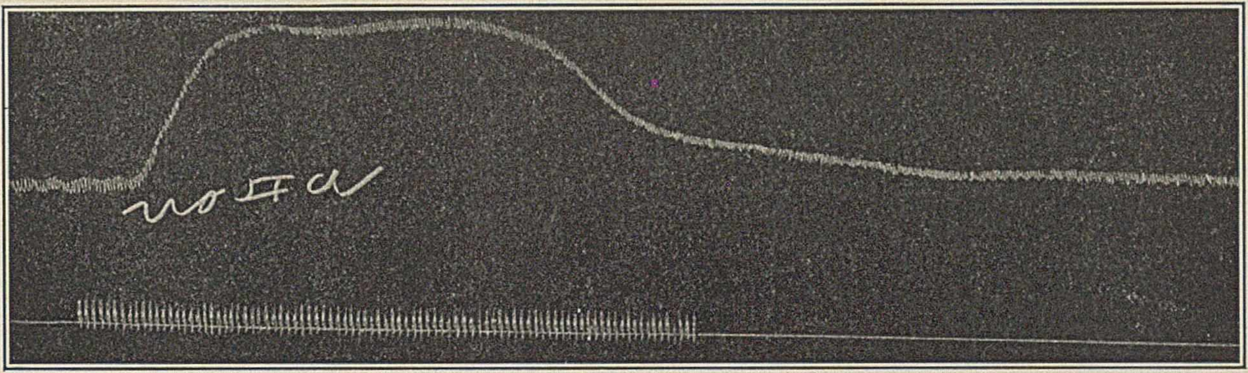


Curve III.

Showing change in blood pressure produced by an intravenous injection of 1 cc. of 1–10,000 parts solution of repurified whale epinephrin. Date under Table IV, Lab. No. II(15). The after-depression is entirely eliminated.

The method for repurifying the epinephrin used in these experiments was to dissolve the base in absolute alcohol, which contained a small percentage of dilute hydrochloric acid. The organic, inorganic and protein material was precipitated by adding ether. The solution was filtered and ammonia added to the clear filtrate until the solution smelled distinctly of ammonia, at which point the precipitation was complete. The precipitate was collected on a filter under pressure and thoroughly washed with water, absolute alcohol and ether. It was dried in a vacuum over sulphuric acid. It was found necessary to take precautions in using this method, as the addition of too strong hydrochloric acid readily decomposes the base.

In Table II the after-depressions are as characteristic as the rise which appeared greater with the commercial than with the purer epinephrin.



Curve IV.

Showing change in blood pressure produced by an intravenous injection of 1 cc. of 1–50,000 parts solution of repurified whale epinephrin. Data under Table IV, Lab. No. II*a*. No depression.

Table II.—Blood Pressure Experiment, Feb. 24, 1912.

Male cat. Approximate weight, 3.5 kilograms. Same method and dilutions as given under Table I. Solutions were prepared by 9.40 A.M. Amount injected, 1 cc.

Solution injected.	Lab. No.	Time of injection.	Blood pressure measured by mercury manometer.			Duration of rise.		Depression.	Duration of depression.	
		A.M.	Before. Mm.	After. Mm.	Rise. Mm.	Min.	Sec.	Mm.	Min.	Sec.
Epinephrin:										
Commercial	I	10.28	160	246	86	1	7	54	2	53
Whale "A"[1]	II	10.33	156	268	112	1	30	6	1	..
Whale "A"	II*a*	10.37	150	262	112	1	30	28	1	..
Whale "B"[2]	III	10.42	146	244	98	1	11	42	2	..
Commercial, 1–1000 Sol.	VI	10.54	152	218	66	..	55	22	1	40
Whale	VII	10.57	150	258	108	2	..	48	2	..
Cattle[3]	VIII	11.14	110	206	96	2	30	10	..	15
Cattle	VIII*a*	11.17	116	216	100	2	..	none	..	..
Commercial	I*a*	11.24	110	220	110	1	20	34	2	30
Cattle "A"[4]	X	11.43	110	198	88	2	15	none	..	..
Whale "B"	III*a*	12.05	110	198	88	1	15	42	2	..
Whale "A"	II(*g*)	12.24	100	208	108	2	..	8	..	10

[1] Repurified.

[2] Impure.

[3] Cattle epinephrin prepared and purified in the same manner as the whale epinephrin.

[4] Second preparation by the same method.

The same method of purification was used, as described under Table I. The increase in the blood pressure was very nearly the same for all the crystalline preparations but was a considerable increase over the commercial 1–1000 solution of the base. The results in the increase in blood pressure for a 1 cc. injection of a 1-10,000 parts solution of the base compare very favorably with those obtained by Schultz.[1]

Table III.—Blood Pressure Experiment, April 27, 1912.

Female cat, 3 kilograms weight. Same method and dilutions as given under Table I. Solutions prepared at 9.00 A.M. Amount injected, 1 cc.

Solution injected.	Lab. No.	Time of injection.	Blood pressure measured by mercury manometer.			Duration of rise.		Depression.	Duration of depression.	
		A.M.	Before. Mm.	After. Mm.	Rise. Mm.	Min.	Sec.	Mm.	Min.	Sec.
Epinephrin:										
Commercial	1*a*	10.10	130	214	84	2	..	30	1	30
Whale 93[1]	2	10.15	90	198	108	3	..	..	..	..
Whale 93	9	10.23	96	192	96	3	..	..	..	..
Whale "B"[2]	10	10.34	120	188	68	2	..	22	3	..
Whale "B"	3	10.52	100	170	70	2	..	10	1	..
Whale 892	15	11.53	90	150	60	3	..	14	2	..

[1] Repurified.

[2] Impure.

Whale epinephrin "93" (Table III) was repurified by dissolving it in dilute acetic acid containing a small per cent. of sodium sulphite and reprecipitated by adding ammonia. This gave an almost pure white crystalline product as distinguished from the commercial preparation, which is of a pinkish color. The polarimetric measurement was $[\alpha]_D^{25} = -52.00°$. This epinephrin failed to give the after-depression, which occurred with the injections of the commercial and impure whale epinephrin.

As can be seen by examining the table, the increase in the blood pressure lasted for a longer time with the pure epinephrin and there was no depression as characterized by the commercial and impure compound. This would indicate that the depression is due to some impurity. The following tables contain sufficient evidence to prove that the after-effect is due to some foreign substance and is not in any way a part of the epinephrin. The base used for the experiments in Table IV was repurified three times by the method

Table IV.—Blood Pressure Experiment, May 5, 1912.

Female cat. Approximate weight 3 kilograms. Method same as given under Table I. The solutions were prepared at 1.30 o'clock and diluted to make 1–10,000 (*a*) and 1–50,000 (*b*) parts solution (base). Amount injected, 1 cc.

Solution injected.	Lab. No.	Dilution.	Time of injection.	Blood pressure measured by mercury manometer.			Duration of rise.		Depression.	Duration of depression.	
			P.M.	Before. Mm.	After. Mm.	Rise. Mm.	Min.	Sec.	Mm.	Min.	Sec.
Epinephrin:											
Commercial	I*a*	b	2.23	136	180	44	.	42	18	1	30
Commercial	I	a	2.27	136	228	92	2	..	34	.	30
Whale "A"[1]	IV	a	2.40	120	134	114	2	..	..	.	..
Whale "A"	II	b	2.48	120	164	44	1	..	..	.	..
Whale "A"	II*a*	b	3.01	130	176	46	.	57	..	.	..
Whale "B"[2]	III	a	3.06	120	208	88	1	18	6	.	15
Whale "A"	II*a,d*	b	3.22	114	166	52	1	30	..	.	..
Whale "B"	III*a*	a	3.26	116	204	88	1	56	..	.	..
Cattle "A"[3]	IV*a*	b	3.37	120	178	58	1	24	..	.	..
Whale "A"	II*a,f*	b	3.41	120	168	48	1	15	..	.	..
Commercial	I*a,b*	b	3.43	126	178	52	1	12	18	2	..
Whale "A"	II*a,g*	b	3.55	112	168	56	1	30	..	.	..
Commercial	I*a,h*	b	4.03	116	174	58	1	18	6	.	15
Whale "A"	II(15)	a	4.10	116	224	108	2	..	none	.	..
Commercial	I*g*	a	4.15	120	212	92	2	..	18	.	30

[1] Repurified.

[2] Impure.

[3] Prepared in the same manner as the whale epinephrin.

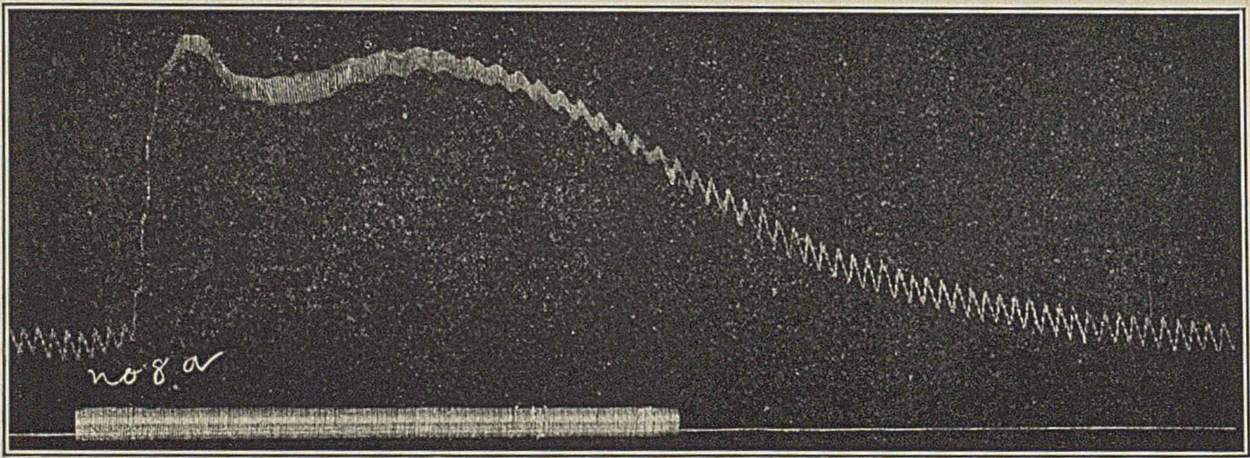
---

[1] *Loc. cit.*

described under Table III in order to be absolutely certain of its purity.

The only depressions obtained were by injecting the impure whale epinephrin and the commercial preparation. The increase in the blood pressure is just about the same with the commercial preparations as with the repurified compound. However, the effect of the drug lasted for a longer time with the pure base. These results are again in agreement with those obtained by Schultz.

It thus becomes evident that the after-effect so commonly given by epinephrin is not a characteristic of the base but is due to some other source. The difference between the pure and impure epinephrin in the increase of the blood pressure shows this depressant substance to be of a very active nature.



CURVE V.

Showing change in blood pressure produced by an intravenous injection of 1 cc. of 1–10,000 parts solution of repurified cattle epinephrin. Data under Table II, Lab. No. VIII*a*. This curve is of the recrystallized cattle epinephrin separated by the same method as that used in obtaining the active principle from the glands of the whale and is identical with the curve produced by the whale epinephrin.

The solutions of epinephrin undergo decomposition very readily and in most cases this is clearly indicated by the color changes. A deteriorated solution will first become pink, then red and finally brown, at which point a precipitate usually is formed. It has been clearly demonstrated by many investigators that solutions having reached this stage are worthless for medicinal purposes.

A few experiments have been made to determine the effect of slightly deteriorated solutions. Only part of the solutions prepared for the physiological experiments given under Table III were used for making those tests. The remaining solutions were placed in white glass bottles, care being taken to see that the bottles were only half filled by the solutions. These were placed aside for one week. On examination, they all showed a change of color, which was more distinct with the commercial solution than with those of the purer epinephrin. The commercial epinephrin had changed to a red color, while the purer base was of a faint pink color. Physiological tests were made of these solutions, the results of which are recorded in Table V.

TABLE V.—AMOUNT INJECTED, 1 CC.

Solution injected.	Lab. No.	Concentration of solution. Base. Gram.	Concentration of solution. Ringer. Cc.	Blood pressure measured by a Mercury manometer. Rise. Apr. 27. Mm.	Depression. (Fresh.) Mm.	Rise. May 5. Mm.	Depression. (Old.) Mm.
Epinephrin:							
Commercial	I*a*	1	10,000	84	30	72	50
Whale "93"	2	1	10,000	108	..	86	22
Commercial Fresh, May 5	1	1	10,000	..	..	92	. 34
Whale Fresh, May 5	IV	1	10,000	..	..	114	none

The injection of a solution after eight days' standing failed to increase the blood pressure to the same degree as a fresh solution of the same strength of the base. The same solution injected into an anesthetized cat eight days previous possessed a stronger vasoconstrictor action than it did after standing. The increase in the blood pressure by an injection of epinephrin varies in the different animals and this is well illustrated in experiments of Table V, in which the fresh solution of epinephrin caused a greater increase in the blood pressure than the fresh solutions injected into a different animal eight days previous; thus if the solutions Nos. I*a* and 2 in Table V had not deteriorated on standing. they should have increased the pressure more in this particular case than they did before, but as denoted by the results, the rise in the blood pressure fell considerably below the previous rise. On comparing these results with those obtained by Schultz,[1] it will be seen that they substantiate his work. As an example, he found that an injection of a 1–10,000 parts solution of "epinephrin"[2] prepared on October 29th gave an increase of 106 mm. in the blood pressure, while a similar solution prepared ten days previous increased the pressure only 75 mm. The results show that this deterioration was just the same with the pure and impure product, as in neither case was the blood pressure increase as great as with the

---

[1] *Loc. cit.*

[2] Schultz uses the name adrenaline instead of epinephrin in this particular case. Adrenaline is often used in the chemical literature for the active principle from the suprarenal glands.

fresh solutions It is also to be observed that the after-depression with the commercial epinephrin has increased and that the pure epinephrin, which a week previous did not give an after-effect, now produces a marked depression. It is quite possible, therefore, that part of the so-called characteristic depressant action of epinephrin is partly due to the decomposition products of epinephrin caused by oxidation, and partly due to the impurities. We may conclude, therefore, that the impurities present in an epinephrin solution perform two functions: first, their presence alone causes the epinephrin to give an after-depression, and second, they tend to accelerate the degree of the deterioration of a solution.

The impurities present in an epinephrin solution consist largely of proteins, lecithins and phosphates. In order to get a control and to see whether the phosphates, which are present in such large quantities in the glands of the whale, have any effect on the blood pressure, physiological tests were made[1] on the various salts of phosphorus and on phosphoric acid alone and in solution with epinephrin. These showed no effect whatever on the blood pressure. On oxidation and decomposition, cholin, or some other substance which is antagonistic to epinephrin, might be formed in small quantities.

CONCLUSIONS.

Epinephrin is present in the suprarenal glands of the whale and can be separated from the glands preserved in chloroform after standing for six to nine months. The highest yield obtained was 0.2 per cent. of the moist glands or about 1.2 grams from each gland.

If the epinephrin is very carefully purified by the method described under Table III and injected intravenously, it gives a marked increase in the blood pressure which is not followed by a depressant action. This so-called depressant property of epinephrin is due to impurities present in the glands and to decomposition products which are formed through oxidation on standing for a short time in aqueous solution. The commercial epinephrin shows this after-depression. The commercial product used in making these comparisons was declared by Schultz to be the best preparation placed upon the market. He gave sufficient evidence to show that it increases the blood pressure to the same degree as a much purer product, and these results were duplicated in the data presented in this paper. However, as is illustrated from these results, the increase in the blood pressure alone cannot be used as an index of purity but the after-depression must also be taken into consideration.

This is illustrated by the following experiments.

Table VI contains an average change in the blood pressure produced by injecting 1 cc. of a 1–10,000 parts solution of the pure and impure epinephrin into a 3 kg. cat. This epinephrin was obtained both from the cattle and the whale.

TABLE VI.

		Concentration of solution.		Blood pressure measured by a mercury manometer.	
Solution injected.	Amt. injected. Cc.	Base. Gram.	Ringer. Cc.	Rise. Mm.	Depression. Mm.
Epinephrin:					
Commercial	1	1	10,000	84	30
Pure	1	1	10,000	108	none

The following table contains an average change in the blood pressure produced by injecting 1 cc. of a 1–50,000 parts solution (base) into a 3 kg. cat.

TABLE VII.

		Concentration of solution.		Blood pressure measured by a mercury manometer.	
Solution injected.	Amt. injected. Cc.	Base. Gram.	Ringer. Cc.	Rise. Mm.	Depression. Mm.
Epinephrin:					
Commercial	1	1	50,000	55	8
Pure	1	1	50,000	58	0

Several different methods were used to detect iodine in the glands and they all gave negative results.

The author wishes to express his gratitude to Dr. Robert Kennedy Duncan, Sc.D., for his helpful assistance in this work.

DEPARTMENT OF INDUSTRIAL RESEARCH,
UNIVERSITY OF KANSAS,
LAWRENCE.

---

[1] These were studied by Mr. Burket and the complete results will be published in his paper in the *Am. J. Phys.*

THE CHLORIDES OF CARBON AS SOLVENTS, I: CARBON TETRACHLORIDE.[1]

By CHARLES BASKERVILLE AND H. S. RIEDERER.

Received June 22, 1912.

INDUSTRIAL CONSIDERATIONS.

Serious endeavors have been made to introduce carbon tetrachloride, which has replaced chloroform for many purposes, as a substitute for benzine in industrial extraction processes, and it has, in fact, been adopted in a number of industries with excellent results. For such a purpose, a solvent, to be of industrial value, should satisfy the following requirements:[2]

1. It should be free from danger of inflammability and explosion.[3] This is, as is well-known, one of the principal advantages in using carbon tetrachloride, and renders it of especial importance in the dyeing industry and in cleaning establishments.[4] When such a non-inflammable material as carbon tetrachloride is employed as a solvent, high premiums for fire insurance and special precautions against fire are reduced.

2. It should be a uniform chemical compound and not a mixture, so that only distillation, and not fractionation, should be required in practice. Carbon tetrachloride complies in full with this requirement.

3. It should be completely volatile without imparting any odor to the solute or extracted material. It has been found that bone fat produced with the aid of carbon tetrachloride is of superior quality to that

---

[1] Read before the New York Section of the American Chemical Society, May 10, 1912.

[2] On these points, see Ganswindt, *Z. angew. Chem.*, **1899**, 537.

[3] Carbon tetrachloride is uninflammable and furnishes no explosive vapors. On the flash-points of mixtures of carbon tetrachloride and light petroleum, see Barrier, THIS JOURNAL, **2**, 16.

[4] A number of processes have been devised for rendering carbon tetrachloride soluble in dilute soap solutions and for rendering it soluble in, or emulsifiable with, water. The products are intended for use in cleansing textiles, etc. Sommerfeld (*Leipziger Färber- u. Zeugdrucker-Ztg.*, **47**, 223) pointed out that carbon tetrachloride could be used for removing grease stains, and that, unlike when petroleum spirit was used, there was no halo left after the stain had disappeared. Carbon tetrachloride has been sold as a grease eradicator for some time.

obtained by means of petroleum ether. In such extraction processes, the favorable results obtained are also to be attributed, in part, to the fact that, with carbon tetrachloride, the extraction is at a lower temperature.[1]

4. It should dissolve fats, resins, and oils as readily as benzine.[2]

5. It should not freeze at the average winter temperature. Carbon tetrachloride freezes at —24.7° C. at the ordinary pressure, and at 0° C. under 620 atmospheres pressure.

6. Its vapors, when inhaled, should not exert any objectionable physiological action. It has been stated that the use of carbon tetrachloride is objectionable from a hygienic standpoint;[3] but its anesthetic action has been investigated, and, notwithstanding many statements to the contrary, carbon tetrachloride has been found to be quantitatively less active than benzine.[4]

7. Its price should be as nearly as possible that of benzine. Comparative high cost has been the principal handicap of carbon tetrachloride.

Other worthy advantages of carbon tetrachloride than those given above, are: It has a lower boiling point—namely, 78.1° C.—than the generally employed petroleum fractions (70°–120° C.); it possesses a specific gravity of 1.63, and therefore shares with carbon disulphide the advantage of being heavier than water; and it possesses both a low specific heat (0.219 at 80° C.) and a low latent heat of evaporation, in consequence of which its use effects a great saving in steam and cooling water.

It has been indicated, however, that these advantages are not a sufficient set-off against the comparative high price of carbon tetrachloride, for, in the extraction processes by the aid of solvents, the volume of the solvent and not its weight must be considered.[5] It is evident that for the same volume of solvent more than twice as much of carbon tetrachloride by weight must be used as of petroleum naphtha.[6] The loss, expressed in actual money value, is also greater than in the case of naphtha; and it has been said that the difference in favor of carbon tetrachloride in cooling water required for condensing the vapors is too small, even though lower insurance premiums be considered, to counterbalance the difference in cost of the amounts of solvents employed. Carbon tetrachloride also attacks iron and copper, especially in the presence of moisture, so that it is necessary to use lead- or tin-lined extraction apparatus, just as in the case of *s*-tetrachloro-ethane.[1]

Pichon and Truchelut have pointed out[2] that the use of carbon tetrachloride has been restricted in many industries by its tendency to decompose, with the liberation of hydrogen chloride,[3] particularly when mixed with light petroleum. They claimed a method for suppressing this decomposition, depending upon the addition of from 1–5 per cent. of oil of turpentine or other hydrocarbon with a great affinity for oxygen.

Baskerville and Hamor[4] find that while pure carbon tetrachloride is subject to oxidation, carbonyl chloride being formed, when exposed to light in partially filled colorless glass containers for long periods,[5] and that this decomposition is accelerated by the presence of hydrochloric or sulphuric acid, yet the oxidation is much slower than in the case of chloroform. The small amount of sulphur or carbon disulphide, or both, present in commercial carbon tetrachloride may act as a preservative, and there has been very little complaint among consumers about the decomposition of the solvent. Carbon tetrachloride should not, of course, be used in the presence of oxidizing agents or mineral acids; and when it is to be kept for some time, should be stored in a dark, cool place, in well filled, or, better still, totally filled containers.

Notwithstanding the objections which have been urged against the employment of carbon tetrachloride, it has admittedly taken a place as an industrial solvent; its high solvent power for various substances, its uniformity, non-inflammability and non-explosibility, have particularly impressed certain manufacturers, and it has replaced benzine and carbon disulphide in some plants where risks from fire or explosion are serious considerations. With suitable extraction apparatus, the losses during extraction processes should be small and the solvent should do its work rapidly and economically.

---

[1] On this point see Brücke, *Chem. Rev. Fett- u. Harz-ind.*, **12**, 100.

[2] Von Schwartz ("Fire and Explosion Risks," p. 256, 1904) refers to carbon tetrachloride as "the best of all substitutes for benzine" and states that it "dissolves fat as readily as benzine."

[3] Von Schwartz, *ibid.*

[4] Lehman, *Chem.-Ztg.*, **1906**, 330; cf., however, Goehrig, *J. Soc. Chem. Ind.*, **22**, 1344.

On the physiological action of carbon tetrachloride, see also B. and F. *Med.-Chir. Rev.*, **1867**, 551; *Lancet*, June, 1867; Richardson, *Sci. Am. Suppl.*, No. 515, 8227; Bianchini, *Stazione Sperimentale Agraria Italiana*, **37**, 171 (1904); Freyss, *Chem.-Ztg.*, **1903**, 1137; Haller, *Ber. ueber die Weltausstellung in Paris*, **1900**: Morel, *Compt. rend.*, **84**, 1460; and Regnauld, *Idem.*, **100**, 1146.

While it is stated that carbon tetrachloride is more toxic and more irritating to the mucous membrane of the trachea and bronchi than chloroform (Francis and Fortescue-Brickdale, "The Chemical Basis of Pharmacology," **1908**, p. 97), Cushny states that its heart depressing action is one-half as strong as that of chloroform, and Marshall found the difference in action between carbon tetrachloride and chloroform to be mainly due to physical characteristics.

Carbon tetrachloride has been used by hairdressers to clean the hair, and a case of accidental poisoning, owing to the inhalation of the vapor, has been reported (*Lancet*, **1907**, i, 1725). This case very nearly had a fatal termination.

[5] See Zänker, *Leipziger Färber- u. Zeugdrucker-Ztg.*, **48**, 237.

[6] In washing operations, generally speaking, equal volumes have to be taken for comparison.

[1] Bolis (*Chem.-Ztg.*, **30**, 1117) found that perfectly dry carbon tetrachloride might be boiled in cast-iron vessels and would exert very slight action on them; but that if moisture was present, the iron was very sensibly attacked, the rate of attack increasing with the proportion of moisture. Brücke (*loc. cit.*) reported that ordinary iron extraction apparatus was quite unsuitable for carbon tetrachloride.

[2] French Patent, 402,235, April 20, 1909.

[3] Carbonyl chloride is produced by the action of powerful oxidizing agents, such as, for example, chromic acid, on carbon tetrachloride (Schmidt, *Pharm. Chem.*, **2**, 148 (1896)). Goldschmidt reported (*Wien. Akad. Ber.*, 2, *Abt.* **83**, 736; *Ber.*, **14**, 927) that water and carbon tetrachloride form hydrogen chloride and carbon dioxide at high temperatures.

For a résumé of the deportment of carbon tetrachloride with various inorganic and organic compounds, see Margosches, *Der Tetrachlorkohlenstoff*, **1905**, 45–72; and on the pyrogenic reactions of the compound, consult Regnault, *Ann.*, **33**, 310; *Ann. chim. phys.*, [2] **71**, 353; Kolbe, *Ann.*, **54**, 147; Basset, *Chem. News*, **20**, 175; Lüdeking, *Phil. Mag.*, [5] **33**, 521; Hodgkinson and Lowndes, *Chem. News*, **58**, 187; Löb, *Z. Elektrochem.*, **7**, 903.

[4] Unpublished investigation.

[5] The exposures were made for one year, to diffused sunlight and at 20° C., in bottles containing varying amounts of air.

In this connection, see Baskerville and Hamor, THIS JOURNAL, **4**, No. 4, 287.

THE SOLVENT PROPERTIES OF CARBON TETRACHLORIDE.

With regard to the solvent properties of carbon tetrachloride, very few data are available with reference to pure chemical substances. For the most part, medicinal preparations have alone been studied, and these are all very sparingly soluble.[1] Inorganic salts have received little consideration; and while such substances as acetic acid, bromine, iodine, and carbon dioxide have been investigated as to their distribution in the system water-carbon tetrachloride, yet the results give no indication of the actual solubility of these in carbon tetrachloride.

The solution of gums, resins, natural pitches, asphalts, etc., in carbon tetrachloride has been reported,[2] but the results have received only partial confirmation,—in fact, many of the statements relating thereto are conflicting. Gum mastic, for example, has been reported to be both soluble and insoluble in hot carbon tetrachloride, while, as a matter of fact, it is completely soluble at +20° C. Andes[3] reported on gums, resins, etc., insoluble, partly soluble, and soluble, which might be more easily dissolved by admixture of other solvents, as alcohol, turpentine, and the like, for producing varnishes.

Carbon tetrachloride has been used for extracting fats,[4] oils,[5] waxes,[6] asphalt,[7] resins,[8] dyes,[9] alkaloids,[10] and for dissolving caoutchouc;[11] but in the published accounts of these applications no mention of quantitative data is made.

This investigation was undertaken with the following ideas in mind:

1. To learn if the chlorides of carbon would answer the purposes of some of the solvents used at present on a large scale commercially or as analytical reagents.
2. To determine, provided they proved commercially desirable, if they supplied a less hazard to life in their use.
3. To learn if some means might be devised whereby these solvents, some already proven of value in specific cases, both as to hygiene and efficiency, could be produced at a less or at least more reasonable price.

This communication presents some new data on carbon tetrachloride as a commercial solvent. Other phases of the topic will be presented in later papers.

EXPERIMENTAL.

In the experimental determinations of the solvent properties of carbon tetrachloride, commercial carbon tetrachloride, 99.70 per cent. pure, was used.[1] All determinations were made at room temperature, which varied from 20°–21° C.—an amply close range for the work. The solvent with an excess of the solute[2] was placed in a glass-stoppered flask of suitable size and occasionally agitated at room temperature until a saturated solution was obtained; the solution was then filtered as rapidly as possible into a covered tarred dish, and weighed; and finally it was evaporated at 60° C. and the residue weighed. Viscous solutions were filtered by forcing them through absorbent cotton by the aid of compressed air. In the case of volatile solids such as camphor, it was found that these could be examined most easily by weighing an amount of solvent in a small ground-glass-stoppered weighing flask and then adding small quantities of solute until saturation was reached; the weight of the solution obtained in this manner gave the weight of actual solute. The results obtained by the authors during the course of an investigation of the solvent action of carbon tetrachloride on various substances are given below.

ASPHALTS, BITUMENS, ETC.—This class of natural and artificial products includes many which differ from each other in a variety of reactions, based mainly, however, on their solubility or insolubility in various solvents. Carbon tetrachloride has been employed in connection therewith principally for analytical purposes.

Richardson and Forrest[3] have called attention to the use of carbon tetrachloride as a solvent for differentiating between bitumens. Some of these are soluble in carbon disulphide and insoluble in carbon tetrachloride, and the quantities of such "carbenes"[4] present give an indication of the weathering or excessive heating, or both, to which a natural asphalt has been subjected.

Gilsonite is almost completely soluble in carbon tetrachloride. It is the purest natural bitumen

---

[1] See appended Tables.

[2] In, for example, *Neueste Erfind. u. Erfahrungen*, **1896**, 3.

[3] *Chem. Rev. Fett- u. Harz-Ind.*, **12**, 157 (1905).

[4] On the determination of fat in food materials, see Bryant, *J. Am. Chem. Soc.*, **1904**, 568. Mention has already been made of carbon tetrachloride as a fat solvent.

[5] *E. g.*, in the determination of oil in cottonseed products (Herty, Smith, and Orr, This Journal, **1**, No. 2).

[6] In the analysis of paraffin, Graefe, *Chem. Rev. Fett- u. Harz-Ind.*, **1906**, 30. In German Patent, 179,449, January 3, 1902, fat or wax is extracted from moist substances by using, among other solvents, carbon tetrachloride; and in English Patent, 741, January 13, 1908, to moderate the chlorination reaction on resins, gums, wax, fats, oils, etc., these are dissolved in carbon tetrachloride.

[7] See Richardson and Forrest, *J. Soc. Chem. Ind.*, **24**, 310.

[8] On carbon tetrachloride as a paint or varnish diluent, see Le Roy, *Rev. Chim. Ind.*, **11**, 173. Le Roy gave the advantages as follows: diminished inflammability, less tendency for the pigment to deposit on keeping, freedom from solidification or resinification during storage, brilliant strong films, and excellent drying power.

In U. S. Patent, 817,141, April 3, 1906, to Ellis, carbon tetrachloride in combination with wax, alcohol, and amyl acetate is claimed as a paint and varnish remover.

[9] In the determination of dyes in confectionery, Pintte and Bentivoglio, *Gazz. chim. ital.*, **1906**, ii, 385. On the solution of fatty color lakes in carbon tetrachloride, see Sommerfeld, *loc. cit.*

[10] See Schindelmeiser, *Chem.-Ztg.*, **1901**, 129.

[11] In the preparation of an antiseptic rubber solution for clinical use, Wederhake, *Med. Klin.*, **1908**, 1302.

[1] The carbon tetrachloride used in this investigation was generously supplied by The Dow Chemical Company, of Midland, Mich.

[2] All of the samples of commercial products used in the work were obtained from reliable concerns. The authors are grateful for the assistance which was rendered by a number of houses in securing correct samples with their true designations, and are particularly appreciative of the following presentations:

Graded varieties of Arabic, Senegal, Indian and Tragacanth gums from Thurston and Braidich.

Animal and vegetable oils from Mr. Henry A. Gardner.

A very fine collection of commercial shellacs, also some natural and artificial bitumens from John R. Anderson and Company.

Vegetable and mineral waxes from Mr. D. Steengrafe.

All grades of commercial rosin from A to WW from George L. Hammond and Company.

Cellulose nitrate and cellulose acetate from The Arlington Company.

The other samples used were purchased in the open market.

[3] *Loc. cit.*

[4] Richardson, "The Modern Asphalt Pavement," 1st Ed., p. 120.

(99.5 per cent. pure) and absorbs carbon tetrachloride, being miscible in all proportions.

Grahamite, while an almost pure bitumen, is, unlike gilsonite, almost entirely insoluble in 62° naphtha and is 55–80.6 per cent. insoluble in carbon tetrachloride.[1]

Albertite is partly soluble in carbon tetrachloride.

Oil asphalt and *Refined bitumens* are from 99.0–99.9 per cent. soluble in carbon tetrachloride.

Andes[2] states that *Syrian asphalt* and probably all others are soluble in carbon tetrachloride.

Other solid bitumens and their deportment with carbon tetrachloride are: *Wurtzilite* (elaterite, tabbyite, aeonite, aegerite), slightly soluble; *Wiedgerite* ("mineral liver"), soluble; and *Impsonite*, partly soluble.[3] Ozokerite is considered among the waxes.

CELLULOSE, ACETATES AND NITRATES.—Like chloroform carbon tetrachloride is a *Pyroxylin* nonsolvent; it dissolves *camphor*, but, unlike chloroform, does not dissolve the *cellulose acetates*. The results of the determinations of the authors show that the *cellulose nitrates* (11.32 and 12.63 per cent. nitrogen) and *cellulose acetates* (three varieties), as well as *Celluloid*, are insoluble in carbon tetrachloride at 20° C.

It may be noted here that the authors found that 100 g. of carbon tetrachloride would dissolve 125 g. of *camphor* at 20° C.

RUBBER.—While carbon tetrachloride is a recognized solvent for rubber, no figures on its solubility can be determined with our present knowledge and methods. Like oils, waxes and fats, rubber will absorb or dissolve considerable quantities of carbon tetrachloride without assuming a liquid state. Furthermore, the amount of solvent necessary to produce a solution of definite viscosity varies with the same grade of rubber; for example, a rubber which has been masticated very much will form a more liquid solution than one which has not been worked in this way. The many grades of rubber which come into the markets all deport more or less differently, aside from the variations in each grade due to mechanical treatment; and besides, the moisture content of two samples masticated to the same extent, but dried differently, will also affect the character of the solution.

In the experiments conducted by the authors, the following grades of rubber were tried: *Up-river pure para, guayule, pale Ceylon crep, dark Ceylon crep, equateur*, and *pontianac*. It was found that 25 g. of the better grades (all except guayule and pontianac) would easily dissolve 200 g. of carbon tetrachloride, and much more carbon tetrachloride was necessary to obtain a flowing solution. It may be noted here that, according to Woudstra,[4] caoutchouc is a true colloid and the viscosity of its solutions decreases with standing.

The use of carbon tetrachloride in the purification of caoutchouc has been claimed in French Patent 404,307, June 22, 1909, of the General Caoutchouc Co., Ltd.[5]

ALCOHOL GUMS.—Of the gums of this class, mastic, sandarac, and sed accroides were tried. *Accroides* showed no solubility in carbon tetrachloride.

Sandarac was found by Coffignier[1] to be 77–79 per cent. insoluble in carbon tetrachloride, while Andes[2] reported that it was insoluble, but, like yellow accroides and mastic, dissolved on adding small amounts of alcohol or turpentine. The authors found that sandarac is partly soluble in carbon tetrachloride, although no attempt was made to ascertain the proportion. Boiling a small amount of sandarac with a large excess of carbon tetrachloride did not effect complete solution; but the soluble portion yielded, on evaporation, a light yellow resinous mass, clear and brittle.

Notwithstanding the findings of Andes, experiments showed that mastic dissolves completely in carbon tetrachloride at 20° C., forming a light yellow, very viscous solution. However, a true solubility can hardly be spoken of, owing to mutual solubility. Filtration was effected through cotton with compressed air; and on evaporating the viscous solution at 60° C., no constant weight was obtained even after 300 hours: decomposition had set in, although mastic alone is unaffected under the same conditions.

COPAL GUMS.—Margosches[3] has stated that melted Zanzibar Copal, and probably all other melted copals, are soluble in carbon tetrachloride. Andes[4] reported that hard Manila copal is insoluble, swells in the solvent when in a fine powder, but is completely soluble upon the addition of a small amount of alcohol or turpentine.

The authors find that the natural copals act differently according to their origin, but that they are all partly soluble at 20° C.; heating does not assist solution, the gums partly melting and decomposing even before all the carbon tetrachloride is expelled. In the experiments made, the ground copals were agitated with carbon tetrachloride.

Zanzibar copal is slightly soluble in carbon tetrachloride and the insoluble portion has a very slight tendency to gum together (swelling).

The *Manila copals* exhibit this gumming or swelling to a marked degree, all the fine particles adhering and forming a soft film on the solution, which film may be pulled, although it possesses no elasticity; *i. e.*, it does not return to its original shape as happens with rubber.

The *Congo copals* deport similarly to Manila copal, while *Pontianac copal* has much similarity to Zanzibar copal.

Sierra Leona copal swells up and gums much more than the above mentioned, and is partly soluble.

Brazilian copal is partly soluble without gumming, while *Brazil gum copal* in small fragments swells in the solvent.

DAMAR GUM.—This gum is completely soluble in carbon tetrachloride, giving a turbid solution which clears up on adding 95 per cent. alcohol or on warming.

---

[1] Richardson, *Ibid.*

[2] *Loc. cit.*

[3] See "Mineral Resources of the United States," **1910**, ii, 836.

[4] *Z. Chem. Ind. Kolloide*, **5**, 31 (1909).

[5] The process is for the purification of a caoutchouc by rendering it viscous with carbon disulphide or carbon tetrachloride, then treating with a solvent which will extract resin, but which will not dissolve caoutchouc.

[1] *Bull. soc. chim.*, **27**, 549 (1902).

[2] *Loc. cit.*

[3] "Der Tetrachlorkohlenstoff," Vol. 10, *Sammlung Chem. u. Chemtech. Vortraege*, **1905**, p. 99.

[4] *Loc. cit.*

The solution filters easily. On evaporating the solvent at 60° C., some decomposition seems to occur, as shown by a darkening of the gum. Evaporation to constant weight showed that 100 g. of carbon tetrachloride dissolve 7.13 g. Batavia damar at 20° C.

KAURI GUM.—Several samples, ranging in quality from the finest to the most ordinary Kauri gum, were powdered and then treated with carbon tetrachloride. After standing, with occasional agitation, for several days, it was found that the gum was attacked to a certain extent, although not uniformly. Coffignier[1] has made an extensive study of Kauri gum. He found that brown hard Kauri gum gave a yellow solution and dark brown residue; that bush Kauri gum swelled and left a dark brown residue; and that bush-gathered gum afforded a pale yellow carbon tetrachloride solution and a dark brown residue. His results are, while interesting, of doubtful value; for the raw material is of variable character, probably between wide limits, and the components have yet to receive careful study. Some of these components deport differently from others, and although two samples of gum may have the same trade grading, yet their chemical and physical reactions may differ widely.

WATER GUMS.—Samples of different grades of *aleppo, Turkey* and *Persian gum tragacanth, Indian gum, gum senegal,* and *gum arabic* were treated with carbon tetrachloride. After standing for several days, with agitation, 50–70 g. of the solution were filtered and evaporated. The residue in all cases amounted to but a trace; consequently, this class of gum shows practically no solubility in carbon tetrachloride. After treatment with carbon tetrachloride, the gums did not exhibit any apparent physical change.

SHELLAC.—Andes[1] reported that shellac is insoluble in carbon tetrachloride, but that it is soluble in a mixture of 70 g. carbon tetrachloride and 30 g. 25 per cent. alcohol. Experiments by the authors on four samples—*Superfine Quality, TN Quality Native Shellac, A. C. Garnet Shellac,* and *Refuse Lac*—confirm the work of Andes.

The authors found that the *superfine* gave a negligible extract residue; that the *TN native* gave 0.2 per cent. residue from the solution, this residue being slightly turbid and brittle; that the *A. C. garnet* gave 0.2 per cent. residue, this consisting of a transparent non-brittle wax-like substance; and that *refuse lac* gave 0.2 per cent. residue also, this being very similar to shellac wax.

ROSIN.—Rosin of four different commercial grades was treated with carbon tetrachloride, and apparently a true solution resulted. This solution was difficult to handle, being exceedingly viscous; to remove undissolved rosin and grit, the solution was forced with compressed air through absorbent cotton into a tared dish. Evaporation, made at 60° C., was very slow.

Even after heating for over 350 hours at 60° C., the filtered solutions did not attain a constant weight; a blank showed only very slight losses under the same conditions. Other experiments seemed to show that not only does rosin dissolve in carbon tetrachloride, but that carbon tetrachloride also dissolves in rosin; furthermore, that a small amount of carbon tetrachloride with rosin gives a solid solution. Under such conditions, it is, of course, impossible to supply exact data as to the actual amount of rosin soluble in carbon tetrachloride.

The experimental results of the authors seem to indicate that the depth of color of a carbon tetrachloride solution of rosin may be employed to fix the grade of the sample.

PINE OIL.—Crude pine oil was found to mix in all proportions with carbon tetrachloride with, however, the formation of a white precipitate. Very small amounts of carbon tetrachloride were found to give no visible precipitate, and it was found that the production of a turbidity or white precipitate was due to the presence of water in the pine oil.

Fractional distillation products, refined and decolorized, were also available; these were: 156°–165°, 165°–177°, and 177°–195° C. None showed any precipitate with carbon tetrachloride and all mixed perfectly in all proportions.

WAXES.—The following waxes were treated with carbon tetrachloride: flora carnauba wax and No. 3 ceara carnauba wax, Japan wax, pure ozokerite, candellila wax, montan wax, yellow Cuban beeswax, bayberry wax, shellac wax (m. p. 75° C.), paraffin wax refined (m. p. 120° C.).

All of these absorb carbon tetrachloride at 20° C.; and, according to the amount of this solvent used, the resulting mass will be more or less solid or semi-fluid.

Ozokerite shows this most plainly, forming a homogeneous product in all proportions with carbon tetrachloride.

The *carnauba waxes* appear to be a distinct mixture of substances of different properties. The addition of a small amount of carbon tetrachloride softens the whole mass and further additions will finally give two layers on standing, the upper layer carrying the insoluble portion of the wax as a bulky flocculent mass, while the lower is very fluid.

Beeswax acts like carnauba wax, except that a liquid portion can be separated from the semi-solid residue without having it all suspended in the solution. It is interesting to note that the liquid portion carries the coloring matter, while the residuum is nearly white. Upon melting the latter on water, a product is obtained which hardly differs from the original wax, except that the color is gone, also some of the characteristic odor, and the product may be slightly harder.

Japan wax absorbs carbon tetrachloride more readily than the others above mentioned, forming at first a turbid semi-fluid mass. Upon the addition of more carbon tetrachloride, the fluidity increases, and finally a perfectly clear solution is obtained, although this point can not be sharply defined since the colorless particles in suspension which form the turbidity cannot be seen when the point of complete solution is approached. A portion of the turbid solution was

---

[1] *Loc. cit.*

filtered and evaporated, and the solubility figures 31.0 g. in 100 g. of carbon tetrachloride at 20° C. were obtained.

Montan wax acts similarly to carnauba wax, and the suspended wax is so sticky that it will totally obstruct any filter almost immediately. The addition of more solvent to permit of filtration would introduce the question as to whether the solution would then be saturated, and no practical method of determining this is known to the authors. The addition of a large excess of solvent leaves two layers on standing—a turbid solution below and the insoluble portion of the wax.

TABLE I.—THE SOLUBILITY OF VARIOUS INORGANIC SUBSTANCES IN CARBON TETRACHLORIDE.

Substance.	Solubility in 100 g. solvent.	Temperature.	Authority.
Chlorine[1]	10.5	0°	Dow Chemical Co.
Chlorine	7.4	15°	Dow Chemical Co.
Chlorine	5.56	25°	Dow Chemical Co.
Chlorine	3.02	40°	Dow Chemical Co.
Chlorine	1.17	55°	Dow Chemical Co.
Chlorine	0.81	65°	Dow Chemical Co.
Iodine	3.033	25°	Jakowkin, *Z. phys. Chem.*, **18**, 590 (1895).
Sulphur	0.717	20°	The authors.
Mercuric chloride	0.002	18°–20°	Sulc, *Z. anorg. Chem.*, **25**, 401.
Mercuric iodide	0.006	18°–20°	Sulc, *Ibid.*
	0.094	75°, b. p.	
Mercuric cyanide	0.001	18°–20°	Sulc, *Ibid.*
Stannic iodide	100 g. sol. (density 1.59) at 22.4° contain 5.25 g.		McDermott, *J. Am. Chem. Soc.*, **33**, 1963 (1911).
Stannic iodide	100 g. sol. (density 1.63) at 50° contain 8.21 g.		McDermott, *Ibid.*

[1] The use of a solution of chlorine in carbon tetrachloride in analytical chemistry is being investigated in this laboratory by Dr. L. J. Curtman.

It would seem that montan wax is undoubtedly a mixture of several components which differ materially from each other in their properties.

Candelilla wax.—What has just been said of montan wax applies equally well to candelilla wax.

All the above-mentioned waxes dissolve completely and easily in carbon tetrachloride at or near its boiling point, although the solutions may show a slight turbidity depending upon the amount of solvent present. A very small amount of carbon tetrachloride introduced into the melted wax dissolves completely. Accordingly, it may be said that waxes are partially soluble in cold carbon tetrachloride, completely soluble at or near the boiling point, and that the melted wax mixes in all proportions with carbon tetrachloride.

TABLE II.—THE SOLUBILITY OF NAPHTHALENE IN CARBON TETRACHLORIDE.

Solubility in 100 g. solvent.	Temperature.	Authority.
9.0	0°	Schroeder, *Z. phys. Chem.*, **11**, 457 (1893).
14.0	10°	Schroeder, *Ibid.*
20.0	20°	" "
23.0	25°	" "
26.5	30°	" "
35.5	40°	" "
47.5	50°	" "
62.5	60°	" "
80.8	70°	" "

Fats, Tallow, etc.—The rendered animal fats, tallow, etc., are soluble in all proportions in carbon tetrachloride, and on melting yield clear solutions. According to the proportion of fat to solvent, the mixture may be from an opaque solid to a clear liquid in the cold (*i. e.*, at 20° C.).

Butter is heterogeneous and only partially soluble, the fatty components being taken up by the carbon tetrachloride. In the presence of water, on heating, an emulsion is formed which, on standing, separates into three layers, namely, the water-extract above, the carbon tetrachloride below, and very likely the casein between, since casein is insoluble in either.

Fatty Oils. — The solubility of the following oils was determined: menhaden, whale, linseed (raw and boiled), corn, untreated Chinese wood, soya, and cottonseed. It was found that all of these are miscible in all proportions with carbon tetrachloride.

TABLE III.—THE SOLUBILITY OF CARBON TETRACHLORIDE IN WATER.

Solubility in 100 g. water.	Temperature.	Authority.
0.097	0°	Rex, *Z. phys. Chem.*, **55**, 355 (1906).
0.083	10°	" *Ibid.*
0.080	20°	" "
0.085	30°	" "

In order to determine the value of carbon tetrachloride as an extracting solvent, 10 g. of each oil, with the exception of cottonseed, were mixed with 25 cc. of carbon tetrachloride and then evaporated at 60° C., a blank with 10 g. of each oil being heated at the same temperature for the same length of time. The period of heating varied from 5$^{1}/_{4}$ hours to 10 hours, depending upon the rapidity with which the solvent evaporated. The following results were obtained:

Menhaden oil, after six hours heating, gained less than 1 per cent. The appearance of the oil was not noticeably altered, although the odor appeared to be stronger than in the original sample.

TABLE IV.—THE SOLUBILITY OF VARIOUS MEDICINAL PREPARATIONS IN CARBON TETRACHLORIDE.

Substance.	Solubility in 100 g. solvent.	Temperature.	Authority.
Aconitine (amorphous)	1.99	18°–22°	Mueller, *Apoth.-Ztg.*, **18**, 2 (1907).
Brucine	0.078	...	Mueller, *Ibid.*, 232.
Brucine	1.937	17°	Schindelmeiser, *Loc. cit.*
Atropine	1.136	17°	Schindelmeiser, *Loc. cit.*
Caffein	0.089	18°	Goeckel, *J. Chem. Soc.*, **74**, 327 (1898).
Caffein	0.702	Boiling	
Chinine, hydrate	0.203	...	Mueller, *Loc. cit.*
Chinine, anhydrous	0.529	...	Prunier, *J. Pharm. Chim.*, [4] **29**, 136.
Chinidine	0.565	...	
Cinchonin	0.0361	...	
Cinchonidin	0.0508	...	
Cocaine	18.503	...	Schindelmeiser, *Loc. cit.*
Codein	1.328	...	Schindelmeiser, *Loc. cit.*
Hydrastine	0.123	...	Mueller, *Apoth.-Ztg.*, **18**, 249.
Hyoscyamine	0.059	...	Mueller, *Ibid.*
Morphine	0.0156	18°–22°	Mueller, *Idem.*, 257.
	0.032	17°	Schindelmeiser, *Loc. cit.*
Narcein	0.011	17°	Schindelmeiser, *Loc. cit.*
Papaverine	0.203	17°	Schindelmeiser, *Loc. cit.*
Strychnine	0.158	20°	Mueller, *Loc. cit.*
	0.645	17°	Schindelmeiser, *Loc. cit.*
Theobromine	0.0212	...	Goeckel, *Chem. Centr.*, **1897**, ii, 401.

Linseed oil, boiled, gained 1.25 per cent. after 5 hours and 40 minutes.

Linseed oil, raw, gained 1 per cent. after 5 hours and 20 minutes.

These oils skinned slightly during the period of heating, and it is probable that the solvent may be removed only under reduced pressure and at a low temperature so as to leave the oil unchanged.

Chinese wood oil.—In 5 hours and 15 minutes the sample to which carbon tetrachloride has been added skinned over to a considerable extent and gained 2.30 per cent. The blank showed only light skinning and an increase of but 0.27 per cent.

Whale oil gained 0.6 per cent. in 6 hours. The appearance and odor were not changed

Corn oil.—Eight hours heating was necessary in order to obtain a constant weight; a very small loss (0.04 per cent.) resulted, due possibly to the presence of water in the sample. There was no apparent change in either odor or appearance.

Soya oil.—After 7 hours the sample to which carbon tetrachloride had been added showed an increase of 0.5 per cent., while there was no gain in the blank. After heating for 3¹/₂ hours longer, the mixed sample had gained 1 per cent. and the blank 0.3 per cent. It therefore appears that Soya oil will stand heating for some time before giving any indications of oxidation. Heating somewhat intensified the odor.

DEPARTMENT OF CHEMISTRY,
COLLEGE OF THE CITY OF NEW YORK.

ON THE SURFACE TENSION OF SILICATE AND BOROSILICATE GLASSES.

By EDWIN WARD TILLOTSON, JR.

Received July 1, 1912.

In a former paper[1] from this laboratory, a simple and convenient method was described for measuring the surface tension of molten glasses. This method consisted, briefly, in the determination of the relation between the weight of the drops falling from glass fibers of known diameter, which were lowered vertically into the carefully regulated flame of a blast lamp. It was found that the weight of the drop was within limits a parabolic function of the diameter of the fiber and to be expressed by the following equation:

$$W = \alpha D + \beta D^2$$

when W is the weight of the drop, D the diameter of the fiber, α a factor proportional to the surface tension and, β a factor dependent on the cohesion of the molten glass. This factor β seemed to be nearly constant for a considerable number of borate glasses, although it varied widely for some of the silicates.

The present paper is a record of surface tension determinations made on some sodium silicates, soda lime and soda-barium glasses, and also soda barium glasses containing boric oxide. For these measurements about ten fibers were drawn from each glass, varying roughly from 0.10–1.00 mm. in diameter, the drops formed in the manner previously described, and weighed. In every glass examined the parabolic relation of the diameter of fiber to weight of drop was observed and it was found that this was satisfied by a value of 15 for β in all of the glasses. This value for β is not an exact one, nor can it be accurately calculated from so few measurements. There are many causes which contribute to variations in the weight of individual drops. Inhomogeneity of the glass, errors in measurement of the diameter of the fiber, momentary changes in the condition of the flame—all may effect the weight of the drop. It is therefore necessary to make many measurements on the same glass in order to fix the exact value of β. But since for these glasses a difference of one unit in β produces a variation in the surface tension of only 2 dynes and since this is small in comparison to that introduced by variations of individual drops, the value 15 was adopted for β in all of these glasses That this procedure was justified is shown by the fact that the values for α were neither progressively higher nor lower as the diameter of the fibers increased.

TABLE I.—SODIUM SILICATE GLASSES.

SiO_2. Per cent.	Na_2O. Per cent.	T = dynes per cm. Obs.	T = dynes per cm. Calc.
49.3	50.7	142	145
59.2	40.8	142	142
66.4	33.6	136	139
73.1	26.9	133	137
74.5	25.5	138	137
77.5	22.5	138	137
77.3	22.7	137	136

TABLE II.—SODA-BARIUM GLASSES.

SiO_2. Per cent.	BaO. Per cent.	Na_2O. Per cent.	T = dynes per cm. Obs.	T = dynes per cm. Calc.
70.10	6.50	23.40	144	140
66.15	13.00	20.85	145	144
61.70	19.80	18.50	150	148
57.30	26.57	16.13	164	151
53.00	33.60	13.40	153	155
48.37	40.70	10.88	155	159
71.70	5.65	22.65	138	140
67.60	12.55	19.85	143	143
64.55	18.45	17.00	151	146
61.36	24.17	14.47	150	149
58.30	29.70	12.00	148	152

TABLE III.—SODA LIME GLASSES.

SiO_2. Per cent.	CaO. Per cent.	Na_2O. Per cent.	T = dynes per cm. Obs.	T = dynes per cm. Calc.
73.60	2.50	23.90	137	141
72.32	5.18	22.50	152	146
70.85	8.25	20.90	146	151
69.30	11.70	19.00	158	158
67.40	15.60	17.00	166	165
65.20	20.20	14.60	172	173

TABLE IV.

SiO_2. Per cent.	B_2O_3. Per cent.	BaO. Per cent.	Na_2O. Per cent.	T = dynes per cm. Obs.	T = dynes per cm. Calc.
63.94	3.88	15.78	16.40	145	142
52.76	6.42	26.90	13.92	142	146
45.70	8.10	34.50	11.70	145	148
36.45	10.62	44.75	9.18	153	153
31.77	11.64	48.40	8.37	159	154
24.40	13.26	55.80	6.54	155	157

The glasses studied consisted of seven sodium silicates, eleven soda-barium glasses and six soda-lime glasses When the results of these measurements were plotted in a system in which the composition of the glass was represented by the abscissas and the surface tension by the ordinates, it was observed that the surface tension was roughly a linear function of the composition. It was therefore possible to compute the surface tension which each oxide showed in its combination in the glass, and with these factors to calculate the surface tension for the several glasses with the aid of the following formula:

$$T = a_1p_1 + a_2p_2 + a_3p_3, \text{ etc.},$$

in which T is the surface tension of the glass, a_1, a_2, a_3, etc., are the surface tensions of the several oxides and p_1, p_2, p_3, etc are the percentages of the respective oxides in the glass. The figures given in the tables

---

[1] Tillotson, THIS JOURNAL, 3, 631 (1911).

under "calculated" are the values of the surface tension obtained in this way, using the following factors:

SiO_2	129
B_2O_3	45
BaO	195
CaO	323
Na_2O	160

In Table I are shown the results of measurements on sodium silicates. The first two columns show the composition of the glass; column three shows the observed and column four the calculated surface tension.

Table II shows the data obtained with the soda-barium glasses, and Table III that for the soda-lime glasses. In both of these tables the first three columns give the composition of the glasses and the last two columns give respectively the observed and calculated value of the surface tension. In Table IV are shown some soda barium glasses containing boric oxide. This series of glasses is especially interesting since it permitted a very wide range in the proportions of the several oxides and offered a severe test for the validity of the additive nature of surface tension.

In the measurements, in the tables given above, it is found that the observed and calculated surface tensions differ, for the most part, by not more than two or three per cent. This is not surprising since the surface tensions of liquids are, as a rule, very sensitive to the presence of small amounts of impurities. The glasses doubtless contain aluminum silicates and other impurities taken up from the crucible, which may perhaps affect the surface tension quite out of proportion to the amount present. The experimental error is not large when ten or more fibers are employed, as shown by the following measurements which were repeated, unknown to the worker, after several other glasses had been investigated. No. 1 is the second of the alkali silicates, as given in Table I and No. 2 is the last one of the same table.

	(α).	T.
1.	45.4	141.6
	45.1	140.8
2.	43.7	136.3
	43.8	136.6

On comparing the values of the surface tensions of the pure oxides, as calculated from that of the glasses, we find in general that the acid-forming oxides, SiO_2 and B_2O_3, show lower surface tensions than the basic oxides. Placed in descending order they are as follows: CaO, 323; NaO, 195; Na O, 160; SiO_2, 129; B_2O_3, 45.

It is interesting to note that this surface tension of B_2O_3 is the same as that obtained by direct measurement on the fused boric oxide, and a little over one-half of that given by Quincke[1] (84.5). Inasmuch as the surface tensions of the lead borates previously described[2] do not show any regular relationship, this coincidence in the two values of the surface tension of boric oxide probably has little significance.

In conclusion, the writer desires to acknowledge his indebtedness to Mr. J. D. Malcolmson for his generous assistance in these measurements.

SUMMARY.

1. The surface tension of a number of soda-lime, soda-barium silicate glasses and of some soda-barium borosilicate glasses has been measured.
2. The surface tension of glasses is roughly a linear function of their composition.
3. The surface tension of silicate and borosilicate glass may be calculated with a fair degree of accuracy from the chemical composition, using the following values for the surface tension of the oxides: SiO_2, 129; B_2O_3, 45; BaO, 195; CaO, 323; Na_2O, 160.

DEPARTMENT OF INDUSTRIAL RESEARCH,
UNIVERSITY OF KANSAS,
LAWRENCE.

---

[1] Quincke, *Pogg. Ann.*, **138**, 141 (1869).

[2] Tillotson, *Loc. cit.*

THE DETECTION AND DETERMINATION OF CYANOGEN AND HYDROGEN CYANIDE.

By F. H. RHODES.

Received June 6, 1912.

The usual method for the detection and determination of cyanogen and hydrogen cyanide in the presence of each other is based upon the difference in the products of the reaction of cyanogen and of hydrogen cyanide with a solution of potassium hydroxide. When passed into a solution of potassium hydroxide, hydrogen cyanide is quantitatively converted into potassium cyanide, whereas cyanogen forms equimolecular amounts of potassium cyanide and potassium cyanate.

The usual method for the detection of cyanogen in the presence of hydrogen cyanide consists in absorbing the gases in a solution of potassium hydroxide and testing for potassium cyanate Potassium cyanate may be detected by acidifying the solution, heating to hydrolyze the cyanic acid liberated by this acidification, and testing for the ammonia formed by this hydrolysis.

The customary method for the determination of cyanogen in the presence of hydrogen cyanide is based upon the same reactions as the qualitative method just described. The gases are absorbed in a solution of potassium hydroxide, the potassium cyanate is decomposed by the addition of an excess of a strong acid, and the resulting ammonia is determined by the addition of an excess of alkali and distillation into standard acid. Both the qualitative and quantitative methods just described are tedious, and are liable to error because of the possibility of the formation of some ammonia by the simultaneous hydrolysis of some of the hydrocyanic acid liberated upon the acidification of the solution containing potassium cyanide.

Wallis[1] states that when hydrogen cyanide is passed into an acidified solution of silver nitrate it reacts quantitatively with the silver nitrate to precipitate silver cyanide. He also states that cyanogen does not react with an acidified solution of silver nitrate, and that any cyanogen which dissolves as such in the reagent may be removed practically completely by passing a current of air through the solution. Upon this difference of behavior of cyanogen and of hydrogen cyanide toward silver nitrate, Wallis based a method for the detection of cyanogen and of hydrogen cyanide when these gases are present together in a gas mixture, but he carried the work no further than to show the

---

[1] Wallis, *Ann. Chem.*, **345**, 353 (1906).

applicability of this method to the qualitative examination of a few special gas mixtures.

The present investigation was taken up to determine the applicability of the difference of behavior of cyanogen and hydrogen cyanide toward an acidified solution of silver nitrate to general qualitative gas analysis, and to ascertain whether this method could be used for the quantitative determination of cyanogen and hydrogen cyanide in the presence of each other.

The behavior of cyanogen when passed into a slightly acid solution of silver nitrate was first studied. Cyanogen was prepared by heating about two grams of mercuric cyanide in a hard glass tube. To one end of this tube was connected a series of four test tubes with side arm. In each of the first three of these absorption tubes was placed 5 cc. of a standard solution of silver nitrate and one drop of dilute nitric acid; in the fourth tube was placed 10 cc. of a 2 *N* solution of potassium hydroxide. A slow current of air was passed through the apparatus and the tube containing the mercuric cyanide was heated to dull redness, the heating being continued until the mercuric cyanide was completely decomposed. The current of air was continued for about twenty minutes after the decomposition of the mercuric cyanide.

A slight white precipitate was formed in the first absorption tube, but no precipitate appeared in any of the other tubes. The fourth absorption tube was disconnected and a portion of the solution contained in it was treated with 10 cc. of a solution of ferrous sulphate and one drop of a solution of ferric chloride. After being allowed to stand for about five minutes, the solution was made slightly acid with sulphuric acid. A heavy blue precipitate indicated the presence of cyanide in the solution of potassium hydroxide. Another portion of the solution from the fourth absorption tube was made acid and heated for a few minutes to hydrolyze any cyanic acid present. The resulting solution was made alkaline with a considerable excess of potassium hydroxide and warmed. Ammonia was copiously evolved, thus proving the presence of a considerable amount of cyanate. This experiment demonstrated that cynaogen will readily pass through an acidified solution of silver nitrate.

To ascertain whether appreciable amounts of cyanogen are absorbed by the solution of silver nitrate, the second absorption tube was removed from the apparatus, and the solution of silver nitrate contained in it was filtered. After thoroughly washing the filter paper with very dilute nitric acid, the combined filtrate and wash water was titrated with a standard solution of potassium sulphocyanate, with 5 cc. of a saturated solution of ferric ammonium alum as an indicator. The results,

5 cc. original solution of $AgNO_3$ = 3.91 cc. KCNS.
Solution from tube 2 = 3.92 cc. KCNS,

showed that cyanogen is not absorbed by a solution of silver nitrate that contains a slight amount of free nitric acid.

To learn whether any cyanogen is held back by the solution of silver nitrate and is not removed by a current of air, the third absorption tube was disconnected and the solution of silver nitrate that it contained transferred to a small beaker. To the solution was added an amount of a 2 *N* solution of potassium hydroxide (chloride-free) slightly in excess of that required to precipitate all of the silver. After standing for about three minutes, the solution was made slightly acid, filtered, and the filter paper thoroughly washed with dilute nitric acid. The combined filtrate and wash-water was titrated with a standard solution of potassium sulphocyanate. The results were as follows:

5 cc. original solution = 3.91 cc. KCNS solution
Solution from tube 3 = 3.91 cc. KCNS solution

If any cyanogen had dissolved as such in the solution of silver nitrate and had not been removed by the passage of the current of air through the solution, it would have reacted with the potassium hydroxide to form potassium cyanate and potassium cyanide, and the latter substance would have reacted with the silver nitrate to form insoluble silver cyanide. The fact that the amount of silver in solution was unchanged by the passage of a considerable amount of cyanogen through the reagent proves that any cyanogen that may dissolve as such in the slightly acidified solution of silver nitrate may be completely removed by the passage of a current of air through the liquid.

The slight precipitate obtained in the first absorption tube was due to the fact that the gas generated by the heating of the mercuric cyanide was not pure cyanogen, but contained small amounts of hydrogen cyanide. That this precipitate was not due to cyanogen is shown by the fact that there was no precipitate in either of the other absorption tubes containing acidified solutions of silver nitrate.

The completeness and rapidity of the absorption of hydrogen cyanide by a slightly acid solution of silver nitrate was next investigated. The hydrogen cyanide was generated by the action of an excess of dilute sulphuric acid upon 0.2452 gram of 96.15 per cent. potassium cyanide, and was passed through a series of four absorption tubes. In each of the first three of the absorption tubes was placed 15 cc. of an approximately *N*/10 solution of silver nitrate acidified with one drop of dilute nitric acid, while the fourth absorption tube contained 10 cc. of a *N*/2 solution of potassium hydroxide. After the complete decomposition of the potassium cyanide by the acid, a current of air was passed through the apparatus to sweep out any hydrogen cyanide remaining in the tubes. A precipitate appeared in each of the tubes containing silver nitrate. As far as could be judged from the volume of the precipitate, the precipitation of the silver in the first tube was almost complete before any precipitate appeared in the second tube. The precipitation in the third tube was slight, and did not begin until the precipitation in the second tube was almost complete. The fourth absorption tube was disconnected and the solution contained in it tested for cyanides by adding 10 cc. of a solution of ferrous sulphate and one drop of a solution of ferric chloride, allowing the solution and precipitate to stand for fifteen minutes, and then adding a slight excess of sulphuric acid. There was produced no blue precipitate or green color which showed that hydrogen cyanide is rapidly and quantitatively absorbed by a slightly acid solution of silver nitrate.

Upon the basis of the foregoing observations the following method for the detection of cyanogen in the presence of hydrogen cyanide was developed:

Two absorption tubes of the form already mentioned, the first containing 10 cc. of a 10 per cent. solution of silver nitrate, and one drop of dilute ($N/6$) nitric acid, and the second 10 cc. of a $N/2$ solution of potassium hydroxide, are connected in series and the gas mixture is passed through these tubes. This is followed by a slow current of air, the passage of which is continued for about 10 minutes. The absorption tube containing the solution of potassium hydroxide is then disconnected, and 5 cc. of a solution of ferrous sulphate and one drop of a solution of ferric chloride are added to the contents of the tube. After about 15 minutes there is added dilute sulphuric acid sufficient to dissolve the precipitated ferrous and ferric hydroxides. The appearance of a blue precipitate or of a distinct green color in the solution after acidification proves the presence of cyanogen in the original gas mixture.

The delicacy of this method was ascertained by passing known amounts of cyanogen gas through the absorbent. Since the cyanogen that is generated by heating mercuric cyanide was found to contain considerable amounts of hydrogen cyanide, the gas used in this test was generated by the action of a warm concentrated solution of cupric sulphate upon potassium cyanide. The cyanogen was collected in small glass tubes that were closed at each end with a stopcock. The volume of each of these small containers was previously determined by filling the tubes and the bore of the stopcocks with mercury, and then weighing the mercury. Several of these collection tubes were filled with cyanogen by connecting them in series and passing through them a current of cyanogen gas freed from hydrogen cyanide by passage through a slightly acid solution of silver nitrate, and dried by passage through a U-tube containing calcium chloride. The current of cyanogen through the tube was continued until the gas issuing from the last tube was completely absorbed by a solution of potassium hydroxide which showed that all air in the apparatus had been displaced. The stopcocks of the tubes were then closed, the tubes disconnected and any cyanogen remaining in the open end of the tubes blown out with air.

The delicacy of the test for cyanogen was then ascertained by connecting one of the above sample tubes with the absorption tubes containing solutions of silver nitrate and potassium hydroxide, and passing the gas through these tubes in the manner above described. The results of these qualitative tests were as follows:

VOLUME OF CYANOGEN, CC.	COLOR DEVELOPED.
10	Blue precipitate
5	Blue precipitate
1	Blue precipitate
0.4	Green color
0.3	Faint green color
0.2	Very faint green color

From the above data it appears that as small an amount as 0.3 cc. of cyanogen may be detected in this manner. That the presence of hydrogen cyanide in the gas does not interfere with the delicacy of this method was demonstrated by passing through the absorbents a mixture of 0.4 cc. of cyanogen and 10 cc. of hydrogen cyanide and obtaining a distinct reaction for cyanogen under these conditions.

Since potassium cyanide is hydrolyzed to a considerable degree in aqueous solution with the formation of hydrocyanic acid, it was thought possible that the passage of a large volume of air through the apparatus might carry with it some of the hydrogen cyanide and thus decrease the delicacy of the test. It was found, however, that this was not the case, 0 4 cc. of cyanogen still yielding a distinct reaction when 20 liters of air was passed through the apparatus subsequent to the introduction of the cyanogen.

A small amount of carbon dioxide in the gas mixture under examination does not interfere with the test for cyanogen, but if an amount of gas containing carbon dioxide sufficient to convert all of the potassium hydroxide into potassium carbonate is passed through the reagent, naturally the reaction for cyanogen is then not obtained.

The presence of hydrogen cyanide in the original gas mixture is detected by collecting on a filter any precipitate that may have formed in the solution of silver nitrate in the first absorption tube, washing the precipitate with very dilute nitric acid, drying it, transferring it to a small sublimation tube, and warming it with a small amount of iodine (five milligrams or less. The formation of a sublimate of cyanogen iodide on the side of the tube proves the presence of silver cyanide in the precipitate and consequently of hydrogen cyanide in the original gas mixture: 0.1 mg. of silver cyanide, equivalent to 0.02 mg. of hydrogen cyanide, may be detected in this manner.

Experiments were next carried out to ascertain whether the difference in behavior of cyanogen and hydrogen cyanide toward a slightly acid solution of silver nitrate could successfully be utilized in the quantitative separation and determination of these two gases in the presence of each other. To this end a mixture of hydrogen cyanide and cyanogen was generated by the action of an *acidified* solution of copper sulphate upon potassium cyanide, and the gas mixture was collected in the tube containers described above. One of these containers was then connected in series with four absorption tubes, each of the first two of the tubes containing 5 cc. of a standardized (approximately $N/10$) solution of silver nitrate and one drop of dilute nitric acid. The third absorption tube contained 10 cc. of an approximately $N/2$ solution of potassium hydroxide free from chloride, and the last tube contained 5 cc. of this solution. The mixture of gases in the collection tube was driven through this absorption apparatus by a slow current of air which was continued for about 30 minutes. The first two absorption tubes were then disconnected and the solution of silver nitrate that they contained was transferred into a beaker and filtered. The precipitate and filter paper were washed with very dilute nitric acid until free from soluble silver salts. The filtrate and wash water were then combined and titrated with a standardized solution of ammonium sulphocyanate (using ammonium-ferric alum as indicator) and the amount of hydrogen cyanide present in the original gas mixture calculated from the volume of ammonium sulphocyanate used.

The contents of the third and fourth absorption tubes was transferred into a beaker and a known volume of a standardized solution of silver nitrate added. The silver nitrate must be in excess of the amount required to precipitate all of the potassium cyanide in the solution as silver cyanide. The solution and the suspended precipitate were then thoroughly stirred, and dilute nitric acid added until the precipitated silver oxide redissolved and the solution became slightly acid. The precipitate of silver cyanide was now filtered off; precipitate and filter paper were washed with very dilute nitric acid until all soluble silver salts were removed, and the filtrate and wash water combined and titrated with a standardized solution of ammonium sulphocyanate using ammonium-ferric alum as indicator. The cyanogen present in the original gas mixture was then calculated, the reactions involved in the calculation being:

$$(CN)_2 + 2KOH = KCN + KCNO + H_2O.$$
$$KCN + AgNO_3 = AgCN + KNO_3.$$
$$AgNO_3 + KCNS = AgCNS + KNO_3.$$

The results of some determinations of cyanogen and hydrogen cyanide are given in the following table, the analyses being expressed in terms of the ratio of hydrogen cyanide to cyanogen by weight because by this means mistakes arising either from error in the determination of the volume of the small containing tubes or from the presence of gases other than cyanogen or hydrogen cyanide in the gas mixture are eliminated.

Mixture No. 1.

Tube.	Weight HCN.	Weight $(CN)_2$.	Ratio.
1	0.0177	0.009005	1.96 : 1
2	0.00586	0.00296	1.98 : 1
Mixture No. 2.			
1	0.00134	0.0116	1 : 8.65
2	0.00044	0.0038	1 : 8.63

The results of the investigation may be summarized as follows:

1. Hydrogen cyanide is rapidly and quantitatively absorbed by a slightly acid solution of silver nitrate with the formation of silver cyanide.

2. Cyanogen is not absorbed by a slightly acid solution of silver nitrate and any cyanogen that may be dissolved as such in the solution is quantitatively removed when a current of air is passed through the liquid

3. Cyanogen may be detected in the presence of hydrogen cyanide even when the total volume of cyanogen in the gas mixture is as small as 0.3 cc. The method is applicable to the detection of small amounts of cyanogen in the presence of hydrogen cyanide and large volumes of air.

4. Hydrogen cyanide and cyanogen may be determined rapidly and accurately in the presence of each other.

I wish to express my indebtedness to Professor Dennis for the assistance and encouragement that he has given me in this work.

CORNELL UNIVERSITY,
ITHACA, N. Y.

RAPID AND ACCURATE METHODS FOR DETERMINING PHENOL.

By L. V. REDMAN AND E. O. RHODES.

Received July 3, 1912.

In 1871 Landolt[1] made the first successful attempt to determine phenol quantitatively by precipitation as tribromphenol, and since that time numerous attempts have been made to obtain an accurate and easy method of determining phenol each experimenter working under varying conditions to suit his particular purpose. As a result of these investigations, many methods have been submitted for which claims of more or less accuracy and rapidity have been asserted. The time of the reaction period in most cases is too long for rapid determination.

A method has been suggested by Lloyd[2] in which he substitutes a hypobromite solution for Koppeschaar's[3] bromide-bromate solution. In his paper he shows that the tribromphenol is formed almost instantaneously and quantitatively (and that the time of the reaction period is reduced practically to zero). This hypobromite method has been adversely criticized by Olivier,[4] who in 1909 and 1910 published results which do not agree with Lloyd's. He did not find as high a percentage of error when a large excess of hypobromite was added to the phenol as did Lloyd, and he doubts the accuracy of Lloyd's numbers and methods. He shows also that the length of time required for Koppeschaar's method, using a bromide-bromate solution, may be reduced from one-half hour to nine minutes.

More recently, Wilkie[5] has published a method for the rapid determination of phenol, in which he used iodine in cold sodium carbonate solution. The reaction period for this method is 5–10 minutes. It has the disadvantage of requiring that the iodine solution be restandardized each time a phenol determination is made.

A more complete bibliography on phenol determination may be found in Lloyd's[2] paper of 1905 or Wilkie's papers of 1911–1912.

Our object in undertaking this research was to shorten if possible the time required for a determination of phenol by the bromide-bromate method and compare the hypobromite method with the bromide-bromate method for accuracy, ease of manipulation and time required for a determination.

Apparatus.—The apparatus used consisted of a shaking machine driven by a water motor, several five-liter bottles fitted with glass siphons, D. R. burettes and one-half liter ground stoppered bottles from the common stock in which the phenol determinations were made.

---

[1] *Berichte*, **4**, 770 (1871).

[2] *J. Am. Chem. Soc.*, **27**, 16 (1905).

[3] *Z. Ann. Chem.*, **15**, 233 (1876).

[4] *Rec. Trav. Chim.*, **28**, 362 (1909).

[5] *J. Soc. Chem. Ind.*, **30**, 399 (1911).

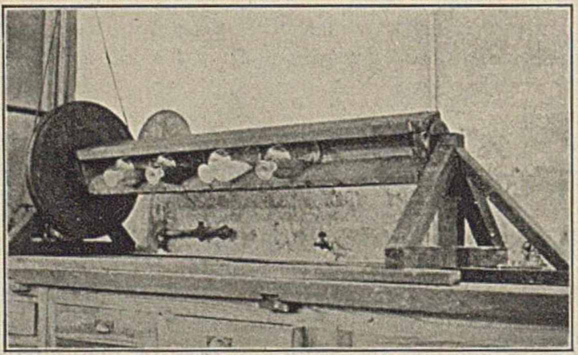
The shaking machine is a long, narrow and shallow wooden box 120 cm. × 9 cm. × 9 cm. inside measurements, lined on the inside with felt-covered pads. This box holds twelve one-half-liter bottles. The trough is fitted at one end with a grooved pulley two feet in diameter At the center of this pulley and also at the center of the box on the end opposite the pulley are steel spindles which fit into the wooden bearings on the supporting frame. The frame is so constructed that this box may be removed and a larger or smaller box substituted. It was possible to rotate the shaker four revolutions per second, but one revolution per second was sufficient.

When a determination was to be made, each of the solutions was run into a 500 cc. bottle. The stoppers were then placed in the bottles and while being pressed inward were given a short sharp twist. This twist brought the two ground glass surfaces together and made it impossible for any of the solution to leak out or for the stopper to be thrown out when revolved rapidly.

The bottle was inserted between the padded sides of the box. The pressure of the pads held the bottles in firmly. By this construction no clamps are needed to hold the stoppers in the bottles during the time of shaking and the bottles are held in the machine by the pressure of the felt pads, no straps or clamps of any kind being used. This is an advantage, since, by eliminating all clamps, much time and labor, which are important factors when time determinations of small duration are being made, are saved.

In our investigations we made a total of two hundred determinations for which the machine was used and in no case did we experience any trouble or lose a determination on account of bottles flying out or stoppers leaking.

A photograph of the shaking machine appears below.



Solutions Used.—The solutions used in the determinations were approximately 0.1 *N* solutions of sodium thiosulphate, potassium hypobromite, a mixture of sodium bromide and bromate and phenol, concentrated hydrochloric acid (sp. gr. 1.2), a 20 per cent. potassium iodide solution and a starch solution used as an indicator.

The thiosulphate solution was prepared by dissolving 125 grams of sodium thiosulphate ($Na_2S_2O_3.5H_2O$) in five liters of water; 40 grams of liquid bromine dissolved in five liters of *N*/4 potassium hydroxide made up the hypobromite solution and the bromide-bromate solution consisted of 3.5 grams of potassium bromate and 55 grams of KBr per liter. The phenol solution for testing was made from the third distillation at 181–2° C. of Merck's c. p. phenol, 1.46 grams being diluted to 1 liter.

THE HYPOBROMITE METHOD.

In each of the following tables, the order given from left to right is the same order in which the solutions were added for the determinations. The tables show in each case the total volume, the volumes of phenol, hypobromite, hydrochloric acid, potassium iodide and thiosulphate used, and also the time of shaking and the percentage of the phenol present which were determined by means of this method.

Table I was prepared in order to determine the effect of time of shaking upon the results obtained, when the total dilution, volume of phenol and volume of hypobromite solution are kept constant and the solution is acid.

The method was as follows: Into a half-liter bottle containing 61 cc. water the following solutions were added in the order given: Five cc. of HCl (sp. gr. 1.2), 15 cc. of 0.1 *N* phenol and 19 cc. of 0.1 *N* hypobromite solution. The stopper was then inserted into the bottle and the latter placed in the shaker where it remained revolving for the desired length of time. After shaking, it was removed; 5 cc. of KI (20 per cent.) solution was added to the mixture and the bottle was returned to the shaker where it revolved for at least three minutes.

The following table shows the results obtained for one minute to one hour's shaking (the reaction period) before the KI solution was added.

TABLE I.—HYPOBROMITE.

No.	H_2O.	HCl.	C_6H_5OH.	KOBr.	Time. Min.	KI.	Time. Min.	$Na_2S_2O_3$.	Per cent. Phenol.
1*a*	61	5	15	19	1	5	3	3.99	100.3
1*b*	61	5	15	19	1	5	3	3.98	100.4
2*a*	61	5	15	19	5	5	3	3.97	99.7
2*b*	61	5	15	20	5	5	3	4.98	99.9
3*a*	61	5	15	19	10	5	3	3.88	100.5
3*b*	61	5	15	19	10	5	3	3.97	99.9
4*a*	61	5	15	19	15	5	3	3.89	100.4
4*b*	61	5	15	19	15	5	3	3.90	100.3
5*a*	61	5	15	19	20	5	3	3.91	100.3
5*b*	61	5	15	17	20	5	3	1.90	100.2
6*a*	61	5	15	19	30	5	3	3.88	100.5
7*a*	61	5	15	19	60	5	3	3.86	100.6
7*b*	61	5	15	19	60	5	3	3.91	100.2

Solutions.

Phenol............	0.1022 N	KI	20 per cent.
KOBr............	0.1016 N	HCl	1.2 sp. gr.
Thiosulphate......	0.1003 N		

The above results indicate that the time of shaking has very little effect upon the percentages of phenol as determined. It will be noticed that the values for one minute's shaking are as correct as those for one hour. There is no result in the table which varies from the correct value by more than 0.6 of 1 per cent. and the average varies by 0.2 per cent. This is the degree of accuracy claimed by Lloyd for the hypobromite method.

In Table II are given the results obtained when the concentration of phenol with respect to the total volume was varied but the relative concentrations of phenol and hypobromite were kept constant. In each case the time of shaking was 1 minute and the total dilution 100 cc.

TABLE II.

No.	H_2O.	HCl.	C_6H_5OH.	KOBr.	Time. Min.	KI.	Time. Min.	$Na_2S_2O_3$.	Per cent.
1*a*	61	5	15	19.0	1	5	3	3.97	100.14
1*b*	61	5	15	19.0	1	5	3	3.97	100.14
2*a*	83.5	5	5	6.5	1	5	3	1.50	99.79
2*b*	83.5	5	5	5.5	1	5	3	1.50	99.79
3*a*	90.4	5	3	3.9	1	5	3	0.92	99.14
3*b*	90.4	5	2	2.6	1	5	3	0.60	99.71
4*a*	92.7	5	1	1.3	1	5	3	0.32	98.90
4*b*	92.7	5	1	1.3	1	5	3	0.31	98.81

Solutions—See Table I.

The results obtained indicate that amounts of phenol as small as 0.000015 gram per cubic centimeter may be determined within 1 per cent. by this method and with a reaction period of one minute.

Table III shows that shaking for one minute is sufficient by the method used for an accuracy not greater than four parts per thousand. Each test was run with a total volume of 100 cc. and in each the concentrations of the various solutions were the same. The six determinations were a single series. All six are submitted, none rejected, thus giving a fair estimate of the amount of the error to be expected generally in a laboratory determination.

TABLE III.—HYPOBROMITE.

No.	H_2O.	HCl.	C_6H_5OH.	KOBr.	Time. Min.	KI.	Time. Min.	$Na_2S_2O_3$.	Per cent.
1	61	5	15	19	1	5	3	3.99	100.3
2	61	5	15	19	1	5	3	3.98	100.4
3	61	5	15	19	1	5	3	4.02	99.6
4	61	5	15	19	1	5	3	4.00	99.8
5	61	5	15	19	1	5	3	4.01	99.7
6	61	5	15	20	1	5	3	5.00	99.8

Solutions—See Table I.

Attention is called to the fact that in each of these tables, the phenol was first diluted with water before the hypobromite solution was added to it. *This* is of interest because of the fact that a number of authors state that in the determination of phenol by bromine,[1] a red compound is formed in the white precipitate which is probably tetrabromphenoquinone. Only once or twice in all our determinations did the precipitate show even a light pink shade, never yellow which would indicate tribromphenol bromide, and in all the other cases the precipitate was perfectly white. In every case where the red compound is mentioned the phenol solution was used with greater concentration than *N*/100; it was found that diluting the phenol to approximately *N*/100 reduced the formation of this compound to zero and possibly increased the accuracy of this method.

The Permanency of a Hypobromite Solution.—In estimating phenol, conflicting determinations were obtained by us when it was assumed that a fresh hypobromite solution retains a constant quantity of available bromine. Allen[2] states that a hypobromite solution made alkaline by dissolving 62.2 grams of pure NaOH (this is 50 per cent. more caustic than is necessary to react with the bromine according to the equation, $Br_2 + 2NaOH = 2NaBrO + H_2O$) and made up to 0.16075 *N* loses not more than 0.8 per cent. of its bromine by boiling it for one hour. Lloyd[1] assumes from Allen's paper that the available bromine in a solution of hypobromite is fairly constant. This is true if the bottle is kept full of solution and corked with a ground stopper. But if the ordinary 5-liter bottle be fitted up with a paraffined bark cork, siphon and inlet for air, the hypobromite solution changes its strength. A fresh solution made up in this laboratory by dissolving 8 grams of bromine per liter in *N*/4 KOH changed its strength in thirty-two days from 0.0865 *N* to 0.0781 *N*, a decrease 0.3 per cent. strength per day. A second fresh solution of strength 0.1654 *N* changed in 12 days to 0.1584 *N*, that is a change of 0.33 per cent. per day. A third solution, which was kept in a ground stoppered brown glass bottle in a dark compartment, changed from 0.1346 *N* to 0.1340 *N* in fifty-seven days. It is evident that this solution, which was quite yellow and smelled of free bromine, retained its strength when kept well corked in a brown glass bottle. This may account for the conflicting statements made regarding available bromine in a hypobromite solution. Owing to the possibility of bromine evaporating from a strongly alkaline hypobromite solution it is necessary to test this strength of hypobromite after each determination if these are more than a few hours apart, especially if the solution has an inlet for air to allow the siphon to operate, or if the bottle is badly corked.

The Acidity of the Phenol Hypobromite Solution.—It is imperative, if hypobromite is used in determining a phenol solution as tribromphenol, to have the solution acid both before and after the hypobromite is added. Otherwise the phenol ring is broken[2] up in alkaline hypobromite and passes over into carbon tetrabromide and possibly higher homologues.

TABLE IV.—ALKALINE PHENOL HYPOBROMITE.

No.	H_2O.	C_6H_5OH.	KOBr.	Time.	HCl.	KI.	Time. Min.	$Na_2S_2O_3$.	Per cent.
I*a*	64.5	2.5	18	1 min.	5	5	3	19.81	167.84
II*a*	64.5	2.5	18	1 min.	5	5	3	19.78	169.01
I*c*	64.5	2.5	18	5 mins.	5	5	3	19.04	197.25
II*c*	64.5	2.5	18	5 mins.	5	5	3	19.06	196.86
I*d*	64.5	2.5	18	10 mins.	5	5	3	18.96	200.39
II*d*	64.5	2.5	18	10 mins.	5	5	3	18.94	201.17
I*e*	64.5	2.5	18	20 mins.	5	5	3	18.90	202.74
II*e*	64.5	2.5	18	20 mins.	5	5	3	18.89	203.13
I*g*	64.5	2.5	18	1 hr.	5	5	3	18.79	205.49
II*g*	64.5	2.5	18	1 hr.	5	5	3	18.76	208.22
I*i*	64.5	2.5	18	18 hrs.	5	5	3	18.08	234.51
II*i*	64.5	2.5	18	18 hrs.	5	5	3	18.07	234.90

Solutions.

Phenol.......... 0.1022 N KI 20 per cent.
KOBr.......... 0.1318 N HCl 1.2 sp. gr.
Thiosulphate.... 0.09816 N
18 cc. 0.1318 N KOBr = 23.72 cc. 0.1 N KOBr
2.5 cc. 0.1022 N phenol = 2.55 cc. 0.1 N phenol

In Table IV the acid was not added until after the hypobromite. Column 5 shows the time during which the solution was alkaline. The table shows the rate at which the bromine is used up in an alkaline phenol solution. The last column gives the per cent. of Br disappearing, calculating as 100 per cent. the amount of Br required to form tribromphenol, when the solution is acid.

---

[1] Beckurts, *Arch. Pharm.*, **5**, 24, 561 (1886); from *J. Soc. Chem. Ind.*, **5**, 5, 546 (1886).

[2] *J. Soc. Chem. Ind.*, **3**, 65 (1884).

[1] *J. Am. Chem. Soc.*, **27**, 10 (1905).

[2] Olivier, *Rec. Trav. Chim.*, **29**, 294 (1910); Collie, *J. Soc. Chem. Ind.*, p. 264 (1894); Wallach, *Ann. Chem.*, **275**, 147 (1893); **159**, 322.

The above table indicates that if the solution be alkaline for only one minute after the hypobromite is added, an error as great as 67 per cent. may be introduced in the determination, and a longer period gives a greater error. Lloyd uses sufficient acid to keep this solution strongly acid although he does not mention the attendant danger if the solution were alkaline. Olivier[1] rather inconsistently expresses surprise at the amount of acid used by Lloyd and at the same time shows that if the solution become alkaline an error of 125 per cent. may be introduced in a single determination.

It may be noted that no precipitates appeared after adding the acid.

THE BROMIDE-BROMATE METHOD.

This method is similar in many respects to the hypobromite method. Instead of using a solution of hypobromite as in the first case, a solution consisting of a mixture of potassium bromide and potassium bromate (Koppeschaar's solution) was used. This is the standard solution used by the United States Pharmacopoeia and is made as follows: 3.5 grams of potassium bromate and 55 grams of potassium bromide are dissolved in water and then diluted up to 1 liter.

This solution has considerable advantage over the hypobromite solution in that it contains no free bromine and therefore does not have the objectionable odor of the hypobromite solution. For the same reason, it is much more stable than this solution[2] and does not require to be standardized with each operation. The chief objection to the use of the bromide-bromate solution, however, has been that it was too slow. Koppeschaar recommends 15 minutes shaking and the U. S. P. 30 minutes, before the KI solution is added.

As shown by the following tables it is not necessary to shake for one-half hour to obtain an accuracy of three parts per thousand. The order of adding the solutions is shown in each table reading from left to right.

TABLE V.—BROMIDE BROMATE.

No.	H_2O.	HCl.	C_6H_5OH.	Bromide bromate.	Time. Min.	KI.	Time. Min.	$Na_2S_2O_3$.	Per cent.
1*a*	61	5	15	19	1	5	3	2.80	99.72
1*b*	61	5	15	19	1	5	3	2.75	100.04
2*a*	61	5	15	19	5	5	3	2.80	99.72
2*b*	61	5	15	19	5	5	3	2.77	99.92
3*a*	61	5	15	19	10	5	3	2.80	99.72
3*b*	61	5	15	19	10	5	3	2.79	99.79
4*a*	61	5	15	19	15	5	3	2.78	99.85
4*b*	61	5	15	19	15	5	3	2.77	99.92
5*a*	61	5	15	19	20	5	3	2.73	100.11
5*b*	61	5	15	19	20	5	3	2.80	99.72
5*c*	61	5	15	19	20	5	3	2.75	100.04
5*b*	61	5	15	19	20	5	3	2.82	99.60
6*a*	61	5	15	19	30	5	3	2.70	100.30
6*b*	61	5	15	19	30	5	3	2.74	100.11
7*a*	61	5	15	19	60	5	3	2.70	100.30
7*b*	61	5	15	19	60	5	3	2.71	100.30

Solutions.

Phenol..........	0.1022 N	KI	20 per cent.
Bromide bromate	0.09493 N	HCl	1.2 sp. gr.
Thiosulphate....	0.09816 N		

Table V was prepared to determine the effect of time of shaking upon the results obtained when the total dilution, volume of phenol and volume of bromide bromate are kept constant and the solution acid.

In Table V the constant volumes of water, phenol, acid and bromide-bromate solution were used, but the time of shaking varied. It will be noticed that for no test was there a greater error than 0.6 per cent. and that with one exception all the results are within 0.3 per cent. The results obtained for one minute's shaking are as accurate as those for 15 minutes, 30 minutes and 1 hour.

In order to confirm the one-minute determinations, a series of five tests were run exactly similar to those in Table V. The five results are submitted, none rejected, thereby giving an idea of the magnitude of the errors to be expected in an ordinary laboratory determination by this method.

The results given below in Table VI show an average error of 0.3 per cent., the greatest error being 0.4 per cent. for a reaction period of only 1 minute.

TABLE VI.—BROMIDE BROMATE.

No.	H_2O.	HCl.	C_6H_5OH.	Bromide bromate.	Time. Min.	KI.	Time. Min.	$Na_2S_2O_3$.	Per cent.
1	61	5	15	20	1	5	3	5.81	100.4
2	61	5	15	18	1	5	3	3.88	100.4
3	61	5	15	18	1	5	3	3.90	100.2
4	61	5	15	18	1	5	3	3.92	100.3
5	61	5	15	18	1	5	3	3.90	100.2

Solutions.

Phenol..........	0.08815 N	KI	20 per cent.
Bromide bromate	0.09493 N	HCl	1.2 sp. gr.
Thiosulphate....	0.09816 N		

Table VII like Table II varies the concentration of phenol with respect to the total volume, but keeps the relative quantity of bromide bromate with respect to the phenol constant. In this table the time of shaking was taken as one-half hour. This length of time was chosen according to the U. S. P., as Table VII was completed before Tables IV and V.

TABLE VII.—BROMIDE BROMATE.

No.	H_2O.	HCl.	C_6H_5OH.	Bromide bromate.	Time. Min.	KI.	Time. Min.	$Na_2S_2O_3$.	Per cent.
1*a*	61.	5	15	19.	30	5	3	2.70	100.36
1*b*	61.	5	15	19.	30	5	3	2.74	100.11
2*a*	72.	5	10	13.	30	5	3	2.12	100.39
2*b*	72.	5	10	13.	30	5	3	2.15	100.10
3*a*	83.5	5	5	6.5	30	5	3	1.02	101.15
3*b*	83.5	5	5	6.5	30	5	3	1.08	100.00
4*a*	90.4	5	2	2.6	30	5	3	0.39	102.02
4*b*	90.4	5	2	2.6	30	5	3	0.43	100.05
5*a*	92.7	5	1	1.3	30	5	3	0.19	102.50
5*b*	92.7	5	1	1.3	30	5	3	0.21	100.58

Solutions—See Table V.

The results for 1 and 2 cc. of phenol are seen to be less concordant than those for larger amounts. However, as one drop is an error of 5 per cent. in 1 cc., and as the phenol solution was measured out from a burette and not weighed, the agreement is fairly good. The table shows that 0.000015 gram of phenol per cubic centimeter may be determined by this method with a maximum error of 2 per cent. The method is probably much more sensitive than this if more dilute solutions are used.

From these tables we have come to the following conclusions for work requiring an accuracy not closer than 0.3 per cent. *First,* it is not necessary to shake the acidified phenol solution with Koppeschaar's solution (bromide bromate) or with Lloyd's hypobromite solution for a longer time than one minute

---

[1] Olivier, *Rec. Trav. Chim.*, **29**, 294 (1910).

[2] See Part V, SUMMARY, page 659; also page 657.

if a continuous shaker is used. *Second*, if the conditions of dilution, etc., are those given in the preceding tables no red or yellow compounds are observed in the white tribromphenol precipitate.

In addition to the above experiments, tests were run by the two methods to determine the error which might be introduced in the determinations due to chemicals, evaporation of bromine due to the use of ordinary one-half liter bottles, methods of working, etc. Thus, an error might be introduced by running the hypobromite solution into the phenol without shaking if the region where the hypobromite was most concentrated became alkaline. Several tests were made to determine this, but no appreciable effect was noticed.

A series of six determinations to find the effect of titrating back with the thiosulphate after periods of 1, 2 and 3 minutes (continuous shaking) from the time when the KI was added, gave results which showed a maximum error of 0.5 per cent. within themselves. Accordingly an error of not more than 0.5 per cent. is introduced if the solution is shaken only 1 minute after adding the potassium iodide.

Blank experiments were run under the same conditions as the original determinations which showed that the maximum error introduced by the solutions, manipulation, bottles, etc., was 0.3 per cent.

Directions.—(1) $N/10$ sodium thiosulphate and a $N/10$ of either hypobromite or bromide bromate, 20 per cent. KI and $^1/_2$ per cent. starch solutions.

(2) Into a 500 cc. bottle, fitted with a ground glass stopper, put 60 cc. water, 5 cc. hydrochloric acid (sp. gr. 1.2) and then add 15 cc. of the unknown phenol solution which is to be determined and which has previously been diluted to about $N/10$. If the solution is weaker than $N/10$ no previous dilution is required. Add quickly enough $N/10$ hypobromite or bromide-bromate solution to make the solution yellow and then add in addition 10 per cent. of the amount already added. Place the stopper in the bottle and shake continuously for one minute. Add to the solution in the bottle 5 cc. potassium iodide solution (10 per cent.) and again shake for three minutes. Wash down the stopper and sides of the bottle and titrate the solution with the $N/10$ thiosulphate, using starch solution as an indicator. The starch must not be added until enough thiosulphate has been run in to make the solution almost colorless. The quantity of thiosulphate used represents the quantity of free iodine, and therefore the quantity of excess bromine. The difference between this quantity and the known quantity of bromine added gives the amount of solution present. Each cubic centimeter of $N/10$ bromine used up is equivalent to 0.00156 gram of phenol.

SUMMARY.

I. The results show that by the above methods of manipulation, either with the hypobromite or with the bromide-bromate solution, phenol determinations can be made within an error of 0.3 per cent. with only one minute of continuous shaking after the solution containing the bromine is added, *i. e.*, the reaction period may be reduced from 30 minutes to 1 minute without sacrificing accuracy.

II. The phenol in each case was diluted until it was approximately $N/100$ before the determination was made. The resulting precipitate with the hypobromite or bromide-bromate solution was white and flocculent in each case and the precipitate showed no traces of red tetrabromphenoquinone or yellow tribromphenol bromide.

III. In order to secure correct results, the phenol solution must be acid after the bromine is added. If it is alkaline, an error is introduced which increases as the concentration of the phenol in the solution diminishes and the reaction period increases.

IV. The error introduced by shaking the solution for only one minute after the KI solution is added before titrating back with thiosulphate is 0.5 per cent. Three minutes shaking eliminates this error and longer shaking has no effect.

V. The bromide-bromate solution has the advantage over the hypobromite of being permanent. When the solution used was first made, its strength was 0.09493 *N*. After three months duplicate tests gave 0.09495 *N*. The hypobromite solution weakened one-third per cent. every twenty-four hours for the first few days after the solution was made. The bromide-bromate solution has not the unpleasant odor or free bromine.

DEPARTMENT OF INDUSTRIAL RESEARCH,
UNIVERSITY OF KANSAS,
LAWRENCE.

THE COLORIMETRIC DETERMINATION OF IRON IN LEAD AND ITS OXIDES.

By JOHN A. SCHAEFFER.

Received June 20, 1912.

The determination of the small percentage of iron always found in lead and its oxides must frequently be made by chemists working in industries where any appreciable amount of iron in raw materials has a deleterious effect on the finished product. This is especially true in the use of red lead and litharge in the manufacture of high-grade cut glass, and lead and its oxides in the manufacture of lead accumulators, where the determinations are constantly made. The gravimetric determination of this constituent necessitates a lengthy and a more or less inaccurate analysis, owing to the many operations entailed. A volumetric determination is also in many cases not sufficiently accurate and rapid for estimating the very small percentages which are often present.

The following colorimetric method was developed to fill this need and it has been found that no other method compares with it in rapidity, ease of manipulation, or in accuracy for the estimation of the small percentages of the above constituent present in lead and its oxides. The method is a modification of Thomson's[1] method, so adapted as to be readily applied to the above mentioned analysis.

It is carried out in the following manner:

In the analysis of litharge or metallic lead, treat one gram of the sample in a beaker with 15 cc. of water

---

[1] *J. Chem. Soc.*, **1885**, 493.

and sufficient nitric acid to convert all the lead present to lead nitrate. Should there be any separation of basic lead nitrate add more water until complete solution is effected.

In the analysis of red lead, treat one gram of the sample with 10 cc. of water and sufficient nitric acid to convert all the oxide present, excepting the lead dioxide, to lead nitrate. Add 10 cc. of hydrogen peroxide (1 : 3.5) to the solution, and boil for a minute until all the oxides of lead pass into solution.

After complete solution of either the metallic lead, litharge or red lead, boil the nitrate solution gently for several minutes to convert all the iron to the ferric condition, cool the contents of the beaker, neutralize the free nitric acid present with ammonium hydroxide and render faintly acid with nitric acid. A solution made from red lead may, after neutralization and the subsequent addition of acid, show the presence of lead dioxide. When this occurs, the solution can be rendered clear by the addition of a few drops of the hydrogen peroxide solution.

Wash the contents of the beaker into a 100 cc. Nessler cylinder, add 15 cc. of dilute ammonium sulphocyanide (1 : 20) and dilute to the mark. The intensity of the blood-red color depends upon the amount of iron present. The color is compared with a blank made in the following manner:

A solution of ferric ammonium sulphate of known strength is required. This is made by dissolving 0.7022 gram of ferrous ammonium sulphate in water. Acidify with sulphuric acid, heat to boiling and add a solution of potassium permanganate until all the iron is converted to the ferric condition. Only the very slightest pink tinge may be present after the addition of the potassium permanganate, as this tinge will fade away, while the presence of a pink color tends to vitiate the results. Allow the solution to cool and dilute to one liter. One cc. of this solution equals 0.0001 gram of iron.

Prepare the blank by pouring into a 100 cc. Nessler cylinder 10 cc. of hydrogen peroxide of the above strength, provided hydrogen peroxide was added for the solution of the oxide, approximately the same amount of nitric acid as was required for the solution of the original metallic lead or oxide, and 15 cc. of ammonium sulphocyanide solution. Dilute to 100 cc. and titrate to the exact color developed in the sample under examination, by the addition of the standard ferric ammonium sulphate solution. One cc. of this solution equals 0.01 per cent. of iron when a one-gram sample is used. The percentage of iron present should not require more than 2 or 3 cc. of the standard to equal it, or the color will be too deep for comparison.

It will be found that the color can be accurately compared to within 0.001 per cent. of iron content. The small percentage of copper present in lead and its oxides does not interfere with the reaction.

Laboratory of Picher Lead Company,
Joplin, Mo.

A RAPID MICROSCOPICAL METHOD FOR THE DETERMINATION OF ARSENIC, AS ORPIMENT, IN SHELLAC.[1]

By Robert Schwarz.

Received July 15, 1912.

As is well known, orpiment, the mineral form of arsenic trisulphid, is very generally added to shellac in India, where this product is collected and prepared for the market. Orpiment is added merely to make shellac more opaque and light straw-colored.

An attempt has therefore been made to obtain from India shellac to which no orpiment has been added, but it has been found that, for some unknown reason, almost all shipments of so-called "arsenic-free" goods contain from small amounts to considerable quantities of arsenic, mostly in the form of orpiment. Therefore it appeared advisable to develop a method of qualitatively determining orpiment in shellac, which method would be more rapid than the Gutzeit or Marsh tests. Such a method has been evolved and bases itself, (1) upon the fact that orpiment is insoluble in alcohol and can be precipitated from alcoholic solution of shellac by centrifugal motion, and (2), upon the characteristic appearance of orpiment under the microscope. When examined in this manner, orpiment appears as transparent to translucent granular masses and imperfect crystals of a distinctly characteristic yellow-greenish color.

The method, therefore, is very simple and rapid, as can be seen from the following:

A 10-gram average sample is ground fine in a coffee mill and then dissolved in 15 cc. of methyl alcohol, solution being hastened by shaking and warming the flask. The varnish is then poured into a graduated tapering tube and this revolved in a centrifugal machine for 5–6 minutes at 1000–1500 revolutions per minute. This causes the precipitation of the greater part of the insoluble material, which contains the orpiment. The varnish is then decanted, the precipitate shaken with methyl alcohol and the tube again revolved in the centrifuge for one to two minutes. The alcohol is then decanted as thoroughly as possible, the amount of the precipitate recorded, and a small portion transferred to a microscopic slide by means of a capillary tube. This preparation is then carefully examined under the microscope, using a magnification of 450–600 diameters.

With an ordinary brewers' shellac or varnish containing a normal amount of insoluble material and above 150 parts of arsenic per million, several pieces of orpiment will be observed in each field. Some shellacs, however, contain a considerable amount of insoluble material, and so the precipitate becomes larger and the number of pieces of orpiment in each field correspondingly smaller. The method has been used not only on the common grades of shellac, but it has also been tried on so-called "arsenic-free" shipments and three bleached shellacs. The results of all tests have been embodied in a table in which is given the number of each test, description of the sample, amount of the precipitate, number of pieces of orpiment

---

[1] Paper presented at the New York Section of the American Chemical Society, June 7,1912.

found in each field or preparation, and the amount of arsenic trioxide, as determined by the Marsh or Gutzeit test. The Marsh or Gutzeit test determines the total amount of arsenic present, and therefore, as Langmuir and White[1] have shown that a certain amount of orpiment may be dissolved in the shellac in the process of manufacture, it is not surprising that in some instances the microscopic tests failed to reveal orpiment, while the chemical tests showed appreciable amounts of arsenic to be present.

Sample Number.	Description.		Sediment.	Orpiment crystals per field.	AS_2O_3. Parts per million. M = Marsh G = Gutzeit.
1	Varnish	Orange	0.1 cc.	4–5	400 M
2	Varnish	Orange	0.05	1	60 M
3	Varnish	Orange	0.05	4–5	155 M
4	Varnish	Orange As-free	0.025	none[1]	none G
5	Varnish	Manheim	none	none	none M
6	Varnish	Manheim	0.02	1–2	112 M
7	Varnish	White	0.05	none[1]	none G
8	Shellac	Grain Lac.	1.5	1	45 M
9	Shellac	R & P garnet	0.1	none[1]	85 M
10	Shellac	Gr. orange	0.075	none[1]	none M
11	Shellac	Reg. orange	0.075	6–8	550 M
12	Com. As-free shellac	....	0.025	1[2]	4 G
13	Com. As-free shellac	....	0.05	1[2]	7.5 G
14	Com. As-free shellac	....	0.025	2[2]	4 G
15	Com. As-free shellac	Grain lac.	1.00	1[2]	20 G
16	Com. As-free shellac	Grain lac.	1.00	1[2]	20 G
17	Bleached shellac	....	0.01	1[2]	6 G
18	Bleached shellac	....	0.25	1[3]	traces G-M
19	Bleached shellac	....	0.01	none[1]	15 G

[1] Three preparations examined.
[2] Number of crystals in each preparation.
[3] One crystal in every third preparation.

It is easily seen from the above table that the sediment from a brewers' varnish (samples 1–6), which is generally made from the ordinary grades of shellac, contains such an amount of orpiment that there are always one or more crystals present in each microscopic field. Sample 4, however, did not show any orpiment in three microscopic preparations, and as experience had shown that this number of preparations would show at least one crystal of orpiment, if any were present, this sample was judged orpiment-free. The Gutzeit test showed that no arsenic in any form was present.

Of the raw or purified shellacs all but two showed crystals of orpiment where arsenic was subsequently found by the Marsh or Gutzeit tests. The two exceptions were No. 9, of which a number of preparations were made and no orpiment found, and No. 19, a bleached, wax-free sample, which gave similar results. It is quite probable that in both instances the arsenic was in solution, and that any orpiment which had been present in the raw lac had been removed in the process of manufacture.

Regarding samples Nos. 12–18, it is interesting to note that the method will show the presence of orpiment even when the total arsenic present is only 4 parts per million, and in one instance—sample No. 18—one crystal was found in every third microscopic preparation, while the Gutzeit and Marsh tests showed the presence of traces only of arsenic.

As regards using the method to obtain quantitative approximation of the amount of orpiment present, it must be stated that, in the first place, the method is suggested only as a qualitative test. However, by using the same microscope, ocular and objective, and by comparing the sediments of unknown shellacs with those of samples containing known amounts of orpiment, a fair idea of the amount of orpiment present can be obtained.

In conclusion I wish to acknowledge my indebtedness to Dr. A. C. Langmuir, at whose suggestion this paper was written, and who has given valuable advice in the preparation of the same.

MICROSCOPICAL LABORATORY,
FIRST SCIENTIFIC STATION FOR THE ART OF BREWING,
NEW YORK CITY.

---

[1] *J. Soc. Chem. Ind.*, **1911**, 786.

SOME PRACTICAL METHODS FOR TESTING AND IDENTIFYING COLORS FOR PRINTING INKS AND SIMILAR PIGMENTS.

By SAMUEL LEVINSON.

Received May 27, 1912.

Every manufacturer, in fact every large user of colors, should be in position to identify and match colors brought to his attention as a producer, jobber or buyer. In this paper we shall consider only the so-called LAKE COLORS, *i. e.*, colors made from coal-tar dyestuffs consisting of the base, coloring matter and usually some substance or substances used to fasten the dye to the base. Analytical methods very often are insufficient to properly identify chemical preparations. A complete analysis giving the percentage of all the constituents which can be properly identified chemically will often be of comparatively little value. But on the other hand a synthetic test, *i. e.*, a combination of different materials which results in a substance identical with the one tested will make the examination complete and at the same time provide all the important analytical data. In very many cases the synthetic test is simpler and takes up much less time, than an analysis. In many factories where there are no or very limited laboratory facilities a complete analysis is out of the question and one must per force take refuge in synthetic methods. Certain conditions, of course, cannot be duplicated in the laboratory and besides the chemist must be familiar not only with analytical methods but must understand the manufacture of the articles in question. Happily in the color line conditions are such that almost any color can easily be prepared in the laboratory and the preparation requires but little time and very limited facilities.

It is relatively easy to find out the percentage of coloring matter in a color and in many instances the manufacturer will state the nature of the dye used, but, if the consumer should pay according to the percentage of dye, as revealed by such analysis, the results might prove disastrous. It is quite a common occurrence for two colors with exactly the same percentage of dye to show different strengths. In examining a new color it is worth while to remember that there are relatively few *lake colors* in the market in shades other than RED, because some of the more important INORGANIC colors, like chrome yellow, chrome green, ultramarine and prussian blue, are much cheaper. So in many instances we can tell by the shade and price without any further examination, whether the article in question is a lake color or an inorganic color. The purpose for which the color is used is a factor of even greater importance; it is evidently useless to look for a heavy gritty base in a color intended for fine printing inks.

Very little apparatus and but few chemicals are required in order to form a definite idea of most of the colors. A few test tubes, a Bunsen burner, and an alcohol lamp will enable one to make most of the necessary tests. When matching is the more important part of the work it very often becomes necessary to make up counter samples, *i. e.*, a color having all or most of the important qualities of the submitted sample. For this work a few Mason jars of one quart capacity can be used as working tanks; glass rods, or even pieces of wood will serve as stirring rods; all the dissolving can be performed without the necessity of boiling by using hot water in enameled ware dishes. As most of the operations included in the manufacture of colors take place with the use of live steam, passing through open iron pipes with a maximum temperature of approximately 170° F., it will readily be seen that the use of boiling water will practically duplicate the working conditions in the manufacture.

Several glass funnels for filtration, or better still a suction pump and a drying oven will complete the outfit In the absence of a drying oven a pot of boiling water covered with a piece of tin can be used ~~for drying.~~ A scale and a set of metric weights will be very convenient, as by figuring 1 gram to 9 cc. as the equivalent of a pound per gallon, it is easy to figure out the dimensions of tanks and vessels required for the actual manufacture. The concentration of the solutions of the materials used is a very important item in manufacture.

The color submitted for examination must be first examined as to the shade and strength. In order to do this properly it is very convenient to have a fair sized collection of standard samples, either prepared in the laboratory or standard market goods; the names of the manufacturers, trade names, prices, etc., should be carefully kept on record. The sample in question is "rubbed out" on a glass plate in some vehicle, either linseed oil, varnish, water or glue solution, depending on the use to which the color is to be put. This mixture is spread out in a thin layer alongside of a sample of some standard color rubbed out in exactly the same way, which appears to be nearest in shade. The two rub-outs can be placed together on a piece of glass. It is also very convenient to spread the colors on white paper, which should not be too heavy. Another method is to put separately very small masses of the colors in oil or varnish on a large palette knife and then rub them out together on a piece of paper in adjoining smears. In this way both the overtone and undertone can be studied and compared with standard samples.

The next in order is a strength test, or a determination of the staining power. For this the color is reduced with a given amount of an inert white base, rubbed out and compared with a standard exactly as before. For reducing I have always used oxide of zinc with very satisfactory results. The color is mixed with ten, twenty or in case of strong color even fifty or a hundred parts of white (by weight). The same concentration of the standard color is prepared. To facilitate matters it is very convenient to prepare dry mixtures of standard colors 1 : 10 or 1 : 20 and keep them in small bottles for further reference. If the shade of the sample and standard are identical and they differ in strength only, the addition of more zinc oxide will help to determine the exact strength. In the course of the above determinations we can also consider the general behavior of the color "bleeding" in oil, in water, resistance toward common reagents, acids and alkalies, etc. If the overtone, undertone, strength, and general behavior of two colors are alike they can be safely considered identical for all practical purposes.

If none of the standards on hand matches the sample it becomes necessary to examine the color more closely, beginning with the base The specific gravity of the color will furnish a good clue in this matter, *e. g.*, a heavy color cannot be a lake made on alumina hydrate base. It must contain some of the heavier bases (barytes, clay, different lead salts, etc.). A few simple tests like the following will suffice to determine the base. A little of the color is treated in a test tube with hydrochloric acid; strong effervescence will show the presence of carbonates, usually either Paris white, or carbonate of barium or lead. The latter are both heavier than Paris white. The following test will clear up the question: A little of the color is boiled in a test tube with strong acetic acid and some hot water and a few drops of a solution of potassium iodide are added The immediate formation of heavy golden crystals will show the presence of lead as a base, as previously confirmed by the heaviness of the color. If the crystals are formed very slowly, we can deduce that lead was used but in small quantities, evidently in order to fasten the dyestuff. The coloring matter can be easily destroyed by boiling the color with a mixture of hydrochloric and nitric acids. The filtrate is tested in the usual way for soluble metals. Large amounts of aluminium for instance will show that the color contains some hydrate of that metal. If a microscope having a magnification of about 100 is handy, it is very convenient to examine the color on a slide rubbed out with a little alcohol. In this way it is easy to determine the difference between barytes and blanc fixe which are identical chemically (natural and artificial sulfate of barium) but act quite differently as bases for colors.

After getting some idea of the base, we shall next proceed to examine the coloring matter proper. The presence of small quantities of lead previously determined in testing for this metal in the case of a red color usually bespeaks the presence of eosines; decided fluorescence of the color with alkalies will confirm it. It is however important to remember that some of the newer coal-tar products show quite a similar behavior; *e. g.*, Pigment Scarlet 3 B (of Meister, Lucius and

Bruening). A bromine test will prove the presence of eosines more positively and exclude Pigment Scarlet.

Having excluded this class of dyes, the identification of so-called Permanent Colors made with Paranitraniline is next in order. When treated with strong sulfuric acid this class shows a cherry-red reaction; boiled with alcoholic caustic soda solution a dark violet will appear. The above method has been used by the author for the last six years, and has been sufficient for the complete identification of this class of colors, nor has confusion with any other class ever occurred.

Using some of the most common reagents like sulfuric acid, hydrochloric acid, caustic soda, also alcoholic caustic soda, alcohol, etc., and comparing the resulting reactions with standard samples made with known coal-tar dyes, or even with the coal-tar dyes *per se*, we can arrive at some conclusion as to the nature of the dye used in the sample. In some cases, especially when dealing with imported colors, we may find that none of the dyes on the market are similar to the one used in the sample. It occurs quite often that manufactured goods with new dyes come to this country, before the corresponding dyes have been imported. It is necessary to have a good collection of coal-tar dyes found on the market. It is very important to keep a record of the name of the original manufacturer (in case the dyes are bought from jobbers), as very often dyestuffs of different make are different, even if they have the same trade name. The trade name should be always noted in full including different letters, B, R, G, etc., and descriptive words like "extra," "fine," etc., in order to be able to get exactly the same products should occasion occur. The record should also contain the price.

After having determined to some extent the nature of the base and coloring matter it becomes often necessary in order to confirm the findings to make a similar or even an identical sample. In this work care must be taken to use always the same grade of raw materials; it is convenient to keep on hand standard samples, of them, with names of the manufacturers, trade names, etc. One cannot make samples with chemically pure materials, as it would not be possible to duplicate them on a large scale. After a sample is made in the laboratory it is compared exactly in the same way as stated above with the tested sample. It is very important to keep a record of the yield of the color, as this will enable us to figure out the price. In computing the price from the raw materials one must always be sure to include a fair estimate for cost of labor, including also as a factor the salary of the chemist and taking into consideration the manufacturers' and jobbers' profit. In this way it is easy to tell whether the price asked for a new color is fair.

Another factor of some importance is that there is usually some little difference between a color made in the factory and one prepared in the laboratory, as it is impossible to have the conditions of work absolutely alike. It would be very wrong for a manufacturer to submit to a customer a laboratory sample for the goods that he will deliver.

The same work of preparing counter samples is often necessary in order to identify and match samples of coal-tar dyes for the use in the color trade. Two samples of dyestuffs may often stain wool or cotton in exactly the same way, but give entirely different results when used in the manufacture of colors.

After separation from the vehicle, thinners, etc., practically the same methods as those given above can be used in the examination of paints and similar goods.

BROOKLYN, NEW YORK.

THE EFFECT OF IGNITION ON THE SOLUBILITY OF SOIL PHOSPHATES.

By CHAS. B. LIPMAN.

Received July 31, 1912.

In common with other soil investigators, the writer has taken occasion to point out recently the dangers involved in applying data obtained with solution cultures of plants to soil problems with the same plants. Time and again results have been obtained in solution cultures of both plants and bacteria which when compared with tests of the same organisms on soils, both sterile and unsterile, were found to be widely divergent and discordant. I have also found the same to be true regarding the purely chemical changes of the same materials in minerals and in soils as brought about by the laboratory treatment involved in their quantitative determination. My remarks apply particularly to the quantitative determinations of phosphates in soil; I employ for this paper the same title that Fraps[1] used for his recently, to call attention to the differences effected in the degree of solubility of phosphates in phosphate minerals and in soils, by ignition. In the work just cited, Fraps has shown that the ignition of phosphate minerals, including wavellite, dufrenite and variscite, for 10 minutes at a low red heat increased about 10 times the solubility of the phosphoric acid contained in them in fifth normal nitric acid and rendered it almost completely soluble in 12 per cent. hydrochloric acid. From these results he concludes that the method for determining phosphoric acid in soils as used by him is not suited to distinguish between the organic and the inorganic phosphorus in soils, since the inorganic phosphates are made more soluble through ignition.

We are not concerned in this paper with the latter conclusion of Fraps as regards the distinction between the organic and inorganic phosphorus of the soil. Having frequently noted, however, in our analytical work on soils that the very opposite effect to that above quoted is accomplished by ignition of soils before determining the phosphoric acid, it was deemed desirable to make some systematic tests with reference to the matter, and determine, if possible, the cause of the different effect of ignition on the solubility of phosphates in minerals and in soils, if such a different effect was definitely shown to exist. Accordingly five different soils were selected, each sifted through a 0.5 mm. sieve and prepared for analysis for phosphoric acid. The soils were as follows:

---

[1] THIS JOURNAL, **3**, 335.

No. 1. A very rich, black, fine silty loam, rich in phosphoric acid and humus, from Arroyo Grande, San Luis Obispo County, California.

No. 2. A fine sandy soil with a good supply of phosphoric acid, but poor in humus, from Escondido, San Diego County, California.

No. 3. A very heavy black, clay adobe soil with sufficient phosphoric acid for fair crop production, from West Berkeley, Alameda County, California.

No. 4. A sandy loam with a fairly good humus and phosphoric acid content from South San Francisco, California.

No. 5. A light sandy loam, of fairly good humus content and phosphoric acid, from Anaheim, Orange County, California.

The analysis was carried out as follows: Four grams of soil were placed in a porcelain cup and digested with concentrated nitric acid for two days on the steam bath. Two samples of each soil were ignited for twenty minutes at a low red heat in a platinum dish and two others of each soil were placed in the cups without ignition. The greatest caution was exercised to prevent loss by dusting in the process of ignition and in the transfer from platinum to digestion cup. After the period of digestion, the soil cups were placed on the sand bath and evaporated to dryness to dehydrate the silica, after which more acid and a little distilled water were added and the cups were replaced on the steam bath for four hours. The solutions were then carefully filtered and the soil residue washed on the filter. The filtrate was warmed to a temperature of 65° to 70° C. and the phosphoric acid precipitated with ammonium molybdate. The precipitate and solution were allowed to stand at 65° to 70° C. for about four hours, then filtered and the precipitate washed with a solution of ammonium nitrate. After this it was dissolved out with ammonia, and precipitated with magnesia mixture, then allowed to stand over night, filtered the next morning and washed with distilled water containing a little ammonia. The precipitate and filter were then dried, ignited, weighed and the phosphoric acid determined in the usual way. The percentages given represent averages of closely agreeing duplicates for each soil both ignited and unignited.

TABLE I.—PERCENTAGES P_2O_5.

Soil No.	1	2	3	4	5
Ignited	0.410	0.150	0.090	0.167	0.151
Not ignited	0.460	0.250	0.130	0.191	0.190

The data given in Table I leave no room for doubt as to the effect of ignition on soil phosphates as existing in various soils. In most cases the loss in percentage is not very great, but it is always definite and in some cases, as in soil No. 2, it is quite marked. In practically all cases the duplicates agreed within one hundredth of a percent. We obtain therefore the very reverse effect of ignition on the soil phosphates as existing in the soil, from that obtained by Fraps on mineral phosphates as existing in minerals. In brief, ignition of soil appears to decrease appreciably and definitely the solubility of its phosphates whether they be largely inorganic or organic. The large variety of soils employed would seem further to strengthen the evidence, in that they doubtless contained largely varying proportions of inorganic and organic phosphates and a large variety of phosphate bearing minerals.

Just why these important differences exist in the effects of ignition on phosphates in minerals and in soils is an explanation that is not as easily found as the facts which obtain in the case. It would appear to be clear that the increased solubility of the phosphoric acid in minerals like wavellite, variscite and others tested by Fraps might be accomplished through the mechanical changes induced by the heat in the mineral employed. We know for example that heating of sand will disintegrate its grains and thus produce more surface. It is altogether likely that the same happens when a phosphate mineral is ignited and the result is the production of a larger surface for the nitric acid to act upon, hence an increase in solubility of phosphoric acid in the ignited over the unignited mineral. On the other hand, in a complex material like the soil, which contains besides many kinds of mineral and rock particles in different stages of disintegration, very considerable quantities of organic matter, both decaying and in living form, and the minerals and salts in different degrees hydrated, it is probable that the mineral particles would be protected from disintegration by heat so long as the water of hydration and the organic matter still remained in the soil; therefore no additional surface would be exposed to the action of the acid and besides, the dehydration of the organic, as well as inorganic phosphates, would seem to make them less soluble. Indeed I have data to show that dehydration without ignition also decreases the solubility of the soil phosphates. This explanation is offered by the writer for the facts noted, merely as a suggestion as to the phenomena probably occurring when mineral phosphates and soils are heated, as regards their phosphate content. It is hoped that an explanation or further suggestions will be forthcoming from my colleagues. This brief paper is offered merely as a partial report on one phase of the subject of the determination of phosphoric acid in soils, the whole of which is now being studied in our laboratory. Other interesting data besides that mentioned has already been obtained which we hope to include in another paper in which the whole subject will be treated more completely.

SOILS RESEARCH LABORATORY,
UNIVERSITY OF CALIFORNIA, BERKELEY.

THE DETERMINATION OF HUMUS IN HAWAIIAN SOIL.[1]

By W. P. KELLEY AND WM. MCGEORGE.

Received May 31, 1912.

In the determination of humus in soils, the difficulty of completely separating the clay from the ammonia soluble organic matter has been appreciated for some time. Certain constituents occurring in varying amounts in clays hold water of hydration which cannot be completely driven off at temperatures below the

---

[1] Published in detail as *Press Bulletin* No. **33**, Hawaii Experiment Station.

point of partial decomposition of the organic matter and, since humus is estimated from the loss upon incinerating the residue obtained by evaporating the ammoniacal extract, the importance of completely removing the clay is at once apparent In soils containing relatively small amounts of clay, this separation is usually a matter of comparative ease, while heavy clay soils present difficulties in varying degrees, depending largely on the specific nature of the constituents contained in the deflocculated clay. Ordinary filtration is ineffective.

TABLE I.—MECHANICAL ANALYSES OF SOILS USED IN EXPERIMENTS (PERCENTAGES).

SOIL NUMBERS.	69	74	97	98	99	100	101	102	103	104	108
Organic matter and combined water	44.60	25.83	14.32	13.65	15.80	15.55	13.06	14.67	17.58	16.17	15.55
Fine gravel	5.94		0.09	0.12	0.86	0.41	0.14	0.29	0.06	0.09	0.96
Coarse sand	26.72		0.43	0.43	0.73	1.65	0.50	0.91	0.26	0.42	
Fine sand	8.65	38.03	1.62	2.11	2.35	1.65	1.33	1.12	0.81	2.36	13.58
Silt	4.07	16.22	3.37	3.06	9.28	6.72	6.23	7.38	5.60	6.44	6.25
Fine silt	5.09	19.99	27.19	26.32	32.69	18.45	28.88	18.87	22.70	29.07	13.35
Clay	5.78	2.05	52.30	55.05	38.60	57.80	47.45	57.80	56.72	44.54	51.26

A number of methods have been proposed for this determination. In some investigations in this laboratory, we have had occasion to compare some of the better known methods with soils representing a wide range both as regards mechanical composition and humus content. The soils under investigation for the most part represent heavy clays of the laterite class, such as constitute the main body of the arable lands of the Hawaiian Islands. In addition, the clay is composed of particles in a very fine state of division and possesses properties which render its separation from ammoniacal solutions extremely difficult. A few samples of highly organic soils have also been examined As will be seen from the tabular results, the humus content[1] varies from 2.64–18.27 per cent.

TABLE II.—COMPARISON OF SEVERAL METHODS IN PRESENT USE. (PERCENTAGES.)

SOIL NUMBERS.	69	74	97	98	99	100	101	102	103	104	108
				Humus.							
Official method	...	...	4.30	5.94	5.12	6.38	4.64	4.34	6.31	3.54	...
Hilgard method	15.63	5.26	2.43	2.61	3.68	...	2.95	2.71	...	...	...
Mooers-Hampton method	18.74	5.32	2.68	2.70	3.17	2.32	3.72	3.20	3.72	2.68	3.84
Cameron-Breazeale method	12.30	3.98	2.34	2.38	2.91	2.24	2.85	2.24	2.94	2.36	2.29
Rather method	20.75	6.49	4.32	4.15	5.01	6.03	5.64	4.38	5.95	4.81	8.24
				Humus Ash.							
Official method	...	...	13.25	20.92	10.54	33.20	15.18	13.15	25.42	7.67	...
Hilgard method	5.44	1.85	2.46	2.56	2.00	...	4.28	1.82	...	...	...
Mooers-Hampton method	6.33	1.33	0.60	0.84	0.65	0.41	1.52	1.70	0.98	1.17	0.44
Cameron-Breazeale method	1.09	1.81	0.28	0.74	0.33	0.33	0.31	0.30	0.57	0.23	0.46
Rather method	7.71	2.51	12.94	11.43	10.40	25.69	17.61	10.28	20.49	12.74	32.69

The type of soil, especially as regards the percentage of clay present, appears to determine in considerable measure the applicability of certain methods now in use for the determination of humus. The mechanical composition of the soils used in this investigation is therefore of some interest in this connection[2] (Table I).

Attention is called to the high content of clay and fine silt in all of these soils save Nos. 69 and 74. One of the pronounced characteristics of Hawaiian soils is a very high content of iron which exists in many cases as ferric hydrate and which imparts to the soil a red color. In connection with humus determinations it is important to know not only the proportion of clay in the soil, but also something regarding its properties, for clay is a sort of general term when applied to soils and usually has reference only to the size of the particles.

In this investigation the following methods have been used. Hilgard, Mooers-Hampton, Huston-Mac Bride or official, Cameron-Breazeale, and Rather. In all the determinations reported in this paper, except those by the Hilgard method, the solutions were made according to the official method. Since the chief obstacle to be overcome is that of removing the clay, the humus ash has been determined in each instance. By this means we were able to check the completeness of the removal of the clay. Table II shows the results as obtained by the several methods studied.

These results show a wide range of variation in the percentage of both humus and humus ash when determined by the various methods, and in addition a strict concordance is not found to exist between the results as obtained by any two methods. The results obtained by the Hilgard, Mooers-Hampton, and Cameron-Breazeale methods, it is true, are in fair agreement in certain instances, but on the whole, they are too discordant to permit of their indiscriminate use. By reference to the data for humus ash, it will be seen that none of these methods save that of Cameron-Breazeale affected a complete removal of the clay in every instance, but this method, when used in its original form, is known to bring about a loss of humus through the absorbing action of the clay filter. The Rather method in most instances brought about no coagulation of clay whatever and therefore, in its original form, is unreliable with these soils. In our use of the Mooers-Hampton method it was found to be necessary to evaporate the humus solutions to dryness in some instances as many as six times, allowing the residue to bake on the water bath for several hours and even then, upon resolution in ammonia, a partial deflocculation of the clay was unavoidable.

---

[1] In this paper the term "humus" is used to signify the organic matter of soils soluble in 4 per cent. solution of ammonia after removing the calcium and magnesium with dilute hydrochloric acid.

[2] Analyses made by the method as outlined by Hall, "The Soil," London, 1908, Second Edition, page 51.

In the main, however, this method can be manipulated so as to remove the clay at least to a point where it is of small importance. The time required, together with the fact that the evaporation must be made in an atmosphere free from acid fumes, makes the method tedious and impracticable. From our studies on these soils and others, it appears that a partial explanation for the disagreement among the several publications dealing with the subject of humus determinations, is probably to be found in the fact that the soils studied were very different in composition and properties. With certain soils a number of these methods will no doubt give reliable results.

A MODIFIED CLAY FILTER METHOD.

From the failure to remove the clay effectively by any means other than by the use of a porous clay filter, attention was directed toward overcoming the difficulties attending its use. The essential feature of the method, as finally adopted, consists in passing a definite aliquot of the humus solution through the filter followed by dilute ammonia solution until all the organic matter is washed through, as was done by Alway, *et al.*[1]

The difficulties of this method have been overcome as follows. The solution is drawn through the filter in the opposite direction from that ordinarily employed. Instead of using the compression chamber, an ordinary suction pump was employed. The tube of glazed porcelain attached to the lower end of an 8-inch Pasteur-Chamberland filter was broken off,[2] so as to leave the end of the tube open, then the tube was inserted into the upper opening of a bell jar, such as is used for filtering under suction, in a manner similar to that employed in the use of a Gooch crucible. A large part of the tube was allowed to extend into the filtering jar and the connection made air tight (Fig. 1). It was also found desirable to coat the upper portion of the tube with paraffin, so as to prevent the passage of the solution except in the lower half of the tube. Otherwise the solution will pass down the sides of the bell jar.

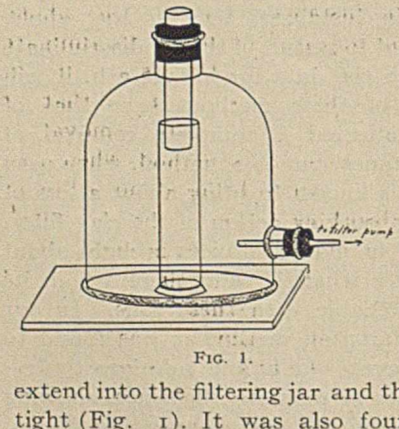


Fig. 1.

A 50 cc. aliquot of the humus solution, representing 1 gram of soil, is drawn through the tube by means of reduced pressure, the filtrate being collected in a cylinder After this aliquot has passed through, a 4 per cent. of ammonia is then drawn through as long as it shows any color; usually about 200 cc. are required. The filtrate and washings are then evaporated to dryness and the determination completed as usual. After each filtration, the clay should be washed out of the filter tube. For this purpose, a test tube brush was found to be serviceable.

The time required to complete a filtration was found to be about 3$^1/_2$ hours and by arranging a number of filtering jars in a series, an ordinary Richardson pump provided suction for at least three filters. With close fitting connections, it is probably possible to operate six filters with one pump. No attention is required other than an occasional moment for pouring in solutions and hence the filtration can be carried out along with other work without interruption. For the sake of comparison, the results obtained by the previously named methods and the modified clay filter method are submitted in Table III.

TABLE III.—COMPARISON OF SEVERAL METHODS WITH THE MODIFIED CLAY FILTER METHOD (PERCENTAGES).

Soil Numbers.	69	74	97	98	99	100	101	102	103	104	108
					Humus.						
Official method	...	...	4.30	5.94	5.12	6.38	4.64	4.34	6.31	3.54	...
Hilgard method	15.63	5.26	2.43	2.61	3.68	...	2.95	2.71	...	...	...
Mooers-Hampton method	18.74	5.32	2.68	2.70	3.17	2.32	3.72	3.20	3.72	2.68	3.84
Cameron-Breazeale method	12.30	3.98	2.34	2.38	2.91	2.24	2.85	2.24	2.94	2.36	2.29
Rather method	20.75	6.49	4.32	4.15	5.01	6.03	5.64	4.38	5.95	4.81	8.24
Modified clay filter method	18.27	5.75	2.64	2.81	3.84	3.48	3.61	3.37	4.74	3.22	3.31
					Humus Ash.						
Official method	...	...	13.25	20.92	10.54	33.20	15.18	13.15	25.42	7.67	...
Hilgard method	5.44	1.85	2.46	2.56	2.00	...	4.28	1.82	...	...	...
Mooers-Hampton method	6.33	1.33	0.60	0.84	0.65	0.41	1.52	1.70	0.98	1.17	0.44
Cameron-Breazeale method	1.09	1.81	0.28	0.74	0.33	0.33	0.31	0.30	0.57	0.23	0.46
Rather method	7.71	2.51	12.94	11.43	10.40	25.69	17.61	10.28	20.49	12.74	32.69
Modified clay filter method	2.14	2.19	0.54	0.75	0.57	0.64	0.78	0.70	1.12	0.76	0.99

From these data, it is obvious that the modified clay filter method gives results higher than those obtained by any other than the official and Rather methods, neither of which can be relied on with Hawaiian soils. By any of the previously used methods, it was found to be extremely difficult to obtain concordant results even with the same soil extract, while by the modified clay filter method, concordant results were easily obtained from separate extractions and in each instance the humus ash had a gray color, indicating the complete elimination of the clay.

The failure of the Rather method and other means of coagulating clay in Hawaiian soils is undoubtedly due to the peculiarities of the clay itself. Some humus solutions in which ammonium carbonate affected an incomplete coagulation of the clay were treated according to the Rather method and the coagulated and uncoagulated clay analyzed. The former appears to be made up of a mixture of ferric hydrate and

---

[1] Nebraska Experiment Station, *Bulletin* **115**.

[2] A Pasteur-Chamberland filter having no tubular would no doubt serve for this purpose.

silicate of aluminum, while the latter contains relatively more silica and iron and correspondingly less aluminum. In some instances it was found that a coagulation could be affected by the use of larger amounts of ammonium carbonate, while in other cases, as much as 40 grams per liter failed to produce coagulation. By the use of still larger amounts of ammonium carbonate, a partial precipitation of humus also took place.

Contribution No. 5, Hawaii Experiment Station,
Honolulu.

THE COMPOSITION OF FUSEL OIL FROM BEET MOLASSES.

By M. C. Boswell and J. L. Gooderham.

Received May 15, 1912.

The published proximate analyses of fusel oil are very few and mostly relate to the distillates from potatoes and corn. This arises from the fact that, until comparatively recent years, fusel oil from any source was regarded as more or less valueless. In Canada, after legislation put a premium on its destruction, this product was allowed to run away in drains or used as a constituent of a cheap burning fluid. The numerous purposes to which it is now applied and for which it is indeed indispensable, have changed this custom, so that it has become four or five times as valuable as the alcohol from which it is separated.

The production of fusel oil from the fermentation of beet molasses depends industrially on a supply of crude material from beet sugar refineries, which did not come into existence on a large scale in Canada until about seven years ago. An alcohol plant, capable of handling from 30,000–40,000 tons of molasses per annum, was established in Toronto in 1905, and very considerable quantities of fusel oil have since been produced, for which a home use, or an export value, has to be found.

The researches of Ehrlich[1] carried on since 1903 ultimately led to the conclusion that the production and composition of fusel oil depend on the character of the substance fermented, mainly with relation to the quantities of leucine and isoleucine present. As beet molasses mash differs very widely from that from potatoes or grain, it might be expected that a corresponding difference would be noted in the quantities and proportions of the amyl alcohols. The particular composition of beet molasses fusel oil is hence a question of considerable technological importance.

The fusel oils of commerce differ very widely in their general characteristics, such as color, specific gravity and solubility in water, being influenced not only by the nature of the material operated on, but by the form of distilling apparatus, the process followed, and the care of the operator. The excise authorities generally look sharply after the presence of ethyl alcohol, and their requirements regarding this affect the presence of other alcohols soluble in water. In the United States, the official and commercial regulations confine the term "crude fusel oil" to that from which the lower alcohols have been so far removed by washing, that a loss of not more than 10 per cent. is realized by agitation with an equal bulk of water. The term is thus used in this paper. Hence the percentage of water-soluble alcohols in fusel oil will depend to some extent on whether the manufacturer has found it necessary to wash his oil in order to meet the excise requirements respecting ethyl alcohol.

The oil examined was amber in color. It was found that the substance or substances causing the color were soluble on shaking in dilute caustic soda. Traces of iron and copper were found, due probably to contact with these metals in the process.

The specific gravity of the sample, taken by the pycnometer, at 15° C. was 0.8370. This is somewhat higher than the figures given for fusel oil from corn, which differ widely as stated by various authorities. Worden[1] gives the range for ordinary samples of washed oil as between 0.810 and 0.835. It is evident that this character will be largely influenced by the amount of water dissolved in the oil, and also by the lower alcohols which have escaped the washing-out process.

In the fusel oil examined, the lower alcohols (ethyl, propyl and butyl) were roughly estimated by agitating equal volumes of oil and water thoroughly in a measuring tube, and noting the increase in volume of the water layer. This amounted to 8 per cent. In a similar manner the amount of water was determined approximately by agitating 10 cc. of the oil with 100 cc. of petroleum benzine and measuring the water layer. This amounted to 5 per cent. Then 500 cc. of crude unwashed fusel oil was thoroughly dried over anhydrous sodium sulphate and fractionated repeatedly until the volumes of the fractions remained constant. The result was as follows:

I.	II.	III.	IV.	V.	VI.	VII.	VIII.	IX.	X.	XI.
75°–80°	80°–85°	85°–90°	90°–105°	105°–115°	115°–120°	120°–125°	125°–128°	128°–130°	130°–133°	residue
7 cc.	18 cc.	6.5 cc.	11 cc.	22 cc.	27 cc.	29 cc.	45 cc.	260 cc.	33 cc.	10 cc.

Total, 473.5 cc. Water, 20.0 cc. Loss, 6.5 cc.

A sample of the crude oil was thoroughly agitated with water, and the oil separated and dried: 500 cc. of this on fractionation gave the following;

I.	II.	III.	IV.	V.	VI.	VII.	VIII.	IX.	X.	XI.
75°–80°	80°–85°	85°–90°	90°–110°	110°–115°	115°–120°	120°–125°	125°–128°	128°–130°	130°–133°	residue
none	none	very little	10 cc.	10 cc.	25 cc.	40 cc.	75 cc.	278 cc.	51 cc.	10 cc.

Total, 499 cc. Loss 1, cc.

On comparing the results of the two fractionations it will be noted that fractions I, II and III have practically disappeared from the washed oil. These were identified, as will be shown later, as lower alcohols which are more or less soluble in water.

Although the boiling points indicated the particular alcohols which were present in the various fractions it was decided to substantiate this by transforming the alcohols into esters. On examining the literature, it was found that the esters of acetic acid were more completely described than those of any other acid, and consequently served best for purposes of identification. Action with acetyl chloride alone was found

---

[1] Summarized in Harden's "Alcoholic Fermentation," **1911**, 75–82.

[1] Worden, *Nitro-cellulose Industry*, **1**, 208.

to be unsatisfactory, yielding a mixture in each case difficult to fractionate, and always leaving a high boiling residue, indicating that the reaction was not one of simple esterification alone.

The method of Einhorn[1] was adopted and proved very satisfactory.

Accordingly 10 grams of each fraction were dissolved in about 60 grams of pyridine, and a little more than the theoretical quantity of acetyl chloride was added. After standing for 6–8 hours the mixture was poured into cold dilute sulphuric acid. The ester which separated as an oil was dried over anhydrous sodium sulphate and fractionated.

The following were the results:

Fraction I (75°–80°).—See table.—The boiling point indicated ethyl alcohol, which was confirmed by the iodoform reaction.

Fraction II (80°–85°).—The b. p. indicated the presence of isopropyl alcohol—b. p. 82.8°. The ester on fractionation boiled chiefly at 90°–94°, the boiling point of isopropyl acetate. This fraction was hence largely isopropyl alcohol.

The boiling points of fractions III and IV, as well as fractions VII and VIII made it difficult alone to decide with certainty as to the particular alcohols present. However, upon transformation into acetic esters, and careful fractionation, it was found possible to identify them.

Fraction III (85°–90°).—As this fraction was very small, it was esterified and added to the ester from fraction IV.

Fraction IV (90°–105°).—The ester distilled chiefly between 110°–120°. It was hence the isobutyl ester—b. p. 115–°117°. A little isopropyl, and traces of amyl esters, were also detected.

Fraction V (105°–115°).—The b. p. indicated the presence of isobutyl alcohol—b. p. 108°. The largest portion of the ester was recovered at 110°–120°, the temperature being very constant at 115°–117°, indicating isobutyl ester. A very small quantity of normal butyl ester, with a boiling point of 125°, was obtained. This fraction hence consisted chiefly of isobutyl alcohol with some normal butyl alcohol.

Fraction VI (115°–120°).—The b. p. indicated the presence of normal butyl alcohol—b. p. 117°. The main portion of the ester came over at 120° to 130°; mostly at 125°, the boiling point of the n. butyl ester. Some methyl normal propyl carbinol ester, with a boiling point of 133°–135°, was recovered also. This fraction hence consisted chiefly of *n.* butyl alcohol with some methyl normal propyl carbinol.

Fraction VII (120°–125°).—The ester of this fraction on distillation separated very sharply into two fractions, the larger with b. p. 133°–136° indicating methyl normal propyl carbinol ester, and the smaller with b. p. 138°–139° indicating isoamyl ester. Hence, this fraction consisted chiefly of methyl *n.* propyl carbinol with some isoamyl alcohol.

Fraction VIII (125°–128°).—A small portion of ester came over between 130° and 137°, containing some methyl *n.* propyl carbinol ester. The largest fraction, which was very constant, distilling between 137–140°, represented the isoamyl ester. This fraction was chiefly isoamyl alcohol, with a little methyl *n.* propyl carbinol.

Fraction IX (128°–130°).—The b. p. indicated the presence of active amyl alcohol, b. p. 128.5°. Practically all the ester came over between 141° and 142°, being the boiling point of active amyl ester, with a small amount of the isoamyl ester, which boils at 137°–140°. This fraction was hence chiefly active amyl alcohol, with a small amount of isoamyl alcohol.

Fraction X (130°–133°).—The b. p. indicated the presence of isoamyl alcohol, b. p. 131.5°. Practically all the ester came over between 138°–140°, proving it to be the isoamyl ester, with a small quantity of active amyl ester. This fraction hence consisted of isoamyl alcohol with some active amyl alcohol.

The Residue (XI), which amounted to 10 cc., was placed in a small flask and distilled. About 8 cc. came over below 150°; a very little up to 180°; and about 1½ cc. was left in the flask. This last residue appeared to have decomposed with the production of brownish vapor. The 8 cc. that came over was esterified and the ester fractionated, and found for the greater part, to distil between 135°–140°, being the boiling point of the isoamyl ester. That which was collected at 140°–150°, and was fairly constant between 141°–142°, was the active amyl ester. Very little came over above 150°, but if a sufficient quantity had been available, would probably have been found to consist of the hexyl and heptyl esters. This residue hence consisted of isoamyl alcohol and active amyl alcohol, with probably small quantities of higher alcohols.

There were no semi-solid substances observed toward the end of the operation as has sometimes been the case with fusel oil from corn.

Ten grams of fusel oil were titrated against a standard potash solution using phenolphthalein as the indicator. 100 grams of fusel oil contained 4.5 cc. normal acid. This is equivalent to 0.5 per cent. free acid in the oil, calculated on C_5H_{11}—COOH as a basis.

Ten grams of fusel oil were boiled with 75 cc. of 0.5 N.KOH for one hour, under a reflux condenser. After cooling, the excess of alkali was titrated against standard acid.

One hundred grams of oil contained 18.4 cc. of normal free acid and acid from esters. Of this quantity, 4.5 cc. were free fatty acids, while the balance (13.9 cc.) represented the acids from the esters. Using $C_5H_{11}COOC_5H_{11}$, the amyl ester of capronic acid, as a basis for calculation, this is equivalent to 2.5 per cent. ester in the oil.

The bases present in the oil were separated in the usual manner. The amount was too small for purification and estimation. However, the distinctive odor of pyridine was recognized.

Furfurol could not be detected.

Consequently, "the composition of fusel oil from beet molasses" may be summarized as follows:

		Cc. from 500 cc.	Per cent.
Ethyl alcohol		5	1
Isopropyl alcohol		20	4
Isobutyl alcohol		30	6
n. Butyl alcohol		30	6
Amyl alcohols	Methyl *n.* propyl carbinol	40	8
	Active amyl alcohol	210	42
	Isoamyl alcohol	130	26
Fatty acids		2.5	0.5
Esters of the fatty acids		12.3	2.46
Pyridine and other bases		Present	Present
Hexyl alcohols, etc.		Traces	Traces
		479.8	95.96
Water		20.0	4.00
Total		499.8	99.96

This composition does not present any marked difference of practical importance from that given for corn by LeBel,[1] and largely quoted, which is as follows:

	Per cent.
Normal propyl alcohol	3.69
Isobutyl alcohol	15.76
Amyl alcohols	75.85
Hexyl alcohols	0.13
Free fatty acids	0.16
Fatty acid esters	0.30
Terpines and terpine hydrates	0.08
Furfurol, heptyl alcohol and bases	0.02
	95.99

---

[1] Liebig's *Annalen*, **301**, 95 (Einhorn).

[1] Maercker's "Spiritusfabrication," p. 53.

The amount of total amyl alcohols, which, industrially, is the chief point, shows a difference of only 0.15 per cent. The respective figures for butyl alcohols differ by 3.76 per cent., though the propyl closely corresponds. This is, however, of little importance, as it shows only that one sample of oil was washed more than the other.

TORONTO, CANADA.

DIFFICULTIES IN THE COLORIMETRIC ESTIMATION OF VANILLIN.[1]

By W. S. HUBBARD.

Received July 19, 1912.

Moerk,[2] in 1891, found in testing for vanillin that he had some difficulty in always obtaining the ferric chloride color reaction, and tried using a ferrous salt and oxidizing it with bromine water. In the latter case, he found the color much more intense than with ferric chloride and was able to detect 1 : 100,000 instead of 1 : 2,000 as before. In a paper[3] a month later he proposed a colorimetric estimation of vanillin in vanilla extracts by this means and his method with a few modifications was later adopted by the Bureau of Chemistry.[4] The procedure is as follows:

"Measure 2 cc. of the vanilla extract into a test tube and add about 5 cc. of lead hydrate; mix thoroughly, pour upon a small wet filter, collect filtrate and washings in a 50 cc. graduated Nessler tube; add an excess of bromine water (3 or 4 drops) and sufficient freshly prepared 10 per cent. ferrous sulphate solution to produce the maximum bluish-green color that will result if vanillin is present, and fill to the mark with water."

"Compare with solutions containing a known amount of vanillin treated as directed above." The lead hydrate is prepared as follows:

"Dissolve 200 grams of lead acetate in 850 cc. of water, filter and add an excess of potassium hydroxide. Let the precipitate settle and wash thoroughly by decantation with repeated portions of water until perfectly neutral. Keep in 500 cc of water in the reagent bottle, and shake to form an emulsion-like mixture before adding to decolorize."

The above method has been used in this laboratory with indifferent success for the past two years. Not until this year were the standards put through the treatment with lead hydrate as is directed in the method: then the troubles quickly multiplied. It was noticed that it was not always possible to match two standards containing the same amount of vanillin and treated in a like manner. An attempt was made to locate the trouble by means of a number of experiments.

Four cc. each of three solutions of vanillin standard made up according to the directions given in Bulletin 107, but containing 0.05, 0.10 and 0.20 gram of vanillin per 100 cc. respectively, were treated with lead cream, centrifuged and filtered, ferrous sulphate and bromine added, and diluted to 50 cc. with water. No difference in color could be noticed among the three and they showed about $^1/_8$ the color of a sample of four cc. of the 0.05 gram in 100 cc. sol. not treated with lead cream. Inasmuch as lead sulphate was precipitated out when the ferrous sulphate and bromine were added it was thought possible that this precipitate mechanically carried down some vanillin.

Since vanilla contains small amounts of oxalic acid and phosphates, 4 cc. of vanillin standard (0.05 in 100) was treated with 5 drops of 85 per cent. phosphoric acid and then with lead cream. It was not necessary to centrifuge as the lead agglutinated immediately, and on the addition of the ferrous sulphate and bromine water no precipitate was formed. The solution matched up to a standard untreated with lead except that it was of a purplish color. But if four drops of phosphoric acid were used instead of five, a precipitate was formed on the addition of bromine water and ferrous sulphate and the color did not match an untreated standard.

A series of experiments were carried on in the same manner with malic acid instead of phosphoric, and it was found that 0.5 cc. of a 10 per cent malic acid gave the best results; the solution had the characteristic bluish green color instead of being purplish as with the phosphoric acid. On standing four weeks, the samples acquired a yellowish tinge in comparison to freshly prepared samples.

In the original method of Moerk[1] a few drops of ferrous sulphate are added and then the bromine drop by drop to a maximum color. In the method of the government, however, an excess of bromine is added and sufficient ferrous sulphate to produce the maximum color. A number of experiments were carried out to see if it made any difference which way it was done and to find the limit in amount of ferrous sulphate and bromine water if any. One cc. of standard vanillin solution (0.05 in 100) was used in all cases.

TABLE I.

Experiment Number.	1.	2.	3.	4.	5.	6.	7.	8.
Drops $FeSO_4$ sol.	1	2	3	4	5	6	7	8
Drops Br sol.	2	2	2	2	2	2	2	2
	Of equal intensity					Lighter but equal		
One more drop Br sol.	Increases intensity					Intensity same as 3, 4 & 5		
One more drop Br sol.						Intensity same as 3, 4 & 5		

TABLE II.

Experiment Number.	9	10	11	12	13	14	15	16
Drops $FeSO_4$ sol.	8	9	10	11	12	13	14	15
Drops Br sol.	4	4	4	4	4	4	4	4
	Of equal intensity				Of equal intensity			
One additional drop Br sol.	All of equal intensity							

TABLE III.

Experiment Number.	17	18	19	20	21	22	23	24
Drops Br sol.	5	5	5	5	5	5	5	5
Drops $FeSO_4$ sol.	1	2	3	4	5	6	7	8
	No color	Darkest and equal					Lighter and equal	

It was found that after obtaining the maximum color in the above tests and then diluting to 50 cc. with water, it was necessary in every case to add at least 2 drops more bromine water to bring the color up to a maximum, and this could not be accomplished by adding the extra

---

[1] Read at the February meeting of University of Michigan Section of the A. C. S. I wish to thank Dean J. O. Schlotterbeck for his interest in my work.

[2] *Am. J. Pharm.*, **63**, 521.

[3] *Ibid.*, 572.

[4] *Bull.* **107**, (revised) p. 157.

[2] *Am. J. Pharm.*, **63**, 521.

2 drops of bromine water before diluting. When the bromine water was added first and the color developed with ferrous sulphate and diluted, a deeper color could not be obtained by the addition of more bromine water (Table III). It was noted too that those which had a larger proportion of ferrous sulphate gave the deeper color, a fact also noted by Flückiger and Nagelwort.[1] In those in which the bromine was added first (Table III) the color was not nearly as deep as in those in which ferrous sulphate was added first (Table I). It was found that it took 2.5 cc. of the vanillin solution (0 05 in 100) when bromine water was added first, to equal 1 cc. when ferrous sulphate was added first.

One cc. of pyrocatechuic acid (equivalent to the one cc. of vanillin) and 2 drops of ferric chloride added gave the same depth of color as 1 cc. of vanillin when treated with ferrous sulphate and bromine water.

Carles[2] in 1872 and Tiemann[3] and Haarmann in 1874 showed that a water solution of vanillin gave a precipitate, soluble in hot water, with a concentrated solution of lead acetate. The lead salt has the formula $(C_8H_7O_3)_2Pb$. In trying lead acetate and also lead nitrate solutions we were unable to get any precipitate with a water solution of vanillin of the strength usually met with in extracts. When, however, the clear, neutral filtrate from lead cream was added to the vanillin solution there appeared immediately a yellow precipitate. This precipitate when dissolved gives the color with ferrous sulphate and bromine water. Some of the yellowish precipitate was extracted with ether and the ether evaporated, leaving a crystalline mass which responded to the vanillin color reaction. On standing 12–24 hours, colorless, rosette like crystals formed in the filtrate from which the yellow precipitate was filtered out. The crystals were soluble in hot water and when massed together in some quantity had a yellow color similar to the first precipitate.

A number of analyses were made of the precipitate which comes down immediately and were as follows: The precipitate was dissolved in a little dilute acetic acid and hydrogen sulphide passed in, the lead sulphide washed, dried and weighed as such.

RESULTS.

	Wt. of lead vanillin. Gram.	Wt. of PbS. Gram.	$\frac{Pb(C_8H_7O_3)_2}{Pb}$.
Theoretical.	0.357	..	1.724
A	0.09695	0.0626	1.771
B	0.1238	0.0858	1.666
C	0.0946	0.0732	1.48
D	0.1130	0.0864	1.50
E	...	..	..
F	0.0642	0.0370	1.98
		Average,	1.687

The filtrate from the lead showed a strong color reaction for vanillin.

CONCLUSION.

In the official colorimetric estimation of vanillin in vanilla extracts, it is difficult to get a maximum color.

The original method of adding the ferrous sulphate first gives a deeper color than that of the present method when the bromine is added first.

In a vanilla extract it is very difficult to add only enough lead cream to decolorize the solution and when different amounts of lead cream are used different depths of color are obtained.

Dilution of the sample influences the color.

It is shown that much larger amounts of ferrous sulphate are necessary in comparison with bromine water to produce a maximum color.

It is shown that the lead cream forms a lead vanillin compound of the formula $(C_8H_7O_3)_2Pb$ and such being the case a quantitative estimation is impossible where lead is used.

It seems quite likely that the vanillin is oxidized to pyrocatechuic acid.

DEPARTMENT OF FOOD AND DRUG ANALYSIS,
SCHOOL OF PHARMACY, UNIVERSITY OF MICHIGAN,
ANN ARBOR.

---

[1] "Reactions," p. 152, by Flückiger.

[2] *Bull. soc. chim.*, **17,** 2.

[3] *Ber. Chem. Geos.*, **7,** 614.

A NEW COLORIMETRIC METHOD FOR THE DETERMINATION OF VANILLIN IN FLAVORING EXTRACTS.

By OTTO FOLIN AND W. DENIS.

Received July 1, 1912.

As the Hess-Prescott method for the determination of vanillin, which in the modified form proposed by Winton and his associates[1] is now universally used in American food laboratories, is extremely laborious, although undoubtedly accurate, it has seemed worth while to attempt to work out a rapid colorimetric method for use in this determination.

The time spent at present by the food analyst on the quantitative determination of vanillin in flavoring extracts is out of all proportion to the value of the results when judged by the weight given them in passing judgment on the quality of commercial extracts.

By the use of the phosphotungstic-phosphomolybdic reagent recently described[2] we have been able to work out a colorimetric method for the determination of vanillin which gives theoretical results with purely artificial extracts containing known amounts of the substance, and gives with authentic extracts values agreeing closely with those obtained by the official method.

Solutions Required.—(1) An aqueous solution of pure vanillin to be used as a standard. This should be made of such a strength that 10 cc. contains one mg. of vanillin.

(2) The phosphotungstic-phosphomolybdic acid reagent, prepared as follows: To 100 grams pure sodium tungstate and 20 grams phosphomolybdic acid (free from nitrates and ammonium salts) add 100 grams syrupy phosphoric acid (containing 85 per cent. H_3PO_4) and 700 cc. water; boil over a free flame for one and a half to two hours; then cool, filter if necessary, and make up with water to a volume of 1 liter An equivalent amount of pure molybdic acid may be substituted for the phosphomolybdic acid.

(3) A solution of pure sodium carbonate saturated at room temperature.

---

[1] *J. Am. Chem. Soc.*, **21,** 256 (1899); **24,** 1128 (1902); **27,** 719 (1905).

[2] *J. Biol. Chem.*, **12,** 239 (1912).

(4) A solution containing 5 per cent. basic and 5 per cent. neutral lead acetate.

Vanillin (and also other mono-, di-, and tri-hydric phenol compounds) when treated in acid solution with the phosphotungstic-phosphomolybdic reagent above described gives on the addition of an excess of sodium carbonate a beautiful deep blue color admirably suited for quantitative colorimetric work.

At first an attempt was made to prepare the color directly from the untreated extract it was found, however, that this gave too high results, due probably to the fact that the tannin and tannic acid present in all true vanilla extracts also react with the reagent.

The following procedure has therefore been devised and has given admirable results with a long series of extracts: 5 cc. of the vanilla extract to be examined are transferred by means of a pipette to a 100 cc. volumetric flask and about 75 cc. cold tap water are added: 4 cc. of the lead acetate solution are then poured in and the mixture made up to volume with water.

The contents of the flask are then rapidly filtered through a folded filter paper, and 5 cc. of the filtrate are transferred by means of a pipette to a 50 cc. volumetric flask. In another 50 cc. volumetric flask is placed 5 cc. of the standard vanillin solution; then 5 cc. of the phosphotungstic-phosphomolybdic reagent is added to each flask, the reagent being allowed to run down the neck of the flasks in order that any vanillin adhering thereto may be washed down. After shaking, the flasks are allowed to stand for five minutes and are then filled to the mark with saturated sodium carbonate solution. After inverting the flasks two or three times, in order that the contents may become thoroughly mixed, they are allowed to stand for 10 minutes, by wihch time the precipitation of sodium phosphate is complete. The contents of the flasks are then rapidly filtered through a folded filter paper and the color of the resulting clear deep blue solutions compared by means of a Dubosc colorimeter. The standard solution is best placed at 20 mm. as experiment has shown that the color produced by the amount of vanillin contained therein (1 mg. in 100 cc.) is most accurately and easily read at this point.

In this, as in all other colorimetric methods, a slight cloudiness of the solution to be read, by cutting off more light than the standard, gives a reading much too low, with correspondingly high results; consequently no solution should be read which is not absolutely clear after filtration.

The calculation of the results is not complicated. When 5 cc. of the solution (previously diluted 5 : 100) is taken, this corresponds to 0.25 cc. of the original solution. If 10 cc. are taken they correspond to 0.5 cc. of the original. Since 0.5 mg. vanillin is used as a standard and with the standard set at 20 (mm.), $0.5 \times 20/R = X$ where R is the colorimeter reading of the unknown and X is the amount of vanillin in mgs. present in the volume of the original extract used in the final color comparison: 100 X divided by the volume of extract taken expressed in mgs. gives the result in per cent.

For example, if 5 cc. of the diluted and filtered solution gave a reading of 18 mm. the result would be $0.5 \times 20/18 = 0.555$ mg.; $55.5 \div 250 = 0.22$. Hence 0.22 per cent. vanillin.

As outlined above, an analyst familiar with the method can in one hour easily make vanillin determinations in from ten to twelve samples of vanilla extract.

Another point in favor of the new method is that by its use the amount of material needed for a vanillin determination is reduced to a minimum, 2.5 cc. of extract being sufficient for from two to four duplicate determinations.

Besides the direct determination of vanillin, the colorimetric method may also be used as a check on the official method.

After the vanillin has been extracted with ether, dried to constant weight, etc., in the usual way, a more or less white crystalline substance is obtained which is usually considered pure vanillin; it is possible by the colorimetric method for the analyst to obtain a check on his results which will at once indicate to him whether the substance extracted and weighed is pure.

This determination is best made as follows:

Dissolve the residue in the dish in the smallest possible quantity of 25 per cent. ethyl alcohol, transfer to a volumetric flask and make up with water to such a concentration that 10 cc. of the solution shall contain 1 mg. of the residue. To 5 cc. of this solution add 5 cc. of the phosphotungstic-phosphomolybdic reagent, as described above, and compare with a similarly treated standard.

For successful use of the above method the following precautions should be noted;

Before beginning a series of determinations the standard solution should be placed in both cups of the colorimeter and the operator should satisfy himself that with the available light he can read the standard to within at least 0.2 mm. We have found that satisfactory readings can be made at night by the use of an ordinary incandescent electric light, the bulb of which is covered by a sheet of white paper. It becomes even more important, however, when artificial light is used, that the standard solution be placed in both sides of the colorimeter, both prisms set at 20 mm. and the instrument moved about until equal illumination of both fields is secured.

We have satisfied ourselves by numerous experiments that it is possible by this method to read against each other solutions containing widely varying amounts of vanillin (as for example, a solution containing 1 mg. vanillin in 100 cc. against one containing 0.5 mg. vanillin in the same vessel); as, however, in all colorimetric work it is a recognized fact that accuracy of reading is increased when the concentration of standard and unknown are not too widely divergent, it is suggested that with the standard at 20 mm. no reading of the unknown be accepted as final if the reading fall much above 15 mm. or below 30 mm. Should the reading obtained fall outside these limits a greater or less amount of the filtrate from the lead precipitate should be taken and the determination repeated.

A new portion of the standard must be prepared for each batch of readings made, as the color darkens slowly for about an hour after the addition of the alkali.

It will usually be found that twelve samples constitute the maximum number that can be satisfactorily manipulated at one time.

Vanilla Extracts Made in the Laboratory According to the Specifications of the U. S. Pharmacopoeia.

		Per cent. vanillin by	
Laboratory number.	Kind and quality of beans from which prepared.	Official method.	Colorimetric method.
1	Mexican first	0.17	0.17
3	Mexican second	0.17	0.16
6	Mexican third	0.19	0.19
10	Mexican fourth	0.19	0.19
11	Mexican fifth	0.15	0.15
14	Bourbon first	0.20	0.20
17	Bourbon second	0.15	0.16
21	Bourbon third	0.20	0.21
24	Bourbon fourth	0.15	0.16
29	Bourbon fifth	0.16	0.16
30	Seychelles first	0.19	0.20
33	Seychelles third	0.21	0.21
37	Seychelles fourth	0.18	0.18
39	Madagascar second	0.23	0.21
42	Madagascar third	0.21	0.20
47	Madagascar fourth	0.24	0.24
48	Comores first	0.19	0.19
51	Comores third	0.19	0.19
54	Comores fourth	0.12	0.13
59	Comores second	0.25	0.24
64	South American first	0.23	0.25
65	South American second	0.19	0.19
66	South American splits	0.22	0.22
	Java fourth	0.23	0.22
	Tahiti	0.11	0.10
	Vanillons	0.06	0.07

Through the kindness of Dr. A. L. Winton we have been able to secure a large number of authentic vanilla extracts which were prepared from various grades of beans in the U. S. Food and Drug Inspection Laboratory at Chicago. Dr. Winton has also allowed us to use as a control on our new method the vanillin figures obtained in his laboratory on these extracts by means of the official method.[1]

Through the kindness of Mr. B. H. Smith, of the Boston Laboratory, and of Mr. R. S. Hiltner, of the Denver Laboratory of the U. S. Food and Drug Inspection Service, we have also been able to secure samples of the vanilla extracts sent out for coöperative work in 1911 by the referee on flavoring extracts of the association of official agricultural chemists. Mr. Hiltner has also sent us the average vanillin figures obtained by the official method on these extracts by the chemists coöperating with him. In all somewhat more than a hundred samples of vanilla extract have been assayed for vanillin by our colorimetric method and in no case has there been any marked deviation from the values obtained by the official method.

Above are given a number of examples of the values obtained by the colorimetric method. These represent but a fraction of the number of results obtained, but the figures agree so uniformly with those given by the official method that it seemed useless to take up more space in this connection.

Below are given results obtained with a few miscellaneous extracts; again the vanillin figures reported as obtained by the official method were furnished us in part by Dr. Winton and in part by Mr. Hiltner.

		Percentage vanillin by	
No.	Prepared from:	Official method.	Colorimetric method.
I	Mexican beans, 60% alcohol and glycerine..	0.20	0.20
II	Bourbon beans, 60% alcohol and sugar (U. S. P.)........................	0.19	0.19
III[1]	Mexican and Tahiti beans and maple syrup, prune juice, synthetic vanillin and caramel	0.18	0.17
IV[2]	25% tonka extract, 75% prune juice, 0.15% vanillin and caramel coloring............	0.15	0.16

[1] A. U. S. P. extract.

[2] An entirely artificial extract.

It is a well known fact that vanillin even in fairly dilute solution may be precipitated by basic lead acetate. We have satisfied ourselves, however, that in the very high dilutions employed in our method no vanillin is precipitated by the lead.

Coumarin, extract of tonka bean and acetanilid give no color with the phosphotungstic-phosphomolybdic acid reagent; the presence of sugar, caramel, or glycerine does not in any way interfere with or alter the color formation.

Biochemical Laboratory,
Harvard Medical School,
Boston.

METHOD FOR DETERMINING FAT IN SUGARED EVAPORATED MILK.

By F. C. Broeman.

Received June 8, 1912.

Ten grams of the milk are mixed with 100 cc. of hot water and 5 cc. $CuSO_4$ solution (Feh. St.) added and stirred. The ppt. contains the fat and it is filtered at once and washed with hot water. It is then transferred to a 150 cc. beaker (after a little experience it can be thrown out without a particle sticking to the paper) and 10 cc. conc. HCl added. Heat on hot plate until solution turns to chocolate brown, cool and then add 2–3 times volume of alcohol and extract 4 times with petroleum ether in separatory funnel. The results obtained agree with those obtained by the extraction methods when carried out under the most exacting conditions. The determination can be completed entirely in one hour.

Laboratories of F. C. Broeman & Co.,
Cincinnati, Ohio.

LABORATORY AND PLANT

A NEW TYPE OF INORGANIC FILTER FOR LABORATORY PURPOSES.

By M. A. Williamson and P. A. Boeck.

Received July 15, 1912.

The use of porous inorganic materials for filtration and separation of liquids and solids in quantitative work has been known for some time. A variety of materials and shapes have been employed for this purpose with more or less success.[1]

---

[1] *Bull.* **107**, 156 (Revised), Bur. of Chem.

[1] See Faraday's "Chemical Manipulation," new edition, 1830, Section 9, page 230, and *J. Am. Chem. Soc.*, **9**, 22, article by Lucius Pitkins on the "Efficiency of Porcelain Filters."

The work encountered in analytical operations is so varied in character and is subject to such extremely severe conditions, that most of the materials tried have been found lacking in some one or more desirable characteristics, such as resistance to the influence of the re-agents employed, with the results that their successful application to quantitative work has been seriously curtailed.[1]

There are two general methods of using porous inorganic filters.

1. A finely divided material which is placed loosely on a perforated or porous body, permitting the passage of the liquids, the solid matter being retained by the finer voids in the filtering medium.[2] Well known examples of this class of filter which are used for quantitative analytical work are sand, glass, wool, kaolin, clay, precipitated alumina, natural porous stones and infusorial earths, which may be used either with or without an organic material.

2. Bonding together these finely divided materials by means of some agglutinant which is insoluble in the solutions filtered and which does not occupy all the space between the grains or voids in the body. A massive but porous filtering bed is obtained which may be made into a variety of shapes whose filtering capacity can be varied by altering the size and number of the voids. This can be accomplished in several ways; by varying

1st, the relative sizes of the particles bonded;

2nd, the proportion of the various sizes of grain used;

3rd, the percentage of bonding material used;

4th, the shrinkage of the bonding material;

5th, the addition of some material which can be subsequently removed by ignition or solution, leaving the volume occupied by it as a void.[3]

For analytical work the use of a porous diaphragm or shape offers so many advantages that it has been the subject of much speculation and a variety of materials have been tried out. The advantage is strongly in favor of the bonded articles, as they are immediately available without previous preparation. The asbestos fiber Gooch crucible and Witte plate are good examples of the first class of these materials, but with the exception of soluble precipitates it has the disadvantage of requiring frequent renewal and preparation.

In carrying out the investigation on refractory aluminous bodies for high temperature work it was found that bodies made up of fused alumina, bonded with a highly resistant bonding material of porcelain nature, were very advantageous.

Tests conducted on the fused alumina alone showed it to withstand the action of both acids and alkalis in solution, quantitatively. Similar tests on the bonding material alone indicated that it was affected by only the strongest acids and alkalis and even then to so small an extent that with the proper precautions it could be used for quantitative chemical operations in practically any solution.

MANUFACTURE OF CRUDE MATERIAL AND PROPERTIES OF FINISHED PRODUCT.

The fused alumina, the material used in the manufacture of the filters to be described, has been used for the past ten years in the manufacture of abrasive wheels and stones under the trade name of "Alundum." It is obtained by fusing calcined hydrated oxide of alumina or bauxite in a water cooled electric arc furnace, from which it comes in the form of an ingot weighing some three tons. The impurities contained in the bauxite as iron oxide, silica, and titanium oxide are reduced to a certain extent and segregated at the bottom of the pig as a low grade ferro-silicon containing some titanium. The resulting pig or ingot consists essentially of pure crystalline alumina. The physical properties of this material adapt it peculiarly well to the manufacture of refractory laboratory articles. On being crushed, it is graded to a uniform mesh and mixed with the required amount of bonding material, the character of which is determined by the uses to which the resulting article is to be put. When made into the form of bonded shapes these materials have been found to possess a high thermal coefficient. The following curves illustrate graphically the relative thermal conductivity of ordinary fire-brick, Seger porcelain, bonded Alundum and bonded Crystolon at comparatively low temperatures. The finished articles also possess an extremely high melting point, approximately 1900° Centigrade, or 3500° Fahrenheit, a comparatively low coefficient of expansion 0.0000071 per degree C., and are non-conductors of electricity. This dielectric property was determined by Dr. Thompson, of the Massachusetts Institute of Technology, and is found to be greater than that of porcelain, even at high temperatures. The specific resistance of centimeter cubes at various temperatures are as follows:

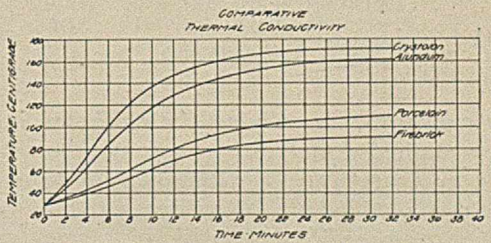


FIG. 1.

Degrees C.	Megohms.
528	130
720	16
892	5.3
1020	1.8

The maximum crushing strength of bonded Alundum is 15,410 lbs. or 7 1/2 tons per square inch while its tensile strength is 1.700 lbs. per square inch. This factor is dependent on the thermal conductivity, coefficient of expansion and other properties desired.

These articles have furthermore been found remarkably resistant to the action of fluxes, especially those of a basic nature even at high temperatures.

---

[1] See *J. Am. Chem. Soc.*, **3-4**, 248, article by P. Casamajor. Also *Chem. News*, **32**, 45, article P. Casamajor, on "Implements of Filtration."

[2] See *J. Am. Chem. Soc.*, **8**, 192, article by J. H. Stebbins, Jr. "The Micromembrane Filter." Also *J. Am. Chem. Soc.*, **27**, by Mr. Porter W. Shimer on a "New Filter."

[3] Article appearing in the German Chemical Society, sixth year, No. 8, page 227, by W. Pukall. "Treatise on Clay Filters, their Properties and Application in Chemical and Bacteriological Laboratories."

GENERAL REQUIREMENTS OF LABORATORY FILTERS.

The general requirements of a filter for laboratory work are, sufficient porosity permitting them to be used for a variety of purposes, rapid cleansing and preparation for subsequent operations. They should possess sufficient strength to resist a high degree of suction and withstand the moderately high temperatures encountered in the ordinary laboratory for igniting the filter; inactivity towards reagents and materials which are ignited in them; constancy in weight within the practical limits of error through ordinary quantitative treatment.

In the platinum Gooch all of these desirable properties are found. It, however, possesses the disadvantage of requiring careful preliminary preparation of the asbestos mat. The cost of platinum, unfortunately, places it beyond the reach of the every-day analyst, also the precautions to be exercised in the use of this ware handicap the operation.

With porcelain, several difficulties are encountered: (1) the time and trouble necessary in preparing the asbestos mat and in varying the thickness in order that any desired degree of porosity may be obtained; (2) the comparatively low thermal conductivity of porcelain is a militating factor in several ways, as in the ashing of organic compounds, burning off precipitates, etc., increasing the time appreciably. Porcelain can be used at only relatively low temperatures in comparison with this new material.

Table I.—Absorption Properties of Alundum as Compared with Porcelain and Platinum.

	Alundum crucibles.								Gooch porcelain crucible.		Platinum crucible.	
	1		2		3		4					
	Wt. Grams.	Difference. Mg.	Wt. Grams.	Difference. Mg.	Wt. Grams.	Difference. Mg.	Wt. Grams.	Difference. Mg.	Wt. Grams.	Difference. Mg.	Wt. Grams.	Difference. Mg.
A	16.2072		12.1658		22.1256		15.4388		19.0030		24.4059	
B	16.2039	—3.3	12.1617	—4.1	22.1194	—6.2	15.4294	—9.4	19.0008	—2.2	24.4055	—0.4
C	16.2018	—2.1	12.1605	—1.2	22.1174	—2.0	15.4290	—0.4	19.0028	+2.0	24.4055	0.0
D	16.2028	+1.0	12.1628	+2.3	22.1193	+1.9	15.4315	+2.5	19.0035	+0.7	24.4056	+0.1
E	16.2032	+0.4	12.1628	0.0	22.1194	+0.1	15.4316	+0.1	19.0035	0.0	24.4056	0.0
F	16.2008	—2.4	12.1600	—2.8	22.1162	—3.2	15.4270	—4.6	19.0007	—2.8	24.4049	—0.7
G	16.2031	+2.3	12.1623	+2.3	22.1182	+2.0	15.4325	+5.5	19.0039	+3.2	24.4059	+1.0
H	16.2031	0.0	12.1623	0.0	22.1188	+0.6	15.4325	0.0	19.0039	0.0	24.4059	0.0
I	16.2007	—2.4	12.1596	—2.7	22.1160	—2.8	15.4286	—3.9	19.0019	—2.0	24.4054	—0.5

The articles made from fused alumina or Alundum will be found to possess most of the desired advantages. They are rapid, always ready, easily cleansed, withstand any temperatures available in the average laboratory; the porosity can be varied to meet any requirement; they will withstand the action of practically all reagents and materials ignited in them. They are not adapted to making fusions with alkaline carbonates or similar material, because of the siliceous nature of the bond. Like porcelain they are fragile, and will withstand but moderately sudden temperature changes. On the other hand, however, they possess a high thermal conductivity which together with the porosity makes them better adapted than porcelain to the burning off of organic materials.

OBJECTIONS TO ALUNDUM.

One disadvantage in making filtrations with the ordinary shaped crucibles of fused alumina was found in that they were not placed in the carbon tube far enough to bring the entire filtering area into the zone of suction. The portion which projected beyond the zone of suction became impregnated with the soluble salts in the solution being filtered which could only be removed after prolonged washing, consuming so much time that in many operations this crucible did not offer any particular advantages over the Gooch. Several methods were developed, employed and found excellent, only they required more time and apparatus than the ordinary porcelain Gooch.

To overcome the foregoing objection, glazing the upper portion of the crucible was attempted. The idea was to obtain a crucible of fused alumina with impervious walls and a porous bottom. This promised a solution of the difficulty in analytical work, but owing to the fact that the walls were impervious to all glazes, it was found that the glaze simply spread over the surface, leaving a porous strata of Alundum between the walls of glaze. This is an extremely unsatisfactory condition in filtering off any precipitate. The porous strata would become impregnated with a solution containing salts impossible of removal, causing an increased weight in the crucible and the possibility of contaminating any solution which would be passed through it afterwards.

The idea of building up crucibles of two parts, that is, glazing the upper portion and cementing it to a porous bottom, was tried out, but found subject to the same objections. Accordingly this scheme had to be abandoned.

Another difficulty experienced by some is the property of Alundum to absorb moisture from the air. This is by no means a chemical action for there is nothing in the bond or the fused alumina which will combine with water at ordinary temperatures. The moisture of the air is simply condensed on the walls of the voids or pores, which action can continue only up to the point of saturation; that is, when a crucible of this material is ignited and immediately weighed it will be found to gain in weight when exposed to the air. Upon again igniting, it will return to the former weight. This variation, however, is so limited that in ordinary determinations it becomes a negligible quantity. The action can be observed more plainly by reference to Table I. Four Alundum crucibles (marked 1, 2, 3 and 4), one 30 cc. porcelain Gooch crucible and one 30 cc. platinum crucible were used for these tests.

All crucibles were carefully weighed before making this test. They were then ignited in the electric furnace at 1000° C., cooled in a desiccator, and weighed. They were then washed with 250 cc. each of hot and cold water, dried in the electric oven at 100° C., ignited in the electric furnace, and cooled in a desiccator, before weighing. The crucibles were then allowed to stand on the scale pan in the balance case for one, two and three hours respectively. Weighings were made at the end of each period of time. The crucibles were then ignited in the electric furnace, permitted to stand in the atmosphere as before and again ignited for the fourth time. Every conceivable precautionary measure was observed in this test in order that the results might be as accurate as possible. The weights taken of these crucibles at the various stages of the operation are marked by letters, as follows:

A, the original weight of the crucible when received.

B, weight of the crucible after igniting in an electric furnace at 1000° C. and cooling in a desiccator.

C, weight after 250 cc. of hot water had been run through by means of a reverse washer, and 250 cc. run through as in direct filtration, and the crucible dried and ignited in the electric furnace at 1000° C. and cooled in a desiccator.

D, weight after allowing the crucible to stand in the balance case one hour and weighing immediately.

E, weight after the crucible had been in the balance case two hours.

F, weight after the crucible had been ignited in the electric furnace at 1000° C.

G, weight after the crucible had been in the balance case one hour.

H, weight after the crucible had been in the balance case two hours.

I, weight after the crucible had been in the electric furnace and cooled in a desiccator.

The fused alumina is crushed to grains of suitable size, mixed with a ceramic bond, moulded, dried and then fired in an ordinary porcelain kiln. The bond becomes more or less vitrified, forming a hard resistant body. During the process of manufacture small particles of the grain adhere to the outside of the article and are retained in the pores. Upon washing, these small particles are dislodged and washed out. Unless this preliminary precaution is observed an appreciable variation in weight is noted, as shown by the following tables.

TABLE II.—EFFECT OF WASHING ON WEIGHT OF ALUNDUM.

Crucible No.	Wt. before washing. Grams.	Wt. after cleaning. Grams.	Loss. Mg.
1	11.6725	11.6708	1.7
2	9.7492	9.7468	2.4
3	11.2629	11.2602	1.7
4	10.0136	10.0094	4.2

Four crucibles were employed. They were weighed, washed with 500 cc. each of hot and cold water, dried in an electric oven at 105° C., ignited in an electric furnace for fifteen minutes at 1000° C., and cooled in a desiccator before weighing. The results are shown in Table II.

After treating these crucibles as above, each was washed with 250 cc. of both hot and cold sulphuric acid, this operation being repeated with hydrochloric acid, 10 per cent. solution. They were then thoroughly washed with distilled water, ignited and weighed. The results of this investigation are summarized in Table III.

TABLE III.—EFFECT OF WASHING WITH ACIDS AFTER TREATMENT WITH WATER.

	Wt. of crucible.	H_2SO_4, cold.	H_2SO_4, hot.	HCl, cold.	HCl, hot.	Total loss.
Crucible No. 1	11.6708	11.6702	11.6693	11.6682	11.6668	
	Loss	0.6 Mg.	0.9 Mg.	1.1 Mg.	1.4 Mg.	4 Mg.
Crucible No. 2	9.7468	9.7464	9.7459	9.7458	9.7448	
	Loss	0.4 Mg.	0.5 Mg.	0.8 Mg.	0.3 Mg.	2 Mg.
Crucible No. 3	11.2602	11.2598	11.2592	11.2587	11.2582	
	Loss	0.4 Mg.	0.6 Mg.	0.5 Mg.	0.5 Mg.	2 Mg.
Crucible No. 4	10.1058	10.1058	10.1048	Crucible broken.		
	Loss	0.0 Mg.	1.0 Mg.			

Comparing Table III with II, the necessity of preliminary preparation is demonstrated by the difference in losses suffered due to the several treatments.

IMPROVED TYPE OF FILTER.

A new type of filter, which differs from the crucible, principally in shape and bond, has been recently developed, giving promise of better adaption to analytical work than any other. It differs from the other types of filters mentioned in that it is compact, filters rapidly, and is always ready. It is made from the same materials as the crucibles but is somewhat more resistant to action of the reagents used in ordinary analysis. This new filter is in the form of a cone and is designed to fit into the 60° funnel. One size found satisfactory measures $1^3/_4''$ in diameter by $1^1/_4''$ high and weighs about ten grams; while this is the most convenient size, the cones can be made up into any desirable shape or size, depending on the specific requirements.

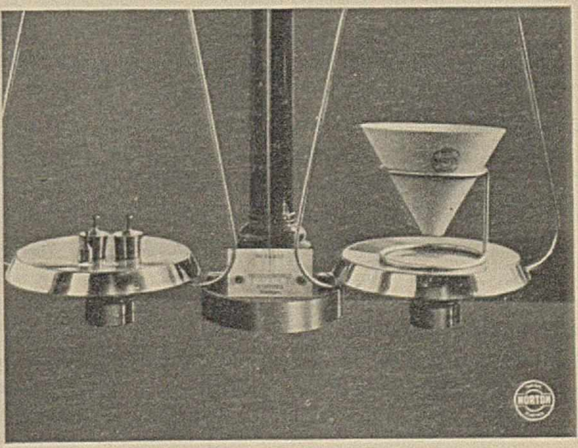


FIG. 2. FILTER CONE ON SCALE PAN.

This type of filter is placed in operation by first stretching over a large end of the funnel a piece of soft rubber tubing about $1^1/_2''$ in diameter and $1^1/_2''$ long, allowing half of the tube to project over the top. The funnel is then connected with the filter bottle and the conical filter placed in the aperture formed by the rubber ring. When suction is applied and the filter moistened, the cone is drawn down against the gasket with a force sufficient to make a gas-tight joint. The efficiency of this joint varies directly with the suction applied. This type of apparatus possesses all the advantages outlined for the best

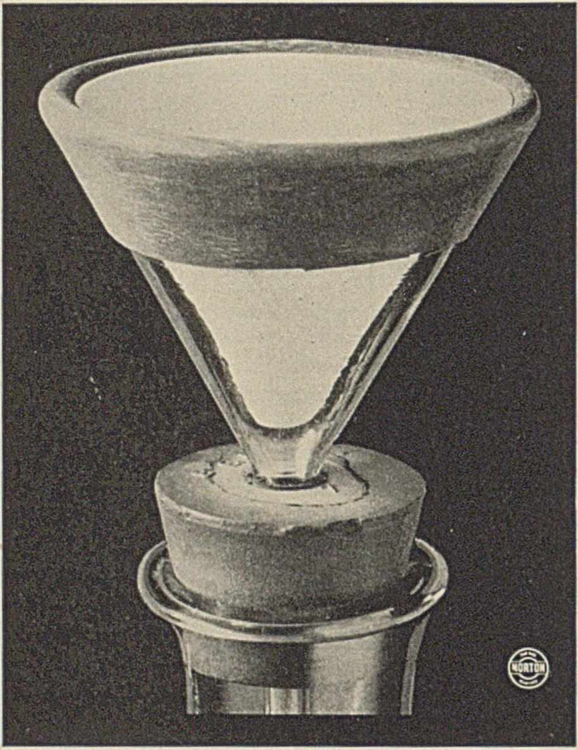


FIG. 3. METHOD OF ADJUSTING CONE.

laboratory filters. It can be used with or without filter paper, depending on the manipulator and the degree of accuracy required.

When using an ordinary filter paper it may be folded in the usual manner and the point turned back about 1/8" so that the paper may fit snugly into the cone, proceeding then as in the ordinary operation. Several advantages are gained by this method, among them being extremely rapid filtration, depending on the fineness and nature of the precipitate to be filtered. In very accurate work the weight of the cone is independent of the weight of the paper and the cone acts only as a support. It permits the use of a paper whose porosity is suitable for the work in hand.

TABLE IV.

Treatment. Soaked in 10% H_2SO_4 and water, then ignited	Cones. 320 Weight. Grams.	Cones. 320 Difference. Mg.	Cones. 321 Weight. Grams.	Cones. 321 Difference. Mg.	Cones. 322 Weight. Grams.	Cones. 322 Difference. Mg.	Cones. 327 Weight. Grams.	Cones. 327 Difference. Mg.	Porcelain Gooch crucible. Weight. Grams.	Porcelain Gooch crucible. Difference. Mg.	Platinum crucible. Weight. Grams.	Platinum crucible. Difference. Mg.
then ignited.......	9.4880		8.0398		5.2539		9.7204		15.6473		11.3184	
Stood 1 hr. in case....	9.4893	+1.3	8.0404	+0.6	5.2552	+1.3	9.7216	+1.2	15.6472	—0.1	11.3184	0.0
Stood 2 hrs. in case...	9.4893	0.0	8.0408	+0.4	5.2552	0.0	9.7216	0.0	15.6475	+0.3	11.3184	0.0
Stood 3 hrs. in case...	9.4893	0.0	8.0408	0.0	5.2552	0.0	9.7215	—0.1	15.6475	0.0	11.3184	0.0
Ignited again.........	9.4881	—1.2	8.0398	—1.0	5.2542	—1.0	9.7205	—1.0	15.6468	—0.7	11.3183	—0.1

The entire filtering area of the cone is subjected to the suction so that any and all soluble salts which might be retained by the porous material can be readily removed by proper washing. The advantages resulting from the use of this filter are obvious.

CONSTANCY IN WEIGHT.

The constancy in weight of the cone has been the subject of considerable speculation and discussion. With the idea of determining this under characteristic conditions, the following test was made.

Four cones, of different mixtures, were chosen for this test, namely, RA-320, 321, 322, 327, and were compared with a porcelain Gooch with asbestos mat and an ordinary platinum laboratory crucible.

All of these were soaked in a 10 per cent. solution of sulphuric acid at ordinary temperatures, washed with distilled water and ignited. They were then allowed to stand on the scale pan for one, two and three hours, weighing at the end of each period of time. They were then ignited and weighed, the results being recorded in Table IV.

This type of filter is subject to the same criticism as the other form, namely, the apparent inconstancy of weight, due to the absorption of moisture from the air. As before stated, this characteristic is in no manner detrimental, since the various articles will remain constant when used under the same conditions each time. This fact is illustrated in Table IV.

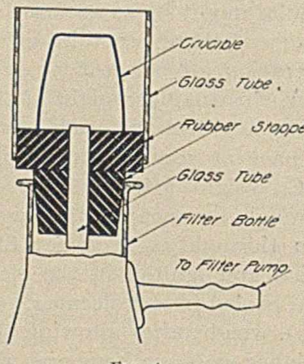


FIG. 4.

The question to be determined is whether they are adapted to quantitative analysis. The favorable results obtained in further tests and recorded in Table V constitute the necessary evidence.

For this final test five conical filters were used and an ordinary porcelain Gooch with asbestos mat. Cones Nos. 1, 2 and 3 were tested without, while cones Nos. 4 and 5 were provided with a lining of filter paper in addition to these a test was made with a filter paper in the usual manner. The 3 precipitates chosen for the test were aluminum hydroxide, barium sulphate and silver chloride, because they are more or less representative of the various classes of precipitates encountered in analytical work. The aluminum hydroxide, barium sulphate and silver chloride were prepared in such a manner as to make standard solutions, 100 cc. of which contained 0.1 gram Al_2O_3, 0.1329 gram $BaSO_4$, and 0.1687 gram $AgCl$, respectively.

The cones were all thoroughly cleaned and ignited before making this test.

From Table V it will be noted that the first cone was found the most satisfactory for all purposes. The time factor as compared with the Gooch and filter paper was reduced considerably without reducing the accuracy to any appreciable extent.

The cleansing of the filter may be readily accomplished by inverting it on a rubber cork and reversing the flow, as is illustrated in Fig. 4.

On the whole the new conical filters proved to be far superior to those ordinarily used.

Table V.—Filtering Properties.

	Al_2O_3.			AgCl.		$BaSO_4$.	
Amount found.	Weight. Gram.	Difference. Mg.	Time required. Min.	Wt. Gram.	Difference. Mg.	Weight. Gram.	Difference. Mg.
By calculation..	0.0500			0.1687		0.1349	
With cone 320..	0.0510	+1.0	2.5	0.1650	—3.7	0.1329	—2.0
With cone 321..	0.0510	+1.0	2.0	0.1644	—4.3	0.1331	—1.8
With cone 327..	0.0502	+0.2	2.0	0.1651	—3.6	0.1331	—1.8
With cone 321 + paper.....	0.0522	+2.2	45.0	0.1647	—4.0	0.1332	—1.7
With cone 322 + paper.....	0.0522	+2.2	30.0	0.1662	—2.5	0.1327	—2.2
With asbestos Gooch.......	0.0536	+3.6	11.0	0.1650	—3.7	0.1328	—2.1
With paper filter	0.0519	+1.9	9.0	0.1642	—4.5	0.1349	0.0

The authors have endeavored to point out the advantages accruing from the use of a filter of this improved type, the value and superiority of which have already been fully demonstrated by their successful application, under varying conditions, in general laboratory operation.

Research Laboratories, Norton Company,
Worcester, Mass.

CALCULATION OF SULPHURIC ACID STOCK BY APPROXIMATE *vs.* ACCURATE METHODS. A SPECIAL SLIDE RULE FOR THIS PURPOSE.

By H. C. Moore.

Received May 25, 1912.

When taking periodical inventories of the amount of sulphuric acid stock on hand in the numerous tanks and chambers around a sulphuric acid plant it is customary to test the acid in each tank for density, in terms of degrees Baumé, and also for temperature. The depth of the acid is also measured, and knowing the dimensions of the tanks and chambers it is a simple matter to calculate the number of cu. ft. of acid in each container.

The next step is to calculate, from the data thus obtained, the acid in each lot to the same basis, as, for instance, to the basis of its equivalent in terms of 50° B., 60° B. or 66° B. acid at 60° F. The whole amount of acid on hand is then determined in terms of one grade.

Among fertilizer factories it is customary to calculate all acid in terms of 50° B. acid at 60° F. Tables, which are available, make it possible to determine the number of pounds of 50° B. acid equivalent to a cu. ft. of acid of any density and temperature. The tables as adopted by the Manufacturing Chemists' Association of the United States in 1904 are generally used as a basis for making all calculations.

Now it is no short task for the superintendent or the chemist of a sulphuric acid plant to take a long row of figures, which represent the density and temperature of the acid in the numerous tanks and chambers, and calculate correctly from this data the exact equivalent in terms of 50° B. acid, unless a very voluminous set of tables has been especially prepared for this purpose. By calculating correctly the writer means that exact corrections are made for density and temperature instead of the rough or approximate corrections ordinarily made.

If, however, one is content when taking the acid inventory, to record the density reading to the nearest even degree Baumé and the temperature to the nearest ten degrees Fahrenheit, then the problem is not such a long task, especially if one also assumes that one cu. ft. of acid testing, say, 52° B. at a temperature from 90° F. to 110° F. is equivalent to one cu. ft. of acid testing 53° B. at 60° F. If all of these assumptions are made the summary of the acid inventory becomes very simple indeed, and if a few simple sets of tables have been compiled, practically no calculations are necessary. Such a method of figuring is not correct, however, and the error will vary, being greater for acid at higher temperatures.

Acid testing, say, 50° B. at 130° F. when cooled to 60° F. would have a density of 53.9° B., but one cu. ft. of this acid at 130° F. would have a volume of less than one cu. ft. if cooled to 60° F. while the shrinkage amounts to about 2.25 per cent., or an error too great to be overlooked.

By mentioning the above incorrect methods of calculating sulphuric acid stock, the writer does not wish to infer that such methods are generally used, but has simply referred to some methods which have come to his knowledge both by hearsay and observation. He has also heard chemists remark that they were not sure they were making their claculations with absolute correctness.

There is another slight error which the writer has often observed, which, however, is scarcely appreciable. In the tables adopted by the Manufacturing Chemists' Association, in 1904, will be found a table marked "Allowance for Temperature." This table indicates the correction necessary to apply to Baumé readings to correct from one temperature basis to another. The allowance for temperature for 50° B. acid is 0.028° B. and for 60° B. acid is 0.026° B., for each degree Fahrenheit. Therefore, acids of densities between these limits probably have an allowance-for-temperature value proportionately between the values given. By interpolation the allowance for 52° B. acid would be 0.0276° B. and for 54° B. would be 0.0274° B. for 1° F.

Take the case of acid testing 52.0° B. at 130° F. This acid when cooled to 60° F. would be about 54° B., and, therefore, the value 0.0274° B. for 1° F. should be applied, and 52.0 plus (70 × 0.0274) = 53.9° B. at 60° F. These allowance-for-temperature values were determined, as the writer understands from the original paper on this work, by heating the acid, starting at 60° F. and noting the density variation for rise in temperature. To further illustrate this point, assume acid testing 50.00° B. at 60° F. Calculating the density of this acid if heated to 203° F. we get 54.00° B. Now suppose we start with acid at 54.00° B. and 203° F. and calculate it back to the basis of 60° F. by applying the temperature allowance of 0.0274° B. for 1° F., which, as above mentioned, would be the temperature allowance interpolated for 54° B. acid, and we would get 50.08° B. at 60° F. The discrepancy, of course, is slight, yet it simply points out a very common error which the writer has observed.

To indicate the error in assuming that one cu. ft. of acid at a temperature above 60° F. is equivalent to one cu. ft. of the acid calculated to its density at 60° F. the following table has been prepared:

	Contraction = error.
50° B. at 130° F. = 51.93° B. at 60° F.	2.03
50° B. at 140° F. = 52.21° B. at 60° F.	2.32
51° B. at 100° F. = 52.10° B. at 60° F.	1.17
51° B. at 90° F. = 51.83° B. at 60° F.	0.88
49° B. at 170° F. = 52.04° B. at 60° F.	3.16
48° B. at 200° F. = 51.86° B. at 60° F.	3.98
47° B. at 240° F. = 52.04° B. at 60° F.	5.14

If the amount of acid used per charge when making acid phosphate is measured and the proper corrections are not made for density and temperature, the error will be greater the higher the temperature of the acid used in mixing. Further, if the amount of acid used per week is computed from records thus obtained the error may be considerable We might assume that the error in calculating the acid in the tanks and chambers is fairly constant from one inventory to another, which assumption would be reasonably correct providing the stock carried in the tanks and chambers remains about constant with small variations in density and temperature.

The writer wishes to state at this point that he is not unmindful of the great difficulty, rather the impossibility, of securing a sample of the acid in the tanks, and especially in the chambers, which is exactly representative of all the acid in each lot. Therefore, the density and temperature of each lot of acid can be only approximately determined. If, however, the acid in each tank and chamber is tested at the same point and in the same manner each time the error will be reasonably constant and the appreciable error, therefore, unless the proper corrections are made as regarding density and temperature, is made in calculating the amount of acid used per week or similar period.

If the acid used at the mixer (acid phosphate) has a temperature of 130° F., the error, resulting by making the incorrect allowance for density and temperature as before described, will amount to about 2 per cent. In other words, the acid department gets credit for 2 per cent. more acid than actually made and the acid phosphate department gets the loss, which is included in the shrinkage allowed.

The writer has known of cases where such errors when unearthed have helped to explain why some acid plants could often get a yield of from 4.95 to 5.20 lbs. of 50° B. acid per pound of sulphur burned.

It might be well to give here two methods by which correct results may be obtained when calculating acid. These methods will not be new to many and yet may be of value to others.

Assume that we have one cu. ft. of sulphuric acid testing 51.0° B. at 100° F. and wish to find its equivalent in terms of 50° B. acid at 60° F. First by reference to the tables and making the calculations before described, we calculate that this acid would have a density of 52.1° B. at 60° F. From this point the calculation may be made by two methods:

Method I:

1 cu. ft. 51.0° B. acid weighs 96.21 lbs. (from table)

1 cu. ft. 52.1° B. acid weighs 97.35 lbs. (from table)

96.21/97.35 = 0.9883 cu. ft. = volume which the cu. ft. of 51° B. acid at 100° F. would have if cooled to 60° F.

1 cu. ft. 52.1° B. acid at 60° F. = 102.20 lbs. 50° B. acid (interpolated from tables).

Therefore, 0.9883 × 102.20 = 101.00 lbs. 50° B acid at 60° F.

Method II:

1 cu. ft. 51° B. acid weighs 96.21 lbs.

52.1° B. acid at 60° F. = 104.98 per cent. of 50° B. acid at 60° F. (interpolated from tables).

104.98 per cent. of 96.21 = 101.00 lbs. 50° B. acid at 60° F.

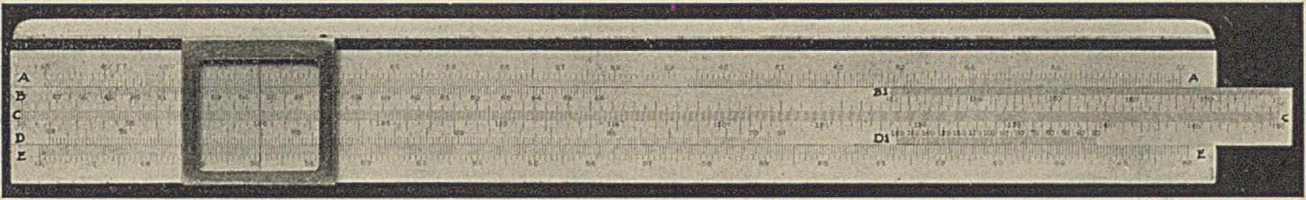
Method I though longer than Method II is interesting in that it will indicate the shrinkage in volume which would result if the acid were cooled to 60° F.

The writer has seen private sets of tables which have been compiled and which make all necessary corrections, thus greatly shortening the time required in making the calculations of acid of different densities and temperature to one basis. At one time he also prepared such a set of tables, but the time required was about three weeks, and the tables then were not thoroughly complete but fulfilled practically all the requirements of the plants at which they were used.

It then occurred to me that some simple means might be found for making all such corrections and calculations in a short time, so my efforts were directed to the problem of determining if it were possible to design a special slide rule by means of which all calculations might be made. After spending considerable time a design for such a slide rule was finally devised and after making many hundred calculations the full details and specifications were worked out. Models were then prepared, which proved that the rule would permit accurate calculations to be made.

By use of this slide rule corrections may be applied to Baumé readings for temperature, thus calculating acid of one density to corresponding density at any other temperature. This requires one adjustment only of the slide rule. Now by making one additional adjustment the final result may be read from the rule directly; that is, one cu. ft. of acid of any density and temperature can be calculated to its equivalent in terms of 50° B. acid at 60° F. (or in terms of 60° B. or 66° B. acid if desired, or in fact to any basis). Also, if desired, 100 lbs. of acid of any density and temperature can be calculated to its equivalent of 50° B. acid at 60° F. (or to any other basis desired) just as easily.

Each case can be worked out by means of this rule in less than ten seconds, which surely allows a wonderful saving of time. The rule is based entirely on the tables of the Manufacturing Chemists' Association of the United States, adopted 1904, and no tables need be used in connection with the rule to give final results.



The accompanying cut shows one of these slide rules, submitted by the manufacturers as a sample, but which is not exactly correct.

The divisions on the slide rule are marked in terms of degrees Baumé, degrees Fahrenheit and pounds per cu. ft. Baumé divisions are to tenths, and in some cases to 0.05° B., the Fahrenheit scale to 1° and the pounds per cu. ft. scale to tenths of a pound per cu. ft. The latter scale can be read to within 0.01 to 0.02 lb. per cu. ft. and the Baumé scale to 0.01° B. In other words, the accuracy of results obtained by the rule are within the limits of error of reading an ordinary hydrometer divided to tenths of a degree Baumé. The scales include Baumé readings between 48° and 66° B. and from 30° to 160° F.

Referring to the rows of divisions by letters: Row D^1 and E are used together to correct Baumé readings from one temperature to another.

Row B^1 is a continuation of Row C, which is likewise a continuation of Row D. This arrangement is adopted to get all of the divisions on a 10″ rule and yet have divisions far enough apart to permit accurate and rapid readings. The value of divisions in these rows represents pounds per cu. ft.

Row B is divided in terms of weight per cu. ft. of acid of different densities. To find from this rule the weight per cu. ft. of acid of densities between the limits included, refer to the division on Row B corresponding to its Baumé reading and project on to Scale C, where the value for its weight can be directly read.

Row A is divided in terms of percentages. (Attention is hereby called to the error on this row, noticeable between the 49 and 50 divisions.) To find the per cent. of one acid as compared to 50° B. acid, adjust the slide so that the 50 division, Scale A, is in vertical alignment as indicated by the runner with 100 on Scale C. Now adjust the runner over the division on Row A corresponding to the density of the acid which it is desired to refer to its per cent. of 50° B. acid and read below on Scale C. To find the corresponding per cent. of 60° B. acid, the operation is similar.

To calculate, for example, 1 cu. ft. of acid testing 51.0° B. at 100° F. to its equivalent in terms of 50° B. acid at 60° F. by this rule, the procedure is as follows:

Line up, by means of the runner, division 100 on Row D^1 and division 51.0 on Row E. Now move runner to division 60 on Row D^1. Read below on Row E and 52.1° B. is indicated as the corrected Baumé reading. Now adjust the slide so that division 50, Row A, and division 51, Row B, are in alignment. Move the runner over the 52.1 division on Row A and read under the runner on Row C, when 101.00 is indicated as the correct result.

Such a slide rule would be of very great value to a chemist or superintendent who has to calculate sulphuric acid stock, and also to a broker who buys and sells acid.

Armour Fertilizer Works,
Atlanta, Ga.

A SIMPLE AND INEXPENSIVE CONDUCTIVITY CELL.

By Carl A. Nowak.

Received June 8, 1912.

Unable to obtain a standard conductivity cell from any of the chemical supply houses in town, and anxious to complete a series of experiments, the author undertook to construct a cell from materials available in the laboratory. This cell, although primarily intended as a makeshift until a standard cell could be obtained, gave such satisfaction, that, for the experiments in hand, it proved practically equal to any of the standard cells now on the market. A brief description of the manner in which this cell was constructed may possibly be of assistance to others, who, like the author, may at some future time be dependent upon a cell of their own construction.

Before going into details it may be well to point out certain of the advantages possessed by this cell: *First*, It requires only 20 cc. of liquid. *Second*, On account of the small volume of liquid the same is more quickly brought to the temperature of the thermostat. *Third*, The cost is considerably lower than that of the cells on the market since the electrodes are made of thin platinum foil, but being concave and themselves fastened directly into the cork cover, are rigid and not easily bent out of shape or otherwise injured, thereby causing a change in the cell constant. *Fourth*, The cell constant can be adjusted to suit the requirements of the test, either by varying the height of the liquid or by reducing the electrode surfaces. The thermometer is directly in the path of the electrodes, and the two loops of platinum foil make it very easy to connect the cell to the circuit. The complete cell can be easily constructed in about one hour from materials to be found in almost every laboratory, and at a low cost.

Fig. 1 is a photograph of the cell and Fig. 2, diagrams giving better the details of construction.

A wide mouthed glass bottle 1¼ inches in diameter and 2¼ inches high was used for the cell body. A flat cork of a somewhat greater diameter than that of the bottle and about $^{3}/_{8}$ of an inch thick was next selected and a disc a little less than 1 inch in diameter cut out of it by means of a sharp penknife, care being taken to cut perpendicular to the surface of the cork and neither to injure the disc nor the ring which remains as the disc must be replaced in the cork after the electrodes and contact strips are inserted. Two pieces of platinum foil 0.002 inch thick, 1 inch wide and 2 inches long were cut, as well as two strips of the same foil two inches long measuring about $^{1}/_{8}$ inch in the center and $^{3}/_{8}$ inch at the ends, cut in the manner shown in Fig. 2, D. The strips were each folded over in the middle so as to form a loop, the ends being then fastened between the ring and the disc of cork together with the two electrodes in the manner shown in the illustrations.

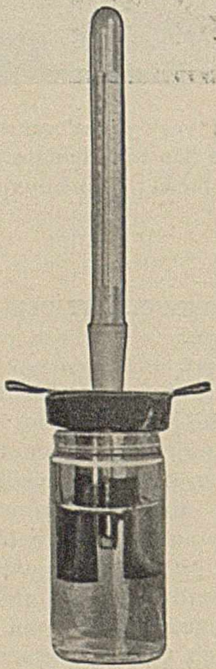


Fig. 1.

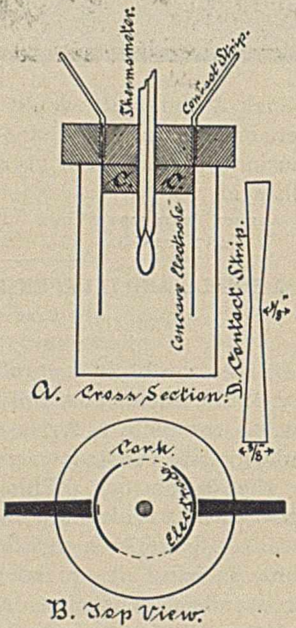


Fig. 2.

The tops of the electrodes should come flush with the top of the cork. If the cork has been properly cut, the electrodes, owing to the now concave shape, will hold firmly in the cork and should be parallel to one another (see Fig. 2, A). Should this, however, not be the case, a short round piece of cork (Fig. 2, C), previously shaped to fit, can be placed between the electrodes and cemented to the cork proper with the aid of a little plaster of Paris.

The cork is now covered with sealing wax on all sides which gives excellent insulation. This can be made smooth by passing a hot, flat piece of steel over it. A knife blade answers very well. For safety's sake, and to prevent short circuit, should any liquid accidentally get on the stopper between the electrodes, the same is dipped into melted paraffine, the loops being again scraped free.

A more finished looking cell can be made by applying plaster of Paris to the cork after inserting the electrodes, instead of the sealing wax. The plaster can be sandpapered down after drying, giving a perfectly smooth surface and covering all imperfections in the cork. If the same is then coated with black enamel or paint the entire cell has a very neat appearance. Of course the cork must be subsequently dipped in paraffine for the reasons given above.

After cleaning the electrodes carefully, the same are coated with platinum black in the usual manner.

The opening for the thermometer is most easily made by heating the point of a round file to redness in the Bunsen flame and then applying it to the cork with a slight pressure, thereby easily penetrating through the sealing wax and cork. After this has been done, the opening in the cork can be filed out by means of the same file, until the thermometer exactly fits it. The author made use of a pycnometer thermometer divided into tenths of a degree and reading from 10°–30° Centigrade.

The general type of the cell, *i. e.*, concave electrodes, makes it especially well adapted for use with poorly conducting fluids, the cell constant of the cell illustrated being 0.237 when 20 cc. of liquid are used.

In using the cell and for determining the cell constant, 20 cc. of liquid are measured into the glass from a standard pipette (always used for this purpose). It will be found that in dealing with the same kind of solution, *i. e.*, one of uniform viscosity, the cell constant will remain unchanged within the permissible limits of error allowed in technical conductivity measurements, provided of course that the same pipette is always used for delivery.

Should one so desire, other volumes of liquid may be used, *viz.*, 30, 15 and 10 cc., the cell constant being determined for each of the respective heights of liquid in the cell.

The cell is very easily cleaned, simple in manipulation and not easily damaged.

2739 Mildred Ave.,
Chicago.

APPARATUS FOR FUMELESS KJELDAHL NITROGEN DIGESTION.

By A. P. Sy.

Received June 4, 1912.

A digestion with sulfuric acid for the Kjeldahl nitrogen determination is practically impossible unless some provision is made for taking care of the large volume of fumes evolved. Even in small quantities these fumes are so objectionable that complete removal is necessary Many devices and arrangements are known and in use, the customary practice being to conduct the digestion in a good hood or closet connected with an efficient natural or forced draught. Such an arrangement is often almost impossible and is always expensive, necessitating an expenditure of several hundred dollars when a fan and motor are used. In addition to the expense, this arrangement is always very noisy, unless the fan is located at some distance from the hood, in which case its efficiency is decreased proportionately. For a number of years the writer used a hood with natural draught, but on some days it was necessary to open all windows and leave the room. Many laboratories, especially those of hospitals and physicians, have no fume closets at all and a

Kjeldahl nitrogen digestion is out of the question. Three years ago the writer began using an arrangement similar in principle to the one here described and shown.

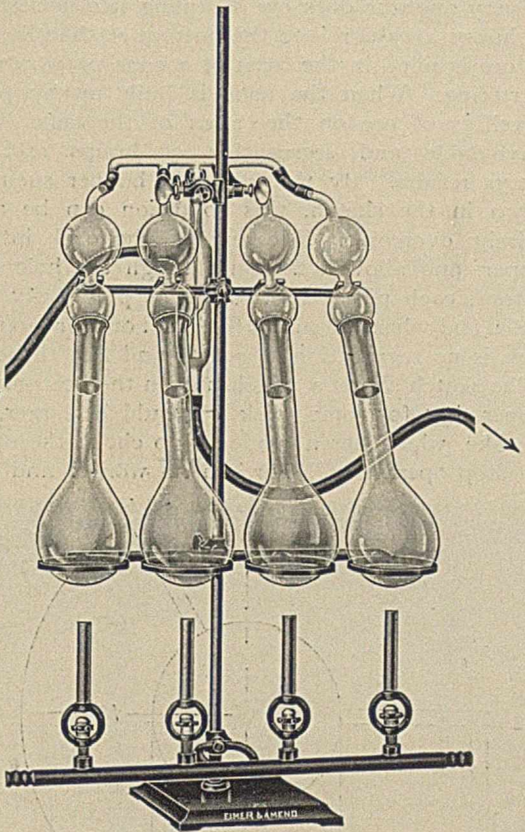


Fig. 1. Front view.

It has been in constant use in the university as well as the writer's laboratory, and in its present form seems to answer all requirements for fume absorption.

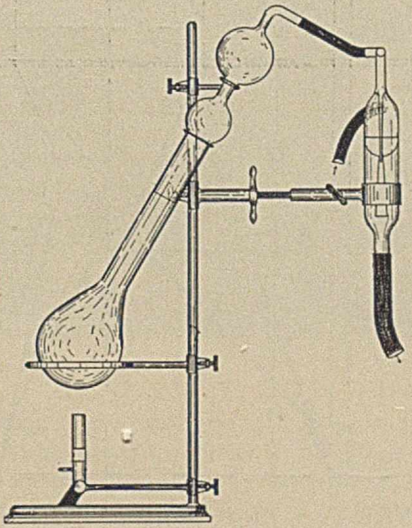


Fig. 2. Side view.

A brief description and reference to Figs. 1 and 2 readily explain the apparatus. The whole is mounted on a portable iron stand, occupies but a little space and is easily moved. In the apparatus here shown, four ordinary long-necked 500 cc. Kjeldahl flasks, suitable for digestion and distillation, are used. The Kjeldahl flasks are supported at the bottom by a special ring-clamp. Into the neck of each flask there is a loosely fitting bulb-tube with two large bulbs and an elbow bend. These bulb-tubes are connected with a large glass suction pump having four branches. Rubber tubing is used for connecting the bulb-tubes and pump, in order to give flexibility to the apparatus, allowing the flasks to be shaken without detaching them. The rubber tubing lasts for many determinations and can easily be replaced. The bulb-tubes are held in position by a special support, allowing their easy removal when shaking is necessary. The bulbs act as air cooled condensers for the acid fumes, and prevent the materials in the flasks from going dry as quickly as when the fumes are allowed to escape. The lower bulb acts as a loose stopper for the flask, while the upper one rests on the support when the apparatus is not in use, always leaving the bulb tubes in position. At the beginning of a digestion, water is driven off, and in order to prevent its dropping into the hot acid and causing spurting, the supports of the Kjeldahl flasks are so arranged as to give the latter a slanting position, allowing the condensed water to flow down the sides gradually. In its present form the apparatus has a quadruple burner on a clamp attached to the iron stand, as shown in the drawings. To operate, connect the pump with the water supply and drain, and start heating the flasks with a low flame. The operation and advantages of this arrangement need no further explanation. The apparatus may be obtained from Eimer and Amend, of New York City.

University of Buffalo,
Buffalo, N. Y.

A SIMPLE METHOD FOR PURIFYING DRINKING WATER.

By J. L. Sammis.

Received July 10, 1912.

Water for drinking purposes is commonly purified on the small scale by distillation. Distilled water is flat and unpalatable and has to be cooled and stored for use.

The possibility of pasteurizing water for drinking purposes, as it flows from the pipes, seems to have attracted little attention. For this purpose, water flowing through a small pipe can be momentarily heated (in a steam jacket or otherwise) to a temperature of 175–180° F. (79–82° C.), by which means disease germs such as those producing typhoid fever, dysentery, etc., are destroyed, while the water under pressure in the pipe does not lose its dissolved gases or its palatability.

The water thus heated can be quickly cooled in the pipe, by means of a cold water jacket. In most buildings, only a small proportion of the water used would require to be heated and cooled for drinking purposes, but the entire quantity used for all purposes could be run through the jacket, to aid in the cooling.

An arrangement of pipes for this purpose can be set up by any pipe fitter at any point where a steam pipe and a water service pipe pass near each other. It is desirable that the steam pressure be uninterrupted, and that the pipe be drained free from condensation. Also the water pipe should be one through which more or less water is flowing continually. The diagram shows the arrangement of the parts.

The steam main is cut at A A′, the water main at B B′, and the cut ends are reconnected through by-passes which constitute the steam jacket C, and the water jacket D, used for cooling the drinking water.

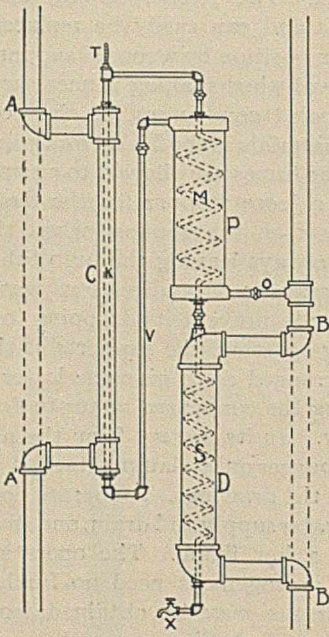


Fig. 1.

A small stream of water is drawn from the main through valve O, passing through the small jacket P, where it partly cools the water in the interior coil M. From the jacket P, the water flows through V and upwards through K, within the steam jacket C, where it is heated to 180–200°F The heated water flows past the thermometer T, through the coil M, and finally into the cooling coil of the water jacket D. The water thus heated and cooled flows out below, when the faucet X is opened, either into a cup or into a bubble fountain.

Very efficient cooling can be secured by making coils M and S of tin lined brass pipe. These can be of thin material, since the water pressure inside and outside of them is always alike. In practice, with such an arrangement, no difficulty was found in cooling the water for drinking to within 2° of the temperature of the cooling water in the jacket D. For some reason, not well understood, the water thus heated and cooled under pressure is more palatable to some observers than the untreated water supply.

The water pressure should be about 25 pounds greater in the main B, than the steam pressure in A, in order that the water may not boil in the pipe K, which may be made of $^{1}/_{4}$ or $^{3}/_{8}$ inch galvanized or tinned iron pipe.

In cities where the municipal water supply is known to be contaminated with sewage, causing typhoid fever, the pasteurization of water as it flows from the pipes for drinking purposes appears desirable.

In large office buildings, factories, schools, etc., where steam pressure is maintained throughout the summer, and where water flows continually through the mains for supplying toilet rooms, work rooms, etc., such an arrangement for pasteurizing water for drinking purposes might find useful application.

The amount of steam used in such an apparatus is small, because the regenerative cooler P prevents waste of heat.

For residences, either gas or electric heat might be substituted for steam in such an arrangement as the one described above.

University of Wisconsin,
Madison.

SAMPLING CONE.

By C. W. Kneff.

Received May 28, 1912.

Every one who does ore sampling has noticed that the lumps always roll to the bottom of the pile, when the ore is piled in the form of a cone preparatory to quartering. When the cone is built up by placing shovelfuls of ore on the apex of the cone, this is unavoidable and segregation of lumps and fines always results. By the use of a hopper such as is shown in the sketch, this condition can be almost entirely overcome. The ore is shoveled into the hopper, and allowed to run through the hole in the bottom; each piece of ore remains practically where it falls and when the pile is flattened out for quartering there is no segregation of coarse and fine to be seen.

The sketch shows a 1 inch hole in the bottom of the hopper, but for some work it should be larger, *e. g.*, for coke, which has a tendency to choke the opening and stop operations. For general work I find a hole of $1^{3}/_{8}''$ diameter most satisfactory, but I have some funnels with smaller openings, which I can drop inside the main funnel, and obtain any size of opening desired.

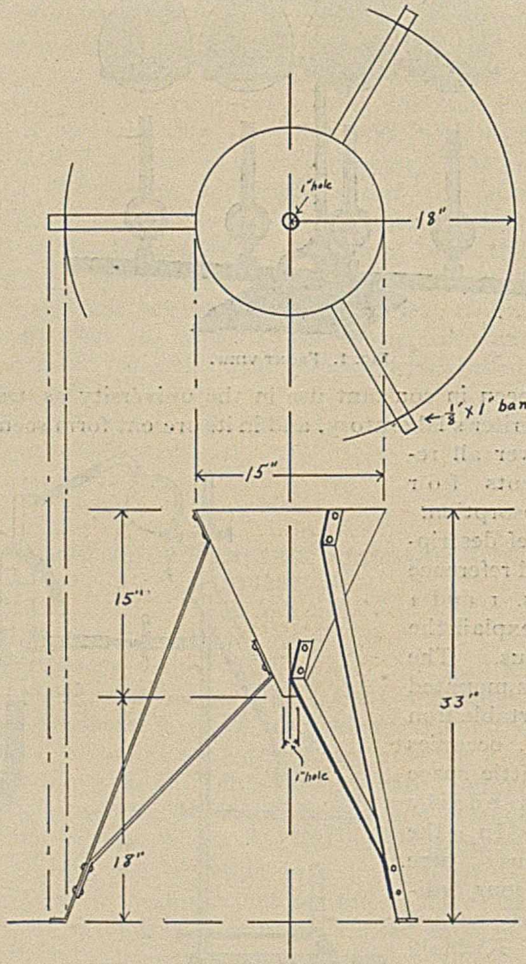


Fig. 1. Cone for sampling ore.

As the sample comes from the crusher, the largest piece is about $^{3}/_{8}$ inch and is mixed with considerable fines. This is passed through the hopper three times, which gives a very uniform mix, much better than can be obtained by the common practice of piling with a shovel. After quartering, the portion retained is passed through the cone again, and so on till the sample weighs from 8 to 10 pounds, after which it is passed through a No. 8 sieve and finished in the usual way.

SHOENBERGER STEEL WORKS,
PITTSBURGH, PA.

A LABORATORY GLASS-FURNACE.

By S. R. SCHOLES.

Received June 17, 1912.

Experimental glass-making has always been attended by the difficulty of getting the necessary temperature. We have installed in this laboratory a furnace burning natural gas and using the regenerative principle common in glass-factory practice. The designing and construction of this furnace, following our rough sketch, were undertaken by Messrs. Armstrong and Lytil, furnace builders, of Pittsburgh.

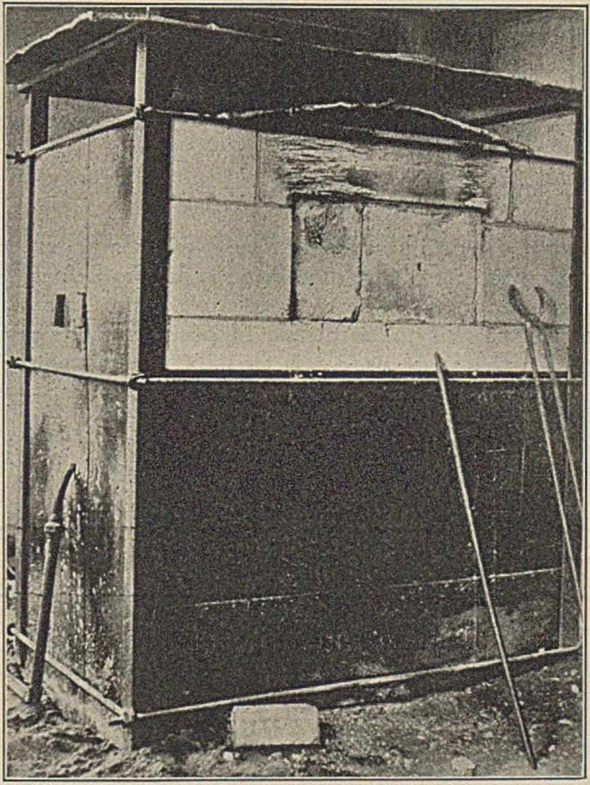


FIG. 1.

The accompanying photograph gives an idea of the general plan of this furnace. It is constructed of standard sizes of furnace blocks. An arched roof of silica brick covers a crucible bench 42 × 27 inches, at the ends of which the gases enter from the vertical regenerators, through openings 9 × 12 inches There is thus a space accommodating several crucibles of generous size, such as size "M" of the Battersea make. The regenerator columns enlarge below the bench to $16^{1}/_{2}$ × 21 inches and are 4 feet high. They are filled with the usual silica checker brick. From the foot of each regenerator a horizontal flue leads to the stack and connects by a suitable valve with an air inlet. A twenty-five-foot stack is used.

Gas is supplied through one-inch pipes, under a pressure equal to eight inches of water. The gas is not "regenerated" but enters, through a three-eighths-inch nozzle, into each regenerator column just below the level of the bench.

The furnace can be brought from room temperature to its full heat in about twelve hours. It is usually maintained at 1350°–1400° C. but a higher temperature can easily be reached, which is practically limited by the softening of the crucibles. The best efficiency is obtained by reversing gas and air supply every twenty minutes. The gas-consumption is about 250 cubic feet per hour.

Much of the credit for the design of this furnace is due Prof. S. L. Goodale, of the School of Mines.

INDUSTRIAL RESEARCH LABORATORY,
UNIVERSITY OF PITTSBURGH.

THE DETERMINATION OF CARBON IN STEEL BY DIRECT COMBUSTION IN THE NEWEST FORM OF SHIMER CRUCIBLE, WITH THE AID OF A PERFORATED CLAY DISC.

By FRANK O. KICHLINE.

Received May 31, 1912.

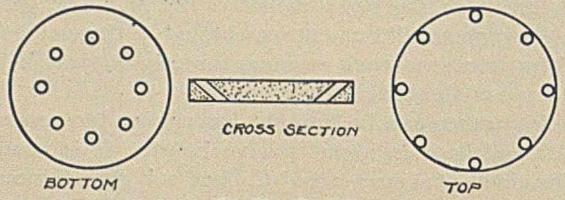
In THIS JOURNAL, for October, 1909, Dr. P. W. Shimer described a simplified form of his crucible for the determination of carbon in steel by combustion. Two improvements have been made in the use of this crucible for direct combustion. These improvements are (1) an increase in the diameter of the crucible, and (2) the use of perforated clay discs instead of asbestos for covering the charge of drillings.

It has been the practice, in the direct combustion of carbon in steel, to place the drillings in a No. 000 Royal Berlin porcelain crucible two-thirds full of silica sand, placing this porcelain crucible inside of the Shimer platinum crucible with a pair of forceps, and covering the charge with a layer of ignited asbestos about $^{3}/_{4}$ inch thick. The asbestos serves to keep the drillings in place and prevents heat radiation to the water-cooled stopper.

A slight increase in the diameter of the Shimer platinum crucible made it possible to use a No. 00 Royal Berlin crucible instead of the No. 000 size. The No. 00 size has at the top an area 1.41 times that of the No. 000 size, and is filled to only one-half its depth with silica sand. This has the obvious advantage of permitting the use of a heavier charge, full factor weight (2.7273 g.), or if the $^{1}/_{2}$ factor weight is preferred it will be less crowded. Dr. Shimer has recently adopted this increased diameter for his standard size crucible.

Ignited asbestos as a covering for drillings is very efficient. While results are not vitiated by the presence of ignited asbestos, it is obvious that the packing in of a layer of asbestos before each burning, and its removal after burning, are both time-consuming and inconvenient, and the source of much dirt around the carbon work table.

In trying to obviate the use of asbestos, the writer tried various materials made up into the form of discs with perforations for the circulation of oxygen. The best results were obtained with a disc about $^3/_{16}$"



CLAY DISC.

thick, of such diameter as to completely cover the No. 00 Royal Berlin porcelain crucible, perforated with slanted holes, leading from the periphery of the upper side of the disc, slanting toward the center on the bottom of the disc, as shown in the illustration. They are best made of china clay. The clay is mixed with water to the proper consistency, moulded into shape, carefully dried, burned and annealed. One of these discs with proper care will last for 100 determinations, which is also the average life of the porcelain crucible. With a little care these discs can be made easily in the laboratory.

The above work has been carried on by the writer in conjunction with Dr. Shimer.

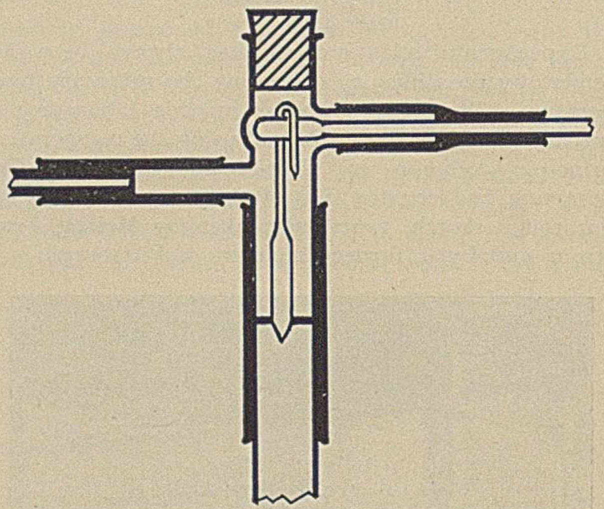
35 First Avenue,
Bethlehem, Pa.

A MODIFIED VICTOR MEYER APPARATUS.

By Harold Canning Chapin.

Received June 24, 1912.

The customary way of introducing a liquid to be vaporized in a Victor Meyer vapor density apparatus is to drop, by some external means of control, a capsule previously supported in the cool upper portion of the tube. This capsule then automatically releases its contents by bursting, expulsion of a glass stopper, or melting of a Wood's metal plug. The first method is preferable, but requiring a completely filled, fragile capsule, is somewhat troublesome. A modification of this, having proved successful with a class of engineering students in this laboratory, seems worthy of more general use. The capsule is made from a piece of 5 mm. tube sealed off at one end and drawn out to a capillary at the other. It is filled to the neck only, bent as shown, and sealed at the tip of the capillary. It is hung in the vaporizing tube instead of being supported in the usual manner from below. For this purpose the ordinary form of tube will serve, but the right angled form here illustrated is preferable because it is more compact, holds the capsule more securely, and allows this to be placed in position more easily through the short neck. A twist of the rod with its flattened end breaks the capillary and drops the capsule.



Walker Laboratory,
Rensselaer Polytechnic Institute,
Troy, New York.

ADDRESSES

THE ANALYST VERSUS THE CHEMIST.[1]

By J. S. Brogdon.

Received July 15, 1912.

There is no subject of greater importance in the fertilizer world to-day than that of Chemical Economy. The chemical units of phosphoric acid, nitrogen and potash in the fertilizer factory are the same as and are equivalent to dollars in the bank. In all the nation you will not find a single bank which for one moment would think of doing business without an efficient and adequate method of keeping account of the money, or without a banker to direct the policy of the bank. Yet in fertilizer factories, systems for keeping account of the income and the outgo of chemical units are not common, and many factories are not under the direction of a chemist. As a result, in the average fertilizer factory, there is a most wanton waste of phosphoric acid in the manufacture of acid phosphate and in the manipulation of mixed fertilizers the losses frequently exceed the profits. To a large extent these losses are caused by improper chemical control or the lack of it.

The days of large profits and splendid dividends in the fertilizer world are over. A new era has dawned—a time of keen competition and close margins—a time when it is necessary that the smallest savings be effected. The wasteful methods of the past cannot be continued and the standard of the quality of the product must be maintained. There is no greater avenue to prosperity for the fertilizer manufacturer than that of applied chemistry. The question naturally arises, who shall apply the principles of chemistry in the fertilizer industry?

Fertilizer managers are occupied with the matter of sales and credits: frequently they are men who have risen from the ranks of the sales force and their training has not fitted them to handle the intricate chemical problems of the factory. On account of this they are accustomed to rely on fertilizer superintendents to look after such matters. The superintendent most

---

[1] Read before the Convention of The National Fertilizer Association at Atlantic City, July, 1912.

frequently is a man who has been promoted from the manufacturing department and often has not given the subject of chemistry as careful consideration as he has the matter of efficiency of machines and the control of labor. It matters little whether this knowledge which we call chemistry is obtained at the fountain head in the factory or through the canned source of text books. It is very important that if a man possess this information, it be harmonized and organized. "Science is organized knowledge." The science of chemistry offers two fields for investigation: analytical chemistry, which takes things apart, or separates them into their component parts, and synthetic chemistry which takes substances and puts them together to form new substances. The man who understands the principles of analytical chemistry and synthetical chemistry and has the ability to apply these principles in a fertilizer factory is a man most worthy of the name of chemist.

The trouble in the application of chemical principles in the fertilizer industry can most frequently be attributed to the fact that managers and superintendents confuse the services of an analyst with those of a chemist. A man who possesses certain chemical information and who is skilled in the manipulation of fancy pieces of glassware and who can perform certain cook book operations, as furnished him by the government, is an analyst. He is capable of disintegrating substances and can express the relation of the component parts in terms of percentages. In other words, an analyst is a man who undoes things; a chemist is a man who does things. It would be well if all chemists were analysts and it is a deplorable fact that all analysts are not chemists. If you have samples to be analyzed, send them to an analyst, but if you have chemical problems to be solved or dividends to be saved, consult a chemist; let him apply the principles of chemistry.

Under the head of Applied Chemistry perhaps there is no question of greater importance in the fertilizer factory than the manufacture of acid phosphate, and it is in an instance like this where the chemist does not receive credit for his labors. A pile of acid phosphate may run 2 per cent. insoluble and look exactly like another pile which runs only $^1/_2$ per cent insoluble. Yet the loss in this case would be $1^1/_2$ per cent. or something like 75 cents a ton. The work of the chemical engineer is not appreciated because it is intangible. A chemical engineer can produce profits which frequently are not audited.

A certain fertilizer factory installed a chemist in their acid phosphate department and at the end of the first year he effected savings which amounted to $20,000; at the end of the second year the auditor credited this department with savings of $40,000 over the old system, and at the end of the third year he was credited with savings of $60,000 over the old system. In the meantime, the quality of the product which at the first had been none too good, had now become recognized as the best on the market. This was the work of a chemist.

A careful and systematic analysis of all raw materials and mixed goods is an advantage that is not appreciated by every manager. Again, the chemical units can be compared to money. Any man will count his money regularly and systematically, yet the same man does not think it necessary to count or audit his chemical units systematically. The matter of 25 cents per ton profit is not to be scorned. If there is a variation in the quality of the materials, it is usually practical and possible to vary the formulae accordingly. This varying of formulae, however, becomes confusing and impossible if the materials have not been properly stored in the shed. Many manufacturers consider that all that is necessary is to unload the material. This is, indeed, a very poor way to handle the matter. Where large quantities of fertilizer materials are being handled, some one should be delegated to know at all times how these materials are stored in order that they can be used to their highest chemical efficiency.

The chemical control of the manipulation of mixed fertilizers is a subject which has been sadly neglected and which amounts to losses of many thousands of dollars per annum. In no other industry is the custom prevalent to give 37 inches for a yard as in the fertilizer world, and frequently the manufacturers of commercial fertilizers are not satisfied with giving away their goods, but they actually throw them away. A loss of $1.50 a ton in averages in a fertilizer factory in the city of Atlanta was reduced to 44 cents per ton through the agency of chemical control. This saving amounted to about $15,000 in one season. This was the work of a chemist.

The packers and the large interests have long since realized the importance of chemical economy and have delegated these responsibilities to a chemist. The independent plants frequently employ a chemist, or rather they maintain a laboratory and pay a man a salary to make chemical analyses, preferring that he occupy his time in this way. Unless there is some one in the factory to interpret the certificate of analysis and apply the principles, the whole procedure becomes a farce. Frequently fertilizer managers fail to consider their chemist in the light of a professional man as they do their lawyer, and superintendents look upon the chemist as a kind of necessary nuisance whom they tolerate rather than seek.

From the early days of Liebig to the modern times of Cameron and Whitney, the devotees of the pure science of chemistry have applied themselves to the study of the nutrition of plants. The chemical engineers have done all in their power to foster the fertilizer industry and have met conditions nobly. I refer to such men as the elder Grasselli who conceived, built and operated the plants of the firm that bears his name. The splendid results of Mr. Herreschoff attest to his interest and ability. All over the South are modern plants which were designed and built by Nathaniel P. Pratt, and at all times the chemical profession has met conditions and now stands ready to meet this new condition, the necessity for chemical economy.

65$^1/_2$ North Broad Street,
Atlanta, Georgia.

CURRENT INDUSTRIAL NEWS

By W. A. Hamor.

FACTORY INSPECTION.

The *Blue Book* containing the annual report of the Chief Inspector of Factories and Workshops for 1911 has just been issued in London, and its contents should prove of great interest to those engaged in the study of industrial diseases. According to the *Chemical Trade Journal*, 51, 4, the points of special interest to the chemical trades dealt with in the report are the following:—

Regulations for Dangerous Trades.—The regulations for the smelting of lead material, etc., render obsolete the special rules for lead smelting and for the manufacture of red, orange and yellow lead. Subject to certain exemptions for materials containing negligible quantities of lead, the code requires the suppression or removal of dangerous dust or fumes; the provision of overalls and respirators in certain processes; the exclusion of persons under 16 years of age and females from lead processes; the exclusion of persons from furnaces, etc., until ventilated; the restriction of the duration of work in flues and condensing chambers; the provision of meal rooms, etc.; and the periodical medical examination of workers in lead processes.

Chemical Works.—Hilditch states that although vats and pans containing liquid of a dangerous character are being fenced in conformity with Rule I, yet the deleterious action of acid fumes upon the stanchions and rails requires careful and periodical examination. Workmen frequently place a plank across a full vat to save themselves the trouble of going around or between pots. Dunolly, owing to two fatalities, gave special attention to the fencing of the waste liquor settling tanks of ammonium sulphate plants. These tanks are about 5 feet deep, and are divided into two sections which are alternatively filled with the boiling waste liquor through a special by-pass channel. He explains that only one section—the one containing the hot liquor—is really dangerous, but the two workmen happened to fall into that tank.

Benzene Derivatives.—Last year one case of dinitro-benzole poisoning was reported, and it was thought that by the careful selection and timely suspension of workmen by appointed surgeons, the cases could be reduced to a minimum. This year, however, 23 cases were reported. These were due to an exceptionally warm English summer, with the consequent greater absorption of the poison by the more open pores. The method of manufacture is said to be still primitive, and more automatic working in places laid with impervious washable floors is considered essential. An improved method of breaking up cake, enclosing of apparatus as much as possible, and provision of much stronger exhaust, are urged as remedies. There were three cases of skin disease reported in 1911 as against 16 in 1910; one case of eczema and one of dermatitis from a factory in which dinitrochlorbenzole is made; and two cases of aniline absorption among workmen in a factory where cotton cloth is dyed.

FACTORY VENTILATION.

It is stated in *Popular Mechanics*, 18, 202, that the heating and ventilating equipment of a new factory building in Springfield, Mass., includes two air-cooling machines of the water-spray type. The air is taken in through an opening in the pent house, enters the cooling machine, is drawn through the water spray, passes a number of baffle plates, continues through the fan into the stair well and passes from there through the louvers into the workrooms. After it has circulated through a workroom it leaves through the upper louvers in the center partitions and is drawn into the main stair well. The water for the machine is taken from the well at a rate of about 60 gallons per minute for each machine and at a temperature of about 54° F. The manufacturers guarantee that air entering at 95° F. and containing 9.3 grains of water to the cubic foot will be cooled to 78° F. It is calculated that under these conditions it will be possible to keep the temperature inside the building about 9 deg. lower than the outside, changing the air four times an hour.

MERCURY POISONING.

A report on "Mercury Poisoning in the Industries of New York City and Vicinity," by Mrs. L. W. Bates, has been issued by the National Civic Federation. Outside of felt hat manufacture, the industries using mercury are not extensive; they are very limited within a radius of fifty miles of New York City. In hatters' fur cutting, a solution of mercury nitrate is employed in carotting, and mercury poisoning is likely to happen in the subsequent process of cutting and brushing by inhalation of particles of fur impregnated with nitrate of mercury. Neither mercury nor any of its salts is used in hat making proper: mercurialism results from the earlier treatment in carotting, yet much more poisoning occurs in the hat making than in the fur cutting processes, owing to the mercurial dust disseminated in certain operations of hat making (blowing, forming, hardening, and sizing). Cases are cited and experiences are recorded to show that mercury is manifestly a poison which, in occupations, is inimical to health and calls for regulation. Mrs. Bates concludes that the unhealthy nature of the trade should be placarded; that eating and drinking should be forbidden in rooms where mercurial processes are conducted; that ample washing facilities should be installed; that proper drinking water should be supplied; that sweeping should be superseded by vacuum cleaning; that the mixing of mercury and acids should be done after working hours; that rubber gloves and respirators should be supplied; that the hat industry should be regulated by special legislation, requiring the elimination from the atmosphere of steam, heat, acid fumes and mercury vapor, fur and dust, at their source of production; that regular medical inspection should be provided; and that compensation and insurance should be supplied for the men working in these processes.

SPECIFICATIONS FOR REFRACTORIES.

The Refractory Material Committee of the Institution of Gas Engineers in their annual report deals with silica bricks, blocks, tiles, etc. (see *J. Gas. Ltg.*, 118, 828). The materials covered by the standard specifications are divided into two classes, namely:

1. That containing 92 per cent. and upwards of silica, and termed "silica" material.

2. That containing 80 to 92 per cent. of silica, and called "siliceous."

The requirements of each class of refractory materials follow.

Refractoriness.—Test pieces of the material shall show no sign of fusion when heated to the following temperatures: "Silica" material—not less than Seger cone 32 (about 1710° C.). "Siliceous" material—not less than Seger cone 29 (about 1650° C.). It is required that the test shall be carried out in an oxidizing atmosphere, the temperature of the furnace being increased at the rate of about 50° C. per 5 minutes.

Surfaces and Texture.—The materials shall be evenly burnt throughout and possess a regular texture; there shall be no holes or flaws, and all surfaces shall be reasonably true and free from flaws or winding.

Contraction and Expansion.—A test piece, when heated in a gas-muffle or electric furnace to a temperature of Seger cone 12 for 2 hours, shall not show, on cooling, more than 0.75 per cent. linear contraction or expansion.

Variations from Measurements.—In the case of ordinary bricks, 9 in. × $4^{1}/_{2}$ in. × 3 in. or $2^{1}/_{2}$ in. thick, there shall not be more than about $1^{1}/_{2}$ per cent. variation in length, nor more than about $2^{1}/_{2}$ per cent. variation in width or thickness; in all cases the bricks shall work out their own bond.

THE UTILIZATION OF SULPHITE LIQUOR.

The waste liquor from sulphite mills contains from 12 to 20 per cent. of highly colored organic matter. In order to use this liquor in the textile industry as a finishing material or in the leather industry as a filling, it is necessary to decolorize it; according to *Paper* (8, 29), it has been found that phosphoric acid under certain conditions possesses the property of separating a red coloring substance from the liquor in an insoluble form; a recent German patent covers a process by which this is effected. To carry out the process, all the free acids stronger than phosphoric acid are first removed from the liquor: insoluble carbonates, such as calcium carbonate, are added, and the excess is removed by filtration. Such an amount of phosphoric acid is then added that about equal parts of liquor and acid are present. The mixture is concentrated, and the organic thio-compounds in the waste sulphite liquor are decomposed by the phosphoric acid; sulphurous acid separates, while the phosphoric acid combines with the lime present as "sulpholignate" to form an insoluble calcium phosphate which may be employed as a fertilizer. The separation of the red coloring matter occurs after the elimination of the sulphurous acid.

ITALIAN SHIPMENTS OF CARBON DISULPHIDE.

According to *The Chemical Engineer* (16, 41), a shipment of 50 tons of carbon disulphide has recently been made from Catania, Italy, to the United States. This shipment, it is learned, is the forerunner of a monthly consignment of like amount. This fact, coupled with several inquiries received from rubber manufacturers, induces the belief that a shortage in the supply of that product exists in the United States. When it is considered that there is a duty of 25 per cent. on the product, that owing to its highly inflammable nature difficulties are encountered in finding vessels which will carry it, that the freight is $18.25 per ton, that the containers (iron drums) are of two-thirds the value of the product and are subject to a duty of 45 per cent., it must be evident that the seeking of this product in a foreign market is hardly a matter of price, but is the result of inadequate production in the United States. There is one establishment producing carbon disulphide at Catania, a sulphur center, Sicily, namely, L'Insulare. It began operations some 12 years ago to supply a local demand, where the article is used in extracting the oil remaining in the residuum of olive oil presses.

THE CONDITION OF THE CHILEAN SALTPETER INDUSTRY.

According to *Die Chemische Industrie*, 35, No. 13, 420, in the period from May 1, 1911, to April 30, 1912, the world's saltpeter consignment was increased by 115,000 tons as compared with a similar period the past year. The total consignments for the year ending April, 30, 1912, were:

	Tons.
In Europe and Egypt	1,848,000
In the United States and remaining countries	550,000
Total consignments	2,398,000

In 1911, the total consignments were 2,285,000 tons, 1,661,000 tons of which went to Europe and Egypt.

The falling off in America is explained by the substitution of cotton-seed residue, much of which was on the market in 1911. This, however, is looked upon as a matter of passing importance. In the last four months, the Chilean production decreased 5,000 tons, owing to the scarcity of laborers and to the low price prevailing for saltpeter. There is also much competition in the saltpeter industry, while the ammonium sulphate industry is practically in one hand. It is stated that the nitrogen price varies 1.31 M. per kg. for saltpeter and 1.39 M. per kg. in the case of ammonium sulphate.

METHYL CHLORIDE AS A REFRIGERATING AGENT.

Methyl chloride has been used to some extent as a means of producing cold and its use has been suggested in refrigerating machines. It is non-poisonous, although anaesthetic, and by its evaporation a temperature of —23° C. is produced, while with air-blowing a temperature of —55° C. may be reached. A mixture of 88 per cent. air and 12 per cent. methyl chloride by volume is exploded only by electric sparks or a powder fuse, and not by flames; when the content of methyl chloride falls below 10 per cent. or is raised above 15 per cent., the mixture does not ignite (*Z. Ges. Schiess- u. Sprengstoffw.*, 6, 304). Lachmann and Heylandt Ges. m. b. H. (French Patent 438,727, 1912) now claim methyl fluoride either alone or mixed with other gases, as methyl chloride, for use as a refrigerating agent. Considerable quantities of methyl chloride are wasted in the chlorination of denatured spirit, and it may be prepared, if required in large quantities, by the chlorination of natural gas.

ACCELERATING PAINT DRYING WITH OZONIZED AIR.

A method of hastening the drying of paint, particularly freshly applied paint on automobile bodies, by means of ozone, has recently been tried out. The ozone was carried by forced draft into the drying room, where it came into contact with "green" paint on a newly painted body selected for the test. Another body, having an equal amount of paint spread over the same area, was placed in a natural atmosphere. At the end of an hour the body kept in the ozonized air had gained 1.67 per cent. in weight, while the other had increased only 1.13 per cent. At the end of a second hour the respective increases in weight were 3.34 per cent. and 1.51 per cent.; while after 15 hours the ozone-treated body had gained 19.74 per cent., as against a total increase of 9.76 per cent. for the other. The treatment with ozonized air thus showed an advantage of more than 100 per cent. over plain air drying.

A NEW PROCESS FOR PRODUCING STEARIC ACID.

Another process for the production of stearic acid from oleic acid is claimed in a recent German Patent (No. 247,454). According to the specification, oleic acid or its esters is treated with concentrated sulphuric acid, and the product, after washing free from sulphuric acid, is reduced to stearic acid by means of an electric current. In more detail, the process is as follows: The sulpho-acid is washed with cold water to free it from sulphuric acid, and is then dissolved in boiling water. The water solution thus obtained is made the catolyte in a diaphragm cell, a 30 per cent. sulphuric acid solution serving as the anolyte. Lead electrodes are employed, with a current density of from 2.5 to 10 amperes per sq. ft. After the passage of the current for about one-fifth of the time indicated theoretically—assuming 100 per cent. current efficiency—as required to complete the reduction, the fatty acids separate out and are again treated with sulphuric acid and electrolyzed. It is said that by repeating the operation several times, oleic acid may be almost quantitatively converted into stearic acid.

THE RAPID PRODUCTION OF PURE CREAM OF TARTAR.

In German Patent 247,452, recently issued, is described a simple means of obtaining cream of tartar of a high grade of purity by a single operation. The discovery was made that the presence of chloride or nitrate of aluminum increases the solubility of potassium bitartrate in hot water while it decreases its solubility in cold water. Accordingly, the process has been patented wherein the raw material is extracted with a hot solution of an aluminum salt instead of with water, with the result, it is claimed, that a very large crop of crystals of at least 99 per cent. purity are recovered on the first crystallization. The presence of aluminum salts in the liquors is said to have the further advantage of arresting fermentation.

"DURIRON."

"Duriron" is a new acid, alkali and rust-proof metal for which there has been considerable demand as a material for acid-cocks, concentrating pans, stirrers, pipe and bowls. It possesses a density of 6.56, a melting-point of 2550° F., tensile strength of 15,000 pounds per sq. in., and a compression strength of 70,000 pounds per sq. in. It is harder than cast iron, and it must be ground and not machined. The manufacturers state that the following tests were made in cold reagents on rough samples, as taken from the sand:

	Percentage losses.		
Period of immersion.	24 hrs.	48 hrs.	72 hrs.
Sulphuric acid, conc.	none	none	none
Sulphuric acid, 10 per cent.	0.0142	0.0226	0.0309
Nitric acid, strong	0.0002	0.0004	0.0005
Nitric acid, 25 per cent.	0.0004	0.0007	0.0008
Hydrochloric acid, conc.	0.0338	0.0641	0.0922
Acetic acid	0.0002	0.0002	0.0003
Tartaric acid, 25 per cent.	0.0006	0.0012	0.0012
Chromic acid, 10 per cent.	0.0002	0.0003	0.0005
Oxalic acid, 25 per cent.	0.0013	......	......
Moist chlorine gas	0.0008	......	......
Ammonium chloride	none	0.0001	0.0002
Sodium chloride	none	none	none
Calcium chloride	none	none	none
Cyanide solution	none	none	none

LEAD FOR CALKING JOINTS.

Lead has been used for centuries to calk pipe joints, the process in vogue being to melt the lead, pour it into the joint, and then calk or hammer the lead to expand it. Recently two new forms of lead have been introduced in England for calking. "Ribbonite" lead, which is used for joint-calking, consists of shavings of lead twisted into the form of ropes, which are calked into water-pipe joints in the place of cast lead. Lead wool is also used for pipe joints and is now employed by many London gas companies; it was lately used in making the joints in $7^1/_2$ miles of water-piping at Staines, England. It is announced that an American company has brought out lead wool and rope for calking purposes (*Pop. Mech.*, 18, 159). Lead rope is said to be made of especially refined metal, very finely stranded, each strand measuring 0.007 inch, and the rope $^1/_2$ inch in diameter. When hammered, this rope becomes very dense and no skill is said to be required to pack it into joints.

"VANALIUM."

"Vanalium" is an aluminum alloy, about 3 per cent. heavier than aluminum. It bears rolling into sheets and drawing into wire, and can be worked very much like brass. It takes a high polish and resembles aluminum in color. "Vanalium" is said to be unaffected by ordinary atmospheric conditions, and by hydrogen sulphide, carbonic acid, sulphurous acid and mineral waters. When cast, the metal has a tensile strength of over 11 tons per sq. in., a yield-point of 8 tons per sq. in., with an elongation of 8 per cent. in 2 in., and can be cast in either iron or sand moulds. By rolling, it is said that the strength is more than doubled, and by drawing, trebled. The alloy retains its hardness after being subjected to heat better than other aluminum alloys, and it melts at about 650° C. It is not affected by sea-water and can be readily soldered.

"ARGILITE."

This new alloy, the invention of G. Jacquier (*Mech. Eng.*, 29, 757), is intended for the manufacture of pipes, tubes and armor plate. It contains 90 per cent. aluminum, 6 per cent. copper, 2 per cent. silicon, and 2 per cent. bismuth, and is said to be light, hard and to possess great resistance to pressure and corrosion.

A WATER FLOW RECORDER.

The Lea Water Flow Recorder, described in *The Engineering and Mining Journal* (93, No. 22, 1089), is said to show all irregularities in the boiler feed, to record the quantity of water evaporated per pound of coal, and to thus show the number of heat units in the coal.

The apparatus works on the V-notch weir principle and is described as follows: A float spindle passes through the bottom of the instrument case, gearing into a small pinion upon the axis of a drum revolving between centers. Upon the body of the drum is a screw thread, the contour of which is the curve of flow for the V-notch, in connection with which the recorder is used. The spiral drum serves a double purpose: Its screw thread rectifies the motion of the recording pen, so that it moves equal distances for equal increments in the rate of flow; it provides a magnified scale for making an accurate observation of the rate of flow at any moment.

The actual depth of water in the notch can always be observed, and the instantaneous rate of flow in pounds or gallons can be seen with accuracy. The recording pen which moves in direct proportion to the rate of flow produces a diagram, the area of which is a measure of the total quantity, and this can easily be deduced by means of a standard planimeter.

Heretofore, the Lea recorder was made on the open or atmospheric principle, but recently the manufacturers added a new type. The notched tank is made of cast iron, similar to the standard open-heater construction. The tank is entirely closed and is suitable for withstanding any pressure or vacuum up to 10 lb. The operating head of the Lea recorder is only about 18 in. and is made in sizes from 200 to 10,000 boiler-horsepower.

Besides being used for the measurement of boiler-feed water, steam consumption, etc., the Lea recorder can also be used for measuring pump discharges, flow of streams, acids, etc. For measuring the flow of acids the apparatus is provided with wooden tanks lined with lead, and the V-notch plate is similarly made. Hard lead or glass, however, can be used.

The apparatus is guaranteed to produce records which shall be within $1^1/_2$ per cent. of absolute accuracy by weight; also that the average error due to variations of temperature over a range of 50° F. (*i. e.*, 25° F. on either side of the normal) shall not exceed 0.5 per cent.

THE MANUFACTURE OF SUCTION HOSE.

The fabrication of suction hose is described in the *India-Rubber Journal*, 44, 22, 73. This type of hose, generally used in connection with pumping operations of all kinds, is armored either inside or out, or both. In suction hose with a spiral wire inside, the canvas used should weigh from 12 to 16 oz. per yard and should be made of Egyptian or American cotton; the wire should be galvanized. For 2 inch suction hose, the following particulars are given:

	1 ply.	2 ply.	3 ply.	4 ply.	5 ply
Wire	12G	12	12	12	12
Inside rubber	17G	17	17	17	17
Width canvas	7½	14	21½	29¼	37
Outside rubber	23G	23	23	23	23

For suction hose up to $1^1/_4$ in. diameter it is usual to run the inside lining on to a mandril by a tubing machine; for larger sizes, it is considered advisable to build these up by hand in the usual manner. For suction purposes, the spiral armoring wire is most satisfactory if put around the inside rubber lining, for it tends then to prevent the drawing-in of the canvas when pumping commences. For pressure hose, it is considered advisable to have the layer of canvas rolled on to the inside rubber coating, the wire armoring then being proceeded with on the top of this. There are three general forms of suction hose: round wire suction, flat wire suction, and internal wire suction. Some times the hose is bound with cord after the cloth wrapping is carried out. Outside armoring is advised only where there is rough usage.

HEAT TRANSMISSION IN VACUUM EVAPORATOR TUBES.

M'Cormack, Dormitzer and Roleson conducted a series of experiments to determine the efficiencies of a Swenson evaporator using tubes of four different materials, namely, copper, steel, lead and tin (*Chem. Eng.*, 16, 1). Since it is known that slight variations in the composition of the metal exert considerable influence on the heat conductivity, the tubes tested were analyzed by standard methods. The results show that the efficiency is highest for the copper tubes and next highest for the steel tubes; this is as one would expect, as copper and steel possess a higher coefficient of heat transmission than the other materials used, and also owing to the fact that the copper and steel tubes used were from one-third to one-fourth as thick as the other two sets of tubes. Although the coefficient of heat transmission for tin is greater than that of lead, and although the lead tubes were about one-eighth thicker, the efficiency of the latter was found to be greater. In general, it may be said that there was found to be very little difference in the efficiencies for the various tubes, the maximum difference being 6.7 per cent. As the authors note, this is doubtless to be attributed to the fact that with tubes of this small thickness the coefficient of heat transmission does not materially effect the efficiency.

A NEW CRUDE OIL ENGINE.

The "Blackstone" semi-Diesel type of crude oil engine, described in *Gas and Oil Power*, 7, 471, is said to be capable of working on all kinds of crude oils, both shale and petroleum, as well as upon petroleum residues, consuming the fuel without leaving any residue and this without the aid of an abnormally high compression. The fuel is injected into the cylinder by means of compressed air at 400 pounds, the main air compression in the cylinder being not more than 150 pounds. The fuel charge is ignited by a flame produced by the combustion of a small auxiliary charge of oil injected at every cycle into a bulb or igniter kept hot by the repeated combustions. The main cylinder fuel spray is regulated by the governor, and the engines run economically on any load. A feature of these engines is the prolonged injection of the main spray fuel, which maintains the initial pressure during a considerable portion of the working stroke, thus ensuring a maximum amount of power with a minimum of cylinder volume. This type of engine is made both stationary and portable, the stationary up to 300 B. h. p. Vertical multi-cylinder engines are also manufactured for marine purposes, driving dynamos, etc.

A DOUBLE-OILING SYSTEM PUMP.

The "Sterling" double-oiling system pump, described in *Power*, 36, 103, is designed to handle clean and dirty oil at the same time. The main casting contains a steel rack plunger which is reciprocated by a gear segment fastened to a shaft extending through the pump and having at its outer end a lever connected to some moving part of the engine. The operating lever has eight adjusting holes to control the amount of oil pumped, and it is also adjustable on the shaft which it drives so that it may be set at any angle. It is therefore possible to arrange the movement of the main pumping plunger so that it will travel from its extreme position at the end of the stroke inwardly much or little and the pump may just comfortably handle the amount of dirty oil which it receives without drawing large quantities of air through the receiving well of the dirty-oil system. The driving rod connecting from the engine to the pump is $^3/_8$ in. pipe. The pump casting has a hollow portion in the top which acts as an air cushion or dome for the discharge of both ends and the steel ball valves at each end are accessible without disturbing any piping or removing their seats.

AIR-JET CHIMNEY VENTILATOR.

A Philadelphia firm is manufacturing a ventilator system in which the draft is created by an air-jet chimney ventilator, the operating air being produced by a rotary blower which creates a suction or negative pressure in the furnace. On the average, the blower consumes 0.5 per cent. of the fuel burned, and at the heaviest load of the grate 1 per cent. The combustion gases do not pass through the blower, so repairs and replacements are not expensive. The system is said to considerably increase the capacity, efficiency, and advantages of the superheater and economizer, as but a small quantity of gases of high temperature are utilized in them. With a varying steam consumption, it is claimed that one boiler may be forced for a time without putting extra boilers in operation, and, most important of all the advantages, it is possible to use low-grade fuels such as lignite, brown coal, etc., in the furnace.

THE UTILIZATION OF PEAT.

In 1907, the peat industry of Europe was investigated by the Department of Mines of Canada, and later a report was published in which the European practice was discussed in detail. In order to determine the possibilities of peat fuel for industrial purposes, the Department purchased some 300 acres of peat bog and has been experimenting with the foreign systems. In the manufacture of air-dried fuel from peat bogs, the peat has been dug by hand, transferred by an elevator into a mill, the resulting pulp conveyed by cable cars to the drying fields, rolled into a sheet about 4 in. thick by a press, and divided by knives into blocks which are then dried on the field. Allowing 140 days for a season's work, the cost of fuel on the field is said to be $1.40 a ton and when stored in the shed $1.65 per ton. In Sweden, the cost of a plant for the manufacture of 20,000 tons of peat powder by the Ekelund system is $86,000, and the cost of producing one ton is $2.30; in Canada, however, the cost per ton is higher, for common labor in Sweden gets a wage of but $1.00 to $1.22 per day of 10 hours. While peat powder has been found to be satisfactory as a fuel in Sweden, because of the expense of production, waste of available nitrogen, etc., Eugene Haanel, the Director of the Department of Mines of Canada, has concluded, after considerable experimentation, that the proper method is to gasify the peat in a suitable producer, along the lines of the ideas advocated by Frank and Caro, and also applied in Ziegler's peat gas-producer; and considers that in order to make the peat industry profitable, a 20 hour day, working 2 shifts, must be adopted, as the real season for working a Canadian bog is not over 110 working days a year.

Thackara (*The Gas Engine*, 14, 318) states that the production of gas from peat having a water content up to 20 per cent. for use in suction gas engines has met with considerable success in Germany, but for a number of years efforts have been made to utilize peat with a water content as high as 50 to 60 per cent. and thus eliminate the expensive drying process. It is now found that peat containing 40 per cent. of water and costing $0.57 per metric ton, may be used with the Gorlitz engine, the consumption per kw.-hr. being 3.43 pounds for one trial and 5.31 pounds for another.

NOTES AND CORRESPONDENCE

SEAWEED, POTASH AND IODINE.

In THIS JOURNAL, Vol. 4, No. 8, page 623, which has just come to hand, there is a note by Hendrick Knudsen, entitled "Sea Weed, Potash and Iodine, A Criticism." The criticism is of a preliminary report prepared by myself, on work done last year under my direction and published as Senate Document 190, Sixty-second Congress, Second Session. The major part of the criticism is captious, indefinite, an expression of personal opinions and calls for no comment. Some of the statements, however, may prove not only misleading but quite mischievous. The author claims to be an expert with more than 20 years' experience. But Mr. Knudsen has not studied nor had any practical experience with the giant kelps of the Pacific Coast and totally misapprehends the conditions existing there in assuming that the methods formerly employed in Norway are applicable. Moreover, he is looking at the matter from the point of view of iodine production, while I was concerned with the possibility of utilizing the kelps as sources of potash. This is clearly evident from a reading of the present critique as it was in a plan for the investigation which Mr. Knudsen submitted for my consideration before the work was undertaken. I disagree absolutely with Mr. Knudsen's conclusion that potash from kelp can come only as a by-product of the iodine industry. Rather, so far as the Pacific kelps are concerned, iodine production is a possible side issue to a very probable potash industry.

It would appear from the critique that *Fucus* was given special consideration. This is not so, as it is discussed only incidentally in a general consideration of the algae. *Laminaria,* the species of especial importance as iodine gatherers, are not particularly prominent on the Pacific Coast, and there is no great promise that an iodine industry *per se* may be looked for there. As the Senate Document clearly shows, the important "potash" varieties are *Nereocystis leutkeana* in northern waters, and *Macrocystis pyrifera,* south of Point Sur. These occur in large beds or groves of practically pure stands. Drift kelp washed ashore is gathered and sold to some extent now, but is not, nor is ever likely to be, worthy of being designated as a commercial industry.[1] It is appreciably lower in potash content than the growing kelp.

Mr. Knudsen's labored calculations to prove that the stand of giant kelps is not sufficient to meet this country's potash requirements ignore the facts. About 1,250,000 tons of potassium salts are imported, varying in composition from 8 to 65 per cent. potash content but far more of the lower than of the high grades, so that the average composition corresponds to appreciably less than 25 per cent. potassium chloride. More than this quantity of potassium chloride, in kelp, is shown in the maps in Senate Document No. 190, and vastly more will be shown when our entire resources are mapped and estimated as will no doubt be done in due course of time. Even more wide from the mark are Mr. Knudsen's calculations of the cost of harvesting. If one man had to row out to the beds, cut and drag ashore and burn enough kelp to make a ton of ash, it might very well cost $22 and probably much more. It will not be done that way, however, and enough has already been done to show that with large scale mechanical devices, the cost of harvesting and drying the kelp should not be a tenth of what Mr. Knudsen estimates.

Knudsen's estimates of cost of production are absurdly wide of the mark. I cannot give any figures with a claim for accuracy, for there is not sufficient existing experience on which to base accurate calculations. From what I have seen done with an experimental plant, I estimate that at several points on the California coast the kelp can be cut, hauled ashore and dried at about 85 cents, and certainly less than $2, a dry ton. This dried kelp can be ground in a ball mill for less than 40 cents a ton. Besides containing organic matter, nitrogenous materials and appreciable amounts of phosphates, all with a value for fertilizer purposes, it will contain 25 per cent. or more of potassium chloride, worth more than 70 cents a unit as present prices go. Consequently I should revise Knudsen's estimates to the following:

Value per ton (2,000 lbs.) of dried kelp		$10.50
Cost of harvesting	$2.00	
Grinding	0.40	
Overhead charges	0.15	
Selling cost, etc	0.10	
Depreciation	0.05	
	$2.70	2.70
Profit		$ 7.80

This estimate does not include the item of containers nor transportation charges. The real problem is whether the margin is sufficient to meet such charges to points of present demand for potash fertilizers. It is expected that the opening of the Panama Canal will answer this question.

This ton of dried kelp will contain about 6 pounds of iodine, worth (Knudsen's figures) $11.52. What it would cost to obtain this iodine cannot yet be estimated satisfactorily. Undoubtedly oil fuel and a retort would be used. It is inconceivable that the archaic kelp ash method assumed by Knudsen would receive any consideration on the Pacific coast. While disclaiming any accuracy for the following figures, I regard them as far more reasonable estimates than those of Mr. Knudsen:

Harvesting and drying per ton of dried kelp	$2.00	
Fuel	1.50	
Labor	0.45	
Chemicals	1.10	
Overhead charges	0.15	
Deterioration, interest, etc	0.10	
Selling cost for potash	0.10	
Selling cost for iodine	0.50	
	$5.90	
800 lbs. salts, 60 per cent. KCl, at 75 cents per unit		$10.60
6 lbs. iodine, at $1.92 per pound		11.52
		$22.12
Expense		5.90
Profit		$16.22

Apparently it would pay better to recover the iodine but, as pointed out in Senate Document No. 190, the market does not exist for all that could be produced from kelp. Moreover, there is good reason to believe that the present price is an artificial one and that iodine from the mother liquors of Chile saltpeter could and possibly would be put on the American market at any figure at which iodine from kelp could be produced. Iodine from kelp, therefore, seems to be largely a question of finding increased uses for iodine, but potash from kelp seems to be a certainty, either when our western states come to use fertilizers or when reasonable transportation charges to the East have been established.

Whether or not it would be profitable to prepare from the kelp salts, potash salts of high purity, is still another question. It can undoubtedly be done since, technically, the problem is not any more, if as difficult, as the preparation of such salts from the Stassfurt materials. The labor and transportation factors

---

[1] There is a company on the Southern California Coast, whose process is to cut the kelp and market the chopped green product for direct application to the soil.

on the Pacific Coast are too uncertain as yet to justify any definite estimates, and opinions only are hardly worth offering.

FRANK K. CAMERON.

BUREAU OF SOILS,
DEPARTMENT OF AGRICULTURE,
WASHINGTON.

ORDINARY WRITING FLUID FOR MARKING PORCELAIN CRUCIBLES.

Editor of the Journal of Industrial and Engineering Chemistry:

In the article on "Marking Porcelain and Silica Crucibles, etc.," published on page 567 of the August issue of THIS JOURNAL, I note the author has experienced a great deal of difficulty in permanently marking glazed crucibles and also note that he has gone to considerable trouble to remedy this difficulty.

While I was employed as "helper" in the U. S. Food and Drug Inspection Laboratory, Portland, Oregon, the same trouble was experienced there, as it is no doubt in most laboratories. We had been marking the crucibles on the bottoms with a piece of magnetite or some other iron ore, but this was impractical, as each crucible had to be lifted up to read the number, so I tried the iron in the form of ordinary black writing fluid from my fountain pen, on the glazed side of the crucibles. The method is as follows:

The crucibles are washed and dried with a clean towel, the numbers put on with the pen and dried carefully so as not to make the outlines of the figures ragged, by holding them about a foot above the Bunsen burner. The ink is applied two or three times, drying after each application and holding in a position so that it will dry in a uniform mark. After the ink is well set, the crucible is held in the flame and heated for about two minutes after it has become red hot. This oxidizes the iron in the ink and burns it into the porcelain, thereby marking it with a beautiful reddish gold numeral which cannot come off. If difficulty is experienced in placing a neat numeral on the crucible it may be outlined in dots, which gives a very pretty effect.

This simple method furnishes a reagent which is always at hand and one that is inexpensive, quick to apply and permanent. After three years' use, marks made in this way show up as bright as when they were taken out of the flame.

Very respectfully,

CLAUDE D. MASON.

IDAHO STATE BOARD OF HEALTH,
BOISE, August 12, 1912.

THE NEED OF CHEMICAL CONTROL IN FURNACE OPERATION.

During the past year I have visited several hundred power plants in this section of the country and as a chemist have been particularly impressed with the lack of instruments for determining furnace efficiency, *i. e.*, automatic CO_2 recorders and continuous gas samplers for sampling flue gas over a period of a number of hours; even the familiar Orsat apparatus is notable by its absence. Furthermore, in 90 per cent. of the cases, in the few plants where something of the kind was found, the instruments had been consigned to the scrap heap or stored and were never used.

The reason seems to lie in the thought that with coal at $1.50 per ton the possible saving would not be worth while. But it has been conclusively proved that the use of these instruments will result, even in this low-priced fuel district, in saving both the cost of instruments and of operation many times over. The losses which take place in furnaces are the most glaring of modern plant operation, yet they receive the least attention.

To the chemists the cause for this is not far to seek. Combustion is essentially a chemical process and it is easier for him to comprehend the chances for loss than one not thoroughly versed in the science. Still more important is the fact that the determination of furnace efficiency involves analysis of the flue gases, a chemical process involving the handling of the delicate gas analysis apparatus, an operation requiring some little skill and more or less constant attention from day to day. This same skill, however, is not greater than necessitated by many other operations carried on daily by the stationary engineer. Why, then, is this not done? Simply because the man who has charge of the boiler room has not been trained in these lines as he has in others.

Right here lies the opportunity for the chemist, if there be one connected with the plant, to make a great saving in operating expenses, with a minimum amount of effort and time on his part. In those plants where I found furnace efficiency at the highest and the instruments for its determination in successful operation, this part of the work was in charge of the chemist. It took very little of his time for a reliable laboratory boy had been trained to do most of the work and make the necessary reports.

R. C. BENNER.

DEPARTMENT OF INDUSTRIAL RESEARCH,
UNIVERSITY OF PITTSBURGH.

THE ESTIMATION OF OXYGEN AND OCCLUDED GASES IN COPPER, ETC.—AUTHOR'S NOTE.

The methods of analysis given in my article under the above title (THIS JOURNAL, 4, 402), may be simplified by the following:

In the purification of Carbon Dioxide (p. 403), for tube (A), substitute: "A bulb tube of $CrO_3 + H_2SO_4$ (sp. gr. 1.84) heated by 1 foot of resistance wire wound over asbestos; then omit (D), the tube of dry chromous chloride."

In the purification of hydrogen (p. 403), for A, B and C, substitute the heated bulb tube of $CrO_3 + H_2SO_4$ described above.

If it is not convenient to use resistance wire for heating these bulbs, a lamp will answer the purpose.

GEORGE L. HEATH.

HUBBELL, MICH.

CHEMICAL INDUSTRIES OF NORWAY.

By CONSUL THOMAS H. NORTON.

Numerous factors have combined to retard the industrial progress of Norway. The climate is severe, coal is lacking, the mineral deposits are not easily accessible, the area of tillable land is very limited, and the industrial education of the people is not advanced.

Less than 3 per cent. of the land is under cultivation, about 25 per cent. is covered by forests, and the reminder consists essentially of moors, mountain pastures, lakes, and marshes. The conditions of life have been comparatively hard and emigration extensive. Exports to other countries have been limited chiefly to timber and the products of the extensive fisheries.

There is, however, now a marked change for the better. Norway bids fair to develop into an industrial state of considerable importance, and the chemical industries are the ones coming most prominently to the fore in the movement. The first step forward was taken in the development of the wood-pulp industry. The second, and most important for Norway's future, was the utilization of the country's magnificent water power for the establishment of electrotechnical and, more especially, of electrochemical industries on a scale impossible in any other European land.

The general movement forward in the manufacturing industries of the Kingdom, and more specifically in the various branches of applied chemistry, may be measured by the growth during the decade 1897–1908. It should be stated, in this connection, however, that a very noticeable increase in the establishment of new factories, mills, etc., began in 1890. It reached its maximum in 1899. There was a decline in the rate until 1904, when a new period of activity set in, and has continued uninterruptedly until the present time.

During the decade ending 1908, there was in Norwegian industry an increase of 45 per cent. in the number of "years of work," *i. e.*, the total number of days of work in a year divided by 300. This increase is five times greater than the increase of population. During the same period there was an increase of 159 per cent. in chemical manufacturing branches. There was an absolute increase of $21,440,000 in the amount of wages paid to operatives, representing an advance of 82 per cent. This advance in chemical industries amounted to 333 per cent.

The average annual wage for all operatives, in all industries, was $210.38 in 1897, in 1908 $264.52, an increase of 26 per cent. In chemical industries the average annual wage advanced 67 per cent. during the period. The average daily wage of adult operatives in all industries was $0.82 in 1900, and $0.92 in 1908.

Statistics of the Chemical and Allied Industries.—In 1897 there was, on an average, 1½ horse power employed per operative in Norwegian factories. In 1908 it had increased to 2½ horse power. The average establishment employed 45 horse power in 1897 and 76 in 1908.

Industries.	Factories.	Operatives.	Average daily wage.	Horse-power.
Chemical industries proper.				
Bone grinding	4	10	$.072	95
Calcium carbide	7	1,158	1.20	59,350
Chemicals:				
Heavy	13	429	0.94	729
Minor (ink, blacking, etc.)	19	80	0.61	61
Colors	8	66	0.84	108
Electrochemicals	9	675	1.18	40,045
Explosives	8	133	0.90	235
Fertilizers	13	132	0.69	638
Glue	2	57	0.76	142
Insulating material	3	11	1.36	12
Matches	5	918	0.73	464
Pharmaceutical products	10	52	0.60	23
Tar paper	2	8	0.72	.....
Varnishes	3	12	0.79	.....
Total	106	3,741	.....	101,902
Candles, oils, power, etc.				
Candles	2	25	$0.47	8
Electric power, centrals	53	459	1.10	137,167
Gas works	6	57	1.00	34
Oils and by-products	17	376	0.88	896
Perfumes	1	6	0.77	.....
Petroleum:				
Briquetting	1	4	0.78	3
Refining	2	56	1.06	37
Soap	39	338	0.72	158
Steam power houses	3	5	1.01	367
Train oil:				
Refining	36	160	0.76	33
Rendering	15	87	0.80	73
Above combined	9	32	0.85	.....
Total	184	1,605	....	138,777
Allied industries.				
Cement	1	160	$0.96	1,360
Copper smelting	4	232	1.00	1,100
Glass	9	1,143	0.84	214
Iron works	4	58	0.89	320
Mining of apatite, minerals, etc.	66	511	0.86	65
Ore mining	111	4,877	1.13	16,016
Paper	33	3,492	0.91	19,006
Tanneries	78	567	0.87	860
Treatment of minerals	6	168	0.73	531
Wood pulp:				
Chemical	23	4,563	1.00	27,307
Mechanical	66	3,475	0.94	108,188
Total	401	19,255	....	174,967
Grand total	691	24,601	....	415,646

The above table has been compiled to show the exact status of the Norwegian chemical industry in 1908, giving data on each separate branch. The classification of the Norwegian census is followed.

Importation of Heavy Chemicals.—In regard to most chemical products, Norway is still largely dependent upon other countries. Apart from her electrochemical industries, there is a fair development of the manufacture of matches, cellulose, fertilizers, oils, candles, iodine, and oxalic acids.

The heavy chemicals are imported chiefly from Germany and Great Britain. Sulphuric acid is manufactured cheaply, as the Norwegian pyrites is of excellent quality and is shipped in large quantities to other countries. The product of the three acid works in active operation is used chiefly for the manufacture of superphosphate and is inadequate to cover the needs of domestic industry. There is an annual import, valued at $42,000. Five small establishments furnish washing soda in crystals, but the main supply of soda ash, caustic soda, Glauber's salt, and bleaching powder is secured from Germany and elsewhere, as the country is dependent upon imported salt.

The utilization of kelp as a source of iodine and potash salts continues to be a prominent industry on the shores of Norway. As in the case of Scotland, Normandy and Japan, conditions seem to enable this time-honored branch still to maintain the competition with Chile iodine. In view of the exhaustion, within a measurable time, of the Chile nitrate deposits, it is well that the kelp industry is kept alive, and that studies are made to perfect its processes. There are nine establishments along the Norwegian coast occupied with this branch. Besides supplying the home demand, they exported in 1910 iodine to the value of $53,000 and 2,318 metric tons of kelp ash, valued at $64,000 (metric ton = 2,204.6 pounds). The current price of the latter is $27.34 per metric ton. Less is done in Norway than in Scotland to extract potash salts in a commercial form from this ash, although all of the kelp works furnish potash fertilizers. There is, however, a process in use for extracting from the kelp, before incineration, a highly mucilaginous substance that is a combination of potash with an acid present in seaweed. It is used to some extent in finishing textiles and is brought into commerce under the name of "norgine."

Manufacture of Oxalic Acid—Copper Pigments—Matches.—One large lumber firm at Frederiksstad carries on very successfully the manufacture of oxalic acid. It is made by fusing sawdust with a mixture of the caustic alkalies. Sodium oxalate is separated by crystallization from the solution of the fused product and transformed into calcium oxalate by treatment with milk of lime. The pure acid is secured from the calcium salt by the usual treatment with sulphuric acid. The export of oxalic acid, amounting to $37,000 in 1910, goes chiefly to the United States. The firm in question manufactures also such oxalates as are demanded in commerce.

The manufacture of copper pigments for use on the hulls of both wooden and steel vessels is highly developed in Norway, as is to be expected in a country possessing so extensive a mercantile marine. Nine establishments make a specialty of this product, and there is an annual export valued at $58,000.

Electrochemical Industries.—It is in the recent establishment of electrochemical industries upon a grand scale that Norway has disclosed her latent power as a coming factor in the field of applied chemistry. The vast, hitherto almost neglected water power is now being harnessed, one factory after another is coming into existence, and soon the Kingdom will present a remarkable exhibit of varied chemical industries, contributing largely to the world's markets and rapidly enriching the land.

This change began in 1899, when the first calcium carbide factory was built. The number of works has steadily increased until now there are seven in operation. In 1905 the first air-nitrate works began operation. Now a second on a much larger scale is about to open, and others are planned. In addition, there is a factory for cyanamide, one for sodium, one for aluminum, one for nickel, one for ferrosilicon, and one for electro steel. There are also several smaller experimental plants.

The products of these factories exported in 1910 had the following values: Calcium carbide, $1,627,000; calcium cyanamide, $184,000; calcium nitrate, $507,000; sodium nitrate, $58,000; sodium nitrite, $309,000; aluminum, $437,000; sodium, $63,000; ferrosilicon, $192,000; total, $3,377,000.

The exported products in the above categories were valued at $2,717,000 in 1909. The annual increase at present in the value of electrochemical products, as far as it can be measured by export statistics, is thus $660,000.

Manufacture of Calcium Carbide—Calcium Cyanamide.—The manufacture of calcium carbide was the pioneer electrical industry in Norway, and considerable English capital has been invested in this branch. A French company operates one plant at Hafslund. The Kellner Partington Paper Pulp Co., at Borregaard, is a good example of foreign investment in Norway. The company utilizes 24,000 horse power, and employs 3,000 workmen in its carbide factory, ferrosilicon works, and large pulp mill. It is the largest industrial establishment in the Kingdom. The Albion Products Co., at Notodden, and the Alby United Carbide Factories at Odda, are two other large English undertakings. At Trondhjem, the Meraker Carbide & Smelting Works have added to their extensive works plants for producing ferrochrome and ferrotitanium. The seven carbide works employ a total of 60,000 horse power. They are all located on the coast or on navigable rivers, and manufacture almost exclusively for exportation. In 1910 they shipped 50,579 metric tons at an average price of $32.16 per ton. The average daily yield per horse power is roughly estimated at $2^1/_3$ kilos, or 843 kilos in the year. In German factories the yield ranges from 3 to 5 kilos, as compared with a theoretical maximum of 8 kilos. The equipment of the carbide factories in Norway is essentially the same as that of the American factories.

An English company, the Northwestern Cyanamide Co., has built large works at Odda, on the Hardanger Fjord, and established on a successful basis the manufacture from atmospheric nitrogen of calcium cyanamide, which is competing with Norwegian calcium nitrate for recognition as the most economic form in which the air can furnish nitrogenous compounds for the needs of agriculture. The firm shipped 752 metric tons in 1909 and 4,281 tons in 1910. The price is $42.88 per metric ton. The industry is evidently on a firm footing and finds a market for its products, as do the similar works in Germany.

Air Nitrates—Sodium.—At Notodden, in 1905, the first factory for manufacturing nitric acid directly from the elementary gases of the atmosphere was erected. In an enlarged form it now gives occupation to 500 workmen, and is daily demonstrating the remarkable possibilities of this new factor in chemical industry and in economic evolution. The factory furnishes all the nitrates required for Norway in agriculture and the arts, and is shipping constantly increasing quantities to foreign countries. The exports for two years were as follows: 1909, calcium nitrate, 9,422 tons; sodium nitrite, 2,577 tons; sodium nitrite, 592 tons; 1910, calcium nitrate, 13,531 tons; sodium nitrite, 3,200 tons; sodium nitrate, 1,074 tons.

During 1911 the manufacture of ammonium nitrate for use in making explosives has been introduced upon a large scale, as it is profitable at present prices. Ammonia is imported from England, and after conversion into the nitrate is shipped back. A much larger factory is nearing completion at Saaheim and will be put in active operation before the close of 1911.

A single factory at Vadheim, on the west coast, is manufacturing sodium very successfully. The export in 1909 was 179 tons. The price is $0.536 per kilo, or $0.243 per pound. The process employed is that of the direct electrolysis of fused anhydrous caustic soda. Fusion vessels and cathode are of iron, and the anode is of nickel iron. The success of the operation depends largely upon the pains taken to keep the temperature of the bath within the narrow limits of 310° to 330° C. and the rapid removal from the cathode of the liberated metal. There is an increasing demand for sodium for use in making sodium cyanide, sodium amide, and especially sodium peroxide.

Production of Aluminum and Ferrosilicon.—One large factory at Christianssand is devoted to the electrolytic production of aluminum. The process is practically identical with that employed in the large American works. The export of the metal was 486 metric tons in 1909 and 1,019 tons in 1910. This is equivalent to one-ninth of the annual American production. The Norwegain aluminum is sold at $0.43 per kilo. A considerable amount is employed in equipping the air-nitrate works, as the large conduits for acid gases and the pipings for nitric acid are all made of this metal.

The demand for ferrosilicon, so indispensable in the modern metallurgy of iron, is rapidly growing, as shown by the exports from both Norway and Sweden to other countries. In 1909 Norway shipped 2,645 metric tons abroad; in 1910 the export reached 5,121 tons. Much of the output is made in the electric furnaces at Borregaard.

Decreased Output of Nickel—Electrolytic Refining.—Norway possesses extensive deposits of nickel ores, much of it containing as high as 2 per cent. of the metal. In former years nickel mining was of some importance, but competition with the richer ores of Canada and the United States could not be maintained, and most of the mines ceased operation. During the closing decade of the last century the annual production of nickel sand amounted to 7 tons. Since 1900 the industry has revived, and there is an annual output now of 70 tons, nearly all of which is used in the Kingdom. In 1909 the only mine worked, that of Eije, yielded 5,770 tons of ore containing 1.1 per cent. of nickel. In the smelting works 2.77 tons of matte are obtained from 100 tons of ore. This matte contains 40 per cent. of nickel and 25 per cent. of copper. It is refined in the new electrolytic works at Christianssand, which are equipped for an annual production of 400 tons of the metal. The production of electrolytic nickel is a much more complicated operation than are those yielding aluminum or sodium. The copper-nickel matte is used as anode in a weak acid bath. Both metals are dissolved and pure copper is deposited on the cathode. At a certain point, when the electrolyte contains in solution a relatively large percentage of nickel, the current is interrupted. The remaining copper is first removed from the solution (by hydrogen sulphide) and then the iron is removed with the customary precipitants. From this purified and heated solution nickel is deposited electrolytically, insoluble anodes being used. The electrolytic nickel has a high degree of purity and is fairly compact. The total consumption of electricity is relatively large and the process can be employed with advantage only where the cost of the current is exceptionally low, as is the case in Norway.

Electric Smelting.—The success which has followed the experimental trials of the Gronwall furnace for the electric smelting of iron ores, first at Domnarfvet, in central Sweden, and later on a larger scale at Trollhattan, near Gothenburg (see Daily Consular and Trade Reports for May 6, July 19, and Oct. 14, 1911), has demonstrated beyond question the economic and technical advantages of this new process. The Norsk Electrometal Co. has promptly secured patent rights for Norway, and two companies are now constructing electric iron-smelting works under their licenses. The Hardanger Electriske, of Staalwerk, is erecting two furnaces at Odda that will use 5,800 horse power from the Tysse fall. The company controls in all 15,000 horse power at this point. At Arendal the Arendals Fosse-Compagni is building furnaces that will utilize 6,000 horse power, and is able to increase it to 30,000.

A somewhat different type of smelter is under construction near Notodden by the Tinfoss Jernoers Aktieselskab, which will use at first 5,000 horse power and can increase it, if necessary, to 15,000. Unquestionably within a few months the electric manufacture of an excellent grade of iron will be established in Norway on a good working basis.

The electric smelting industry promises much for the country. In earlier years Norway possesses a flourishing iron industry, but saw it gradually decline as the fuel became more and more expensive. The land is rich in iron deposits, most of which are too remote to permit of advantageous mining at present. The Norwegian magnetite is not rich enough to warrant its export, and it is too hard for English smelters. If exported at all, it must usually be previously concentrated and briquetted, involving considerable expense. This magnetic iron ore, however, frequently contains sufficient lime to be self-fluxing. When adequate and cheap water power is near the mines, not only the magnetic ore, but the low-grade ores not worked at all now can easily be turned into first-class steel billets and offer a large margin of profit at present prices. It may be that Norway will rank eventually among the prominent iron-producing countries of Europe, as but little is known about the full extent of its mineral wealth, especially in the northern less-accessible regions.

Electric Steel Furnace.—Active steps are also being taken to introduce the electric steel furnace. The Hardanger Company is installing one requiring 800 horse power, and other plans are on foot. The fine grade of iron obtained by an electric smelter with the use of charcoal is almost free from manganese and silicon. If brought into a mixer heated with gas, and then refined in an electric furnace, the steel produced should be of an exceptional quality.

All of these plants and projects are dependent upon the continuance of the cheap rate for water power in Norway. In Sweden the cost per annual horsepower is apt to range above 50 crowns, or $13.40. In Norway, rates vary usually between $5.40 and $10.70. There are some cases where the cost is even as low as $4.

In addition to the foregoing enterprises, Norwegian capitalists are discussing the establishment of electric works for zinc smelting, for nickel smelting and for the combined electric smelting of copper ores and the electric refining of the metal.

Statistics of the Mines and Metallurgical Plants.—The following table shows the condition of the mines and metallurgical plants in 1909. Comparative figures of production for 1896 are added:

	Metric tons.			Miners and operatives in
Ores.	1896.	1909.	Value in 1909.	1909.
Apatite	1,485	1,364	$ 18,000	.....
Copper	36,956	42,612	450,000	2,243
Feldspar	15,568	36,489	127,000	.....
Gold	....	.....	2,000	47
Iron	6,510	40,389	79,000	681
Lead and zinc	452	983	6,000	262
Molybdenum	1	30	12,000	46
Nickel	422	5,770	27,000	78
Pyrites:				
Arsenical	.....	160	2,000	4
Iron and copper	87,867	282,806	1,638,000	1,867
Rutile	33	83	19,000	....
Silver	400	2,729	150,000	264
Metals smelted.				
Cobalt compounds	1	.....	....	....
Copper	1,112	1,594	445,000	116
Nickel	7	70	29,000	57
Pig iron	366	.....	......	....
Silver	4.8	7.8	134,000	11

In 1910 Norway purchased iron and steel to the amount of $4,581,000 and manufacturers of iron and steel valued at $4,832,000. Imports of other metals reached $1,397,000, and other metal manufactures, $6,243,000.

Striking Features of Norway's Chemical Industries.—In surveying the chemical industries of Norway there are several features worthy of careful study by the American economist. First and foremost is the systematic and exhaustive manner in which the abundant water power of the country is now being regulated, stored up, and pressed into service by the steadily increasing group of electrochemical industries. The best talent in the nation is enlisted in this cause, and the way is rapidly being opened for Norway to assume an industrial position commensurate with its geographical size and admirable facilities for maritime transportation.

In another field Norway has shown her ability to develop an industry, fitting in well with her enormous lumber interests, and that is in the manufacture of oxalic acid. It is a source of wonder that no attempt has yet been made to organize this branch of manufacture in the vicinity of some of the great American lumber centers, where sawdust, the primary raw material, is without value except as fuel. The United States buys annually oxalic acid from Norway to the value of $43,000, and from Germany to the value of $65,000. The American market should not be dependent upon European manufacturers for a chemical, the preparation of which is so comparatively simple.

As a market for American chemicals, Norway offers less of a field than the neighboring Scandinavian States, on account of the limited extent to which many industries consuming such products are developed at present. The character of the demand is much the same as in Denmark and Sweden. The quantity is relatively less.

CEMENT PRODUCTION AND TRADE OF THE FAR EAST.

According to Consul General George E. Anderson, of Hongkong, the cement industry of Hongkong and vicinity, which is the enterprise of one corporation but includes works in various portions of the colony and at Macao and Canton as well, has long dominated the cement trade of Southeast Asia and at times has had a not unimportant share in the import cement trade of the Pacific coast of the United States.

At the last general meeting of this company attention was called to the growing competition in cement making in the far East. In the course of his discussion of the situation the presiding officer at the company meeting said:

"Competition continues unabated but has somewhat changed in form. European shipments to the far East have decreased and in the main can be ignored. The establishment of new factories in near-by territory is what interferes with us most, and some of these are gradually improving the quality of their product and increasing their output. There are probably more factories in the East than the average man realizes; for, besides, the numerous Japanese establishments, including Manchurian, we have those at Tongshan (Tientsin), in Hupeh on the Yangtze at Haifong, at Kuala Lumpur, and a new one at Padang in Sumatra, and there may some day be one at Manila. To offset the rise of these establishments we have the ever-increasing call for cement. And if this increase continues in years of stagnation and troubled trade such as we have experienced lately, what may it be when China settles to a steady course and the inevitable railway building comes into full swing?"

No mention was made of the plant under the control of the Chinese Government at Canton, which is not in operation for the time being. The chief competition for Hongkong at present is coming from Haifong. The Manila enterprise referred to is under the control of a Philippine corporation organized for the purpose and is reported as well under way.

The total ordinary maximum output of the plants mentioned, which are now serving to a great extent much of China, particularly south of the Yangtze, the Philippines, Indo-China, the Malay States, and Siam, as well as other countries in lesser degree, probably aggregates more than 2,000,000 barrels annually. The maximum output, according to the best information available, consists of the following, in barrels of 375 pounds each:

	Barrels.
Green Island Cement Co. (Hongkong)	780,000
Ciments P. A. de l'Indo-Chine (Haifong)	300,000
Chee-Hsin Cement Co. (Tongshan, Tientsin)	300,000
Hupeh Cement Co.	288,000
Others	300,000
Maximum output	2,028,000

Competition with each other has prevented any one of the establishments concerned in this eastern trade from running at maximum capacity, and this is likely to be the case for sometime in the future. But, while competition has been and is likely to continue to be exceedingly keen, there appears to be no sound reason why all these plants shall not remain in the field. Each of these has more or less difficulties to overcome, but each has notable advantage either in the way of convenient and abundant supplies or unusually good shipping facilities, and all have cheap labor, fuel, and other supplies, and a constantly increasing demand for their product.

It seems quite likely, therefore, that the prospective increased demand for cement in China will be met with a complete and satisfactory supply in or near China.

Consul Stuart K. Lupton, of Karachi, India, states that the cement trade of northwestern India is comparatively small, as may be seen from the accompanying table of imports for the past five years, which means practically the entire consumption in a district with a population of some 45,000,000 people:

Year.	Casks.	Value.
1906–7	15,591	$38,126
1907–8	20,107	51,934
1908–9	22,729	59,181
1909–10	36,497	83,390
1910–11	33,095	75,579

Most of the cement imported is of British manufacture. The brands chiefly used are Victor, Rhinoceros, Gillingham, Peters, Elephant, Red Cross, and Pyramid among the English marks, with Gladiator as the principal German brand.

British cement is quoted by the manufacturers for March 23rd at $1.95 per cask, c. i. f. Karachi, and after paying a duty and handling charges is sold in smaller quantities to the consumer at $2.09 to $2.13 per cask. As freight rates from Great Britain are 20 to 25 shillings ($4.87 to $6.08) per ton, this means that cement must be produced at the shipping point for 50 or 60 cents a cask to realize a profit.

At the present time the Port Trust and the Karachi municipality are using about 1,200 casks of 400 pounds each every month; but this extraordinary work will soon close, and I am credibly informed that the average monthly consumption of cement for all purposes will be about 200 casks for the next eight months or a year.

SULPHUR, PYRITE, AND SULPHURIC ACID.

Mineral Resources of the United States, issued by the Geological Survey, states that the production of sulphur in the United States in 1911 amounted to 265,664 long tons, valued at $4,787,049, as compared with 255,534 tons, valued at $4,605,112, in 1910. In determining the value of most of the sulphur produced in 1911 the current market prices in New York were taken, from which the value at the mine was then computed. It is estimated that the production for the year 1911 is very close to the present rate of consumption.

Prices remained fairly constant throughout the year at approximately $22 per long ton at New York for prime Louisiana sulphur, and at $22.50 at Boston, Philadelphia, and Baltimore. Quotations on roll sulphur were from $1.85 to $2.15 per 100 pounds; for flowers of sulphur the range was from $2 to $2.40 per 100 pounds; and for sublimed sulphur it was from $2.20 to $2.60 per 100 pounds. Sicilian sulphur was held at the same figure.

In 1911 there were imported for consumption into the United States 29,144 long tons of sulphur, including crude, refined, flowers of sulphur, and other kinds. This sulphur was valued at $552,836. In 1910 the imports amounted to 30,833 long tons valued at $558,611. The great bulk of the sulphur imported comes from Japan.

In 1909 the United States exported 37,142 long tons of sulphur, valued at $736,928; in 1910 the exportation amounted to 30,742 tons, valued at $552,941; in 1911 the exports totaled 28,103 tons, worth $545,420.

The production of pyrite in the United States in 1911 amounted to 299,904 long tons, valued at $1,162,261. This was an increase in quantity of 58,292 long tons and in value of $184,283, as compared with the production of 1910. The figures are also the maximum ever recorded by the survey for the pyrite industry. Though low-grade sulphide ores of copper containing considerable quantities of pyrite and pyrrhotite and zinc sulphide concentrates have been used in recent years in the manufacture of sulphuric acid, this condition of affairs does not seem to have curtailed the output of pyrite, as it was feared it might. As a matter of fact, the output of pyrite has shown a great increased ring the last five years, notwithstanding this was a period of rapid development by the by-product sulphuric-acid industry. It is estimated that the quantity of sulphides other than straight pyrite used in the manufacture of sulphuric acid in 1911 was equivalent to 200,000 long tons of pyrite, which would bring the tonnage of this mineral theoretically produced in 1911 up to nearly 500,000 long tons. This does not include copper-bearing Spanish pyrite used in making sulphuric acid.

The importation of pyrite still greatly exceeds the domestic supply, as appears from the following statement of imports for consumption for the last three years: 1909, 688,843 long tons, value $2,428,580; 1910, 803,551 tons, value $2,748,647; 1911, 1,006,310 tons, value $3,788,803.

For the first time in the history of the volume, *Mineral Resources*, published by the Geological Survey, a brief statistical statement is made by the sulphuric-acid industry. One of the reasons for adding the subject of sulphuric acid is that, owing to the fact that so large a percentage of the output of sulphur and pyrite is converted into acid for use in the industries, the acid production becomes in a way a check on the statistics of sulphur and pyrite, especially of pyrite, which is practically all used in the acid industry.

The 1911 production of sulphuric acid in the United States aggregated 2,210,330 short tons, valued at $17,369,871, as follows: 50° Baumé, 1,026,896 tons, value $5,447,958; 60° Baumé 421,165 tons, value $2,624,042; 66° Baumé, 751,541 tons, value $9,176,297; other grades, 10,728 tons, value $121,575.

CHEMICAL INDUSTRY OF GERMANY.

Consul General A. M. Thackara, of Berlin, reports that with but few exceptions, conditions in the various branches of the German chemical industry during the year 1911 were most favorable. Heavy orders were received both for home and foreign consumption, and in many lines the prices for natural and artficial preparations were higher. The demands for drugs and chemicals were so large that the manufacturers of raw materials, such as acids, ammonia, etc., experienced great difficulty in filling their orders. There were especially notable increases in the demands for medicinal preparations on account of the numerous cases of illness, such as influenza, scarlet fever, diphtheria, and other ailments due to the heat of last summer. Many orders were received by the German manufacturers for disinfecting and other materials which were used in stamping out the plague in the far East.

Luftsaltpeter or air saltpeter manufactured from nitrogen extracted from the air by the Norwegian and Swedish plants is slowly finding its way to the market. It is expected that, in the near future, the Norwegian saltpeter can be shipped in large quantities to the centers of consumption. Its success as a competitor with the Chile product will naturally depend upon the price. At present the artificial saltpeter is selling at 8 to 9 pfennigs (1.9 to 2.1 cents) more per kilo (2.2 pounds) than Chile saltpeter, but it is thought that the prices will soon be equalized. In 1911 there were only 493.3 metric tons of soda saltpeter (natron saltpeter) imported from Norway, as against 730,939 tons received from Chile. In 1911 there were also imported 473.4 tons of nitrate of ammonia from Norway and 139.2 tons from Sweden, and 14,494 tons of nitrate of lime (Saltpetersäures Kalk) from Norway and 1,033.6 tons from Sweden. Not only in Sweden and Norway are new plants in course of construction for extracting nitrogen from the air, but also in Upper Bavaria, in the Tyrol, in Switzerland, and in the Valley of the Rhine.

The favorable business year of the German chemical industry is reflected in the increased dividends declared by many of the chemical companies, in the amount of capital invested in new companies, and in the capital used in extending existing industries. The total amount of new capital invested in the chemical industry last year was $16,226,840, compared with $6,333,180 for 1910. For last year $10,010,280 was employed for the creation of new companies and $6,216,560 for the extension of existing industries.

The drought of last summer unfavorably affected the crops of medicinal roots, leaves, and seeds, in consequence of which the prices of these raw materials were much higher. The prices of certain bulky products used in the chemical industry were also affected, owing to the difficulty of securing water transportation.

GERMAN POTASH AND SALT STATISTICS.

Consular Assistant Louis G. Dreyfus, Jr., of Berlin, reports that statistics recently published by the Ministry of the Interior giving the production of potash and salt mines in Germany, show that in 1910 there were 82 works, employing 27,790 persons, to whom was paid $8,869,678 in salaries and wages. Each of these figures was an advance over 1909, the record for that year being 78 works, 27,445 employees, and $8,400,077 paid in salaries and wages. Below is summarized the production for these two years.

Potash and salts.	1909. Metric tons.	1909. Value.	1910. Metric tons.	1910. Value.
Raw salts:				
Rock salt	1,103,562	$ 1,296,045	1,136,776	$ 1,344,269
Potash salts:				
Carnallite, inclusing kieserite	3,502,658	7,541,709	3,729,409	7,644,105
Kainite, sylvanite (sylvite)	3,570,286	11,508,021	4,610,152	13,862,702
Boracite	144	5,587	166	6,704
Salts to be used in further manufacture:				
Carnallite	3,353,993	7,262,482	3,569,937	7,382,753
Kainite, sylvanite	926,556	2,873,156	1,329,523	3,808,893
Products ready for sale:				
Stone salt	1,097,491	1,312,191	1,112,562	1,346,673
Carnallite with 9 to 12 per cent. K_2O	328,386	734,627	402,476	908,250
Crude salt with 12 to 15 per cent. K_2O	2,594,179	8,386,873	2,924,709	8,756,404
Salt with 15 to 19 per cent. K_2O	33,543	151,088	153,297	437,472
Fertilizer salts:				
With 20 to 22 per cent. K_2O	84,585	610,868	136,233	850,184
With 30 to 32 per cent. K_2O	43,713	505,370	55,556	626,330
With 40 to 42 per cent. K_2O	265,706	4,214,486	335,671	5,196,046
Potassium chloride:				
With 50 to 60 per cent. K_2O	266,911	8,295,233	304,145	8,673,969
With over 60 per cent. K_2O	107,537	3,662,667	130,767	4,336,013
Potassium sulphate of over 42 per cent. K_2O	69,730	2,608,336	90,389	3,239,079
Potassium magnesium sulphate	40,105	729,654	39,011	688,366
Magnesium sulphate	65,771	217,908	68,862	224,623
Magnesium chloride	28,983	84,848	31,012	92,911
Sodium bisulphite	4,445	34,452	2,540	19,078
Boracite	102	3,990	135	5,412
Bromine, etc	11,390	501,623	14,293	472,496
Total	17,499,776	62,541,214	20,177,621	69,922,723

Among numerous references to the German potash industry that have appeared in Consular and Trade Reports were the articles published on Sept. 18, 1909; June 15, Aug. 30, Nov. 25, and December 12, 1910; Jan. 26, July 25, and Nov. 11, 1911.

THE WIDE USE OF ARSENIC.

The production of white arsenic in the United States in 1911 was 3,132 tons, valued at $73,408, against 1.497 tons, valued at $52,305, in 1910, according to a report on arsenic by Frank L. Hess, just issued by the United States Geological Survey. The arsenic was obtained as a by-product of smelting operations. This output is much the largest ever made in this country, but owing to the low price and the distance of the smelters from New York, the freight charges absorbed a large proportion of the profit.

During the year 4,996 tons of white arsenic, metallic arsenic, and arsenic sulphides, valued at $247,323, were imported. Of this amount 1.921 tons was white arsenic, with a value of $116,948. In addition, 126,191 pounds of Paris green and London purple, valued at $4,972, were imported. The total production and importation in 1911 of arsenic and all arsenic compounds amounted to 16,256,000 pounds.

The principal uses of arsenic are in glass making, in pigments, and in insecticides. The use of Paris green (acetoarsenite of copper) in paint is somewhat limited on account of its poisonous quality. As an insecticide it is used largely by gardeners, orchardists, and farmers. If pure, it is comparatively harmless to plant life, owing to its insolubility, but the trioxide is often present in some quantity and if Paris green is then used it is fatal to plants, especially in dry climates, where it is not soon washed off by rains. Experiments conducted by a number of the State Agricultural experiment stations have demonstrated the value of arsenic when combined with lime as an effective spray against insect pests.

A number of arsenic salts and oxides are used medicinally, among them the bromide, iodide, trisulphide, trioxide, sodium arsenate, and potassium arsenate. Disulphide of arsenic, both natural and artificial, is used as a paint pigment; in calico printing and dyeing; in tanning; and, as it burns with an intense white light, in fireworks. Orpiment, the trisulphide, called also king's yellow, is used as a paint pigment and as a reducing agent in chemical work. The trioxide is used in paints; for preserving hides, both for taxidermists and in the leather industry; as an antiseptic; and in killing animal pests. Sodium arsenate is used in dyeing with turkey-red oil and in printing fabrics; the arsenite in making soaps for use on skins and hides. Potassium arsenite is used as a reducer for silver in the manufacture of mirrors.

A copy of the report on arsenic may be obtained free on application to the Director of the United States Geological Survey at Washington, D. C.

SWISS FACTORY STATISTICS.

The following statistics, reported by Commercial Agent Archibald J. Wolfe, show the preliminary results of the Swiss Federal census of 1911 regarding Swiss factory enterprises:

		Employees.		
Trades.	Factories.	Male.	Female.	Total.
Cotton trades	326	11,617	17,932	29,549
Silk industry	215	7,735	23,802	31,537
Woolen industry	67	2,190	3,135	5,325
Linen industry	24	440	567	1,007
Embroidery	866	11,787	16,822	28,609
Other textile trades	112	1,517	2,633	4,150
Clothing and outfitting	660	8,789	16,061	24,850
Provisions and alimentary trades.	694	13,440	12,604	26,044
Chemical industry	198	6,967	1,725	8,692
Centrals for power, gas, and water	263	4,254	1	4,255
Paper and graphic trades	625	13,227	4,930	18,157
Woodworking trades	1,268	23,333	432	23,765
Metal working	623	21,865	1,460	23,325
Machinery, apparatus, etc	640	45,313	1,122	46,435
Jewelry and watchmaking	856	21,445	13,538	34,983
Clay and stone trades	441	17,160	1,000	18,160

TITANIUM AND ALLOYS OF STEEL.

Much experimenting with various alloys of steel has been carried on by railroads and rolling-mill operators to produce a rail that will give more satisfactory service than the ordinary rail now in use. One of the principal metals used in these experiments, according to the United States Geological Survey, is titanium. More than 250,000 long tons of rails were rolled in 1910 from steel to which ferrotitanium had been added. More than 150,000 tons of steel rails in which nickel or nickel and chromium were used as alloy were also made during 1910, and experiments were made with about 80,000 tons of steel rails in which chromium, manganese, vanadium, and other metals were used. Certain steel makers, according to the Survey, are now advertising titanium steel, claiming that although no titanium is left in the steel, the removal of gases and impurities effected by it greatly increases the good quality of the steel.

GOOD INCREASE IN PLATINUM PRODUCTION.

California and Oregon produced all the platinum mined in the United States in 1911; this, as shown by Waldemar Lindgren, of the United States Geological Survey, in an advance chapter from "Mineral Resources" for 1911, was $8,631 greater in value than the output for 1910. The following is a statement of production in Troy ounces and the values for the two years:

	1910.		1911.	
	Ounces.	Value.	Ounces.	Value.
California	337	$8,386	511	$14,873
Oregon	53	1,121	117	3,265
	390	9,507	628	18,138

The average price paid for platinum in 1911 was $28.87 an ounce, compared with $24.38 in 1910, the higher price undoubtedly resulting in an increased production.

Importations in 1911 of crude platinum sands resulted in an estimated refined product of 27,500 ounces, nearly four times the domestic production. An additional amount was derived from imported ores and mattes, so that the total quantity of refined platinum produced in domestic refineries is estimated by Mr. Lindgren at approximately 29,140 fine ounces, of which about 940 ounces, valued at $40,890, was derived from domestic sources of various kinds—platinum sands, copper and gold bullion, etc. The corresponding estimate for 1910 was 773 ounces, valued at $25,277.

The platinum imported and entered for consumption in the United States in 1911, including ores and manufactured products, was valued at $4,866,207, an increase over the 1910 figures of $1,212,543. The exports amounted to only $8,139.

The world's production of platinum in 1911 was 314,323 troy ounces, compared with 288,952 ounces in 1910.

Mr. Lindgren's report of platinum contains an interesting discussion of the platinum-bearing minerals, the uses of the metal, its sources in the United States, and the possibility of new discoveries. It also contains notes on the other platinum metals such as iridium and palladium.

PAINT PRODUCTION IN 1911.

In 1911, according to the United States Geological Survey, the value of the paint produced from all sources was $31,822,827. Paints are divided by the Survey into three groups—natural mineral pigments, pigments made directly from ores, and chemically manufactured pigments. Of the total production of paint in 1911 $498,821 is to be credited to natural mineral pigments, $7,343,762 to pigments made directly from ores, and $23,780,244 to chemically manufactured pigments. The production of natural pigments was less than in 1910; that of pigments made from ores increased; that of chemically manufactured pigments decreased. There was a total decrease in value, compared with the value for 1910, of $241,495.

The report on mineral paints, by W. C. Phalen, of the Survey, has been issued as an advance chapter of the volume "Mineral Resources" for 1911. It contains tables showing imports of the pigments of different classes, thus giving an idea of the magnitude of their consumption in the United States; descriptions of the characters of the natural mineral pigments, and brief data on the methods of preparation of the prepared pigments. The report also contains a summary of the results of paint tests recently published by the American Society for Testing Materials.

WASTE IN COKE MAKING.

If the 27,703,644 short tons of coke manufactured in 1911 in ovens of the beehive type had been made in by-product ovens the value of the by-products thus recovered, which were wasted in the beehive ovens, would have been between $35,000,000 and $40,000,000. This interesting statement is made by Edward W. Parker, of the United States Geological Survey, in an advance chapter on coke from the volume "Mineral Resources" for 1911. This estimate is based on the value of the by-products resulting from the 7,847,845 tons of coke made in by-product ovens in 1911. The value of these by-products recovered in 1911 was equal to the value at the mines of the coal used in making the coke.

From information received by the Survey from the superintendent of motive power of the Pennsylvania Railroad Company, Mr. Parker estimates that the quantity of power which might be obtained from the coking operations in the Connellsville and Lower Connellsville districts by substituting non-recovery retort ovens for beehive ovens and using the heat which is now wasted would be more than twice the quantity of power necessary to move every train on the Pennsylvania Railroad between Pittsburgh and Harrisburg. The amount of boiler horsepower obtainable from these coking districts is estimated by Mr. Parker at about 400,000 horsepower per hour for every day in the year.

COAL EXPORTS IN 1911.

The exports of coal from the United Staes during 1911, according to the United States Geological Survey, were 17,432,753 long tons, valued at $52,593,274, compared with 13,805,866 long tons, valued at $41,470,792, in 1910. The exports in 1911 comprised 3,553,999 long tons of anthracite, valued at $18,093,285, and 13,878,754 long tons of bituminous coal, valued at $34,499,989. The exports of bituminous coal increased over 3,000,000 tons, or about 30 per cent. Anthracite exports increased about half a million tons.

The imports of anthracite amounted in 1911 to only 2,463 long tons, valued at $12,550, and those of bituminous coal decreased from 1,497,709 long tons, valued at $3,975,561, in 1910, to 1,234,998 tons, valued at $3,604,797.

BOOK REVIEWS

CORRECTION.

Review of Thorpe's Dictionary of Applied Chemistry. Vol. I. This Journal, 4, 550.

The price of $50.00 quoted in our review for the 5 volumes of the above work was a mistake. The price given by the publishers, Longmans, Green & Co., for the complete set of the second edition of this dictionary is $67.50.

A Dictionary of Applied Chemistry. Second Edition. By Sir Edward Thorpe and other eminent contributors. To be issued in five volumes. Revised and enlarged, Volume II., 786 pages. Price, when complete, $67.50 per set and $13.50 per volume. Longmans, Green & Co. 1912, London and New York.

The issue of the first volume, reviewed in This Journal, July, p. 550, has been followed with gratifying promptness by Volume II. This completes the treatment of subjects in alphabetical order up to and through Gold. A large number of new names has been added to the list of special contributors to this work and the same general policy of treating each subject by well known experts has been followed.

A comparison with the individual subjects treated in the first edition shows careful revision and enlargement of many articles. For example, the treatment of Chlorine has been enlarged to include the electrolytic production of this now important industrial product and includes reference to the commerical production of liquid chlorine.

New chapters have been added on Chromophores and Chromogens; Coke and its by-products and appliances used; Colloids; Condensers, laboratory; Corrosion of Iron; Crops; Desiccation and Drying; Diazo Compounds; Diffusion; Edible Oils and Fats; Egg; Esterification; Factis; Feeding Stuffs; Fertilizers and Manures; Fire Extinction and Prevention; Flame; Frits and Glazes.

The additions of new material together with the revision and modernizing of the chapters carried over from the previous edition bring this volume up to the high standard set by Volume I in both material and workmanship M. C. Whitaker.

Portland Cement. By Richard K. Meade. Second Edition. 8vo. Pages viii + 385; 100 illustrations. Easton, Pa.: Chemical Publishing Co. 1911. Price, $3.50.

This excellent treatise, which was much sought after in the first edition, has been greatly improved in the second. The classification of cements is good, as is also the historical review, particularly that dealing with the development of the industry in America. The theories of composition are prudently dealt with mostly in the language of the chief investigators, such as Le Chatelier, Newberry, Richardson, Törnebohm and Day and Shepherd, who are all given the full credit due them. The chapter on raw materials is one of the best on that subject in any language. That on proportioning could well be cut down. The descriptions of the stages of manufacture are replete with detail. The review of the development of kilns, grinders and general mechanical appliances leaves nothing to be desired, at least as regards American practice. The author is strangely brief in speaking of the Universal Company's manufacture from slag and limestone. This is hardly fair, since such an enormous proportion of our American output is now made thus. The latter half of the book is taken up with treatises on analysis and physical testing of cement. In volume-constancy tests all are mentioned except high pressure steam tests.

This work on Portland Cement will always remain a monument to the industry and ability of the author. It is a pity that such flimsy paper should have been used in the embodiment of it.

Charles F. McKenna.

The Cement Industry in 1911. Published as an advance chapter from Mineral Resources, 1911, and may be obtained free by application to the Director, U. S. Geological Survey, Washington, D. C.

The statistics of cement production in 1911, prepared by Ernest F. Burchard, of the United States Geological Survey, show an increase over 1910 of only about a million and a half barrels. The increase in quantity is the smallest recorded within the last 13 years.

The total quantity of Portland, natural, and puzzolan cements produced in the United States during 1911 was 79,547,958 barrels, valued at $66,705,136. The year 1911 showed an increase of 2.27 per cent. in quantity, but a decrease of 1.48 per cent. in value.

The total production of Portland cement in the United States in 1911 as reported to the United States Geological Survey was 78,528,637 barrels, valued at $66,248,817.

This output represents an increase in quantity of 2.58 per cent. and a decrease in value of 2.87 per cent.

The United States has been divided into 11 subdivisions based on the grouping of plants in direct relation to the trade territory covered by each group. This grouping is also logical when the raw materials are considered.

Production of Portland Cement in 1911 by Commercial Districts.

District.	Active plants.	Production 1911. Barrels.	Per cent. change, 1911.	Average factory price per bbl.
New Jersey and Eastern Pennsylvania (Lehigh District) ...	24	25,972,108	— 1.30	0.715
New York....................	7	3,314,217	+ 0.54	0.805
Ohio and Western Pennsylvania.	9	6,756,313	+11.25	0.766
Michigan and Northeastern Indiana..........................	13	4,519,726	— 0.11	0.827
Kentucky and Southern Indiana	3	2,818,820	— 0.21	0.793
Illinois and Northwestern Indiana..........................	6	8,617,341	+ 2.88	0.791
Southeastern States (Maryland, Virginia, West Virginia, Tennessee, Georgia and Alabama)	11	4,049,063	+31.85	0.793
Iowa and Missouri...........	7	6,067,449	+ 6.02	0.862
Great Plains States (Kansas, Oklahoma and Central Texas)	17	7,010,396	— 9.23	0.834
Rocky Mountain States (Colorado, Utah, Montana, Arizona and Western Texas).........	7	2,124,930	— 4.99	1.186
Pacific Coast States (California and Washington)............	11	7,278,274	+13.98	1.406
Total.......................	115	78,528,637	+ 2.58	0.844

Lehigh district produces eighteen million dollars worth.

The Lehigh District of Eastern Pennsylvania-New Jersey has, with three exceptions, shown a steady increase in production each year from 1890 to the present time. The years in which slight decreases are recorded are 1893, 1908, and 1911. The first two decreases were coincident with years of general business depression, but the decrease in 1911 may perhaps be in large part attributed to an over-production in 1910. The production for 1911 was 25,972,108, valued at $18,568,670, or 71.5 cents per barrel. This production represented a decrease in quantity of 343,251 barrels, and in value of $619,845 as compared with the production of 1910, an average decrease in price of 1.4 cents a barrel. There was no net gain or loss in the number of producing plants in the Lehigh district, but the starting of new plants in the South and West resulted in lowering once more the Lehigh district's proportion of the total output of cement in the United States.

The year opened with the prices on the downward grade, and there were only temporary revivals. Taken as a whole and judged by the personal testimony of representative cement manufacturers from all States east of the Rocky Mountains, prices appear to have been very unsatisfactory.

In 1911, 115 plants reported a production of Portland cement as compared with 111 plants in 1910. The total number of rotary kilns in the producing plants was 916 as compared with 902 in 1910. These kilns ranged in length from 40 to 240 feet. The kiln lengths were as follows: 40 to 60 feet, 208 kilns; 60 to 90 feet, 149 kilns; 100 feet, 84 kilns; 110 feet, 140 kilns; 120 feet, 86 kilns; 125 feet, 163 kilns; 125 to 140 feet, 60 kilns; 150 feet or more, 26 kilns.

The gains were all in kilns 100 feet or more in length and these gains more than balanced numerically the smaller kilns which were shut down, giving a total of 559 kilns 100 feet or more in length in 1911 as against 473 kilns in 1910. The 125-foot kiln is apparently still the most common length for modern kilns. From the reports received, it is apparent that the total annual capacity of the country in 1911, allowing for reasonable loss of time for repairs, should have been about 112,500,000 barrels, and that the total production of 78,528,637 barrels represented about 70 per cent. of the total capacity. The capacity in 1911 increased 14,830,000 barrels, or far in excess of the actual increase in production. The apparent average output per kiln in 1911 was about 85,730 barrels, as compared with 84,867 barrels in 1910. This increase is explained by the greater average size of the kilns operated during 1911. According to the mill reports all but about 30 of the producing plants in the United States were shut down part of the time for causes other than repairs, for periods ranging from 2 to 10 months. Shutdowns for repairs ranged from 2 to 6 weeks. The following 9 new plants reported their first commercial output in 1911: Golden State Portland Cement Co., Oro Grande, Cal.; Piedmont Portland Cement Co., Portland, Ga.; Lehigh Portland Cement Co., Mason City, Iowa; Chanute Cement Co., Chanute, Kans.; Tidewater Portland Cement Co., Union Bridge, Md.; Michigan Portland Cement Co., Chelsea, Mich.; Knickerbocker Portland Cement Co., Hudson, N. Y.; Clinchfield Portland Cement Corporation, Kingsport, Tenn.; and Inland Portland Cement Co., Metaline Falls, Wash. In addition, one plant in the Lehigh district, which was idle in 1910, reported a production in 1911. Against these there were 6 plants idle in 1911 that produced cement in 1910, distributed as follows: One each in Arizona and Pennsylvania, 2 in Michigan, and 2 in New York.

A committee composed of Government engineers and representative consumers and manufacturers, and of the national engineering societies, has recently formulated a set of specifications for Portland cement to be used by all departments of the Government. These specifications are described in the advance chapter from Mineral Resources on cement production for 1911.

The importance of testing cement just before using it is generally recognized by large consumers, but it is entirely overlooked by the great majority of those who employ cement on a small scale, as in building sidewalks and small houses, cementing cellars, etc. These suggestions are therefore addressed only to consumers who have ever looked into the matter of having tests made. A few important reasons why tests are essential are as follows: On account of the nature of the manufacture of cement from raw materials which are rarely constant in composition, the resulting product can hardly be expected to be invariably uniform. Manufacturers generally take precautions to prevent the shipment of defective cement, but the tests made at the mill cannot always reveal imperfections in manufacture. The properties in cement are subject to alteration after leaving the mill. Cement that is found slightly inferior when tested at the mill may be sold where it is not likely to be tested. Cement that is tested by large purchasers at the mills and rejected by them may be sold to smaller consumers.

In order best to ascertain the quality of cement shipped the tests should be made after the cement arrives on the work, and they should be made with the greatest care and only by responsible and trained men in laboratories where the instruments have been properly standardized.

For the purpose of correcting any misapprehensions that may arise it should be stated that the United States Geological Survey maintains no testing laboratories and does not make any kind of tests of cement or of any other structural materials either free or for compensation. Such work should be intrusted to private commercial laboratories, such as are in operation in all the large cities of the United States.

In response to a demand for a way in which to render cement mortar and concrete water-tight, a series of tests were carried on at the Structural Materials Laboratories of the United States Geological Survey at St. Louis, Mo. This work has since been transferred to the Bureau of Standards and the unpublished data delivered to that bureau. These data, which have recently been made public, have received attention in this paper.

Tests of iron ore cements and of various Portland cements, both in sea water and in fresh water, which extended over 52 weeks, were made at the Atlantic City Structural Materials Laboratories, organized by the United States Geological Survey, but recently part of the Bureau of Standards. These tests are discussed in the chapter on cement.

Practical Chemistry for Engineering Students. By ARTHUR J. HALE, B.Sc., Lecturer and Demonstrator in Chemistry at the City and Guilds Technical College, Finsbury, with an Introductory Note by Professor R. MELDOLA, D.Sc., LL.D., F.R.S. London: 1912. Longmans, Green & Co. pp. xix + 192. Price, $1 net.

This book purports to offer a course in chemistry which is specially adapted to the needs of the prospective chemical engineer or of the student of engineering who would add some knowledge of chemistry to his equipment. The distinctive feature claimed for it is, "The teaching of the subject with a bias towards the use of materials familiar in constructive industry—a bias becoming more and more pronounced as the student progresses, and leading finally to actual specialization." The course, as laid down, is designed to cover one hundred and eight two-hour periods, of which forty-five to fifty are to be given to general inorganic chemistry, twenty-two to twenty-seven to simple qualitative analysis and volumetric analysis, and thirty-six to "quantitative analysis for engineers," which includes the examination of such materials as iron ores, coals, cements, alloys, and water. An appendix contains some twenty-five useful tables.

In his introductory note, Professor Meldola commends the principle upon which the above course is constructed, namely, that of arousing and holding the interest of the student by the use of materials which are selected because of their "engineering" significance, as pedagogically sound, but he also warns against the danger of losing sight of "the educational, as distinguished from the technical value of the subject, of its discipline as mental equipment quite irrespective of immediate utility."

In the opinion of the reviewer, the course offered by Dr. Hale is very much of the sort to which these words of warning should apply. It is not, as it stands, a course which will lead to the mental development of the student, because he is not required to develop ability to observe independently (he is, in general, told what to look for or what will happen) or to reason from one observation to another. The attempt to cover the ground which should demand two college years in two hundred and sixteen hours must obviously lead to a superficial treatment of the subject, and it may fairly be questioned if, at the end, the engineering student has gained "practical chemistry." It is certain that this procedure will not train him as an engineer of any sort should be trained in an important field, and it is much to be regretted that the endorsement of this course by Professor Meldola seems to make it apply to "chemical engineers" who above all else should have a thorough grounding in all the main branches of chemistry, especially with respect to underlying principles and theories. In the absence of a statement by the author, it is always difficult to determine how far reliance is placed upon supplementary class-room instruction to round out the course, but in this instance the time allotted by the author (two hundred and sixteen hours) leaves little opportunity for class-room exercises.

The experiments in general inorganic chemistry are mostly quantitative, or semi-quantitative, in character. The directions for qualitative and quantitative analysis are brief, but generally well-chosen. The general statements of fact are often too brief and isolated to be of value taken by themselves.

The book is of interest as another conscientious attempt to meet a demand which is very insistent just now for a course which will afford adequate instruction for students of engineering with whom chemistry is a side issue, with the least possible expenditure of time. Thoughtful teachers, especially those concerned with earning or trade schools, will find many helpful suggestions whether they adopt the course as a whole or not.

H. P. Talbot.

Snap Commercial Analysis. By Fred W. Babington. Ottawa. Thorburn and Abbott, 1912, 68 pp. Price, $1.50.

From the preface it appears that the author is Analyst in the Custom Service at Ottawa, Canada. With the exception of urine, the topics considered are commercial articles of a varied nature. The title of the booklet leaves the reader somewhat in the dark as to its meaning, but illumination is afforded by the statement that the methods outlined or referred to "are notes from a rough notebook." This tells the tale but partly. The composition is bad, gross errors of spelling, punctuation and of formula abound, and typographical mistakes are frequent. Proof reading has evidently not been attempted. The author knows "of no general taste for the analine dyes" in essences, "but as a rule an ignition will reveal the characteristic napthol odour." The following directions will, no doubt, interest coal analysts. "Results depend largely on sampling, a small piece about the size of a hazel nut being broken off each lump and about 100 grams roughly ground. This is sieved through three sieves the first (coarse) rejected; second, medium, kept for moisture; the third used for volatile and fixed carbon and ash."

One's first thought is that the booklet was written in jest. However this may be, it is one for the serious analyst to let alone unless he seeks mild entertainment for a leisure moment or an additional argument for a censorship of chemical literature.

W. F. Hillebrand.

NEW PUBLICATIONS

By D. D. Berolzheimer, Librarian, Chemists' Club, New York.

Analysis of Metallurgical and Engineering Materials. By Henry Wysor. L. 8vo., pp. 82. Price, $2.00. Chemical Publishing Co., Easton, Pa.

Analysis; Methods of Volumetric—Part II. By H. Beckerts and O. Luening. 8th Edition. L. 8vo., pp. 360. Price, $2.50. F. Vieweg & Sohn, Braunschweig. (German.)

Arsenic; The Estimation of Minute Amounts of—in Foods. By Edmund Clark and A. G. Woodman. 8vo., pp. 7. U. S. Dept. of Agriculture, Bureau of Chemistry, Circular 99.

Carbon; Lexicon of the— Compounds. By M. M. Richter. Vol. 4· 3d edition. Lex 8vo., pp. 4751. Price, $50.00. L. Voss, Leipzig. (German.)

Celluloid and its Substitutes. By W. Main. 8vo., pp. 163. Price, $0.75. Gauthier-Villars, Paris. (French.)

Chlorids; The Electrolytic Decomposition of Alkali— by Means of Immovable Cathodes. Part I. By J. Billiter. 8vo. Price $4.00. Wilhelm Knapp, Halle.

Dyeing; The Significance of Oxygen in—. By G. Unna and L. Golodetz. 8vo., pp. 128. Leopold Voss, Leipzig. (German.)

Engineers; Transactions American Institute of Chemical—, IV. By John C. Olsen. 8vo., pp. 505. D. Van Nostrand Co., New York.

Explosives; Magazines and Thaw Houses for. By Clarence Hall and S. P. Howell. pp. 32 and 1 pl. U. S. Bureau of Mines Technical Paper 18.

Explosives; The Effect of Stemming on the Efficiency of. By W. O. Snelling and Clarence Hall. pp. 20. U. S. Bureau of Mines, Technical Paper 17.

Foods; The Manufacture of Preserved— and Sweetmeats. By A. Hausner. Cr. 8vo., pp. 246. Price, $2.00. Scott, Greenwood & Co., London.

Furnace; Chemical Arithmetic and Calculation of— Charges. By Regis Chauvenet. 8vo. Price, $4.00. J. B. Lippincott & Co., Philadelphia.

Glass and Glass Painting. By C. J. Stahl. 8vo. Price, $1.25. A. Hartleben, Vienna.

Ketenes; The—. By H. Staudinger. Lex 8vo. Price, $1.50. Ferdinand Enke, Stuttgart. (German.)

Metallurgy; Text-book of Chemical Technology and—. By Bernhard Neumann. 8vo., pp. 900. Price, $4.75. S. Hirzel, Leipzig. (German.)

Mine Explosions; The Prevention of—; Report and Recommendations. By Victor Watteyne, Carl Meissner and Arthur Desborough. U. S. Bureau of Mines, Technical Paper 21.

Mine Gas; Ignition of— by Miniature Electric Lamps. By H. H. Clark. pp. 5. U. S. Bureau of Mines, Technical Paper 23.

Organic; Text-book of— Chemistry. By F. Holleman. 10th edition. 8vo. Price, $2.50. Veit & Co., Leipzig. (German.)

Organic; Text-book of Pharmaceutical— Chemistry. By M. Scholtz. 8vo., pp. 513. Price, $4.50. Carl Winter, Heidelberg. (German.)

Paints; White Zinc. By Paul Fleury. Cr. 8vo., pp. 280. Price, $1.75. Oil and Color Trades Journal, London. (Translation.)

Paper; The Treatment of— for Special Purposes. By Louis E. Andes. Cr. 8vo., pp. 250. Price, $1.75. Scott, Greenwood & Son. (Translation.)

Perfumery; The Manufacture of Modern—. By H. Mann. L. 8vo., pp. 370. Price, $2.50. Verlag fuer Chemische Industrie. Ausburg. (German.)

Photochemistry; Text-book of—. By A. Benrath. L. 8vo., pp. 287. Price, $1.75. Carl Winter, Heidelberg. (German.)

Producer Gas. By J. Emerson Dowson and A. T. Larter. 3d edition. 8vo., pp. 319. Price, $3.00. Longmans, Green & Co., New York.

Proteins: The Chemical Constitution of the—. By R. H. Aders. Plimmer. 8vo., pp. 188. Price, $1.50. Longmans, Green & Co., New York.

Quantitative; An Introduction to— Analysis. By S. J. M. Auld. Cr. 8vo., pp. 228. Price, $1.25. Methuen & Co., London.

Rubber; The Synthesis of—. By R. Ditmar. 8vo. Price, $0.75. Theodor Steinkopff, Dresden. (German.)

Sewage Disposal. By George W. Fuller. 8vo., pp. 767. McGraw-Hill Book Co., New York.

Smokeless Combustion; The— of Coal in Boiler Furnaces; with a Chapter on Central Heating Plants. By D. T. Randall and H. W. Weeks. pp. 188. U. S. Bureau of Mines, Bulletin 40.

Steam Boilers, The Transmission of Heat into—. By Henry Kreisinger and W. T. Ray. pp. 180. U. S. Bureau of Mines, Bulletin 18.

Steel; Its Metallurgy and Mechanical Treatment. By F. W. Harboard and J. W. Hall. 3d edition. 8vo., pp. 758. Price, $9.00. J. B. Lippincott Co., Philadelphia.

Sugar; The —Industry. By R. Teyssiec. 8vo., pp. 183. Price, $0.75. Gauthier-Villars, Paris. (French.)

Tanning: The Puering, Bating and Drenching of Skins. By Joseph T. Wood. 8vo., pp. 293. Price, $3.25. E. & N. Spon, Ltd., London.

Theoretical and Physical Chemistry. By S. Lawrence Bigelow. 8vo., pp. 544. Price, $3.00. The Century Co., New York.

RECENT JOURNAL ARTICLES.

Analytic Separation and Determination of Pyridine and Ammonia. By Alexander Bayer. *Fuer Gasbeleuchtung*, 1912, June 1.

Arsenic; The Quantitative Determination of—. By E. Rupp and F. Lehmann. *Archiv der Pharmazie*, Vol 250, 1912, No. 5, pp. 382-389.

Asphalt; Differentiation of Natural and Petroleum—. By J. Marcusson. *Chemiker Zeitung*. Vol., 36, 1912, No. 84, pp. 801-803.

Bismuth; Extraction of— from Carbonaceous Ores. By F. W. Frerichs. *Transactions American Institute of Chemical Engineers*, Vol. 4, 1912, pp. 90-111.

Cellulose; Comparative Acetylization of—, Hydrocellulose and Alkaline Cellulose. By H. Ost and T. Katayama. *Zeitschrift fuer angewandte Chemie*, Vol. 25, 1912, No. 29, pp. 1467-1470.

Coal; The Determination of Ash in—. By Franz Weisser. *Chemiker Zeitung*, Vol. 36, 1912, No. 80, pp. 757-759.

Coal; Practical Value of the Determination of British Thermal Units in Testing Anthracite—. By S. F. Peckham. *Transactions American Institute of Chemical Engineers*. Vol. 4, 1912, pp. 284-296.

Explosives Used in Engineering and Mining Operations. By Clarence Hall. *Transactions American Institute of Chemical Engineers*. Vol. 4, 1912, pp. 304-330.

Furnaces; An Improved Method of Drying Air for Blast—. By Bruce Walter. *Proceedings of the Engineers' Society of Western Pennsylvania*, Vol. 28, 1912, No. 4, pp. 277-310.

Gelatine; The Action of Water Vapor on—. By Wilder D. Bancroft. *Journal of Physical Chemistry*, Vol. 16, 1912, No. 5. pp. 395-406.

Health; Public— Chemistry and Bacteriology. By D. McKail. 8vo., pp. 409. Price, $1.75. John Wright & Sons, Ltd., London.

Inorganic; The— Compounds. By A. L. Voge. L. 8vo. Price, $12.00. Orell Fuessli, Zuerich.

Lamps; A Laboratory System for Testing Electric Incandescent —. By W. M. Skiff. *Transactions of the Illuminating Engineering Society*, Vol. 7, 1912, No. 5, pp. 212-228.

Nitrates; Manufacture of— from the Nitrogen of the Air. By Ernest K. Scott. *Chemiker Zeitung*, Vol. 36, 1912, No. 82, pp. 784.

Patents; Symposium on the U. S.— System. By Wm. M. Grosvenor, E. B. Moore, Walter D. Edmonds, Robert N. Kenyon. *Transactions American Institute of Chemical Engineers*, Vol. 4, 1912, pp. 417-505.

Physical; Problems in— Chemistry with Practical Applications. By E. B. R. Prideaux. 8vo. Price, $2.00. Constable & Co., London.

Rubber; Artificial— from the Scientific Standpoint. By C. Harries. *Zeitschrift fuer angewandte Chemie*, Vol. 25, 1912, No. 29, pp. 1457-1462.

Rubber; Artificial— from the Technical Standpoint. By Fritz Hofmann. *Zeitschrift fuer angewandte Chemie*, Vol. 25, 1912, No. 29, pp. 1462-1467.

Rubber; The Production and Polymerization of Butadiene, Isoprene, and their Homologs. By W. H. Perkin, Jr. *Journal of the Society of Chemical Industry*, Vol. 31, 1912, No. 13, pp. 616-624.

Soils; The Determination of Humus, Especially in Heavy Clay—. By William Beam. *Cairo Scientific Journal*, Vol. 6, 1912, No. 68, pp. 93–103.

Sulphuric; Volumetric Determination of— Acid. By George Finch. *Chemiker Zeitung*, Vol. 36, 1912, No. 82, pp. 782-783.

Textile; New Methods in the Chemistry of the —Fibres. By Richard Loewenthal. *Chemiker Zeitung*, Vol. 36, 1912, No. 82, pp. 777-779.

Water; Boiler— Purification and the Permutite Process. By E. E. Basch. *Chemiker Zeitung*, Vol. 36, 1912, No. 81, pp. 769-770.

Water; The Treatment of—.with Chlorine. By Joseph Race. *Journal of the Society of Chemical Industry*, Vol. 31, 1912, No. 13, pp. 611-616.

Yarn; Woodpulp—; —Its Manufacture and Uses. By W. P. Dreaper. *Journal of the Society of Dyes and Colourists*, 1912, No. 5.

RECENT INVENTIONS

Reported by C. L. Parker, Solicitor of Chemical Patents, McGill Building, Washington, D. C.

ATTACHING RUBBER TO METALS.

English Patent No. 2,306 (1912), to E. R. Royston.

The claim is made that it has been found that alloys containing antimony are best adapted to the production of a "chemical" bond between rubber and metal on vulcanization. The most suitable alloy is said to consist of copper, $3^{1}/_{4}$ oz.; zinc, $1^{3}/_{4}$ oz.; and antimony, 3 oz. The proportion of antimony should, it is found, be decreased when the rubber contains a relatively large amount of antimony sulphide. When the metallic base to which the rubber is to be fastened cannot be conveniently made of this alloy, another metal may be plated with a coating of the alloy.

ALKALI SILICATES IN POWDER FORM.

English Patent No. 23,391 (1912), to Justice.

The patentee observes that an industrial need has long existed for a readily soluble alkali silicate (waterglass) in powder form, this being more convenient than the usual solutions, the use of which is precluded for such purposes as colors, etc.

The preparation of a water glass in powder form on a large scale has, however, been hitherto attended with serious difficulties. The water glass solution cannot be directly transformed into the dry state, because in the process of concentration a skin that is impenetrable by water forms on the surface at once; at best, only a more or less solid jelly is obtained.

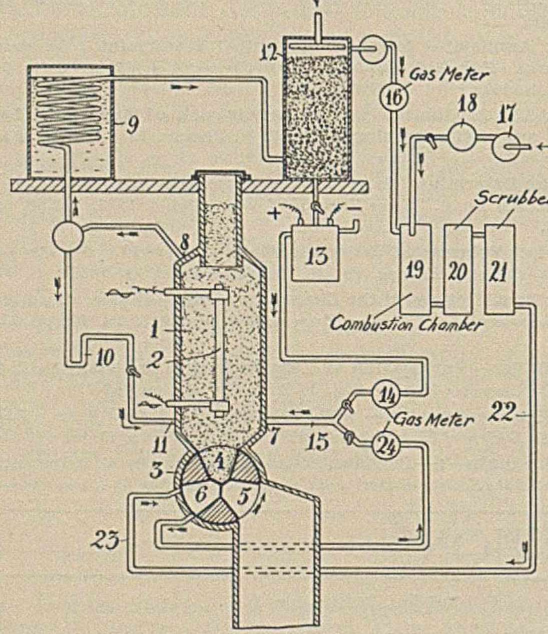
The present invention relates to a method of manufacturing fine-grained, readily soluble alkali silicates, by which the disadvantages specified are avoided and a product is obtained that is soluble even in cold water. The method consists essentially in bringing a hot, highly concentrated, thick solution of water glass (*e. g.*, solution of soda or potash water glass) under heavy pressure (for example, out of a pressure vessel, and through fine openings or spraying nozzles) into contact with cold air under relieved pressure. Under the heavy pressure the water glass assumes the form of spray, and after being suitably cooled, falls down as a dry dust.

The anhydride of sodium silicate is dissolved in water in an ordinary water glass autoclave in which a heavy pressure (about 6 to 8 atmospheres) is produced. The anhydride, being a fusion product, is a vitreous mass, which dissolves with difficulty; and therefore the dissolving process is preferably performed in a rotary apparatus under heavy pressure and at a high temperature, until the thick solution has a specific gravity of about 1.44. The resulting solution is thick while hot, and assumes, on cooling, the condition of a tough, set jelly. The hot solution is next forced out of the autoclave, under a heavy and constant pressure of about 8 atmospheres, through a spraying nozzle with orifices about 1½ mm. in diameter. The atomized solution is immediately transformed—under the influence of cold air—into a dry, solid condition. This operation is assisted by causing the dusty material to ascend through a shaft, for instance by means of a fan, and then allowing it to fall gradually to the ground as a perfectly dry powder.

PROCESS OF BINDING AND UTILIZING ATMOSPHERIC NITROGEN.

U. S. Patent No. 1,031,477, to Alf Sinding-Larsen, Assignor to Messrs. Storm, Bull & Co., of Christiania, Norway.

In the practice of this process to produce silicon-nitrogen compounds of varying nitrogen content, a mixture of coke and quartz is heated to a white heat in a blast furnace. Somewhat above the bottom of this furnace, a mixture of nitrogen and chlorine is first introduced. Tetrachloride of silicon is formed which then reacts with the excess of quartz and coke to form silicon trichloride. At the high temperature present this trichloride will be acted upon by the nitrogen, so that silicon-nitrogen compounds are formed, then silicon tetrachloride is again formed, and so on. A part of the volatile silicon chlorine compounds is liable to escape, together with the carbon monoxide which is formed, and which has to be removed. In order to keep these back, the current of carbon monoxide is conducted through a suitable cooler, where the volatile compounds will be condensed and thereupon led back to the furnace.



HYDROGENATING FATTY MATERIALS.

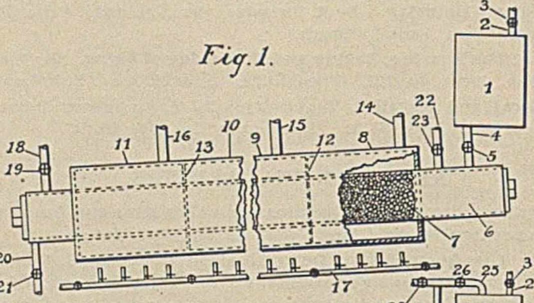
U. S. Patent No. 1,026,156 to Carleton Ellis, Assignor to New Jersey Testing Laboratories, of Montclair, New Jersey.

This is a continuous process of treating unsaturated fats and the like by means of hydrogen or hydrogen adding substances for the purpose of saturating, to a greater or less extent, such unsaturated bodies, in order to raise their melting point or otherwise improve their quality.

The addition of hydrogen to unsaturated organic compounds as brought about by the catalytic agents has been the subject of many investigations, which embrace the work of Sabatier and Senderens, Mailhe, Henle, Willstatter and Mayer, Paal and Amberger, Paal and Gerum, Paal and Roth, Paal and Hartmann, Ipatiew and Philipow, Jakowlew, Rakitin and others.

In the practice of this process unsaturated fat is placed in the tank 1 and is allowed to flow slowly into the conduit 6 or 6*a*, respectively. Hydrogen gas or water gas is admitted through the pipe 18 as a counter-current, the hydrogen traveling in a direction contrary to the traveling liquid stream of oil. The conduit is inclined from the horizontal to secure any desired rate of travel of the oil stream. The latter flows past the stationary mass of catalytic material 7 while contacting with the counter-current of hydrogen. The heating jackets may be filled with paraffin wax or a fusible alloy maintained at the requisite temperature. The treated oil discharges at the lower end of the conduit through the pipe 20, and the spent or excess gas is removed by the pipe 22. When using a nickel catalyzer and differentially heating the conduit, the temperature in 6*a* may, for example, be 150° C.; in 6*b*, 165° C.; and in 6*c*, 180° C., when converting oleic acid or olein into stearic acid or stearin, respectively.

Fig. 1.



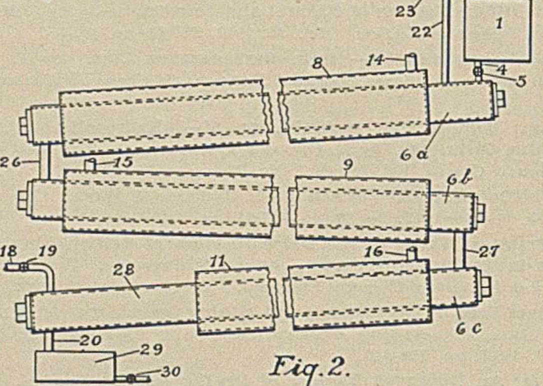


Fig. 2.

METHOD OF TREATING CARBON.

U. S. Patent No. 1,032,246, to William Acheson Smith, Assignor to International Acheson Graphite Company, of Niagara Falls, New York.

This is a process of treating carbon or carbonaceous material for the purpose of converting it in a progressive or substantially continuous manner into a homogeneous, uniform, commercial product. As between the several forms of carbon which may result from the application of heat to commercial carbonaceous materials, no mechanical separation is practicable, and it is essential in order that a given raw material may be converted throughout its mass into a commercial product of the desired density and electrical conductivity that the conditions as regards time and temperature of heating should be susceptible of accurate control and close adjustment, and that the heat should be so applied as to result in a practically uniform treatment of all particles traversing the furnace. According to this invention, the body of carbon or carbonaceous material to be treated is moved progressively through a heating zone located between terminals connected to a source of polyphase current, the arrangement of the terminals and the construction of the furnace being such as to secure a practically

Fig. 1.

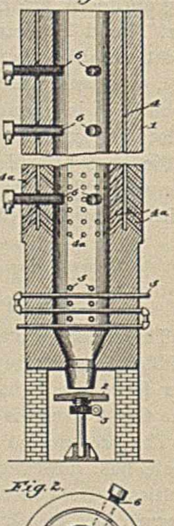
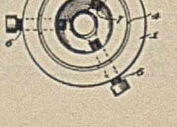


Fig. 2.

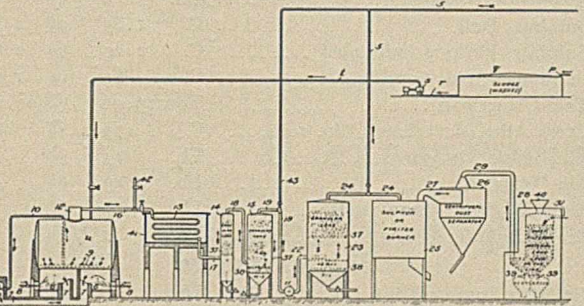


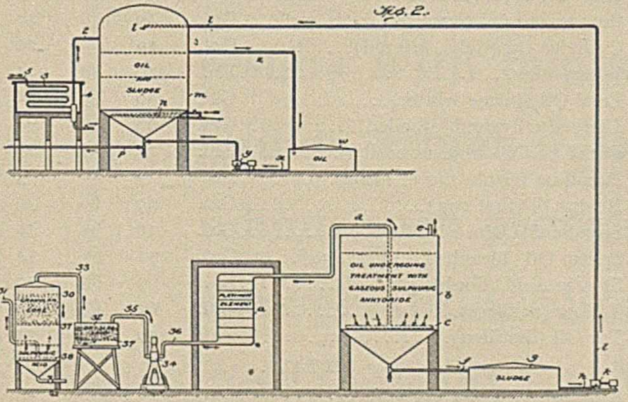
uniform heating of the entire cross section of the charge. One or more heating zones may be provided according to the results desired.

UTILIZING ACID SLUDGE FROM REFINING PETROLEUM.

U. S. Patent No. 1,031,413, to John C. Black and Marvin L. Chappell, of Richmond, California, Assignors to Standard Oil Company, of Richmond, California.

This is a process for utilizing the sulphur content of acid sludge for the production of sulphuric anhydride. The sludge is first heated in the presence of a solvent of hydrocarbons to effect a partial decomposition of the sludge. The solvent with the hydrocarbons in solution is then withdrawn and the residual sludge subjected to a decomposing temperature (not above 425° F.). The aëriform products from both decompositions are purified by contact with a solvent of hydrocarbons, the resulting aëriform products being passed over catalytic material for converting their sulphur dioxide content into sulphuric anhydride.





PRODUCTION OF LEAD COMPOUNDS.

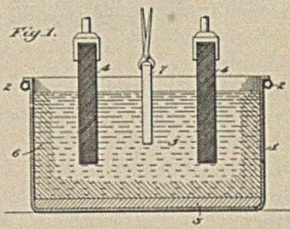
U. S. Patent No. 1,033,405, to Louis S. Hughes, of Chicago, Illinois, Assignor to Picher Lead Company, of Joplin Missouri.

A process of producing lead compounds such as lead hydrate, litharge, minium, lead carbonate, arsenate, nitrate, chromate and similar lead salts from lead sulphate. Lead sulphate is converted into lead hydroxide which in some cases is the ultimate product of the process and in other cases is an intermediate product thereafter converted into other compounds. In practice lead suphate and an alkaline base are placed in a grinding mill, a small quantity of water is added to the mixture, and the mass is thoroughly triturated. By triturating the wet mixture of lead sulphate and the alkaline base a thorough and rapid conversion of the lead sulphate is obtained. The trituration is effected in a double cone ball mill of well-known type, employing pebbles or metal balls. Crusts or coatings of lead hydrate are successively formed on and rubbed off of each kernel of the lead sulphate until finally the entire kernel is converted. After the conversion is completed the mixture of lead hydroxide and sulphate of the alkaline base is run out of the mill and the lead hydrate separated.

REFRACTORY ARTICLE AND METHOD OF MAKING IT.

U. S. Patent No. 1,030,999, to Samuel F. Hall, of Niagara Falls, New York, Assignor to Norton Company, of Worcester, Mass.

Attempts have been made to cast molten alumina or other refractory oxides or combinations of these in molds, but such efforts have not proved wholly successful. According to the patentee's process articles consisting of such refractory oxides are produced by heating the oxide, for example alumina, to a state of quiet fusion in an electric furnace, then dipping or immersing in the fused mass a mold or form, usually of carbon or graphite, withdrawing the mold together with the adhering or contained oxide, and separating or detaching the solidified oxide from the mold. By proceeding in this manner the patentee has found it practicable to produce a variety of articles, such as rods, tubes, vessels or the like, without flaws, cracks or objectionable irregularities, and, in the case of tubes or hollow articles, with any desired thickness of wall.

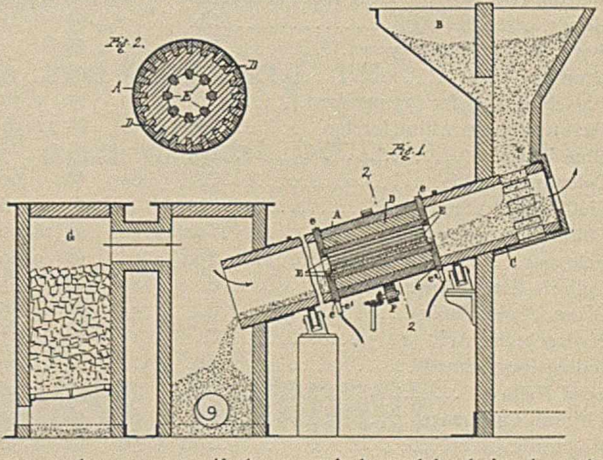


PROCESS OF MANUFACTURING ALUMINIUM NITRIDE.

U. S. Patent No. 1,030,929, to Ottokar Serpek, Assignor to Société Generale Des Nitrures, of Paris, France.

It is well known that if alumina be heated to a high temperature, for example in the neighborhood of 1800° C., in the presence of carbon and nitrogen it will combine with nitrogen to form aluminium nitride.

Heretofore it has been customary to pass an electric current through a mass of comminuted and intimately mixed carbon and alumina in an electric arc furnace through which nitrogenous gas is simultaneously blown. This is in a measure unsatisfactory, the heat beng too high in certain zones and too low in others. The patentee has discovered that this disadvantage may be overcome if the mass is heated by being brought into contact with resistance elements through which alone the current passes. The resistance elements are preferably composed of a mixture of carbon and aluminium nitride and these, during the reaction, are set in motion so as to form stirrers which agitate the finely divided mixture of carbon and alumina and thus not only serve to evenly heat the mixture but to subject it more thoroughly to the action of the nitrogen which is blown through the reaction chamber.



MARKET REPORT.

AVERAGE WHOLESALE PRICES OF STANDARD CHEMICALS, ETC., FOR MONTH OF AUGUST.

ORGANIC CHEMICALS.

Acetanilid	Lb.	$20^{1}/_{2}$	@	23
Acetone (drums)	Lb.	17	@	18
Alcohol, grain (188 proof)	Gal.	2.55	@	2.57
Alcohol, wood (95 per cent.)	Gal.	50	@	52
Alcohol, denatured (180 proof)	Gal.	40	@	42
Amyl Acetate	Gal.	2.90	@	3.00
Acetic Acid (28 per cent.)	C.	2.00	@	2.15
Aniline Oil	Lb.	$10^{3}/_{4}$	@	$11^{1}/_{2}$
Benzoic Acid	Lb.	23	@	27
Carbon Tetrachloride (drums)	Lb.	11	@	14
Carbon Bisulphide	Lb.	$10^{1}/_{2}$	@	$11^{1}/_{2}$
Chloroform	Lb.	20	@	30
Carbolic Acid (drums)	Lb.	15	@	16
Citric Acid (domestic), crystals	Lb.	$38^{1}/_{2}$	@	39
Camphor (refined in bulk)	Lb.	44	@	—
Dextrine (imported potato)	Lb.	6	@	7
Dextrine (corn)	C.	3.20	@	3.21
Ether (U. S. P., 1900)	Lb.	14	@	20
Formaldehyde	Lb.	$8^{1}/_{2}$	@	$9^{1}/_{2}$
Glycerine (dynamite)	Lb.	$17^{1}/_{4}$	@	$17^{1}/_{2}$
Oxalic Acid	Lb.	$7^{7}/_{8}$	@	$8^{3}/_{8}$
Pyrogallic Acid (bulk)	Lb.	1.35	@	1.45
Salicylic Acid	Lb.	32	@	34
Starch (corn)	C.	2.43	@	2.54
Starch (potato)	Lb.	$5^{1}/_{4}$	@	$5^{3}/_{4}$
Tannic Acid (commercial)	Lb.	35	@	$35^{1}/_{2}$
Tartaric Acid crystals	Lb.	$30^{1}/_{2}$	@	31

INORGANIC CHEMICALS.

Acetate of Lime (gray)	C.	2.50	@	2.60
Acetate of Lead (brown, broken)	Lb.	$7^{3}/_{4}$	@	8
Alum (lump)	C.	1.75	@	2.00
Ammonium Carbonate, domestic	Lb.	$8^{1}/_{4}$	@	$8^{1}/_{2}$
Ammonium Chloride, gray	Lb.	$6^{1}/_{8}$	@	$6^{1}/_{4}$
Aluminum Sulphate	C.	90	@	1.75
Aqua Ammonia (drums) 16°	Lb.	$2^{1}/_{4}$	@	$2^{1}/_{2}$
Arsenic, white	Lb.	$4^{7}/_{8}$	@	$5^{1}/_{8}$
Brimstone (crude, domestic)	Ton	22.00	@	22.50
Barium Chloride	C.	1.40	@	1.55
Barium Nitrate	Lb.	$4^{3}/_{4}$	@	5
Borax, crystals (bags)	Lb.	$3^{1}/_{2}$	@	4
Boric Acid, crystals (powd.)	Lb.	7	@	$7^{1}/_{2}$
Bromine, bulk	Lb.	25	@	30
Bleaching Powder (35 per cent.)	C.	1.30	@	1.50
Barytes (prime white, foreign)	Ton	18.50	@	22.50
Blue Vitriol	Lb.	$5^{1}/_{2}$	@	$5^{3}/_{4}$
Calcium Chloride	C.	65	@	90
Chalk (light precipitated)	Lb.	$4^{1}/_{2}$	@	6
China Clay (imported)	Ton	11.50	@	18.00
Feldspar	Ton	7.00	@	9.00
Fuller's Earth, powdered	C.	80	@	85
Green Vitriol (bulk)	C.	55	@	60
Hydrochloric Acid (18°)	C.	1.15	@	1.55
Iodine (resublimed)	Lb.	3.05	@	3.10
Lead Nitrate	Lb.	$8^{1}/_{4}$	@	$8^{1}/_{2}$
Lithium Carbonate	Lb.	65	@	70
Magnesite (raw)	Ton	7.50	@	8.50
Nitric Acid, 36°	Lb.	$3^{7}/_{8}$	@	$4^{1}/_{4}$
Phosphorus	Lb.	35	@	90
Phosphoric Acid, sp. gr. 1.75	Lb.	22	@	26
Plaster of Paris	Bbl.	1.50	@	1.70
Potassium Bromide	Lb.	31	@	34
Potassium Permanganate (bulk)	Lb.	$9^{1}/_{4}$	@	$9^{7}/_{8}$
Potassium Cyanide (bulk) 98–99%	Lb.	$19^{1}/_{2}$	@	21
Potassium Iodide (bulk)	Lb.	2.60	@	2.65
Potassium Chlorate, crystals	Lb.	$8^{1}/_{4}$	@	$9^{1}/_{2}$
Potassium Nitrate (crude)	Lb.	$4^{3}/_{4}$	@	5
Potassium Bichromate, 50°	Lb.	$6^{7}/_{8}$	@	7
Quicksilver, Flask		42.50	@	44.00
Salt Cake (glass-makers')	C.	55	@	65
Silver Nitrate	Oz.	$38^{1}/_{2}$	@	$40^{1}/_{2}$
Soapstone in bags	Ton	10.00	@	12.00
Sodium Acetate	Lb.	$4^{1}/_{4}$	@	5
Sodium Chlorate	Lb.	$8^{1}/_{4}$	@	$9^{1}/_{2}$
Sodium Bicarbonate (English)	Lb.	$2^{3}/_{4}$	@	3
Sodium Bichromate	Lb.	$5^{1}/_{8}$	@	$5^{1}/_{4}$
Sodium Hydroxide, 60 per cent.	C.	1.70	@	1.75
Sodium Hyposulfite	C.	1.30	@	1.60
Sodium Nitrate, 95 per cent., spot	C.	—	@	2.45
Sodium Silicate (liquid)	C.	65	@	1.50
Strontium Nitrate	Lb.	$6^{7}/_{8}$	@	$7^{5}/_{8}$
Sulphur, Roll	C.	1.85	@	2.15
Sulphur, Flowers (sublimed)	C.	2.20	@	2.60
Sulphuric Acid, 60° B.	C.	85	@	1.00
Talc (American)	Ton	15.00	@	20.00
Terra Alba (American), No. 1	C.	75	@	80
Tin Bichloride (50°)	Lb.	$13^{1}/_{4}$	@	$13^{1}/_{2}$
Tin Oxide	Lb.	45	@	47
Zinc Chloride (granulated)	Lb.	$4^{1}/_{4}$	@	$4^{1}/_{2}$
Zinc Sulphate	Lb.	$2^{1}/_{4}$	@	$2^{1}/_{2}$

OILS, WAXES, ETC.

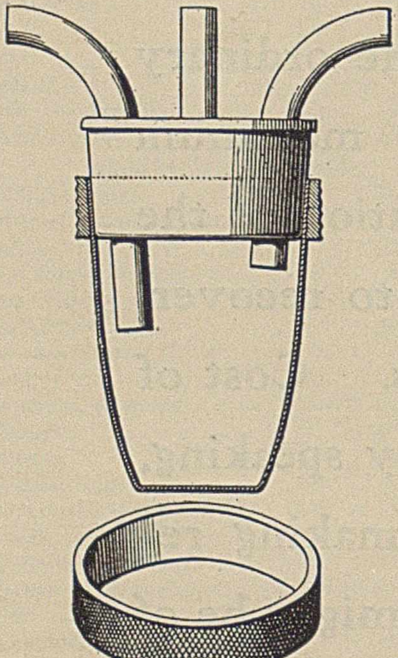
Beeswax (pure white)	Lb.	40	@	44
Black Mineral Oil, 29 gravity	Gal.	12	@	$12^{1}/_{2}$
Castor Oil (No. 3)	Lb.	$9^{1}/_{2}$	@	$10^{1}/_{2}$
Ceresin (yellow)	Lb.	9	@	15
Corn Oil	C.	5.90	@	5.95
Cottonseed Oil (crude), f. o. b. mill	Gal.	40	@	41
Cylinder Oil (light, filtered)	Gal.	$19^{1}/_{2}$	@	20
Japan Wax	Lb.	10	@	11
Lard Oil (prime winter)	Gal.	86	@	90
Linseed Oil (double-boiled)	Gal.	68	@	—
Paraffine Oil (high viscosity)	Gal.	$25^{1}/_{2}$	@	26
Paraffine (crude 120 & 122 m. p.)	Lb.	3	@	$3^{3}/_{8}$
Rosin Oil (first run)	Gal.	37	@	39
Spindle Oil, No. 1	Gal.	16	@	$16^{1}/_{2}$
Sperm Oil (bleached winter), 38°	Gal.	72	@	74
Stearic Acid (double-pressed)	Lb.	9	@	10
Tallow (acidless)	Gal.	62	@	65
Tar Oil (distilled)	Gal.	30	@	31

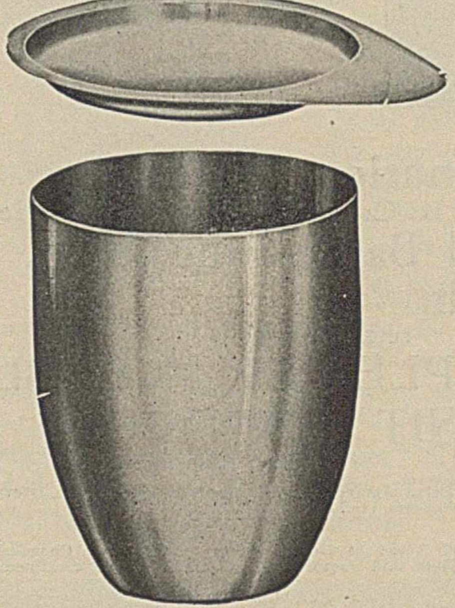
METALS.

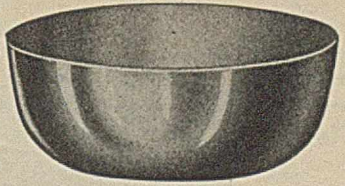
Aluminum (No. 1 ingots)	Lb.	22	@	23
Antimony (Hallet's)	Lb.	$7^{5}/_{8}$	@	$7^{7}/_{8}$
Bismuth (New York)	Lb.	2.10	@	2.15
Copper (electrolytic)	Lb.	$17^{1}/_{2}$	@	17.55
Copper (lake)	Lb.	$17^{1}/_{2}$	@	17.55
Lead, N. Y.	Lb.	$4^{1}/_{2}$	@	4.35
Nickel	Lb.	50	@	55
Platinum (refined)	Oz.	46.35	@	47.00
Silver	Oz.	63	@	—
Tin	Lb.	$45^{3}/_{4}$	@	—
Zinc	Lb.	6.95	@	7.15

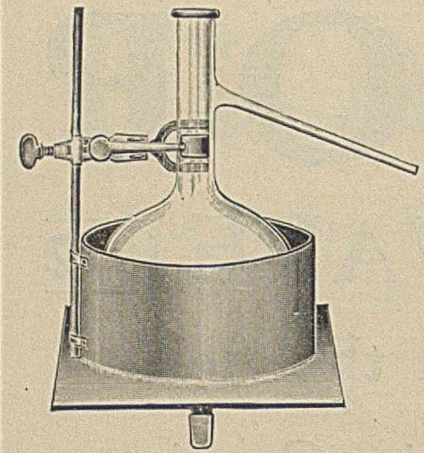
FERTILIZER MATERIALS.

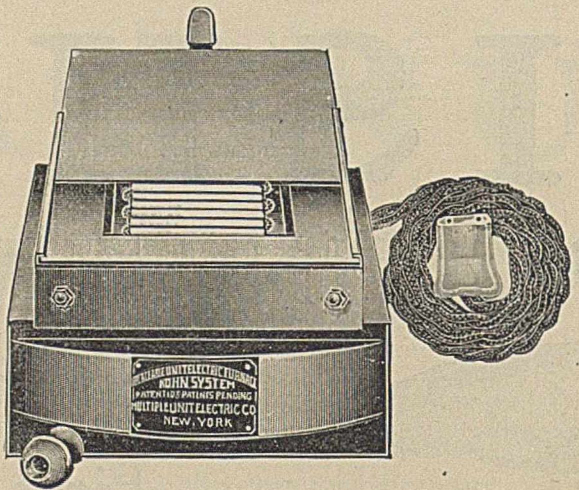
Ammonium Sulphate	C.	3.20	@	3.30
Fish Scrap, domestic, dried	Unit	2.45	&	10
Blood, dried	Unit	$2.72^{1}/_{2}$	@	2.75
Tankage, high grade	Unit	2.55	&	10
Bone, $4^{1}/_{2}$ and 50, ground, raw	Ton	27.00	@	—
Potassium, "muriate," basis 80%	Ton	38.55	@	—
Phosphate, acid, 16 per cent.	Ton	7.00	@	7.25
Phosphate rock; f. o. b. mine:				
Florida land pebble, 68 per cent.	Ton	3.70	@	3.80
Tennessee, 68–72 per cent.	Ton	4.25	@	4.50
Pyrites, furnace size, imported	Unit	$0.13^{1}/_{8}$	@	$0.13\ /_{4}$
Castor meal	Unit	nominal		
Mowrah meal	Ton	8.50	@	9.00

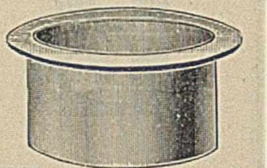












D. F. H. Combination

Indispensable in the Laboratory because it Combines in One Device

Flask Heater, Hot Plate, Oil Bath, Sand Bath, Water Bath

SEVERAL OF THE

MULTIPLE REPLACEABLE UNIT FURNACES

USED BY

Chemists, Metallurgists, Assayers, Steel Experts, Machinists, Jewelers, Scientists, Glass Workers, etc., etc.

IN

Chemical, Steel and Board of Health Laboratories, also in Chemical Industries and in Shops and Factories for all kinds of steel treatment and general heating work.

BECAUSE

Heating Unit is immediately replaceable.
Heat is discharged directly in the furnace chamber.
Replaceable Unit system gives heat just where needed and absolute temperature control.
Hence adaptability, reliability and utmost efficiency are obtained.
Special shapes and sizes for all purposes. Write.

Multiple Unit Electric Co.

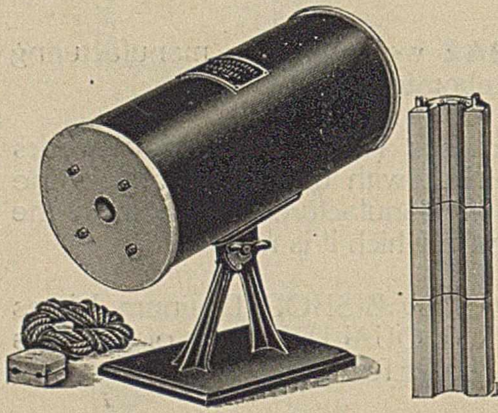
136 Liberty Street, New York

Standard goods carried in stock by

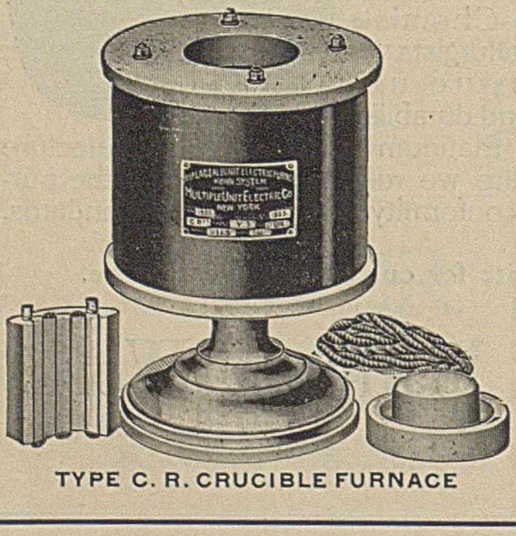
EIMER & AMEND
New York, N. Y.

ARTHUR H. THOMAS CO.
Philadelphia, Pa.

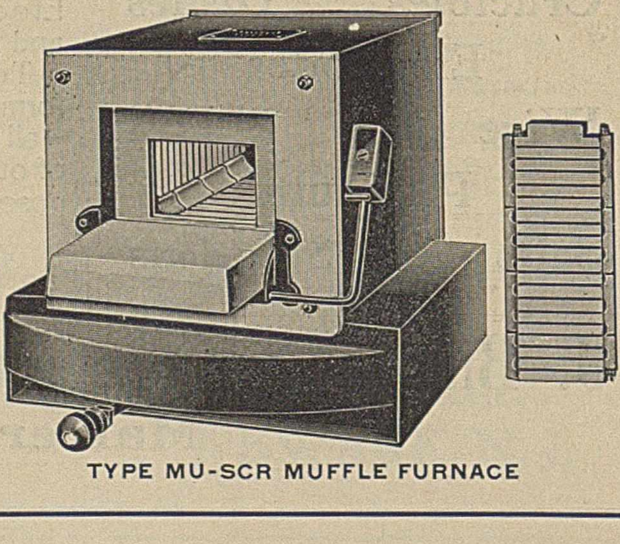
BAUSCH & LOMB OPTICAL CO., Rochester, N. Y.



TYPE CO COMBUSTION FURNACE



TYPE C. R. CRUCIBLE FURNACE

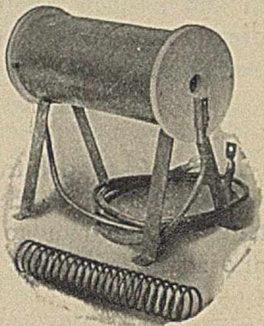


TYPE MU-SCR MUFFLE FURNACE

HOSKINS

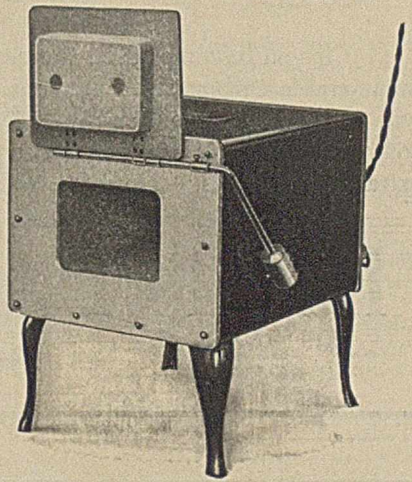
HOSKINS ELECTRIC LABORATORY FURNACES

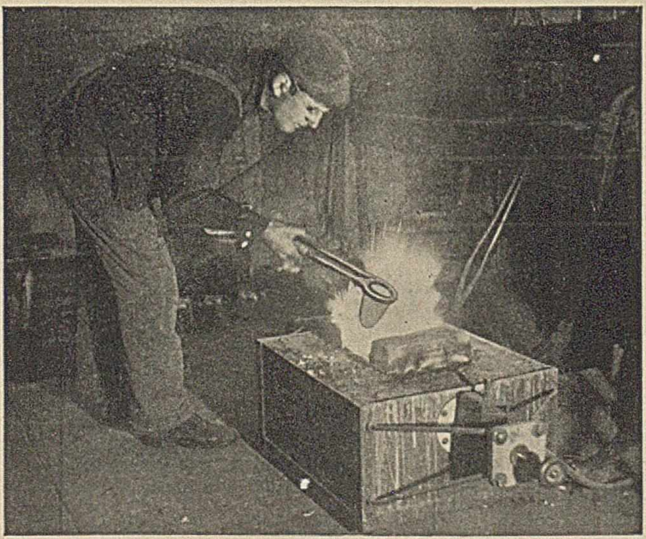
—have proved the superiority of electric heat and of themselves in all kinds of laboratories and in every section of the country. Their wide adaptability, high efficiency and all-round satisfactory service are indicated by, and are the reasons for their use in so many well known laboratories, a few of which are mentioned below. They offer the same advantages to your laboratory.



The United States Isthmian Canal Commission, U. S. Dept. of Commerce & Labor, American Sheet & Tin Plate Co., Henry Souther Engineering Co., and Carnegie Steel Co. are among the many users of Hoskins "Type FB" Combustion Tube Furnaces. Crucible, tube and muffle chamber designs of the "FB" type for working temperatures of 1100° C. (2000° F.) are supplied and all have heating units removable by the operator.

The United States Dept. of Agriculture, Swift & Co., Pillsbury Flour Mills Co., Milwaukee Coke & Gas Co., Borden Condensed Milk Co., Chicago Dept. of Public Works, Armour Grain Co., Iowa Dairy & Food Commission, Minnesota Grain Inspection Dept. and hundreds of others have Hoskins "Type FA" Muffle Furnaces like the one shown here. "Type FA" Furnaces produce working temperatures up to 1000° C. (1832° F.) and are made in muffle, crucible and tube chamber designs.





Taking a Crucible from the Hoskins "Type FC" Electric Furnace.

HOSKINS MANUFACTURING COMPANY

Electric—Furnaces, Pyrometers and Heating Appliances
"International" Ammeters and Voltmeters

449 Lawton Avenue, DETROIT.

Otis Bldg. CHICAGO
Oliver Bldg. PITTSBURGH.
30 Church St. NEW YORK.

The Consolidated Gas Company of New York in its Chemical Laboratory uses a Hoskins "Type FC" Crucible Furnace for determining the fusion points of coal ash. Massachusetts Institute of Technology, School of Mining at Kingston, Ont., University of California and University of Illinois are other users. Temperatures above 2000° C. (3600° F.) are readily obtained for melting metals, alloys fire brick and refractory materials.

This coupon is for your convenience. Tear off, sign and mail to nearest address, to-day.

HOSKINS MANUFACTURING COMPANY
449 Lawton Avenue, DETROIT.

Otis Bldg. CHICAGO.
Oliver Bldg. PITTSBURGH.
30 Church St. NEW YORK

You may send me full information concerning Hoskins Electric Furnace for..............................

....

(Kindly mention nature of work contemplated)

Name..............................

Position..............................

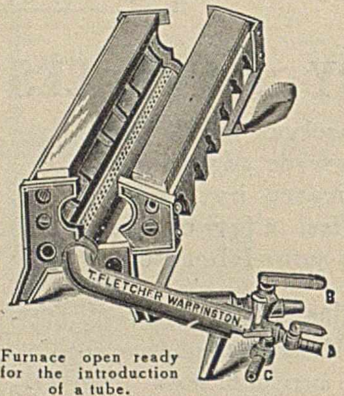
Firm..............................

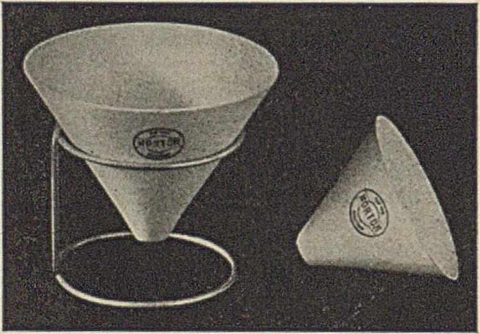
Address..............................

....

Jl. of I. & E. C.

359


T. FLETCHER WARRINGTON
B
B
C



These authorities cannot all be wrong in their endorsement of Titanium Alloy

Among them are numbered some of the world's leading chemists and metallurgists and men who are now using Titanium Alloy in their mills and foundries. Let them tell you why it pays to use Titanium Alloy

¶ "The combination of Titanium with nitrogen is attended with the evolution of heat. It is the *only* indisputable example of the combustion of an element in nitrogen."

—**Moissan,**
Celebrated French Chemist.

¶ "Titanium introduced as an alloy at once combines with the gaseous nitrogen present in the molten metal, forming a stable nitride. It is the formation of this stable nitride which prevents blowholes and thereby produces solid ingots or castings."

—**Dr. F. C Weber.**

¶ "The reducing agents last added to the bath, carbon, manganese and silicon, destroy to a certain extent the existing over-oxidation, but they are able to remove the final traces unsatisfactorily and with the greatest difficulty. This service must therefore be performed by a very powerful reducing agent, such as Titanium, which should be regarded as one of the best and most available."

—**E. von Maltitz,**
Formerly with Illinois Steel Co.

¶ "A hard steel with one per cent. carbon becomes fragile and useless when it contains 0.03 per cent. nitrogen, even when not tempered, and when tempered it will show numerous 'shakes' even when nitrogen is as low as 0.0116."

—**Dr. Hjalmar Braune.**

¶ "Titanium has one advantage which has caused its use to be recommended, namely, its high affinity for nitrogen."

—**Bradley Stoughton,**
Author "Metallurgy of Iron and Steel."

¶ "Titanium * * * has a stronger affinity for oxygen than have the other well-known deoxidizers; * * * it probably gives the slag such a consistency that it separates more completely from the molten iron."

—**Prof. Henry M. Howe,**
Author "Metallurgy of Steel."

¶ "The treatment of all steels with ferro-titanium for the purpose of the purification of the metal is strongly recommended, the presence of nitrogen to the extent of .02 or .045 or .035 in certain steels being enough to cause the metal to break asunder, destroying all elongation and reduction of area."

—**H. LeChatelier,**
Prof. of Metallurgy, University of France.

Titanium Alloy is as easy to use as silicon or manganese. Like any other alloy, however, it must be used properly to secure the best results. For instance, it should never be used with aluminum and should always be added before the slag begins to run.

In view of its high efficiency the low cost of Titanium Alloy is most remarkable. The cost of adding it to iron varies from 25c and upwards per gross ton. For steel, the cost ranges from 50c to about $3 per gross ton, depending upon the results desired.

Output of Titanium steel in 1910 was 326,300 gross tons. In 1911 the output increased to 410,600 gross tons.

¶ "We have lately been using Titanium in all of our castings and are getting results very much superior to those when this alloy is not used, particularly so in certain small pipe fittings and castings of this character which are subject to high pressure, and where the denseness of the metal is an important factor."

—**Keystone Steel Casting Co.,**
Chester, Pa.

¶ "The action of Titanium is to increase the strength of the mixture and to facilitate the throwing off of the impurities contained, and also to give a tougher and more durable chill."

—**New York Car Wheel Co.,**
Buffalo, N. Y.

¶ "We have just received reports from a test bar, having seven pounds of ferro-titanium to the ton, which pulled 90,000 pounds to the square inch with 28 per cent. elongation. The carbon in this steel was only .19. The castings in this heat were subject to specifications which called for tensile strength not less than 60,000 and not more than 70,000 pounds."

Strong Steel Foundry Co.,
Buffalo, N. Y.

¶ "We have taken steps to have Titanium Alloy used in our output of Transformer Boxes and Tanks, in order to secure the benefits of stronger and closer grained castings produced by the use of Titanium Alloy in cast iron, particularly as applied to this class of work where the requirements are so severe."

—**Pittsburg Transformer Co.**

¶ Tests made by the American Foundrymen's Association showed that the crushing strength of gray iron was increased 52% by the use of one-half of 1% of Titanium Alloy.

¶ Tests made by Professor M. Hokanson at the Carnegie Technical Schools demonstrate that the crushing strength of chilled iron is increased nearly 100% by the use of Titanium Alloy.

¶ In summation: Every claim made for Titanium Alloy has been proved in service, and is based upon the careful researches of Enrique Touceda, C. E., Rensselaer Polytechnic Institute; Charles McKenna, eminent metallurgist; E. von Maltitz, for five years with Illinois Steel Co.; Prof. Bradley Stoughton, late of Columbia University; Prof. John J. Porter, of the University of Cincinnati; Prof. Henry M. Howe, Author of "Metallurgy of Iron and Steel;" H. Le Chatelier, Prof. of Metallurgy, University of France; Auguste J. Rossi, M. E., C. E.—and many others.

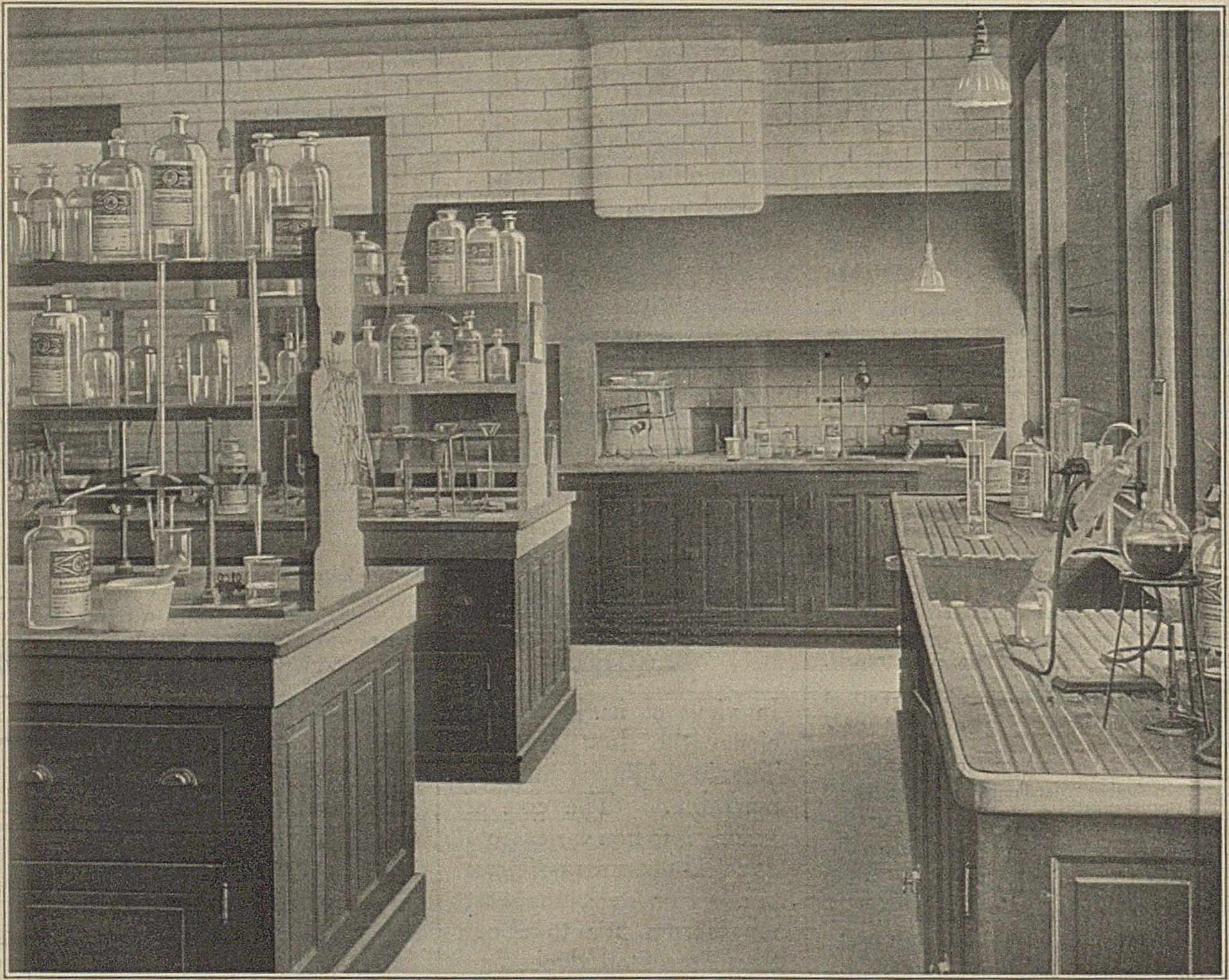
Ask for Booklet No. 33 and we will send literature explaining in detail the action of Titanium Alloy and how it can be used to your advantage. If you are particularly interested in rails, ask for rail diagrams showing superiority of Titanium Rails over plain open-hearth or Bessemer rails.

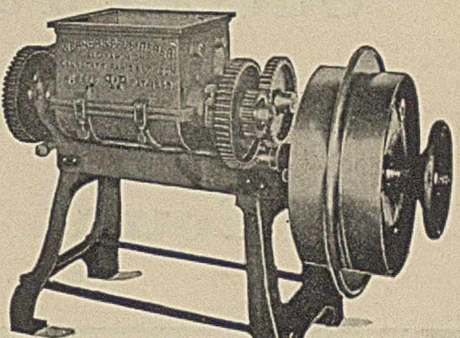
TITANIUM ALLOY MANUFACTURING COMPANY

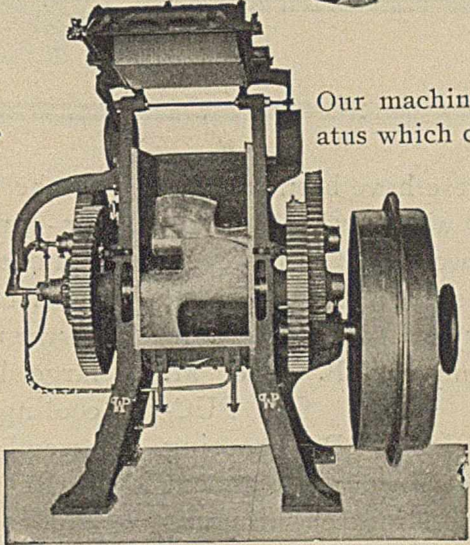
OPERATING UNDER ROSSI PATENTS
Pacific Coast Agents
ECCLES & SMITH CO.
Los Angeles, San Francisco and Portland
Canadian Agents
R. J. MERCUR & CO.
Montreal

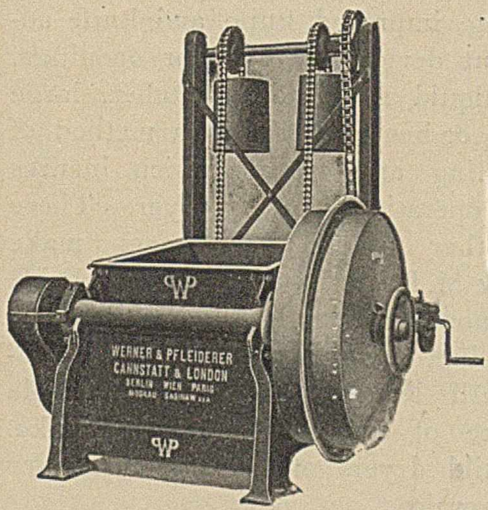
CHAS. V. SLOCUM
General Sales Agent
630-631-632 Oliver Bldg.
PITTSBURGH, PA.

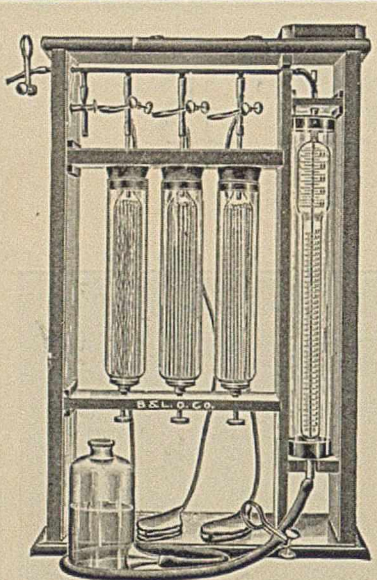
PROCESSES AND PRODUCTS FULLY PATENTED
H. H. COOK
District Agent
People's Gas Building, Chicago, Illinois
THE PRIMOS CHEMICAL CO.
Primos, Delaware County
Pennsylvania

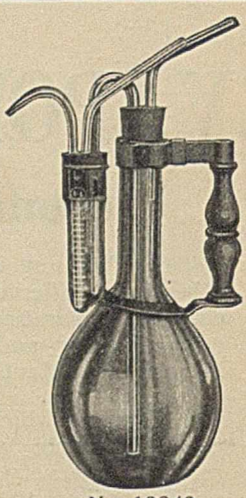




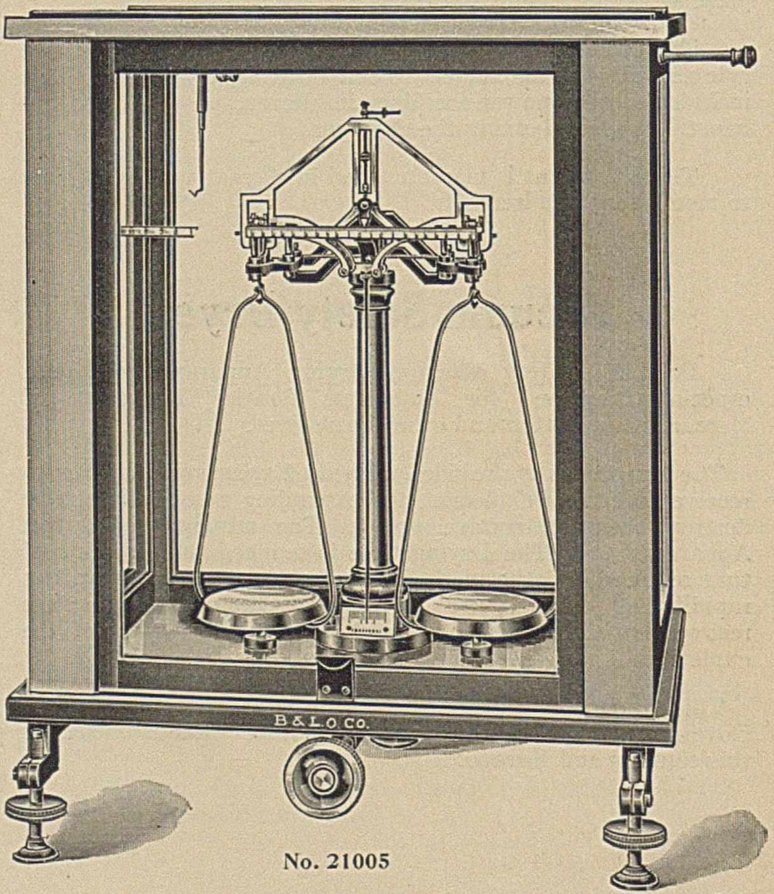



WERNER & PFLEIDERER
CANNSTATT & LONDON
BERLIN WIEN PARIS
MOSKAU SAGINAW U.S.A.

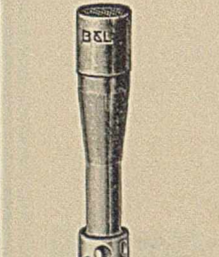




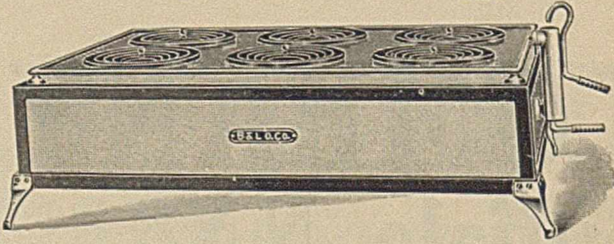
No. 19840



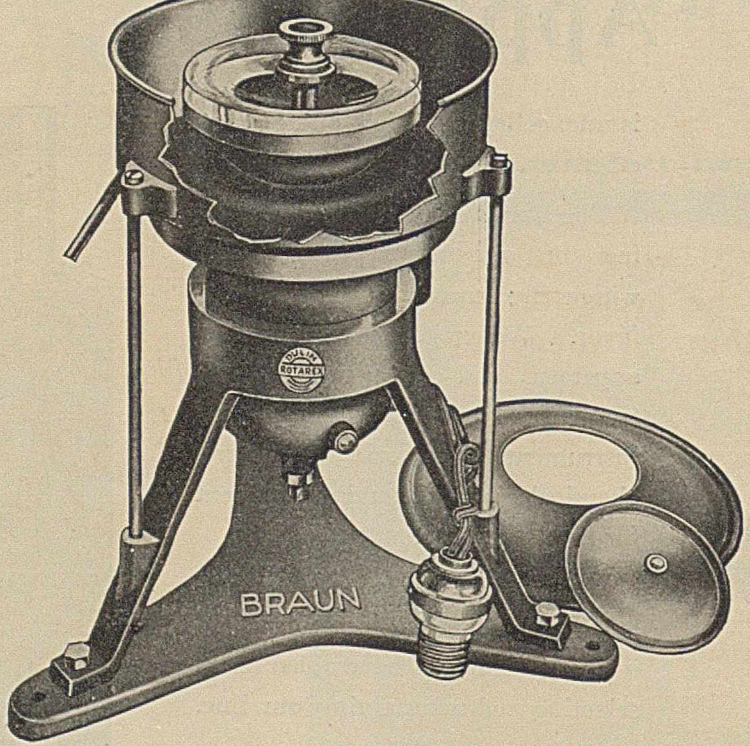
No. 21005

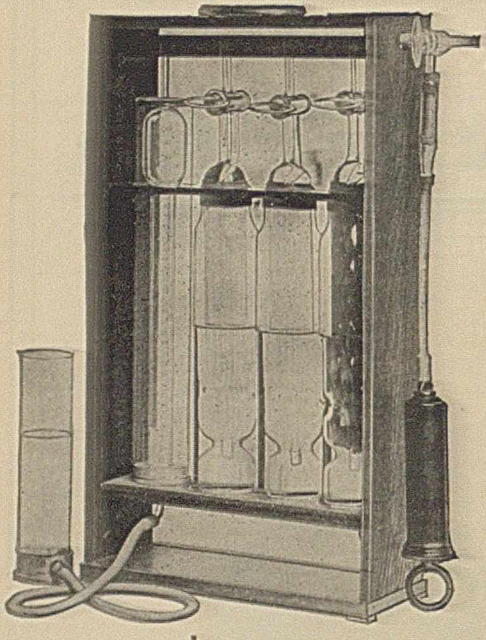


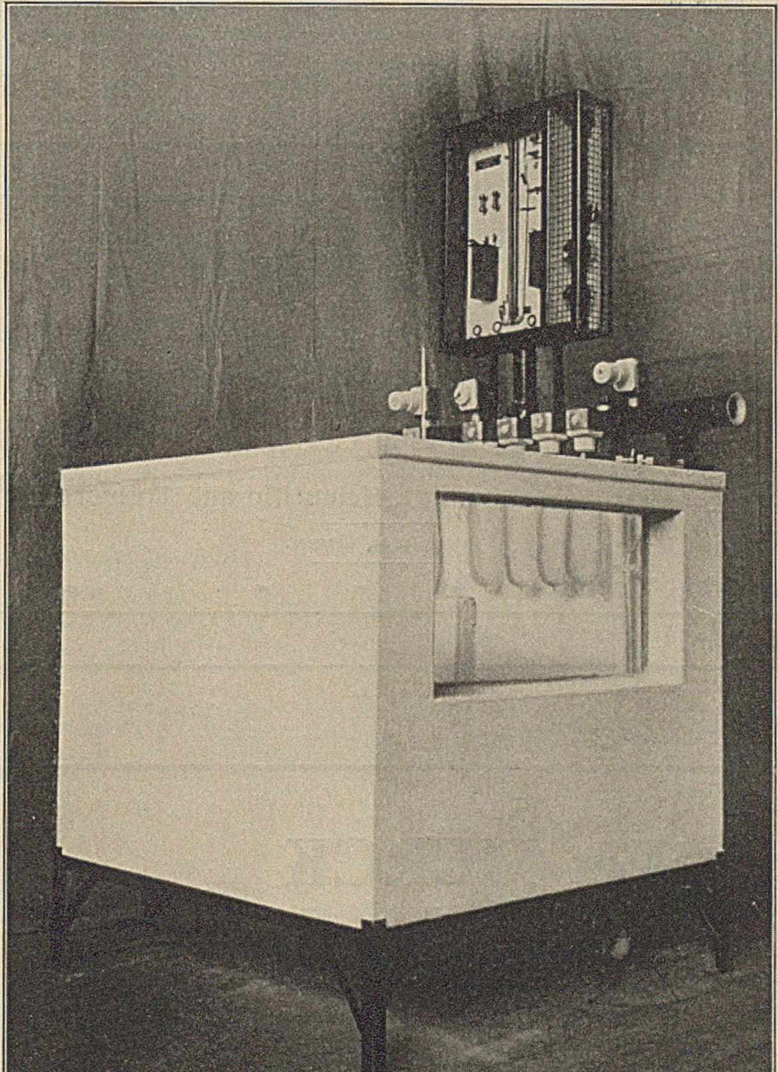
No. 19700

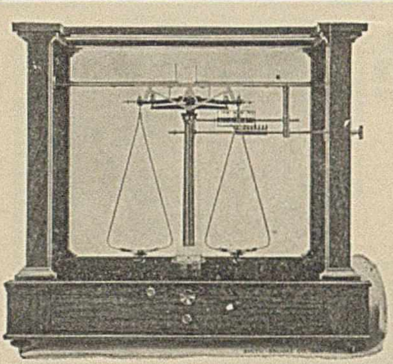


No. 19880


DULIN
ROTAREX
BRAUN

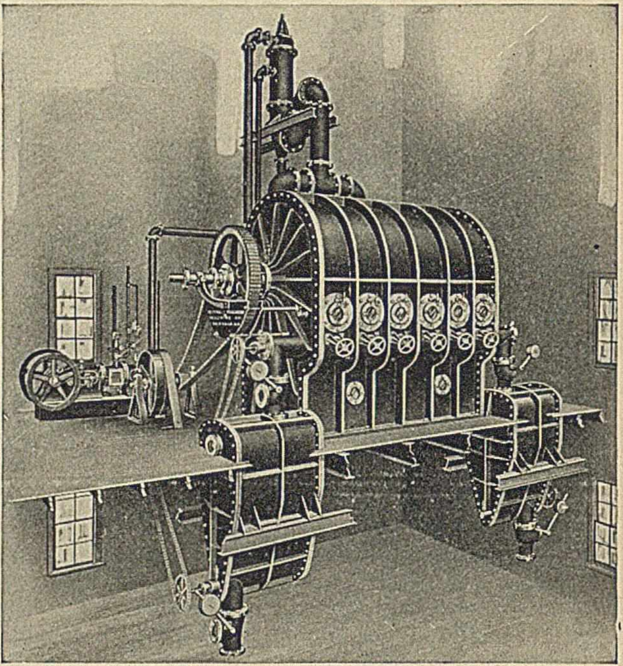






B. F. & M. Vacuum Dryers

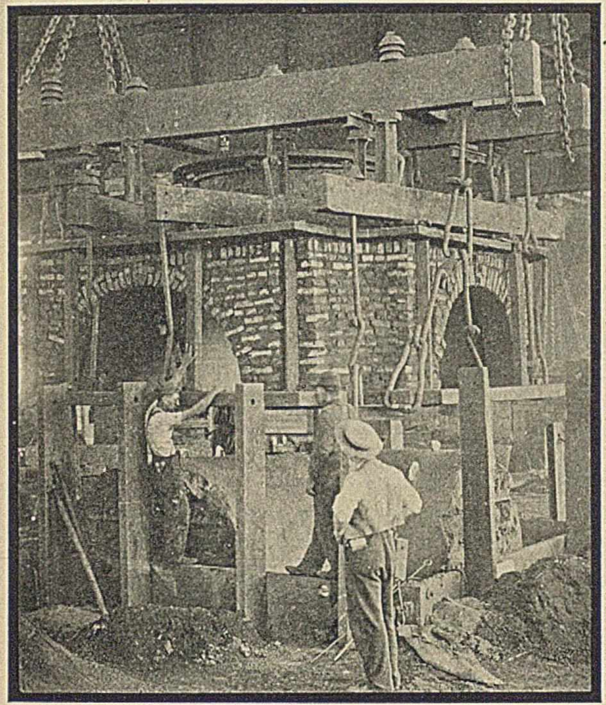
Only
Successful
Installations
Count



Unfortunately there have been vacuum dryer installations which were not successful. But they were not B. F. & M. Dryers. We can show a clear record of success for our dryers. Our record in this respect is unique. B. F. & M. Dryers hold the record for SUCCESSFUL installations. By choosing B. F. & M. apparatus your investment is safeguarded by a guarantee that means *absolute* safety.

B. F. & M. Vacuum Drum Dryers are an example of the "Highest Attainment in Vacuum Dryers." B. F. & M. Design offers distinctive advantages including an improved method of applying liquid to the drum, large working drum area, air-furnace metal drum, one-piece chamber, accessibility of interior for scouring, improved knife and knife adjustment device, large vapor openings, large liquid sealed dust catcher, large cooling or heating coils and a method of assembling and testing which insures perfect operation for every dryer. These and other unique advantages make B. F. & M. Drum Dryers unapproachable for economy in operation and excellence of product manufactured. Investigation will lead you to incontrovertible evidence of every assertion we make. We build dryers of various types for every service.

Large Castings for Chemical Work



Service,
the Keynote
of our
Product

The fact that we have one of the largest and best foundries in the country is directly due to the fact that for years we have been recognized as headquarters for the highest quality castings. Our product built our business. Facilities count heavily when it comes to handling 200-ton castings involving perhaps 600 tons of rigging in preparing the molds. Not only our ability to handle large work is of interest to users of chemical castings. The quality of the smallest as well as that of the largest casting we turn out is safeguarded at every step. We know exactly how metal should be treated for a given service, and by means of our laboratory and metallurgical staff we see that the proper treatment is actually used. A system of continuous, interlocking checks and counterchecks eliminates every possibility of defect in the finished product. Not even a dimension can go wrong.

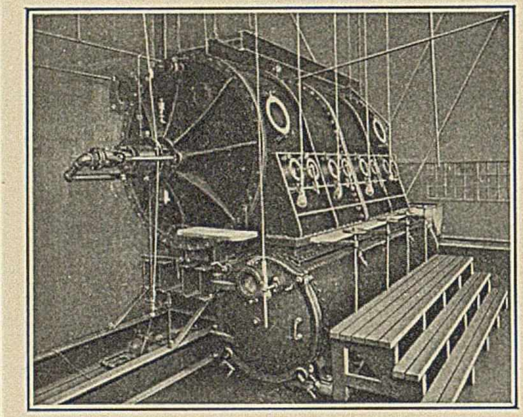
Evidence of the quality of our chemical castings is seen in the fact that users report from 3 to 5 times the service from ours as compared with those procurable anywhere else in the U. S. or abroad.

You buy service, not merely metal when you buy B. F. & M. Chemical Castings.

Buffalo Foundry & Machine Company, Buffalo, N. Y.

VACUUM DRYING AND EVAPORATING APPARATUS

Vacuum Drum Dryers



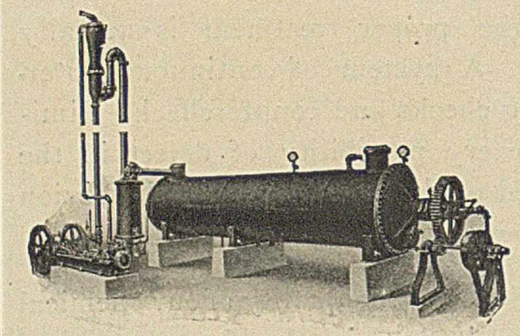
The Patented Vacuum Drum Dryer is especially adapted for the drying of Dyewood and Tannin extracts, albuminous substances, milk, eggs, vegetable and meat extracts and other food products.

The apparatus is equipped with patented device to prevent solution coming in contact with ends of drum or any portion of heating surface not in contact with scrapers; and other auxiliaries to prevent frothing and to insure a rapid and uniform drying without risk of spoiling or deteriorating the material being dried.

The advantages of the Vacuum Drum Dryer are automatic and continuous Drying; superiority of dried product by reason of rapidity of drying at low temperature and absence of air impurities; freedom from dust and elimination of danger to health of employees and destruction of property; a minimum cost of operation, including labor; the combination of evaporation and final drying in one operation.

Capacity and quality of dried product imitated, but never equalled.

Vacuum Rotary Dryer



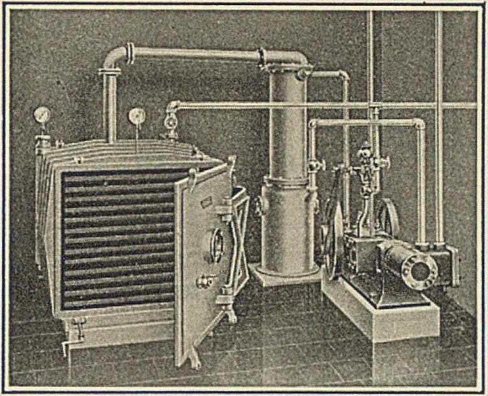
Rotary Vacuum Drying Apparatus for Granular substances, Starch, Dextrine, Cereals, Brewery and Distillery Grains, Fish Guano, by-products of chemical manufacture, etc.

Concentric with the steam jacketed shell is a revolving inside drum, heated by live or exhaust steam with stirring blades attached. The material being dried between inside drum and outside cylinder, every particle comes into close contact periodically with the heating surfaces and thereby effecting a very thorough and even drying process.

By means of a Special Device, small samples may be taken from time to time, without breaking vacuum. The dried material is discharged by its own gravity into sacks or a conveyor. If large quantities are to be dried continuous charging and discharging can be accomplished by a special automatic device.

The Apparatus is manufactured in a variety of sizes to meet every requirement.

Vacuum Chamber Dryers



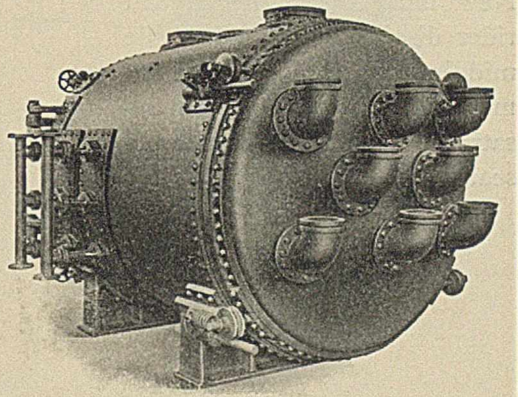
Our Vacuum Chamber Dryer is adapted for Aniline and other Dyes, Effervescent Salts and other chemical and pharmaceutical preparations and extracts, milk, chocolate and biscuits, Rubber and materials used in compounding, Fruit, Incandescent Mantles, Artificial Boards, etc.

Materials which are difficult to dry or cannot be dried in the atmosphere without decomposition have all moisture removed in a very short time without the least danger of impairing their character by overheating; if hot water be used, the evaporation of moisture contained in the materials takes place at as low a temperature as 63° F.

The consumption of steam is reduced to a minimum: as a rule 1.2 lbs. of steam suffices to evaporate 1 lb. of water. This includes motive power for Vacuum Pump, provided the exhaust is used for heating the chamber.

The Apparatus is manufactured in a great variety of sizes to meet every requirement.

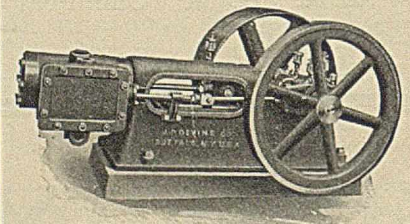
Vacuum Safety Dryer



Passburg Safety Vacuum Drying Apparatus has been especially designed for Smokeless Powder, Fulminate of Mercury, Gun Cotton and other Explosives.

The Apparatus is provided with an Expansion Chamber to receive, in case of explosion, the expanding gases and thereby destroy their destructive power. The advantages of this Apparatus are: The Drying time is reduced to a fraction of that required by othermethods; the solvents, notwithstanding rapidity of drying, are thoroughly eliminated; complete recovery of the solvent in closed vessels; the quality of the explosives is superior, more powerful and keeps better.

This Apparatus and System has been adopted by various Governments and by the leading private establishments in this country and Europe.



J. P. DEVINE COMPANY

428 Brisbane Bldg. Buffalo, N.Y.