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EDITORIALS

THE FUTURE OF SCIENTIFIC RESEARCH

For the last fifty years it has been assumed that the proper home for scientific research is the university, and that scientific discovery is one of the most important—if not the most important—function which a university can fulfill. In spite of this only a few of the American universities, which are admittedly among the best equipped and most energetic of the world, devote a very large portion of their energies to research work, while quite a number prefer to divert as little energy as possible from the business of teaching, which they regard as the primary function of the university.

This neglect of research work by the universities is generally deplored by leading scientific men, and one of the objects of the Committee of One Hundred on Scientific Research, appointed by the American Association for the Advancement of Science, is to assist the universities in increasing their facilities for research work and the inducements which they offer to young men to enter into it. But it seems that the time has come for us to consider the whole question of the relation of scientific research to the university; how far that relation will continue, and to what degree we may expect it to be modified in the near future. Looking back on the history of science we can perceive that so far as research work has been associated with institutions, it has always been because those institutions required the results of the research for the effective performance of their own essential duties; and that when the progress of science ceased to be an advantage to the other work of the institution, the furthering of that progress was abandoned.

The earliest scientific men were ecclesiastics, who regarded the knowledge which they derived from their inquiries as a means of developing the fullness of the religious belief both of themselves and of those whom they taught, and who felt that the opening up of the marvels of natural science was a fitting part of worship. As the advance of knowledge came to demand more and more modification of creeds and dogmas, so that the increase of knowledge, instead of being an advantage to any particular religious body, was a danger in that it might introduce dissention and doubt, the ecclesiastical world abandoned the pursuit of natural science, and the mantle which the church dropped fell upon the university.

The readiness of the university to accept the burden of being responsible for the advancement of knowledge was due essentially to the fact that the results obtained were immediately applicable to the purpose of teaching, and that, indeed, only by assiduous investigation and discovery could the facts of natural science be sufficiently correlated to make it possible to present them in orderly manner, so that they could be understood by the immature minds with which a university has to deal. This necessity for continual investigation on the part of a teacher was so marked, and the success of teachers who themselves were engaged in fresh investigation was so pronounced, that it was generally recognized that the best advanced training in science could be obtained only under a man who was himself actively engaged in promoting the science which he taught. But of recent years the advancing specialization of science and the complexity of each branch have made it more and more difficult for any but the specialists in that subject to appreciate or even to understand the work which is being done in its advancement until the new results obtained through the pushing forward of the ever advancing frontier of knowledge have been digested and brought into line with the general scheme of the subject; and as it becomes more difficult for the ordinary learner of a science to appreciate the work of those who are advancing the science, so the value of contact with those workers diminishes until now it is even thought by some that the ordinary scientific student is best taught by those who are specialists in teaching rather than specialists in research, and many of the university authorities are beginning to feel, even when they do not actively display, distrust of the research specialist in his capacity as a teacher.

It may be suggested then that there is a possibility that as the progress of scientific research lessened its usefulness to the ecclesiastical profession, so in a similar sense its further progress is beginning to lessen its usefulness to the teaching profession, and if this is so, then we may be sure that, however desirable for the community at large it may be for the progress to go on, yet the universities, whose primary and essential business is teaching, will feel less and less at liberty to divert energy from teaching to work which has no direct bearing upon their own chief function.

This view will, of course, be unwelcome to those who hold—as does the writer—that the progress of scientific research is the progress of the human race, and that the race or people or nation which devotes the most time and energy to the furtherance of research will itself be the leader in civilization. But, however important one may feel the progress of research to be, nothing can be gained by merely insisting that it shall be continued by institutions to whom its benefit is diminished, and our energies should, therefore, be directed towards the development of institutions which will prosecute scientific research because it in turn is of use to them as in the past it has been of use to the ecclesiastical and to the teaching professions.

In the case of the natural sciences the usefulness of investigation to the teacher still continues, so that in agriculture and biology and in such subjects as philosophy or psychology the universities are very active in advancing the frontiers of knowledge, but in the physical sciences this is much less the case, and it is for these sciences that some new form of institution, which is actively interested in the results, is required to supplement the activities of the universities.

Fortunately, it seems as if such an institution is already available and that we may hope before long to find new hands prepared to take up the responsibility for the execution of scientific research, as the universities may find it necessary to be relieved of it.

For many years the greatest gainers by the direct progress of scientific knowledge have been the manufacturing industries, and ever since their start they have been coquetting with the idea of advancing scientific progress directly, and of turning it into those directions which seem to be of immediate advantage to themselves.

When research laboratories were first started by industrial corporations the men employed in them were expected to confine their attention very strictly to the immediate requirements of the industry with which they were associated, and general investigation even of the general theory of the industry itself was discouraged, while publication of original work done in such a laboratory was regarded as almost out of the question. Wider experience, however, has shown that the more general the work done by the research laboratory, the greater are the results reaped by the industry likely to be, while the advantage to the worker of being allowed to publish any results of general, as opposed to technical, interest, has become so obvious that all the more important laboratories permit free publication of scientific papers. It seems likely that the proportion of purely scientific work done in the research laboratories will increase rapidly as the advantages of such fundamental theoretical work to industry become better known, and it would not seem too much to hope that before long the industries will devote themselves to scientific research with a definite enthusiasm and energy which must make them the predominant factors in the production of new knowledge. So that it would appear that it is to the industrial research laboratories that we must look in the future for progress in all branches of science which are affiliated in any way with manufacturing industries.

Organic chemistry has for some years been advanced largely through the work of men associated with industrial corporations; analytical chemistry shows every sign of following in the same path, while the other branches of chemical research are so closely associated with industry that they will be adequately provided for in the immediate future. In physics, electricity and optics are already directly associated with large and important industries maintaining adequate research laboratories, and the other branches of physics will surely be associated in due course with cognate industries.

It must be stated, however, that there are some branches of science—and these by no means the least important ones—which have so little direct relation to industry that the industrial laboratories will certainly neglect them to some extent, and it is for these branches of science, which may be termed the "nonpaying" ones, that special provision must be made.

The whole argument of this article is intended to show that only an institution which benefits by the knowledge which is developed can be expected adequately to provide for the furtherance of that knowledge, and if the industries do not directly profit by the advancement of some branches of science, and yet the progress of those branches is essential to the welfare of the people as a whole, it is the people as a whole that may be justly expected to provide for their advancement. This is already recognized in the case of some branches of science which have a more obvious and direct bearing on the general life of the community. Agriculture, forestry—even zoölogy in some of its phases, such as entomology and pisciculture—are already provided for by state or federal institutions, but new institutions are urgently required for theoretical physics, theoretical chemistry, mathematics and some other branches of physical science. Astronomy is provided for by private benefaction, provision for the means of obtaining knowledge about the universe at large having apparently been regarded by a number of wealthy men as a deserving object of charity. It would seem, therefore, that the energies of those who are interested in the furtherance of scientific research should be directed toward obtaining adequately staffed and equipped institutions for the prosecution of those sciences which have little direct relation to industry, leaving the furtherance of the branches of science directly associated with manufacturing processes to the industrial laboratories, which are now rapidly springing up to take their share in the advancement of knowledge.

C. E. Kenneth Mees

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ORIGINAL PAPERS

OZONE IN VENTILATION[1]

By J. C. Olsen and Wm. H. Ulrich

In spite of the fact that a great many investigations have been carried out in recent years on the effect of ozone on air bacteria and odors and also on the physiological effects of ozone, the most diverse conclusions have been reached and opinions expressed with reference to the questions investigated. This confusion is due somewhat to faulty scientific technique and deductions from improperly chosen experiments as well as *ex parte* point of view. The most recent criticisms against ozone in ventilation are found in two articles which were published in the issue of September 27, 1913, of the *Journal of the American Medical Association*, one by Jordan and Carlson and the other by Sawyer, Beckwith and Skolfield on the bactericidal, physiologic and deodorizing action of ozone. A number of errors in the methods used in the experiments given in these articles have been noted and these seem so serious and the articles have been so

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[1] Read at the 6th Semi-annual Meeting of the American Institute of Chemical Engineers, Troy, New York, June 17–20, 1914.

widely quoted that it seems desirable to correct the misapprehensions which have been produced. Both of these articles refer to the fact that exaggerated claims were made by agents selling ozone machines.

In the article by Jordan and Carlson, it is stated, on page 16, that the concentration of ozone is determined by drawing the ozonized air through a solution of potassium iodide which has been acidified with sulfuric acid. The liberated iodine is then titrated with thiosulfate solution. It is well known among chemists that an acidified solution of potassium iodide is readily oxidized by the ordinary oxygen of the air, and, therefore, if an acidified solution of potassium iodide is used for the determination of ozone, the results will be high. The amount of the error will vary with the concentration of the ozone and may easily give results double the true concentration of ozone. This error can easily be demonstrated by drawing air free from ozone through such an acidified solution of potassium iodide. It is evident, therefore, that no reliance can be placed on the figures given for the concentrations of ozone which are reported in this article. In the article by Sawyer, Beckwith and Skolfield, the concentrations of ozone were not determined.

It is universally recognized by ventilating engineers who are familiar with the use of ozone that it is of the greatest importance to regulate the concentration of the ozone and that ozone is useful only when employed in the proper concentration. This well known principle seems to have been so little understood by these investigators that they failed to make careful and accurate determinations of the concentrations of ozone used and therefore many of the conclusions which they reached are entirely vitiated.

Another very serious error in experimental procedure is found in the tests which were made on the effect of ozone on odorous substances. A considerable number of such substances were experimented with and the conclusion was reached that the ozone *masks* these odors but does not destroy them and that, therefore, ozone is not useful in the removal of such odors.

The method of procedure consisted in exposing the substance giving off the odor until a marked odor was noticed in the small closed room which was used for the experiments. The ozone machine was then operated until a strong odor of ozone was produced. Observations were made from time to time of the odor in the room and it was observed in a good many cases that the ozone odor gradually disappeared and the odor of the substance experimented upon returned. In some cases ozone was again generated until its odor was pronounced and observations again made with reference to the disappearance of the ozone odor and the reappearance of the odor of the substance experimented upon. The conclusion was drawn that the ozone did not destroy the substance giving the odor but masked it; this conclusion was based upon the disappearance of the ozone odor and the return of the other odor. No other evidence, whatever, on this point is presented.

In these experiments, no attempt seems to have been made to determine the amounts of the odorous substances which were present in the air except by the odor. The experimenters apparently did not consider the fact that the odors of substances differ a great deal in intensity and that the quantities of substances which would be present, even though the intensity of the odor was the same, would differ very much. These authors also failed to keep in mind that the destruction of odors by ozone is an oxidizing process and that this, as well as all chemical reactions, is quantitative in the sense that a definite amount of oxygen is required to oxidize a definite amount of an oxidizable substance.

The following reaction takes place when ozone oxidizes hydrogen sulfide:

$$H_2S + O_3 = H_2O + S + O_2$$

That is, 34 parts of hydrogen sulfide would require 48 parts of ozone for their oxidation. When the hydrogen sulfide is dissolved in water, the sulfur liberated is still further oxidized by the ozone to sulfuric acid which would require a still larger quantity of ozone, but according to the reaction given, a somewhat larger amount of ozone than hydrogen sulfide would be necessary for the destruction of this substance. Now, if the intensity of the ozone odor is much greater than that of the odor of hydrogen sulfide, the hydrogen sulfide would be oxidized by the ozone in the experiments reported by Jordan and Carlson and some other authors quoted, and the hydrogen sulfide odor would then return as reported by these investigators.

In order to verify these conclusions, experiments were carried out to ascertain the amount of hydrogen sulfide which will give a distinct odor. A large balloon flask of 30 liters capacity was used. The hydrogen sulfide was produced by treating known weights of carefully analyzed iron sulfide with dilute sulfuric acid. The reacting substances were placed on a watch crystal suspended in the center of the balloon flask. In addition to the odor, tests were made with lead acetate paper.

INTENSITY OF ODOR OF HYDROGEN SULFIDE

MG. H_2S PER CUBIC METER	TEST WITH LEAD ACETATE PAPER	ODOR
977	Very black	Very strong
244	Very black	Strong
61	Very black	Distinct
30	Turned black slowly	Fairly distinct
15	Brown on edges	Faint
7.6	Turned brown very slowly	No odor

While to obtain a distinct odor of hydrogen sulfide, 61 parts are required, the odor of ozone is very marked when present to the extent of one part per million, the limit being one-tenth part per million. In the experiments of Jordan and Carlson, the concentration of the hydrogen sulfide must have been from 30 to 60 mg. One part of ozone would have given a strong odor which could mask the odor of the hydrogen sulfide until, by the oxidation of the latter, the ozone was decomposed. Less than one part per million of the hydrogen sulfide would be destroyed by this oxidation, leaving a sufficient amount of hydrogen sulfide to give a very distinct odor. On again generating ozone until a strong ozone odor was obtained, the hydrogen sulfide would be again "masked," and when the ozone odor had disappeared the hydrogen sulfide odor would reappear. This could be done repeatedly as reported by Jordan and Carlson. The conclusion which they drew, however, is entirely unjustified, namely, that their experiments showed that the hydrogen sulfide odor was merely masked and hydrogen sulfide not oxidized or destroyed by the ozone.

In order to verify this conclusion, the following experiment was carried out: A concentration of 25 mg. of hydrogen sulfide was treated with ozone of a concentration of 35.6 mg. per liter. In these concentrations there would be just enough ozone to oxidize the hydrogen sulfide. In this experiment the ozone odor was at first very pronounced but after this odor had disappeared there was no hydrogen sulfide odor. A slight acidity was indicated by the reddening of blue litmus paper. The ozone used had been very carefully tested for nitrous oxides but none were found.

Another experiment was carried out in which the ozone concentration was 7.6 parts per million, while the hydrogen sulfide concentration was 60.7 mg. per cubic meter so that only a small part of the hydrogen sulfide could be oxidized by the ozone present. At first only the odor of the ozone could be detected. The hydrogen sulfide odor gradually returned so that within one hour a faint and after two hours a distinct hydrogen sulfide odor was detected while the ozone odor had entirely disappeared.

This experiment could be repeated three or four times, as reported by Jordan and Carlson on page 33 of their article. They further state: "The mechanism of this masking action of ozone does not concern us here." If the authors had considered the "mechanism" of this action, they might have reached entirely different conclusions and would have seen that their experiments were in exact accordance with the theory that ozone oxidizes hydrogen sulfide and other substances. They still further refer to the fatigue of the olfactory end-organs by the ozone. They say "Strong concentrations of ozone rapidly fatigue or anesthetize the olfactory epithelium." One wonders why the authors did not make this statement general and state what every chemist has frequently observed that *hydrogen sulfide* and the numerous other odors which are present in chemical laboratories produce the same effect on olfactory epithelium so that these odors are not noticed by workers in the laboratory.

Hydrogen sulfide is also oxidized by the air as is shown by the fact that the odor slowly disappeared in a duplicate experiment in the absence of ozone.

In some cases ozone acts as a catalytic agent. This was shown by the action of ozone on linseed oil. Weighed quantities of linseed oil were exposed to air and ozone. The oil exposed to air gained 17 mg. while an equal quantity exposed to the action of ozone gained 110 mg. during the same time. The amount of ozone generated was 11.4 mg. The ozone, therefore, acted as a catalytic agent, causing the absorption of 82 mg. of oxygen which is nearly five times as much oxygen as was absorbed by the oil exposed to air alone. It is reasonable to suppose that ozone would act as a catalytic agent and cause the oxidation of other oils and organic substances similar to linseed oil.

In the case of ammonia, the same considerations apply. Ammonia is oxidized by ozone in accordance with the following equation:

$$2NH_3 + 3O_3 = N_2 + 3H_2O + 3O_2$$

In this case, one part of ammonia is oxidized by about four parts of ozone. A study of the intensity of the odor of ammonia gave the following results:

INTENSITY OF THE ODOR OF AMMONIA

MG. NH_3 PER CUBIC METER	TEST WITH LITMUS PAPER	ODOR
1000	Turns blue readily	Strong
659	Turns blue slowly	Fairly strong
329	Turns blue slowly	Fairly strong
165	Turns blue very slowly	Fairly strong
82	Turns blue very slowly	Quite distinct
41	Turns blue on edges very slowly	Faint
21	Turns partially blue on edges very slowly	Very faint
10	No action	No odor

Experiments were carried out in which known amounts of ammonia were treated with definite amounts of ozone and the ammonia remaining was determined by absorption with sulfuric acid and nesslerizing. Ammonia is acted upon very slowly so that 24 hours were allowed for the reaction. The concentration of the ozone was 35.6 mg. and of the ammonia, 125 mg. per cubic meter. After 24 hours, 78 mg. of ammonia remained in the flask containing air and 75 mg. in the flask containing ozone. The quantity of ozone present was sufficient to oxidize 8$^1/_2$ mg. of ammonia per cubic meter. The experiment indicates some oxidation of ammonia by ozone. Erlandsen and Schwartz[1] state that their results showed no action of ozone on ammonia.

Experiments were also carried out to ascertain the intensity of the odor of oil of cloves. It was found that 66 mg. per cubic meter would give a strong odor. The amount of ozone necessary to oxidize oil of cloves cannot be calculated exactly but it would probably require several times more than an equal weight. On subjecting the oil of cloves vapor in a concentration of 36.6 mg. per cubic meter to the action of ozone of a concentration of 33 mg. per cubic meter, it was found that at first a distinct odor of ozone could be detected which gradually disappeared and was replaced by a sweet odor which had no resemblance to the strong odor of the oil of cloves. Very evidently the oil of cloves or one of its strong smelling constituents is oxidized, at least partially, so as to leave an organic compound having an entirely different odor. The flask was allowed to stand a total of 21 hours although the reaction was practically complete within 2 to 3 hours. The reaction did not seem to be entirely regular. The experiment was repeated several times and the formation of the sweet aromatic substance repeatedly observed but at times the odor of cloves persisted. Any excess of ozone was removed by shaking with 10 per cent ferrous sulfate solution. Control experiments were also made with a balloon flask containing oil of cloves and air only. Erlandsen and Schwartz have made a similar observation with respect to skatol and indol. They state that these substances are completely decomposed by ozone with the formation of pleasant smelling substances similar to coumarin. They also state that mercaptan is rapidly decomposed by a large excess of ozone. These authors also found that hydrogen sulfide is oxidized by ozone. Jordan

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[1] *Zeit. of Hyg.*, **1913**, pp. 81–100.

and Carlson also mention the work of Erlandsen and Schwartz but state that the results of the latter agree with those of Jordan and Carlson in showing that ozone *masks* odors and does not oxidize the substances discussed. Jordan and Carlson even state that "The inability of ozone to oxidize (to any appreciable extent) ammonia vapor and oil of cloves is very striking." Franklin gives the results of experiments showing the oxidation of a great many organic substances and demonstrated that carbon monoxide is oxidized to carbon dioxide.[1]

Undoubtedly many of the conflicting conclusions which have been reached are due to the failure of experimenters to take into account the quantitative relations between ozone and the substances to be oxidized and have generally failed to realize that on account of the much greater intensity of the odor of ozone than that of other substances producing odor far too little ozone has been employed in the experiments. The odor of ozone is at least 100 times as intense as that of other substances having a pronounced odor.

The common method of using ozone to destroy odors seems to be justified by these considerations. The ozone machines in good practice are operated so that a very small concentration of ozone in the air is produced. The continued renewal of this small amount of ozone oxidizes the odorous substances and gives the total quantity of ozone required by chemical theory.

Jordan and Carlson undertook to prove that ozone does not destroy smoke by coating a piece of glazed paper uniformly with a thin film of lampblack and subjecting the carbon to the action of ozone for 10 hours and state that there was no effect on the lampblack. They regard this as evidence that ozone does not destroy smoke although they state that smoke also contains carbon monoxide, sulfurous acid, etc. They seem to have made no attempt to study the effect of ozone on carbon monoxide and sulfurous acid but state that the assertion that "ozone destroys smoke" is equivalent to a deliberate deception because ozone does not oxidize carbon particles suspended in the air. Not being chemists, Jordan and Carlson might not have known that carbon is extremely difficult to oxidize but they should have known that carbon monoxide and sulfurous acid as well as creosote and other pungent and aromatic organic substances present in smoke produce disagreeable and toxic physiological effects. It is just these constituents of smoke which are easily oxidized by ozone. The carbon which is not acted upon is totally inert and harmless.

Jordan and Carlson also carried out investigations on the action of ozone on air bacteria. As has already been stated, their determinations of the concentration of ozone cannot be relied upon because acidified solutions of potassium iodide were used which give high results. The authors admit that the plate method which they used was not an exact one and that therefore the results were irregular. They obtained a reduction of bacteria from 64 to 38, 49 to 18, 61 to 67 (increase), 78 to 34; that is, the bacteria were reduced to 40.6 per cent, 63.3 per cent and 56.4 per cent in three tests, while in the fourth there was an increase to 109.8 per cent. Most authors would discard the fourth test and consider the reduction to be about 55 per cent. Jordan and Carlson then tried Winslow's more exact method but did not use a large enough sample for the test (4.5 liters) so that the highest number of bacteria counted was 7. It is not good practice in bacteriological work to rely on counts of so small a number. Jordan and Carlson draw the following strange conclusion from their results:

"2—The alleged effect of ozone on the ordinary air bacteria, if it occurs at all, is slight and irregular even when amounts of ozone far beyond the limit of human physiological tolerance are employed."

There is no reason to suppose that the ozone used in these experiments was "Far beyond the limit of human physiological tolerance." The reduction in the number of air bacteria is not "slight and irregular." The experimental results of Jordan and Carlson agree with the results obtained by one of us[1] in New York school rooms showing a reduction in air bacteria and moulds of 75 per cent, 91 per cent and 91 per cent, the greater reduction resulting from longer exposure to ozone. No ill effects were observed on the children and adults present during these tests.

Jordan and Carlson (p. 34) state: "Some bacteria are undoubtedly killed by ozone, especially if they are in a moist condition." This statement is correct as it is generally recognized that ozone destroys moist bacteria very rapidly. The conclusion drawn by Jordan and Carlson is very far from being correct. They say: "In practice, however, the fact is of very slight importance." The works of Chapin, Doty and of Winslow and Robinson have fairly disproven the belief held so long that bacteria existed as a menace in rebreathed air. It has been shown that infection occurs but rarely from air-born bacteria and then only when the *bacteria are in the moist condition.* It is just these virulent bacteria which are quickly destroyed by ozone even in low concentrations. The bacteria which resist the ozone are powerless to transmit disease.

It is by no means necessary to show that ozone is capable of sterilizing the air in order to show that it is useful in ventilation. There is in fact no other disinfectant which can be used even in low concentrations in living rooms. All other known disinfectants are highly dangerous in concentrations high enough to be at all effective. Ozone in low concentrations will both remove odors and will materially reduce the bacteria content of the air.

Jordan and Carlson attempted to show that ozone is dangerous by subjecting guinea pigs to high concentrations until the animals died. They also forced strong ozone (10 parts per million) directly into the lungs of dogs and rabbits after performing tracheotomy under ether and inserting a tube well below the larynx and treating the wound with cocaine. They say they did this because at least three-fourths of the ozone is decomposed by the mucous membrane of the respiratory

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[1] *Heating and Ventilating Magazine*, **10**, No. 11.

[1] "Purification of Air and Water by Means of Ozone," Olsen, Fourth International Congress of School Hygiene.

passages. It is difficult to see what bearing this experiment can have on the use of ozone in ventilation. The ozone which was forced into the lungs must have been several hundred times as concentrated as it is ever used in ventilation. It would have been quite as logical to place animals in pure oxygen or even in an atmosphere of 50 per cent oxygen and also force these gases directly into the lungs. When the animals died and the lungs were found to be inflamed, the conclusion might be drawn by highly academic experimenters that it is dangerous to breathe air containing 20 per cent oxygen.

Jordan and Carlson carried out experiments with what might be called low concentrations of ozone. They subjected 4 cats, 4 rabbits, 6 guinea pigs and 12 rats to ozone of 1 part per million nine hours daily during two weeks so that irritation of the eyes and nose was produced. Body weight, appetite and general condition were noted. No ill effects on appetite and body weight or general condition could be observed. The conclusion could, therefore, be drawn that ozone in moderate concentrations is harmless but Jordan and Carlson warn us that this conclusion is not justified.

They say: "We desire to state, however, that this test does not warrant the conclusion that the ozone in concentrations that may be used in practical ventilation is harmless to man. Two weeks is a short time in the life of a man. If ozone in ventilation should come into general use, it would mean in the case of office and shop workers exposure to ozone from six to ten hours a day, six days of the week, from nine to twelve months of the year for from twenty to fifty years. And even if this prolonged exposure to ozone should prove harmless to the robust person, what about the unfortunate person whose lungs have only slight power of resistance?"

Jordan and Carlson seem to have fallen into the error of assuming that because they have not tried to, and therefore have not demonstrated actually, benefit from the use of ozone, this is equivalent to having demonstrated the reverse, *i. e.*, the harmfulness of ozone.

If the facts presented in this paper are properly interpreted they will be found to be in accordance with the view that ozone is a powerful disinfectant and deodorizing substance, which, in suitable concentration, is without any injurious effects whatever. The elimination of odor is by no means the least important function of ozone and there is no other agency available except dilution with fresh air. In many cases it is impossible to introduce enough air for this purpose without producing annoying and dangerous drafts of air not to mention expense of blower installation and operation as well as heating the air. As a matter of fact, before ozone was available, disagreeable odors have often been considered unavoidable nuisances which could not be eliminated or overcome.

With reference to the alleged harmful effects of ozone, no single instance of harm to a person from the proper use of ozone in ventilation has been published but all adverse opinions have been deduced, by inference, as in the paper by Jordan and Carlson, from experiments performed with very high concentrations while all efforts to produce harm experimentally with weak ozone have failed.

Jordan and Carlson report that twenty-six animals, exposed for fourteen days, during nine hours each day, to concentrations high enough to cause irritation of the eyes and nose, suffered no ill effect whatever. Hill cites the cases of the numerous workers in the London underground tubes who have shown no ill effect in three years. Gminder cites the unharmed workers in the spinning mills at Reutlingen, and numerous similar instances of prolonged proper use of ozone without a single complaint are today in existence. The Jordan and Carlson report is the most elaborate and convincing laboratory test that has been published.

Polytechnic Institute, Brooklyn

THE FLUORESCENCE OF PETROLEUM DISTILLATES[1]

By Benjamin T. Brooks and Raymond F. Bacon

Fluorescence is one of the most striking characteristics of petroleum distillates but its cause is not known, at least some of our best authorities attribute it to causes which have nothing to do with the phenomenon. The heavier distillates from Pennsylvania and certain other crude petroleums have a marked greenish fluorescence, and the trade has come to associate this property with Pennsylvania oils. For some uses it is common practice to "debloom" the oils by sun-bleaching or by the addition of certain "deblooming" substances. The subject therefore has some practical as well as theoretical interest.[2]

Engler considers that the fluorescence of mineral oils is due to their colloidal character. Crude oils and the heavier distillates are optically nonhomogeneous and show a marked Tyndall effect, but this property cannot be considered as indicating colloidal properties since many organic compounds having large molecular weights show the Tyndall effect when in true solution. Schneider and Just[3] claim to have observed ultramicroscopic particles in a "yellow mineral oil" and a sample of "paraffin oil." Holde,[4] studying the physical condition of lime soaps in grease, stated that colloidal particles are not discernible as such under the microscope. It is probable, however, from the researches of Holde that such greases, as well as oils containing asphaltic or resinous matter, are to be regarded as colloidal, not *true* solutions. Schulz[5] claimed that the effect of adding "deblooming" substances, such as nitrobenzol and nitronaphthol, was merely that of adding something having a high refractive index, thus making the oil optically homogeneous.

This theory of the fluorescence of mineral oils seemed very plausible. However, since many examples of nonfluorescent oleo-resinous solutions and mixtures

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[1] Presented at the 49th Meeting of the American Chemical Society, Cincinnati, April 6–10, 1914.

[2] Cf. "Relations between Physical Properties and Constitution," Kayser, "Handbuch d. Spectroscopie," Vol. IV, p. 839; Kauffmann, "Beziehungen zw. Fluoreszenz u. Chem. Konstitution," *Samml. Chem. u. Chem.-techn. Vorträge*, **11**, 1906.

[3] *Z. f. wissensch. Mikroscopie*, **1905**, p. 489.

[4] *Z. f. angew. Chem.*, **31** (1908), 2138; *Koll. Ztschr.*, **3** (1908), 270.

[5] *Petrol. Berl.*, **5**, 205.

are known and since the fluorescence of mineral oils persists after repeated distillation and is quite marked in distillates boiling as low as 200° C., we believed that resinous or asphaltic matter could not be a contributing factor. Our experiments have shown that, in general, oxidizing agents partially or wholly destroyed the fluorescence. Certain facts suggested to us that sulfur or carbon in colloidal suspension might be the cause of the phenomenon. Stable colloidal suspensions of carbon, in water and various organic liquids, have been prepared[1] and described as nonfluorescent and brown to black in color. Sulfur, on the other hand, often shows bluish colors when in colloidal degree of dispersion and the blue color of ultramarine blue is undoubtedly caused by so-called colloidal sulfur.[2]

We have succeeded in proving that colloidal suspensions have nothing to do with the fluorescence of mineral oils.

Working on the theory that ultramicroscopic particles were present, 100 cc. of a highly fluorescent lubricating oil were diluted with kerosene to about 500 cc. in order to decrease the viscosity. The solution was placed in a suitable cell containing two round copper plates spaced 2 cm. apart. The oil between the plates was subjected to a unit direction field of 30,000 volts potential difference for thirty minutes without any visible change in the fluorescence or flocking out of any kind of substance.

A sample of the same solution, carefully dried by calcium chloride, was filtered through the finest filter paper and examined under an ultramicroscope of the Zsigmondy-Siedentopf type but no particles whatever were visible. It was found that unless the oil was carefully dried and filtered, particles were visible in the light cone. These may have been minute drops of water or dust. The fact that the ultraviolet light cone is made visible to the eye with bright fluorescence has no significance so far as the colloid theory is concerned since as a general rule the wave length of the emitted fluorescent light is always greater than the incident ray, in this case from ultraviolet to visible blue. Furthermore, the ultraviolet cone contains a certain amount of the visible rays. No more rigid proof of the nonexistence of substances in colloidal suspension in carefully purified fluorescent mineral oil, could be desired. In order, further, to test the arrangement and efficiency of our instrument, a colloidal gold "solution" was made by the formaldehyde reduction method, one of platinum by the Bredig method, and one of palladium by reducing with hydrogen according to Paal, and the beautiful results characteristic of this instrument were obtained.

Percolation through Fuller's earth is an excellent and well known method for clarifying and bleaching oils. A sample of a highly fluorescent lubricating oil was allowed to run through a five foot tube packed with fine Fuller's earth. The resulting oil was very light in color but highly fluorescent and when a little tarry matter, which gave brown nonfluorescent solutions in kerosene, was added to the oil until the color matched the original oil, the two could not be distinguished. The fluorescent material is therefore only slightly absorbed by Fuller's earth and is probably not of very great molecular complexity.

While working on the colloidal suspension theory, the marked solubility of sulfur in mineral oils was noted. A 200 cc. sample of a light machine oil was heated to 100° C. with an excess of flowers of sulfur, filtered hot, and on cooling about 0.5 gram of sulfur crystallized out. Guiselin[1] states that benzine dissolves 0.5 per cent sulfur at 20° C. It is extremely improbable that a *stable* colloidal suspension could exist in which the solubility of one phase in the other is as great as in the case of sulfur and petroleum oils.

Carbon disulfide added to a fluorescent lubricating oil weakens the fluorescence almost to the point of extinction; what remains is dark greenish. Before making the experiments with the ultramicroscope, this was thought to favor the sulfur suspension theory, or the theory of Schulz based on optical homogeneity.[2]

Further experiments with other solvents showed that the character of the fluorescence was affected by the various common solvents in the same way as in the case of the diamino derivatives of terephthalic acid methyl esters, studied by Kauffmann.[3] The effect of the various solvents was even more marked with solutions of the purified fluorescent material described below. The fluorescence colors observed were as follows:

Amyl alcohol	Brilliant sky-blue
Aniline	Very faint green, no blue
Benzol	Pure clear blue
Carbon bisulfide	Faint green, no blue
Chloroform	Bluish green, passing into green on concentrating
Ether	Clear blue
Ligroin	Blue
Phenol	Greenish blue
Pyridine	Bluish green

In most cases the addition of *small* amounts of solvents having high refractive indices has practically no effect on the fluorescence. The effect of adding nitro compounds therefore must have an explanation different from that offered by Schulz.

The introduction of a nitro group into the molecule of a fluorescent benzol derivative, such as the terephthalic esters, completely destroys its fluorescence. It appears that a nitro group in the solvent has the same effect as a nitro group in the molecule of the active compound itself. This is not surprising in view of the marked effect of other solvents. We believed that possibly the fluorescent substance in mineral oil owed this property chiefly to the presence of one or more amino groups as auxochromes but, as will be shown below, this cannot be the case. Although we have found that oxidizing agents destroy the fluorescence, it is probable that the action of nitro compounds is purely physical since we have added N_2O_4, nitrated kerosene or nitrobenzol to fluorescent lubricating oils chilled to —10° C. and destroyed the fluorescence. It is highly improbable that oxidation of any hydrocarbons could take place under these conditions since

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[1] Thomae, *Koll. Ztschr.*, **11** (1912), 268; Vanzetti, *Koll. Ztschr.*, **13** (1913), 6.

[2] Liesegang, *Koll. Ztschr.*, **7** (1910), 307; Hoffmann, *Chem. Ztg.*, **1910**, p. 1079.

[1] *Petroleum*, **1913**, p. 1309.

[2] The refractive index of carbon bisulfide is $N_{D-20°}$ —1.6276.

Ann. d. Chem. (Liebig), **393** (1912), 1.

at 0° C., N_2O_4 merely adds on to ethylene bonds without oxidation.[1] There is also the possibility that such compounds as picric acid and nitrobenzol form non-fluorescent addition products, or double compounds, such as is the case with pyrene and chrysene. However, the simple nitro paraffines are not known to form such double compounds and "nitro kerosene" is fully as efficacious as nitrobenzol for neutralizing fluorescence. The following experiment is interesting in this connection: A sample of a highly fluorescent lubricating oil was "debloomed" by the addition of nitrobenzol. This oil was then shaken out six times with one-half its volume of 96 per cent alcohol, after which treatment the blue fluorescence had reappeared and exactly matched a sample of the same oil not treated with nitrobenzol, but shaken out with alcohol in the same way as the first sample. Refining such a "debloomed" oil with sulfuric acid yields a fluorescent oil identical in this respect with that obtained by refining the original oil. The action of nitro compounds in neutralizing fluorescence must therefore be purely physical in character.

The fact that exposure to the atmosphere for some time partially destroys and changes the character of the fluorescence suggested that what took place during this process was slow autoxidation.

Nitrous acid readily neutralized the fluorescence of lubricating oils, but the oils gradually became dark colored and resinous. Distillation of the latter dark colored oil *in vacuo* or with superheated steam yielded oil having a bluish fluorescence. Repeated washing with alkali removes only a small part of the coloring matter. Shaking a part of a sample of pale engine oil with nitrous acid for three minutes, followed by washing with water and filtering through Fuller's earth, gave a less resinous, light colored oil, very similar to that obtained by sun-bleaching. Oxides of nitrogen, generated by the action of dilute nitric acid on a metal, were then tried and it was found that the sun-bleached oil could be matched, with respect to color and fluorescence, provided the temperature of the oil was not permitted to rise above 10° C., before washing with dilute alkali. At low temperatures addition of oxides of nitrogen to unsaturated compounds probably results as shown by Jegorow. Unless the oil is chilled before passing in the oxides of nitrogen, oxidation appears to result, accompanied by rise in temperature, darkening in color and formation of resinous material. No method of removing the resinous coloring matter without at least partially restoring the bluish fluorescence was found. The effect, on the color of the oil, of nitric acid in sulfuric acid when used for refining is well known and constitutes one of the advantages of acid made by the contact process over that made by the chamber method.

We then made a series of experiments to determine the chemical properties of the fluorescent substance. The efficiency of sulfuric acid, particularly fuming acid, in removing fluorescence is well known. It was found that the wash water from freshly prepared acid sludge tar, made by refining lubricating stock, was highly fluorescent. This suggested that the fluorescent material formed water-soluble sulfonic acids, or that the fluorescent substance was a base and removed as a soluble sulfate. The latter hypothesis can hardly be true since dilute acids do not extract the fluorescent material from the oil. A quantity of such fluorescent aqueous solution was made alkaline and extracted with ether but no fluorescent material was obtained indicating that the substance in question is not a base. A dilute acid solution of the fluorescent substance was nearly neutralized with lime to remove the excess of sulfuric acid. The filtered aqueous solution was evaporated nearly to dryness and the crystalline residue, containing sulfate of lime, extracted with alcohol. Twelve liters of lubricating distillate yielded, in this way, about 1 gram of an impure crystalline residue which was intensely fluorescent when dissolved in the different solvents named above. The amount obtained was too small to be thoroughly investigated, but we hope that we shall have an opportunity in the near future to prepare a quantity of this highly interesting material sufficient for further work. The above results were enough to show the general character of the substance. The crude fluorescent substance probably contains one or more compounds of the benzene series resembling or perhaps identical with chrysene, fluorene or pyrene. Such compounds are known to be formed by the pyrogenic decomposition of many organic substances. Klaudy and Fink, in 1900, isolated a yellow crystalline substance, giving highly fluorescent solutions from the residuum of a cracking still. They give it the formula $C_{24}H_{18}$.

A large proportion of the fluorescent substance or substances is formed during the distillation of the crude. This was shown by distilling a sample of Oklahoma crude at atmospheric pressure and under a pressure of 5 mm. of mercury. The distillates in the first series were very much more fluorescent than the latter. This is also true of the distillates from coal when distilled at atmospheric pressure and under a pressure of 5 mm. Parallel with this difference it should be noted that substances of the benzol series form a much greater proportion of the coal tar obtained at ordinary pressures, paraffines and olefines constituting over 80 per cent of the coal tar obtained by distilling *in vacuo*.[1] It is also well known that no fluorescent substances are known belonging to the paraffin series.

Halogenation destroys the fluorescence, as is to be expected. Hydrogenation also destroys it.

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THE MANUFACTURE OF ETHYL ALCOHOL FROM WOOD WASTE—PRELIMINARY EXPERIMENTS ON THE HYDROLYSIS OF WHITE SPRUCE[2]

By F. W. Kressmann

THE PRESENT VALUE OF WOOD WASTE

The value for most of the wood waste produced today is limited to its fuel value for the production of power at the mill. In some cases, methods of closer utilization have been worked out, but compared with the

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[1] Jegorow, *J. prakt. Chem.*, **86** (1912), 512.

[1] Jones and Wheeler, *J. Chem. Soc. (London)*, **1914**, 140.

[2] Presented at the 49th Meeting of the American Chemical Society, Cincinnati, April 6–10, 1914.

total amount of wood waste produced, the amount of material so utilized is almost negligible. Furthermore, most of the large lumber mills produce waste greatly in excess of the amount necessary for power production and the waste burners are still in use, involving not only a loss of large amounts of wood, but also a definite fixed charge to get rid of it. The utilization of this material is limited, due to a number of considerations which may be classified as follows:

1—LARGE BULK—The bulkiness of the waste material makes a minimum amount of handling imperative and almost prohibits its transportation.

2—MECHANICAL CONDITION OR FORM—The mechanical condition or form of the waste is one of the greatest stumbling blocks to its more complete utilization. Sawdust and shavings are too finely divided to be of value for paper and pulp production or for destructive distillation. For the former, the fiber length has not only been reduced, but the fibers have also been torn and lacerated much as in the production of mechanical ground wood. The destructive distillation of sawdust and shavings is not practicable for two reasons: *First*, the small size of the material makes it such a poor conductor of heat that it is impossible to char it completely in the ordinary forms of retorts and kilns in use; *second*, the charcoal produced is so finely divided that it is difficult to cool and handle and there is no ready market for it. In addition, the waste, as it comes from the mill, is usually a mixture of all the forms enumerated above and any attempt at a separation other, perhaps, than a simple blowing or screening to remove the very fine stuff will increase the cost of the raw material to a prohibitive figure, as shown by the experience of several pulp and paper mills in the yellow pine region of the south. A satisfactory process, therefore, for the utilization of wood waste should be able to handle practically any and all forms of waste as they happen to come from the mill.

3—NON-HOMOGENEITY AND NON-UNIFORMITY—Except in some cases, as in factories using only one or two species of wood or in some mills manufacturing only a few species, as, for example, the "yellow pine" (longleaf, shortleaf, loblolly) mills of the south, the non-homogeneity of the waste has operated against its efficient utilization, for many processes such as pulp and paper or destructive distillation require particular species to give a yield and quality of product that will make the processes commercially feasible.

THE VALUE OF WOOD FOR ALCOHOL PRODUCTION

All woods, however, have one point in common and that is the fact that they all contain more or less cellulose which makes up the fibers of the wood along with an incrusting substance called "lignin." Any process which could chemically utilize this cellulose would, therefore, overcome the objections laid down above as the form of the material, length of the fiber, species, etc., would not be a consideration since finely divided material would permit of a quicker and more complete reaction and coarse material could readily be reduced to a finer condition.

The production of sugars and ethyl alcohol from cellulosic materials such as straw, linen, cotton, peat and wood, in fact, all plant fibers, has engaged the attention of chemists and technologists for nearly a century, although it is only within the last two decades that serious attempts have been made to utilize wood waste by this means.

The principal sources of fermentable sugars from which alcohol is derived at present are:

1—Hydrolytic products of starch.

2—Sugars from fruits; sugar factory residues, such as molasses, etc.

The cost of the raw material for alcohol derived from such sources, however, has been so high that alcohol had not been able to compete in certain fields where its properties and worth are recognized. The technical application in the arts and industries is gradually increasing, due to a rather liberal denaturing policy which has permitted special denaturants for special industries, but its use in this country as a source of liquid fuel is comparatively limited and it is this field that offers greatest possibilities in the future. A study of the motor fuel problem will show that the production of mineral fuels such as gasoline, motor spirits, etc., is not keeping pace with modern automobile production, and alcohol appears to be the only solution of the problem, for if alcohol can be produced from wood waste at a reasonable figure a tremendous supply of raw material is not only available at present but will continue to be so in the future from a natural growing raw material which is not a foodstuff.

PROCESS

The process of producing ethyl alcohol from wood consists, in general, of digesting sawdust or hogged and shredded wood with a dilute mineral acid at from 60 pounds and more of steam pressure. This converts part of the wood into a mixture of pentose and hexose sugars. The latter are then fermented, producing alcohol.

The processes using concentrated sulfuric acid, in which the wood is really attacked and dissolved by the acid as in the Ekström[1] process, have not received commercial attention, notwithstanding the fact that Flechsig,[2] many years ago, showed that cotton cellulose could be converted into dextrose and alcohol almost quantitatively thereby. The more recent work of Willstätter[3] and Feichmeister has confirmed these results with fuming hydrochloric acid, but in all cases the amounts of acid have been so large compared to the procesess in which the acid is used merely as a catalytic agent, that the large initial and recovery costs for acid have prevented commercial development.

The source of the fermentable sugar, that is, whether derived from the cellulose or lignin of the wood, has long been a mooted question and has been the occasion of considerable investigation, but the fact remains that a wood cellulose like soda or sulfite pulp will produce about twice as much fermentable sugar and

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[1] French Patent 380,358, German Patents 193,112, 207,354.

[2] *Z. phys. Chem.*, **1882**.

[3] *Ber.*, **1913**, 2401.

alcohol as the original wood, the yields being proportional to the cellulose content.

HISTORY

The earlier work in the field from the time of Braconnot in 1819 until the work of Simonsen[1] in 1898, although exceedingly interesting historically, may almost be disregarded so far as its scientific value is concerned. It contains many inaccurate and impossible statements, and many contradictions, and is in many cases very vague in regard to yields.

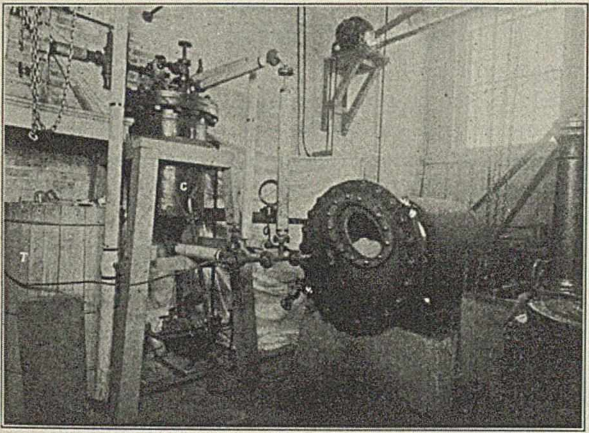

PLATE I—EXPERIMENTAL ALCOHOL APPARATUS
Showing digester with both manhole covers off, loaded with sawdust, and also tank T containing condensing coil and acid tank C.

Simonsen carried out the first systematic investigation of the subject in which the effect of different variables such as the amount of water, pressure, temperature, amount of acid, and time of inversion were studied in some detail. As shown later[2] by Neumann, Simonsen's work is also contradictory in some cases, due mainly to the fact that only a single experiment under each set of conditions was made. In his work on a large scale he was in general unable to duplicate the results obtained in the small autoclave cooks. The yields of alcohol varied considerably, although under the most favorable conditions he obtained in a few exceptional cases yields which were higher than those obtained on the small scale (6 per cent of dry weight of sawdust).

Since Simonsen published his work and took out patents on his process practically all over the world, the production of ethyl alcohol from sawdust has received considerable attention and a large amount of money has been spent in its technical development. Four plants have been built in this country, but none of them up to the present are considered to have achieved commercial success.

OUTLINE OF EXPERIMENTAL WORK

Although other investigators have duplicated Simonsen's yield, which is about six per cent by weight in alcohol of the dry weight of the wood, no systematic study has been made reinvestigating the variables studied by Simonsen, except the work of Cohoe in which hydrochloric acid was used as the catalytic agent instead of sulfuric.

The data to be presented in this paper are the result of the first part of a systematic study of the variables in this process carried on at the Forest Products Laboratory and cover the first two of the following:

1—The influence of pressure and temperatures of digestion.

2—Length of time of digestion.

3—Ratio of water to dry sawdust.

4—Concentration of catalyzing agent in the water.

5—Ratio of catalyzing agent to dry sawdust.

6—Size of the sawdust, hogged slabs, etc.

7—Effect of adding catalytic agent (acid) after preliminary heating of the wood.

8—Effect of varying amounts of bark in the sawdust, or, more specifically, tannins, etc.

9—Special chemical treatments other than acid catalysis or in addition to acid catalysis.

10—A study of the fermentation variables.

11—Steam consumption per ton of sawdust inverted.

12—Variations of yields from different species and mixtures.

EXPERIMENTAL APPARATUS AND PROCEDURE

The apparatus used and method of procedure in each experiment were as follows: A rotary digester consisting of thin cast-iron inner shell lined with acid-proof enamel and an outer shell of steel, the two being separated by several inches from each other, was used for the digestions. The internal length of the inner

PLATE II—EXPERIMENTAL ALCOHOL APPARATUS
Showing leaching tank, L, the settling tanks S and S_2, the single effect vacuum evaporator E, and the hydroextractor H, in the foreground

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[1] See E. Simonsen, *Zeitschrift für angewandte Chemie*, **1898**, 195, 962, 1007; Theor Körner, *Ibid.*, **1908**, 2353; Neumann, Dissertation, Dresden, 1910.

[2] Neumann, Dissertation, Dresden, 1910.

shell is about five feet, and the diameter about $2^1/_2$ feet, making a total capacity of about 22 cubic feet. Steam is admitted to the inner shell and space between the inner and outer shell simultaneously, the digester being similar to a steam-jacketed apparatus except that the inner shell is removable and can readily be taken out and replaced. After a cook has been completed the digester is blown off, the blow-off vapors being condensed in a quartz coil. A cast-iron tank also lined with acid-proof enamel is connected to the digester so that its contents may be introduced into the digester when the latter is under pressure. This tank is used for acid storage and mixing. The steam flows to the inner shell and space between the two shells through separate pipes; the one leading to the inner shell also connects with acid tank. All pipes in contact with acid liquor or acid vapor are enamel-lined and valves are of special bronze so as to reduce corrosion to a minimum and to avoid complications in fermentations due to the presence of iron, copper, and zinc salts.

The pressure is taken by means of a gauge protected from the acid vapors and temperatures are taken on a recording thermometer, the bulb of which projects into the sawdust in the digester.

The digester is filled and emptied through a pair of concentric manholes in the inner and outer shell. The usual procedure is to load the digester with sufficient sawdust to be equivalent to about 100 pounds of dry dust. The exact weight and moisture content are recorded. The diluted acid is then added, the manhole covers bolted on, steam admitted, and rotation begun. Before the temperature reaches 100° C., the air in the inner shell and space between the two shells is vented so as to get a more accurate gauge reading. The admission of steam is continued until the desired pressure is reached, after which the steam is throttled to maintain that pressure for the desired length of time.

At the completion of the latter (or, in cooks of 15 minutes or more, two or three minutes before the time was up) the rotation was stopped and the vapors were then blown off and condensed as rapidly as possible. The time of blow-off varied somewhat, depending on the pressure at which the cook was made and the total amount of liquid and sawdust in the digester. The condensing and cooling capacity of the coil was not equal to the demands placed upon it so that the blowing off of the digester took much longer than it should (about two hours from 7 to 8 atmospheres to atmospheric pressure).

The condensed blow-off was weighed and analyzed. The steam which condensed between the two shells was drained out and weighed. It was also tested qualitatively for dextrose to detect any leakage from the inner shell. The liquor in the inner shell was drained out. After as much of the liquor as would do so had drained off the digester was rotated so that the manholes were at the bottom and the sawdust was raked out. In the later experiments this sawdust was then centrifuged.

Both the digester liquor and treated sawdust were weighed and analyzed for acidity, total solids, dextrose, etc.

The treated sawdust was next placed in the leaching tank, where the remainder of the sugar was extracted from it with warm water. The liquor from the digester and leaching tank was then neutralized with calcium carbonate and allowed to settle. The clear liquor was then concentrated in a single effect vacuum evaporator to a concentration of 10 to 15 per cent sugar for fermentation. The liquors were usually saved until the concentrations from two or three runs were obtained. Where possible, these were divided into two or more parts and fermented with brewers' yeast under varying conditions.

RESULTS

SUGAR YIELDS—Figs. 1, 2 and 3 show the effect on yield of varying the pressure and time of cooking. The curves give the yields in total sugar instead of alcohol since the fermentation end of the work is being taken up in detail at present and was not standardized at the time these experiments were made so as to give check results. The greatest variation on duplicate digestions made with sawdust from the same batch was only 0.11 per cent of total sugar, so the sugar data may be accepted as fairly accurate.

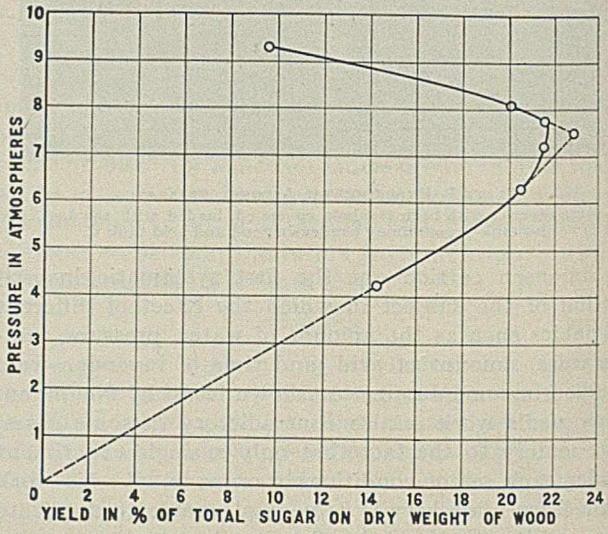

Fig. 1—Showing the Variation of Yield of Total Sugar with Pressure of Digestion. Cooking Period, 15 Minutes

In each run the amount of sawdust used was very nearly equal to 100 pounds dry material; the amount of acid added was the same in all, 2.00 pounds of 90 to 95 per cent sulfuric; and the amount of water in all cases at the end of the cook was equal to four or more than four times the dry weight of wood used. The ratio of acid to dry wood was about 1.8 per cent, while that of water to dry wood was 400 per cent or more. Many of the charges were made up so that the initial amount of water present was exactly four times the dry weight of the material. These, however, showed no change from others in which the amount of water added was allowed to vary within certain limits.

Fig. 1, with a cooking period of 15 minutes, shows a decided maximum in yield at a temperature equal to 7.5 atmospheres steam pressure.

A new lot of sawdust was used for part of the work which included the cooks at 7.5 atmospheres and which probably accounts for the increase in yields shown at that point and which has been indicated by the dotted lines.

On comparing the yields shown in Fig. 1 with those of Simonsen a much greater decrease in yields at pressures above 7.5 atmospheres was noted. From the work of Neumann it is known that dextrose decomposition is very rapid above 175° C., which corresponds very closely with 7.5 atmospheres pressure; in addition to this decomposition, however, the reaction seems to be reversible at this pressure, a fact which has not been recognized heretofore.

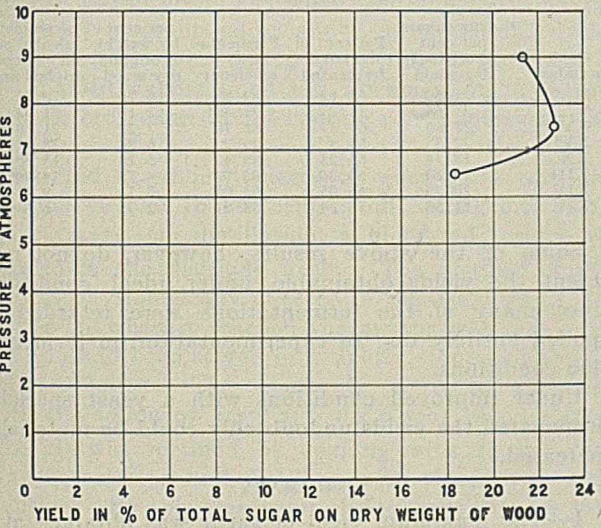

Fig. 2—Showing the Variation of Yield of Total Sugar with Pressure of Digestion. Cooking Period, Zero Minutes

Fig. 2, with a cooking period of zero minutes (blowing off as soon as the pressure is reached), shows the same pronounced maximum at the same pressure and also shows a smaller decrease in yield at high pressures. Using the pressure of 7.5 atmospheres as a constant (at which the best yields were obtained as shown by Figs. 1 and 2) and varying the time of cooking, as shown in Fig. 3, practically no increase or decrease in yield of sugar is shown; in other words, the rates of formation and decomposition of the sugars formed at this temperature are the same and, therefore, maintain a constant yield of sugar. At higher temperatures, however, the rate of decomposition seems to be decidedly greater than the rate of formation which was shown in Figs. 1 and 2. In Fig. 1 the curve crosses the abscissae corresponding to 9 atmospheres at a point showing a yield of 14 per cent of sugar, while in Fig. 2 the yield of 9 atmospheres was 21.29 per cent of sugar. This decided difference in sugar values shows clearly the injurious effect of increasing the time of cooking, especially at pressures greater than 7.5 atmospheres.

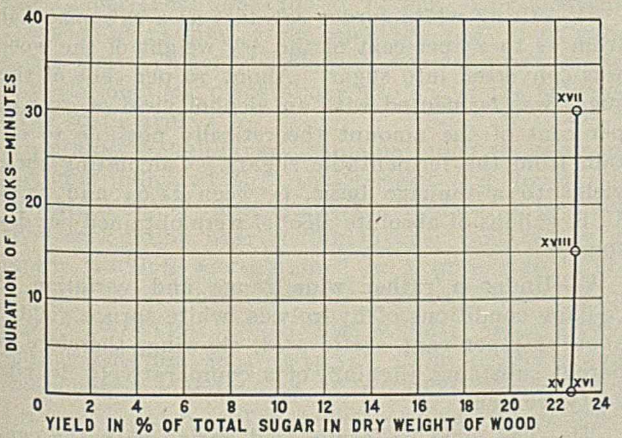

Fig. 3—Showing the Variation of Yield of Total Sugar with Varying Periods of Digestion. Cooking Pressure, 7.5 Atmospheres

The injurious effect of increased time of cooking is also shown in several other ways; the sawdust, of course, is rotated longer in the longer cooks and more fine stuff is formed which makes leaching and handling more difficult. The sawdust is also more friable and larger amounts of fine stuff were formed while being stirred in the leaching tank. And finally, as shown, by the ratio between sugar and total water-soluble solids, more of the sawdust was attacked so that the amount of extraneous water-soluble material other than sugars was greater.

Cohoe[1] was the first one to state that given the proper adjustment of the various phases the reaction is practically instantaneous and our work is in entire agreement with this statement.

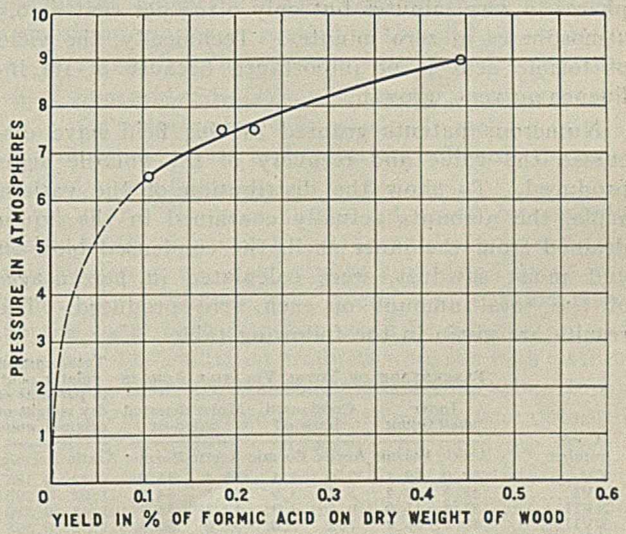

Fig. 4—Showing Variation of Formic Acid Yield with Pressure of Digestion. Cooking Period, Zero Minutes

VOLATILE ACID YIELDS—In addition to the sugars formed as a result of hydrolysis, acetic and formic acid are also produced, probably from a splitting off of acetyl and formyl groups in the lignin complex. The yield of acetic acid has been fairly constant over a wide range of cooking conditions averaging 1.42 per cent of the dry weight of the wood. This is of particular interest not only because of its influence on the subsequent fermentation of the neutralized extract but also because it is practically the same yield obtained by destructive distillation of the wood. Numerous observers such as Klason, Büttner, and Wislicenus have shown that this decomposition does not take place until a temperature of 280° C. or more has been reached, whereas the temperatures of hy-

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[1] *Jour. Soc. Chem. Ind.*, **1912**, 513.

drolysis in this work have averaged 100° C. less than that. The yield obtained, however, is in very close agreement with the work of Bergström,[1] although the latter used no acid, merely hydrolyzing with 4 parts by weight of water at 6 atmospheres pressure for two hours.

The yield of formic acid, however, varies with the cooking conditions as shown by Fig. 4, the amount increasing with increasing cooking pressures. Increasing the time of cooking also materially increases the yield, for as shown at $7^{1}/_{2}$ atmospheres and a zero-minute cook the yield is about 0.2 per cent, while at the same pressure for a 15-minute cook the yield is about three times as great (0.58 per cent). This increase in formic acid production also shows the rate of sugar decomposition since formic acid and levulinic acid are both products of such decomposition. The exact amount hydrolyzed from the wood is difficult to determine since it is also a product of sugar decomposition. Bergström obtained 0.19 per cent at 6 atmospheres cooking for two hours with water alone, whereas we have obtained that figure at $7^{1}/_{2}$ atmospheres in zero minutes but only 0.105 per cent at 6.5 atmospheres in zero minutes. Technically, the yield of formic acid is of importance because of its influence on yeast growth.

Numerous patents granted in this field have discussed the value and recovery of the volatile acids produced. To show the distribution of the various acids, the amounts actually contained in the liquor drained from the inner shell, the condensed blow-off and moist sawdust, were calculated in percentages of the total amount of each acid produced. The results are given in the following table:

	PERCENTAGE OF TOTAL VOLATILE ACID IN						Total amt. of volatile acid in per cent of dry weight of original wood	
	Inner shell liquor		Condensed blow-off		Moist digested sawdust			
Cook number	Acetic	Formic	Acetic	Formic	Acetic	Formic	Acetic	Formic
XV.........	62.0	62.1	2.6	2.1	35.4	35.8	1.22	0.185
XVI........	48.5	49.4	5.7	5.9	45.8	44.7	1.62	0.220
XVII.......	37.8	41.0	9.5	4.3	52.7	54.7	1.48	0.570
XVIII......	40.2	46.2	7.2	7.0	52.6	46.8	1.32	0.598
XIX........	35.0	32.6	6.8	6.1	58.2	61.3	1.60	0.443
XX.........	49.5	39.2	6.3	5.9	44.2	54.9	1.25	0.105

The average amount of acetic acid recovered in the blow-off was 6.4 per cent of the total, and 5.2 per cent of the total amount of formic acid produced.

With an average yield of 1.42 per cent of acetic acid, this would be equivalent to 1.81 pounds of acetic acid per dry ton of wood and since the average concentration of acetic acid in the condensed blow-off was only 0.20 per cent, commercial recovery is obviously out of the question.

ALCOHOL YIELDS—As mentioned heretofore, the fermentation work on the experiments outlined in this paper had not been standardized. Ordinary brewers' yeast, a bottom yeast, has been used without attempting to acclimate it to the mashes used. The main difficulty encountered was the slowness of fermentation which, in some cases, permitted infection of the mashes with wild growth. It was found, however, that the latter could be controlled and excluded by judicious sulfiting and for this purpose potassium metabisulfite[1] was used. Various forms of organic and inorganic nitrogen nutrients were used, of which freshly killed yeast (boiling for two minutes in part of the mash) and ammonium nitrate seemed to be the best.

The following table gives part of the results obtained:

Cook number	Total reducing sugars per cent of original dry wood	Per cent of total sugars fermented	Fermentation efficiency	Yield of alcohol per cent by weight of original dry wood	Yield of alcohol in U. S. gallons of absolute alcohol per dry ton of original wood
II.........	21.50	68.63	89.59	6.76	20.35
V..........	21.54	71.27	91.49	7.18	21.63
XVII......	22.95	69.27	88.70	7.22	21.70
XVIII.....	22.85	55.5	96.2	6.24	18.75
XX........	18.34	65.25	85.42	5.24	15.80
XIII.......	18.81	59.20	83.93	4.78	14.90
XIV.......	20.29	46.05	65.05	3.11	9.35
XII.......	11.58	55.24	68.87	2.25	6.8

Some of the above results, however, do not represent the yields obtainable under ideal conditions since many of the fermentations were retarded or spoiled entirely due to experimentation on fermentation conditions.

Under improved conditions with a yeast specially propagated the yields undoubtedly could be materially increased.

SUMMARY

I—The maximum yield of sugar was obtained at a pressure of 7.5 atmospheres and above and below this point yields decreased very rapidly.

II—A cooking period of zero minutes, that is, blowing off from 7.5 atmospheres as soon as that pressure is attained, was the most advantageous for sawdust.

III—Increasing the time of cooking did not increase the yield and greatly influenced the mechanical condition of the sawdust with greater subsequent difficulty and cost of handling. Economically speaking, the yield decreased as the time of cooking increased.

IV—Using white spruce sawdust as a raw material, from 22 to 23 per cent of the dry weight of the wood was converted into sugar. About 70 per cent of this sugar was fermented with an alcohol yield of over 91 per cent of the amount theoretically possible to obtain from the fermentable sugars. Calculating these yields to a tonnage basis, between 21.63 and 21.70 U. S. gallons of absolute alcohol were obtained per dry ton.

V—Under a rather wide range and variation of cooking conditions of hydrolysis, white spruce yielded about 1.4 per cent acetic acid, showing, therefore, a parent substance (lignin?) of a comparatively definite acetyl content.

VI—The yield of formic acid varied with the conditions of hydrolysis. In cooks longer than zero time, the formic acid yield was indicative of hexose decomposition rather than increased formyl hydrolysis.

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[1] *Der Papierfabrikant*, **2**, 305.

[1] See "Enological Investigations," F. T. Bioletti and W. V. Cruess, *Bull.* **230**, Agr. Expt. Sta., Berkeley, Cal.

THE OIL OF PORT ORFORD CEDAR WOOD AND SOME OBSERVATIONS ON *d*-α-PINENE

By A. W. Schorger

Received May 4, 1914

The Port Orford cedar [*Chamaecyparis lawsoniana* (Murr.) *Parlatore*] occupies a very restricted range. It is found along the Pacific coastal region from Coos Bay in southwestern Oregon to the Mad River in northwestern California. The wood contains an oil having a strong, pleasant odor, and a pronounced physiological action on the kidneys. Owing to the effect of the inhaled vapors upon the workmen, mills cutting Port Orford cedar do not operate continuously on this species.

Selected "resinous" pieces of wood on steam distillation yielded 10 per cent of oil having $d_{15°}$ 0.891, $n_{D_{15°}}$ 1.477. On distillation, a blood-red residue remained in the distilling flask. (The distiller of this oil was physiologically affected in the usual way.)

The oil when it reached the author was *four years* old and had been stored in a tightly stoppered amber-colored bottle. The constants were redetermined with the following results: d_{15} 0.9061, $n_{D_{15°}}$ 1.4806. The oil was rectified by shaking with 10 per cent Na_2CO_3 solution and distilling with steam over soda solution. By this treatment the oil lost 16.4 per cent by volume. In the subsequent examinations of the oil no physiological effects were noted and no red residue on distillation. It is possible that the cause of both phenomena was destroyed by aging.

EXPERIMENTAL

The rectified oil had the following constants: $d_{15°}$ 0.8905; $n_{D_{15°}}$ 1.4758; $\alpha_{D_{25°}}$ +39.60°; acid no. 0.30; ester no. 32.8; ester no. after acetylation 71.57. The ester numbers before and after acetylation are equivalent to 11.48 per cent bornyl acetate and 10.90 per cent of free borneol. The oil distilled as follows: 155–157°, 60.5 per cent; 157–170°, 3 per cent; 170–180°, 4 per cent; 100–130° at 15 mm., 20.5 per cent; 130–160° at 15 mm., 7 per cent; 160–190° at 15 mm., 1 per cent. When distilled at normal pressure decomposition took place above 180° with the splitting off of acetic acid.

α-PINENE—Preliminary examination of the α-pinene fractions indicated that this terpene was present in an exceptionally pure state for a natural product. By fractionation over sodium 65 per cent of the α-pinene fraction was obtained in a pure state. The carefully determined constants were as follows: B. p. 156.0–156.1 (760 mm.); $d_{15°}$ 0.8631; $n_{D_{15°}}$ 1.4684; specific rotation $[\alpha]_D$ +51.52°. The molecular refraction was found to be M = 43.88; calculated for $C_{10}H_{16}\,|^{=}$, 43.54. The highest previously recorded specific rotations for α-pinene are: $[\alpha]_D$ +48.4° for *d*-α-pinene from Grecian turpentine oil;[1] $[\alpha]_{D19°}$ —48.63° for *l*-α-pinene from silver-top stringy-bark eucalyptus oil (*Eucalyptus laevopinea*).[2]

Ten grams of the α-pinene fraction did not yield a trace of crystalline pinene nitrosochloride. One hundred grams of the terpene were then oxidized with 233 grams $KMnO_4$ in 1.5 liters of water and 500 grams of ice in an ice bath. On completion of the oxidation 25.3 grams of oil were recovered by steam distillation. The recovered oil after standing a week deposited a few fan-shaped clusters of needles. This product was evidently pinol hydrate, since it melted at 144–145° after one crystallization from water. After removal of the manganese sludge the oxidation liquor was evaporated to one liter and extracted several times with ether. The pinonic acid precipitated by dilute sulfuric acid was extracted with chloroform and the solvent removed by distillation. The residue distilled between 185–190° at 17 mm., mainly between 187–188°. The distillate weighing 34.8 grams soon crystallized on standing and 16.6 grams of the crystalline keto-acid were obtained. The crystalline *d*-pinonic acid melted at 68–69°, its semicarbazone at 203–205°. The specific rotation of the acid $[\alpha]_D$ +92.69° was determined from a 5.37 per cent chloroform solution. The semicarbazone of the liquid pinonic acid melted at 203°.

DIPENTENE—The fractions, b. p. 157–180°, consisted mainly of dipentene. The portion, b. p. 170–180°, comprising the major portion of the oil had a rotation $\alpha_{D_{23°}}$ +51.16°. Phellandrene was not detected and the dihydrochloride from this fraction melted at 48–49°. On bromination a tetrabromide melting at 124° was obtained. The high rotation indicates the presence of active limonene.

BORNEOL—The free alcohol obtained by saponification of the fraction, b. p. 100–130°, at 15 mm. distilled between 205–230° and was collected in 5° fractions. By oxidation with acetic and chromic acids on the water bath camphor could be detected in each fraction. The oxidation products were oils with a strong camphor odor. On treatment with semicarbazide hydrochloride, crystalline semi-carbazones were obtained, melting at 236–237°. However, by oxidizing the oil, b. p. 205–215°, $\alpha_{D_{20°}}$ +32.16, with saturated permanganate solution and distilling with steam, solid camphor collected in the receiver. An alcoholic solution of the camphor was *d*-rotatory.

COMBINED ACIDS—The combined acids were recovered from the ester saponification liquor by distillation with phosphoric acid. A small amount of oily material appearing on the surface of the distillate was removed by extraction with ether. The solvent was allowed to evaporate spontaneously, the residue neutralized with caustic soda and extracted with ether, to remove resinous matter. On addition of $AgNO_3$ solution a precipitate was obtained and analyzed as follows:

0.0814 gram silver salt gave 0.0313 gram Ag = 38.45 per cent Ag.

Silver caprinate, $C_9H_{19}COOAg$, requires 38.66 per cent Ag.

The acids in the aqueous portion of the distillate were neutralized with caustic soda and precipitated with silver nitrate. The precipitates were found to contain silver formate, as shown by the decomposition on attempting to recrystallize them from hot water. The silver formate was accordingly destroyed by alternate

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[1] Vezes, *Bull. soc. chim.*, [4] **5** (1909), 932.

[2] Smith, *Jour. and Proc. Royal Soc.*, N. S. W., **32** (1898), 195.

heating and filtration of the aqueous solution until decomposition had ceased. The shiny leaflets of silver acetate finally obtained were analyzed as follows:

0.1245 gram silver salt gave 0.0802 gram Ag = 64.42 per cent Ag.
Silver acetate, $CH_3.COOAg$, requires 64.64 per cent Ag.

FREE ACIDS—The acids recovered from the liquors remaining after rectifying the oil with sodium carbonate solution and steam distillation were treated as above. The acid obtained from the other extract was precipitated in two fractions and their silver content determined:

(1) 0.0621 gram silver salt gave 0.0241 gram Ag = 38.81 per cent Ag.
(2) 0.0836 gram silver salt gave 0.0325 gram Ag = 38.87 per cent Ag.

Both precipitates evidently consist of silver caprinate since this salt requires 38.66 per cent Ag.

The aqueous portion was found to consist of acetic and formic acids. In this case the formic acid was destroyed by heating the distillate with mercuric oxide. Analysis of the silver salt of the remaining acid follows:

0.1993 gram silver salt gave 0.1283 gram Ag = 64.38 per cent Ag.

CADINENE—The fractions boiling above 130° at 15 mm. contained cadinene. The portion, b. p. 270–280°, $d_{15°}^{24°}$ 0.9329, $\alpha_{D_{24°}}$ +14.69, yielded the characteristic cadinene dihydrochloride, m. p. 117–118°. A 6.04 per cent ether solution of the dihydrochloride had the rotation $\alpha_{D_{25°}}$ —1.95°.

SUMMARY

The rectified oil has approximately the following composition: *d*-α-pinene 60–61 per cent; dipentene 6–7 per cent; free *l*-borneol 11 per cent; ester as bornyl acetate 11.5 per cent; cadinene 6–7 per cent; losses 5 per cent. The combined borneol occurs mainly as bornyl acetate, but also evidently as the esters of formic and caprinic acids. In the old oil, formic, acetic, and caprinic acids occur in the free state.

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THE RELATION BETWEEN ALUMINUM SULFATE AND COLOR IN MECHANICAL FILTRATION[1]

By Frank E. Hale

The older literature, especially the English, frequently speaks of the humic acid of swamp waters, particularly in connection with the solution of lead by drinking water. In recent years the tendency has been to consider free acidity due to carbonic acid and to be rather skeptical of the existence of free organic acid in water. The experiments described in this paper seem to prove that free organic acid in water is no myth, but actually exists as a property of the coloring matter, and in all probability the removal of color by the action of aluminum sulfate depends upon this acid property. The acid coloring matter combines with the base, aluminum hydrate, and in definite proportions, the ratio varying with the chemical character of the color in different waters.

This theory is in keeping with the fact that practically all organic coloring matter extracted from wood or vegetable growth combines with almost any hydrate, *e. g.*, tin, bismuth, aluminum, chromium, iron, etc. Recently, at Grand Rapids, Mich., in the softening of water, it has been found that excellent decolorization is obtained by means of an excess of magnesium hydrate.[1]

THE REACTION BETWEEN ALUMINUM SULFATE AND THE ALKALINITY

It is usually stated that this reaction results in the formation of aluminum hydrate, $Al(OH)_3$. In elementary courses in chemistry it is taught that the reaction between aluminum salts and sodium carbonate results in the cold in the precipitation of basic aluminum carbonate, which only upon boiling changes completely to the hydrate. This is undoubtedly the reaction occurring in water between aluminum sulfate and calcium bicarbonate. Indeed, judging from the amount of alkalinity reacting with one grain per gallon of basic aluminum sulfate and from the amount of carbonic acid set free, there is good reason to believe that the precipitate formed is a basic sulfate-carbonate.

The usual aluminum sulfate employed is a basic salt containing about 18 per cent alumina (Al_2O_3). The analyses of seventeen samples, representing several years, of the aluminum sulfate used at the Brooklyn filters were as follows:

Percentages	Al_2O_3	SO_3
Average	18.2	39.3
Minimum	16.6	35.9
Maximum	20.6	41.4

The sulfate varied from a few per cent to twenty per cent below the amount theoretically required by the alumina to form a neutral salt. The average deficiency was 11 per cent. This average salt may be expressed by the formula $Al_2(SO_4)_3.Al(SO_4)(OH)$, but I prefer the doubled formula $2Al_2(SO_4)_3.Al_2(SO_4)_2(OH)_2$, since when written graphically it better explains the probable reactions with the alkalinity. Theoretically an aluminum sulfate containing 18 per cent alumina requires 9 p. p. m. calcium carbonate to react completely, thus:

P. p. m. alkalinity = $300/102 \times 17.1 \times 18/100 = 9$
in which 300 is the molecular weight of $3CaCO_3$
102 is the molecular weight of Al_2O_3
17.1 is the p. p. m. equivalent of 1 grain per gallon
18 is the per cent of alumina

But it is not the alumina that combines with the alkalinity. It is the sulfate. As the sulfate is 11 per cent short in the average aluminum sulfate the maximum alkalinity that can react with the average coagulant is 8.3 p. p. m. It will vary with the actual composition and is also governed by other conditions such as a low or a high alkalinity, and a low or a high turbidity. With a high alkalinity the figures approach the upper limit but with a low alkalinity they fall short, even as low as 5.5; in fact figures have been published as low as 3.4, using alum containing 18 to 22 per cent alumina. The following table gives some of the figures found in practice:

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[1] Presented at the 49th Meeting of the A. C. S., Cincinnati, April 6–10, 1914.

[1] "Report of Committee on Water Supplies," *Am. Jour. Pub. Health*, **3** (1913), 1335.

LOCATION	Years	Color	Alkalinity	Alum, grains per gallon	Alkalinity reacting with 1 gr. per gal. of alum
Louisville Water Co. (*a*)	1912	..	55	1.18	8.5
Elmira Water Works (*b*)	1907	20	52	1.55	7.4
Springfield, Mass. (*a*)	1912	40	8	0.27	7.3
Little Falls, N. Y. (*a*)	5 months	41	28	1.30	7.1
Rensselaer, N. Y. (*b*)	1901–1908	25–65	18–65	2.04	6.8
Harrisburg, Pa. (*b*)	1906	17	27	0.95	6.4
Harrisburg, Pa. (*b*)	1907	13	25	1.06	6.2
Harrisburg, Pa. (*a*)	1910	4	49	0.61	5.4
Harrisburg, Pa. (*a*)	1911	7	29	0.7	6.6
Croton water, N. Y. City(*c*)	1912	25	35	1.0	6.2
Brooklyn water, N. Y. City(*c*)	1912	5	12	1.0	6.0
Baisley Filter, Brooklyn	1907	30	31	1.69	5.8
Norwich, N. Y. (*b*)	1905–1908	12	20	0.54	5.6
General average					6.6

(*a*) Reports.
(*b*) J. A. Caird, *Proc. Am. W. W. Assoc.*, **1908**, p. 371.
(*c*) Laboratory experiments.

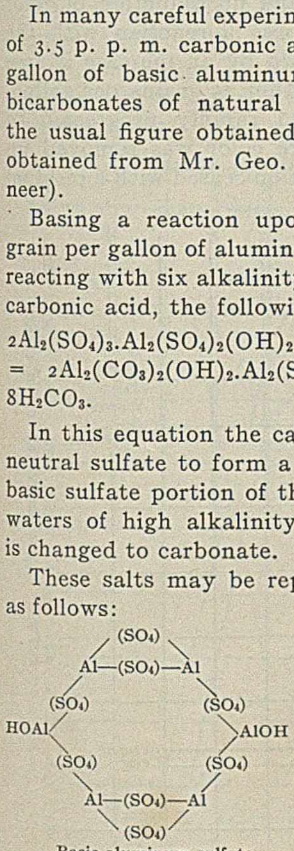
In many careful experiments I have found an average of 3.5 p. p. m. carbonic acid set free by one grain per gallon of basic aluminum sulfate reacting with the bicarbonates of natural waters. This is also about the usual figure obtained at Little Falls (information obtained from Mr. Geo. W. Fuller, Consulting Engineer).

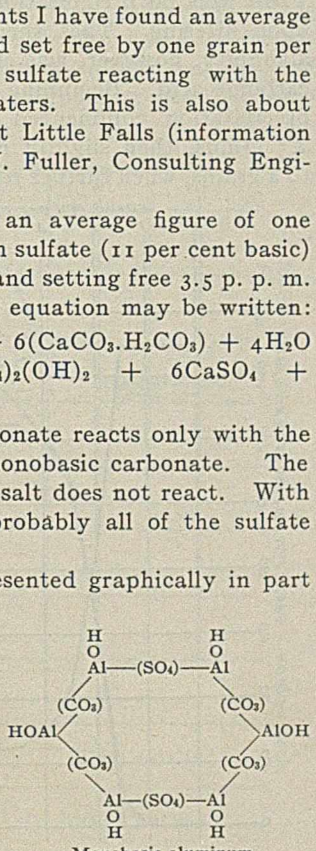
Basing a reaction upon an average figure of one grain per gallon of aluminum sulfate (11 per cent basic) reacting with six alkalinity and setting free 3.5 p. p. m. carbonic acid, the following equation may be written:

$$2Al_2(SO_4)_3.Al_2(SO_4)_2(OH)_2 + 6(CaCO_3.H_2CO_3) + 4H_2O = 2Al_2(CO_3)_2(OH)_2.Al_2(SO_4)_2(OH)_2 + 6CaSO_4 + 8H_2CO_3.$$

In this equation the carbonate reacts only with the neutral sulfate to form a monobasic carbonate. The basic sulfate portion of the salt does not react. With waters of high alkalinity probably all of the sulfate is changed to carbonate.

These salts may be represented graphically in part as follows:


Basic aluminum sulfate


Monobasic aluminum sulfate-carbonate

It may be conceived that all of the sulfate is replaced by carbonate except where there are two sulfate radicles between two aluminum atoms, where only one is replaced. A strain is thus produced at this point, the carbonate hydrolyzes and the result is a hydroxyl radicle attached to each aluminum atom. With high alkalinity, that is, a large excess of carbonate, the remaining sulfate radicles become replaced.

THE REACTION BETWEEN THE COLOR AND THE ALUMINUM SALTS

The acid coloring matter combines with the hydroxyl radicles of the above and is removed from solution only because of the insolubility of the carbonate of aluminum.

The above reactions take place at ordinary temperatures. Mr. G. C. Whipple[1] in a comprehensive discussion of decolorization of water (page 161) gives a table in which 1.2 grains per gallon of aluminum sulfate were required to decolorize a water of 50 color at 44° F., and 0.8 grains at 98° F. This is probably due to the formation of a dibasic aluminum carbonate $[Al_2(CO_3)(OH)_4]$ so that the same amount of aluminum sulfate can react with twice the amount of color. At boiling temperature, however, when $Al(OH)_3$ is formed I have found that 3 grains per gallon of aluminum sulfate did not reduce a color of 90 but intensified it to 130, although the same amount in cold reaction reduced the color to 36. I believe this must be due to the formation of a compound in which the aluminum is entirely combined with the coloring matter and that this compound is soluble. This would explain the fact that as the color of a water increases it requires more aluminum sulfate to reach the starting point of the precipitation and color removal, the excess color at first having a solvent action. This is in line with the fact that iron in combination with coloring matter is soluble.

The reactions may be represented as follows, letting HR represent the coloring matter and ignoring the complex combinations when sulfate does not completely react:

$$Al(CO_3)OH + HR = \underset{\text{insoluble}}{Al(CO_3)R} + H_2O \text{ (ordinary temperatures)}$$

$$Al_2(CO_3)(OH)_4 + 4HR = \underset{\text{insoluble}}{Al_2(CO_3)R_2} + 4H_2O \text{ (100° F.)}$$

$$Al(CO_3)OH + 3HR = \underset{\text{soluble}}{AlR_3} + H_2O + H_2CO_3 \text{ (boiling)}$$

Likewise $Al(OH)_2R$ and $Al(OH)R_2$ should be insoluble.

On pages 156 to 159 (previous citation), Mr. Whipple discusses a direct reaction between aluminum sulfate and coloring matter in the absence of all alkalinity and on page 157 gives a chart showing greater color removal for the same amount of alum. It must be borne in mind, however, that aluminum sulfate acts as a dilute acid upon color, changes it to a greenish hue and lightens it as any acid will, so that the effect of color removal is heightened. If the color be neutralized again the apparent color at the end is about doubled. There is, however, a direct reaction, as shown by the formation of a precipitate whether aluminum sulfate is added to a neutral water or added in excess to an alkaline water. It is probable that not all of the color is of acid character and if such color is represented by NaR the reaction with aluminum sulfate to acidify the color may be written:

$$Al_2(SO_4)_3 + 2NaR + 2H_2O = 2Al(SO_4)OH + 2HR + Na_2SO_4.$$

The precipitation and decolorization may be written:

$$Al_2(SO_4)_3 + 6NaR + 2H_2O = \underset{\text{insoluble}}{2Al(OH)R_2} + 3Na_2SO_4 + \underset{\text{residual color}}{2HR.}$$

It will be noted that this equation requires a residual color one-third the original color. Mr. Whipple states, on page 161 (previous citation), that such resid-

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[1] *Trans. Am. Soc. Civil Eng.*, **46** (1901), 141–181.

ual color usually resulted, as much as 50 in one case of 300 original color. As he used 6.5 grains per gallon of aluminum sulfate, this reaction was probably an excess alum reaction, the color would be acid in character and would represent about 100 original color neutral, or one-third of the original total color if that were all neutral. In my experiments, to be described later, the Great Swamp water neutralized had a color of about 200. In the acid treatment with excess aluminum sulfate the residual color was 25, representing when neutralized 50 p. p. m. or one-fourth the original color neutralized.

During the last two years this acid reaction has had practical application at Springfield, Mass.[1] The supply has been treated with excess aluminum sulfate for a definite period and then allowed to mix and react with untreated supply for another definite period. The results for 1912 are summarized in the following table:

Month	Color orig. P. p. m.	Reduction in color P. p. m.	Alkalinity original P. p. m.	Reduction in alkal. P. p. m.	Alum. sulf. Grs. per gal.	Reduction per one gr. per gal. alum. Color P. p. m.	Reduction per one gr. per gal. alum. Alk. P. p. m.
Jan. (*a*)	32	17	7.5	1.6	0.19	89	8.4
Feb. (*a*)	37	24	8.0	...	0.29	83	..
Mar.	33	20	6.8	1.1	0.21	95	5.2
Apr.	34	21	6.4	1.5	0.22	95	6.8
May	38	25	8.1	1.9	0.25	100	7.6
June	38	21	11.0	2.5	0.25	84	10.0
July	38	21	9.6	1.4	0.20	105	7.0
Aug.	36	19	9.5	1.9	0.19	100	10.0
Sept.	42	25	10.3	1.6	0.26	96	6.2
Oct.	50	32	9.3	1.2	0.27	119	4.4
Nov.	58	40	7.8	3.9	0.58	69	6.7
Dec.	46	31	6.5	3.2	0.38	82	8.4
Average	40	25	8.4	2.0	0.27	93	7.3

(*a*) Days included only when alum was used.

It will be noted that double the usual amount of color has been removed per grain per gallon of aluminum sulfate. The probable reason for this rests in the reactions already given and there is probably produced a mixture of AlR_2OH and $Al(CO_3)R$ and possibly $Al_2(CO_3)R_4$. The acidifying effect of the aluminum sulfate upon the neutral coloring matter renders it more active and at the same time tends to produce apparently an aluminum precipitate containing twice the amount of color that is combined in the usual cold reaction.

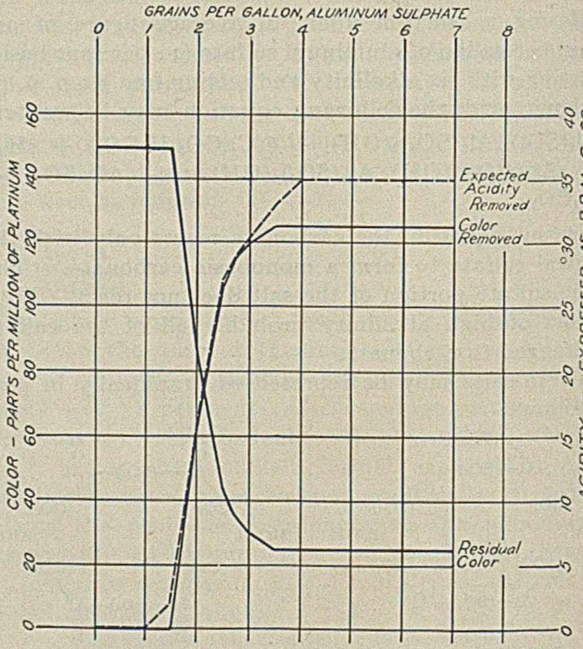
With waters of a high alkalinity a greater amount of aluminum sulfate is required to decolorize a water by the usual method than in a water of low alkalinity. This is probably due to a solvent effect of the alkalinity by a tendency to form alkaline aluminates and in fact precipitation will not take place in many cases until sufficient alum is added to neutralize the excess alkalinity. I have noticed this especially in trade wastes and it was noted at New Orleans with a natural water.[2]

It might be advisable to call attention also to an article on "Hot Water Problems,"[3] in which considerable space is given to color discussion by Mr. G. C. Whipple, since it does not appear in the title.

THE ACIDITY OF COLORING MATTER IN NATURAL WATERS

These experiments were performed upon the Great Swamp water of the south and upon Charleston, S. C., water.

The Great Swamp water had an alkalinity of 9 p. p. m. and a color of 150 p. p. m. Using 200 cc. portions, varying amounts of aluminum sulfate solution were added, allowed to react for a definite period, usually one-half hour, and filtered through two layers of S. & S. No. 589 paper, previously washed twice with some of the water to be filtered. The amounts of aluminum sulfate added ranged from one to seven grains per gallon. The alkalinity of this water, on a basis of 6 p. p. m. alkalinity reacting with one grain per gallon, could react with 1.5 grains per gallon of alum. With this amount no apparent reaction took place. There was no precipitation and no reduction of color upon filtering. That there was a reaction with the alkalinity, however, was shown by an increase in free carbonic acid. Beginning with 1.75 grains per gallon, precipitation commenced and rapidly progressed to 2.5 grains, then slightly more color was removed up to 4 grains, when further reaction ceased with a residual color of 25 p. p. m. This reaction of coloring matter in the presence of excess aluminum sulfate was practically the same phenomenon mentioned by Whipple and now practiced at Springfield, although at the time these experiments were performed I was not acquainted with this work and discovered the reaction by accident. I desire at this point to thank Mr. Geo. W. Fuller for calling my attention to this work of Whipple and of Lockridge.



EXCESS ALUM REACTION—GREAT SWAMP WATER

As the aluminum sulfate and the alkalinity react in colorless waters the free carbonic acid is increased, an average of 3.5 p. p. m. for each grain of alum per gallon, when 6 alkalinity reacts and the alum contains 18 per cent alumina, due to the setting free of bicarbonic acid and a small part of the neutral carbonate.

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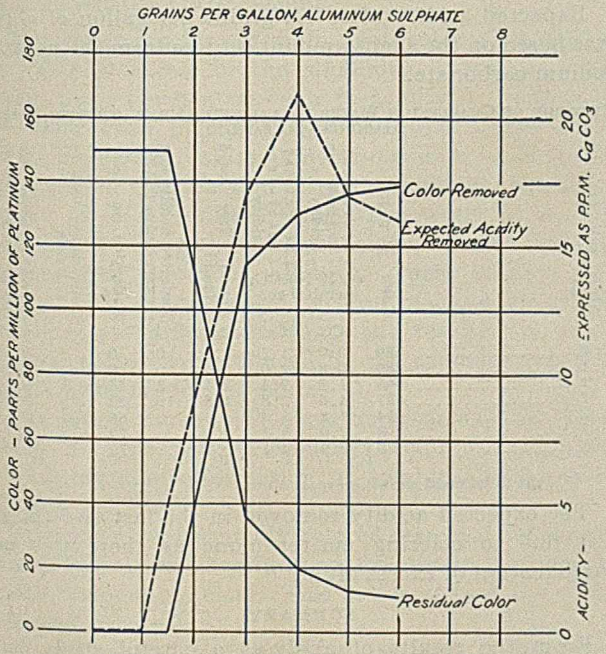
[1] *Eng. News*, **70**, Nov. (1913), 974; *Am. Jour. Pub. Health*, **3**, 1333.

[2] *Trans. Am. Soc. Civil Eng.*, **46** (1901), 168.

[3] *Proc. Am. W. W. Assoc.*, **1911**, pp. 261–276.

The equation for this reaction was given in connection with the graphic formulae. With the highly colored Great Swamp water the theoretical increase of acidity was produced up to 1.5 grains per gallon of alum *while no color was being removed,* but as the color was removed a certain amount of the expected increase of acidity failed to appear and just in proportion to the amount of color removed. After the removal of color stopped, the theoretical increase of acidity commenced again. The accompanying tables and charts show this strikingly. The expected increase of acidity after the alkalinity was used up was due to the excess of aluminum sulfate added. The acidity removed from the solution in the above reaction was undoubtedly due to the removal of acid coloring matter with possibly a small amount of included alum. Titration of the filtrate with $N/50$ sodium carbonate using lacmoid and boiling indicated about one and two-thirds grains per gallon of aluminum sulfate reacting and removed from the solution as against one and one-half theoretical.



NEUTRAL REACTION—GREAT SWAMP WATER

The above experiments were repeated adding as exactly as possible neutral sodium carbonate solution ($N/50$) to supplement the alkalinity. Again the expected increase of acidity was reduced directly proportional to the amount of color removed, but the lost acid was only about one-half the quantity of acid removed in the previous experiment. This was undoubtedly due to the removal of acid in the coloring matter only since the excess of aluminum sulfate was neutralized by the sodium carbonate. The color removal in neutral solution was again very rapid between 1.5 and 3 grains per gallon of alum and progressed slowly up to 7 grains, at which only a color of 9 p. p. m. was left.

About 40 p. p. m. color were removed per grain of aluminum sulfate per gallon and about 7 p. p. m. color possessed 1 p. p. m. acidity, expressed as $CaCO_3$.

The water of Charleston, S. C., possessing an alkalinity of 15 p. p. m. and a color of 80, was tried in the same way with similar results, the removal of expected acidity proportional to the removal of color. With this water about 30 p. p. m. color were removed per grain of aluminum sulfate per gallon and 5 p. p. m. color possessed 1 p. p. m. acidity.

It is interesting and important to note also that the amounts of color removed in these two waters bear a relation to the acidity, *e. g.*, 30 : 40 = 5 : 7.

Several other experiments appear to confirm the existence of free organic acid in natural waters. Free carbonic acid may be removed from water by blowing air through it or by boiling. The Great Swamp water originally contained considerable free acid, but upon standing the free acid became greatly reduced to a point at which it became practically constant, 1.8 cc. $N/50$ sodium carbonate per 100 cc. water, equivalent to 18 expressed as $CaCO_3$. This residual acidity was probably due entirely to the coloring matter and agrees fairly well with the results obtained by loss of expected acidity upon removing the color, 17. Charleston water showed the same phenomenon, a residual acidity of 12 upon standing a long time, against a loss of expected acidity with removal of color of 10.

Upon aerating the Great Swamp water when it contained an acidity of 34, expressed as $CaCO_3$, for five minutes the residual acidity was 14 p. p. m., upon aerating for one hour 14, upon aerating for fifteen minutes with air drawn through lime water 14. Upon boiling one hour the acidity was reduced to 10, the boiling probably causing some change in the coloring matter.

Upon adding dilute acid to the water the color was greatly decreased and brought back by alkali. Upon adding alkali, sodium carbonate, to the original water the color was considerably increased. Upon neutralization Great Swamp water increased in color from 150 to 192. Upon adding 4 cc. excess of $N/50$ sodium carbonate the color became 212 and 8 cc. excess produced no further increase of color. To a portion treated with alum and soda in which the color had been reduced to 13, excess soda raised the color to 26.

Upon neutralizing exactly the residual free acidity of Charleston water probably due entirely to color, with either soda or lime water, 2 grains of alum per gallon reduced the color to only 68 and 70, respectively, although in the unneutralized water 2 grains reduced the color from 80 to 27 p. p. m. The setting of the color in presence of excess alkali, so that the color is more difficult to remove by alum, has been noted at New Orleans (local citation) and was noticed by the author during investigation of corrosion of iron pipes by water. This effect may be due to one or all of three causes: (1) Neutralization of the acidity of the color so that it does not properly react with the aluminum sulfate; (2) increase of color intensity by the neutralization; (3) formation of soluble alkaline aluminates.

It is well known that iron frequently exists in organic combination in water and in such condition is very difficult to remove. The author examined a series of samples of water from northern New York state in which in some samples the color could not be reduced beyond about 15 p. p. m. even with a large excess of alum up to 5–7 grains per gallon. The residual unremovable color[1] in different samples was found to vary almost exactly with the iron content as follows:

Residual color	Iron p. p. m.
4	0.15
13	0.45
16	0.60

This may have been due to the combination of the iron with the acid radicle of some of the color so that it could not react with the alum. In this water also 1 grain per gallon of alum removed only 12 p. p. m. color and the precipitation did not take place until about two, three and four grains, respectively, were added. This water had an alkalinity of about 75 which also was probably partly responsible for the slow start of reaction.

The following tables and charts give the results of these experiments with Great Swamp water and Charleston water. In order to estimate correctly the expected acidity, experiments were made which showed that: (1) one grain per gallon of the aluminum sulfate used reduced the alkalinity 6 p. p. m., using either methyl orange or lacmoid (boiling) as indicator; (2) one grain per gallon of aluminum sulfate (11 per cent basic) reacting with calcium bicarbonate produced an acidity to phenolphthalein of 0.8 cc. *N*/50 sodium carbonate per 100 cc. of water, equal to 3.5 p. p. m. carbonic acid (CO_2) or 8 expressed as $CaCO_3$ p. p. m.; (3) one grain per gallon of aluminum sulfate in excess produced an acidity to phenolphthalein of 1.8 cc. *N*/50 sodium carbonate per 100 cc. of water or 18 expressed as $CaCO_3$. This last reaction may possibly be represented by the following equation: $Al_2(SO_4)_3 + 8Na_2CO_3 + 4H_2O = 2NaAlO_2 + 4(Na_2CO_3.H_2CO_3) + 3Na_2SO_4$.

This equation is equivalent to 1.6 cc. *N*/50 sodium carbonate per 100 cc. water when one grain per gallon of basic alum reacts with 6 alkalinity. The equation for neutral alum as expressed, calls for 2.4 cc. of the carbonate.

Reaction of Great Swamp Water, Alkalinity 9 p. p. m., with Basic Aluminum Sulfate

Alum. sulf. grs. per gal.	Color P. p. m.	Theoretical increase in acidity	Theoretical total free acidity	Actual free acid found	Expected acidity lost expressed as $CaCO_3$	Reduction in color P. p. m.	Color equivalent to one acid	Color removed by 1 gr. per gal. alum.
		N/50 Na_2CO_3 per 100 cc.						
		Cc.	Cc.	Cc.				
0	150	0.0	2.7	2.7	0	0	..	0
1	150	0.8	3.5	3.5	0	0	..	0
1.5	150	1.2	3.9	3.7	2	0	..	0
2	86	2.1	4.8	3.2	16	64	4	32
2.5	44	3.0	5.7	3.0	27	106	4	42
2.75	35	3.4	6.1	3.2	29	115	4	42
3	30	3.9	6.6	3.7	29	120	4	40
3.5	25	4.8	7.5	4.2	33	125	4	36
4	25	5.7	8.4	4.8	36	125	..	..
5	25	7.5	10.2	6.7	35	125	..	..
6	25	9.3	12.0	8.5	35	125	..	..
7	25	11.1	13.8	10.3	35	125	..	..

It was also assumed that one grain per gallon of aluminum sulfate reacting with neutral sodium carbonate formed a monobasic carbonate of aluminum in the precipitation and set free carbonic acid equivalent to 0.2 cc. *N*/50 sodium carbonate per 100 cc. of water. Expected acidity up to 1.5 grains per gallon of alum was due to carbonic acid set free from 9 p. p. m. alkalinity, after that due to excess of alum.

The ratio of color to acid removal in this reaction differs from the following neutral reaction value and rightly since the excess alum turns the color greenish and lightens it by half. Therefore, the color equivalent to one acidity is about half that in the following table:

Reaction of Great Swamp Water with Basic Aluminum Sulfate—and Added Sodium Carbonate to Produce Just Sufficient Alkalinity for Reaction

Alum. sulf. grs. per gal.	Soda *N*/50 per 100 cc.	Color P. p. m.	Theor. increase in acid	Theoretical total free acidity	Actual free acid found	Expected acidity lost expressed as $CaCO_3$	Reduction in color P. p. m.	Color equivalent to one acid	Color removed by 1 gr. per gal. alum.
			N/50 soda per 100 cc.						
	Cc.		Cc.	Cc.	Cc.				
0	0.0	150	0.0	3.4	3.4	0	0	..	0
1.5	0.0	150	1.2	4.6	4.1	5	0	..	0
3	0.9	36	1.5	4.9	3.2	17	114	7	38
4	1.5	20	1.7	5.1	3.0	21	130	6	35
5	2.1	13	1.9	5.3	3.6	17	137	8	27
6	2.7	11	2.1	5.5	3.9	16	139	9	23
7	3.3	9	...	...	...	..	141	..	20

Expected acidity after 1.5 grains per gallon of alum was based on the slight amount set free from the neutral sodium carbonate.

Reaction of Charleston Water (Alkalinity 15 p. p. m.) with Basic Aluminum Sulfate

Alum. sulf. grs. per gal.	Color P. p. m.	Theoretical increase in acidity	Theoretical total free acidity	Actual free acid found	Expected acidity lost expressed as $CaCO_3$	Reduction in color P. p. m.	Color equivalent to one acid	Color removed by 1 gr. per gal. alum.
		N/50 Na_2CO_3 per 100 cc.						
		Cc.	Cc.	Cc.				
0	80	0.0	1.2	1.2	0	0	..	0
1	80	0.8	2.0	2.0	0	0	..	0
1.5	65	1.2	2.4	2.1	3	15	5	10
2	27	1.6	2.8	1.8	10	53	5	26
2.25	14	1.8	3.0	...	..	66	..	29
2.5	8	2.0	3.2	...	..	72	..	29
3	8	2.9	4.1	...(a)	..	72	..	..

(a) Acid to lacmoid showing excess alum.

The expected acidity removed in the last two tables was due to coloring matter alone as there was no complication of excess alum.

SUMMARY

From the results of analyses a careful study has been made of the reactions occurring between basic aluminum sulfate and the alkalinity of natural waters on the one hand and between the alum and the color on the other.

The average basic aluminum sulfate from analysis may be represented by the formula $2Al_2(SO_4)_3.Al_2(SO_4)_2(OH)_2$, a mixture of two parts neutral sulfate and one part monobasic sulfate.

The maximum alkalinity that can react with 1 grain per gallon of this average alum is 8.3 p. p. m. Practice for waters of low alkalinity show only about 6 p. p. m. reacting. High alkalinity waters approach the upper figure.

The amount of carbonic acid set free by one grain per gallon of alum is usually about 3.5 p. p. m.

Based upon this amount of acid produced and six alkalinity used up the equation is written to show the precipitation at ordinary temperatures of $2Al_2(CO_3)_2$-

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[1] Page 161, local citation.

$(OH)_2.Al_2(SO_4)_2(OH)_2$, a mixture of two parts monobasic carbonate and one part monobasic sulfate. When represented graphically these reactions seem explainable by uneven stress.

It is maintained that a large part at least of the color is of acid character. The color combines with the hydroxyl radicle of the aluminum precipitate and is removed from solution merely because of the insolublility of the aluminum carbonate, or hydrate. At 100° F. a dibasic carbonate is probably formed and twice as much color is removed for the same amount of alum. At boiling temperature the aluminum probably is completely combined with the color forming a compound that is soluble as are iron compounds. At boiling temperature no precipitation takes place but the color is intensified. This is in line with the fact that with highly colored waters precipitation and color removal does not begin with small amounts of alum, the excess color exerting a solvent effect. These compounds are represented in simple form, neglecting complex sulfates, as $Al(CO_3)R$ insoluble, $Al_2(CO_3)R_2$ insoluble, and AlR_3 soluble.

The direct reaction of alum upon color when added to water in excess of the alkalinity is explained by action upon the neutral color to acidify it, hydrolysis by water then precipitating two-thirds of the color as a monobasic aluminum compound, $AlR_2(OH)$. The color in this reaction in reality acts like the alkalinity. A high residual color when water is treated with excess alum, the greenish tint produced and the lightening of the color as by an acid confirm this theory. The application of this reaction of excess coagulant at Springfield, Mass., has resulted in color removal twice that produced by the ordinary reaction for the same amount of alum.

The larger amount of alum necessary to use with highly alkaline water, especially sodium carbonate, is probably due to formation of soluble alkaline aluminates.

Experiments with highly colored waters have shown a removal of expected acidity exactly in proportion to the removal of color. This indicates that the color is of acid nature.

The amount of color removed per grain of alum per gallon in different waters was found to be proportional to the color acidity.

Aeration of these highly colored waters left a residual acidity which agreed with the color acidity. Boiling failed to remove the acidity.

Alkalies deepen the natural color of waters, while acids lighten them.

Neutralization of the color acidity by soda prevented decolorization with as small amounts of alum as before neutralization.

Residual colors which cannot be removed by large amounts of alum are frequently explained by combination with iron, the iron preventing the alum from combining.

The fact that definite amounts of alum remove definite and proportional amounts of color points to a definite chemical reaction rather than a physical inclusion.

The recent successful removal of color at Grand Rapids, Mich., by excess magnesium hydrate also points conclusively to the acid character of color.

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SOME FURTHER RESULTS OF THE HYPOCHLORITE DISINFECTION OF THE BALTIMORE CITY WATER SUPPLIES—A COMPARISON OF THE REDUCTION OF THE DIFFERENT MEMBERS OF THE B. COLI GROUP[1]

By J. Bosley Thomas and Edgar A. Sandman

We have shown in a previous paper[2] some of the results obtained in the hypochlorite disinfection of the Baltimore City Water supplies during 1912, when the disinfectant was applied at the effluent of the impounding reservoir. During 1913 the treatment was continued, pending the completion of a filtration plant, but the chemical was applied at the effluent of the first storage reservoir, after the water had been subjected to a longer period of sedimentation, and had received, during periods of high turbidity, a preliminary treatment with aluminum sulfate. After receiving the hypochlorite treatment the water passes through about a mile of conduit to a second storage reservoir where it is retained for a period of from five to seven days before entering the distribution system.

In addition to the use of the water from this supply, known as the Gunpowder River, another supply, which was seldom used during the previous year, was brought into service again. The water from this supply, known as the Jones Falls, was treated at the impounding reservoir, from which it flows through about a mile of conduit to the first of two storage reservoirs.

The amounts of available chlorine applied to these supplies varied between 0.65 and 2.00 parts per million parts of water. The averages per month are shown in Tables I, II and III.

As in the work of the previous year, the *B. coli* averages were obtained from daily tests made with portions of water varying by a multiple of ten from 0.001 cc. to 100 cc., sufficient tubes being used in each case to secure at least one negative and one or more positive tests, excepting when no fermentation was obtained with 100 cc. Lactose bile was used as an initial medium and Endo's agar for isolating the *B. coli*-like organisms in pure culture. In our previous work no differentiation was made in the members of this group, but later these organisms were divided into four sub-groups by the use of dulcite in addition to the commonly used sugars and gelatin. For the purpose of this classification those organisms causing gas production in lactose, dulcite, saccharose and dextrose without liquefaction of gelatin were considered to be *B. coli communior;* those causing gas production in lactose, dulcite and dextrose without liquefaction of gelatin were classified as *B. coli communis;* those

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[1] Read before the Section of Water, Sewage and Sanitation at the 49th Meeting of the American Chemical Society, Cincinnati, April 6–10, 1914.

[2] This Journal, **5**, 476.

TABLE I—MONTHLY AVERAGES OF BACTERIAL COUNTS OF THE BALTIMORE CITY WATER SUPPLIES BEFORE AND AFTER TREATMENT—GUNPOWDER RIVER SUPPLY

	FIRST STORAGE RESERVOIR								SECOND STORAGE RESERVOIR				
	INFLUENT				EFFLUENT				INFLUENT		EFFLUENT		
	G. per gal. coagulant added	Turbidity	Bacteria per cc. growing at 37° C.	Bacteria per cc. growing at 20° C.	P. p. m. available chlorine	Turbidity	Bacteria per cc. growing at 37° C.	Bacteria per cc. growing at 20° C.	Bacteria per cc. growing at 37° C.	Bacteria per cc. growing at 20° C.	Turbidity	Bacteria per cc. growing at 37° C.	Bacteria per cc. growing at 20° C.
January	...	11	270	2,800	0.65	9	75	27,000(a)	..	..	8	32	14,000(a)
February	...	9	55	5,500	0.80	7	24	750	..	..	6	12	14
March	...	8	36	1,900	0.85	6	32	1,200	..	..	5	9	39,000
April	0.692	49	1,100	8,500	0.80	8	110	4,800	..	..	9	16	11,000
May	0.532	38	600	13,000	0.80	7	140	1,800	13	15	7	27	2,100
June	0.803	44	170	1,100	0.85	6	160	450	34	95	10	10	85
July	0.931	85	280	950	1.00	8	47	180	20	42	11	10	12
August	1.237	80	470	7,000	1.50	8	55	90	11	14	9	5	3
September	1.207	95	850	6,500	1.75	8	90	140	1	1.5	8	1	2
October	1.144	80	750	850	2.00	7	60	110	0.6	0.3	6	0.4	0.3
November	0.633	45	2,200	15,000	1.75	7	160	2,100	0.8	1	6	3	0.9
December	0.604	19	200	31,000	1.50	6	42	28,000	4	5	5	0.9	1.1

(a) After-growths resulting from treatment formerly conducted at the impounding reservoir.

causing gas production in the three sugars but not in dulcite with or without liquefaction of gelatin as *B. lactis aerogenes;* and those causing gas production in lactose and dextrose only were called *B. acidi lactici.* It should be borne in mind that this is but a general classification, and it cannot be claimed that the organisms in all cases were strains identical with the classical types. Some of the cultures classified as *B. lactis aerogenes* A_3, in accordance with the last report of the Committee of the American Public Health Association on standard methods of water analysis, no doubt, were species of cloacae capable of causing gas production in lactose, while some others which at first could cause no gas production in lactose were found, after repeated rejuvenation, to produce this change. Furthermore, it is doubtful whether four weeks is long enough time for the observance of liquefaction. We made readings at the end of two weeks and again after four weeks, and found that many of the liquefactions occurred after the first two weeks and that some showed only slight signs of liquefaction at the end of a month. And, again, it is an open question whether the *B. acidi lactici* is a true type or, after all, only a form of *B. coli communis.* It is not within the province of this paper to consider this matter further, but we would say that, although some of the strains of so-called *B. acidi lactici* undoubtedly show signs of motility, there seems to be a fundamental difference between them and the classical type of *B. coli communis* in that they cannot be made to cause gas formation in dulcite.

TABLE II—MONTHLY AVERAGES OF BACTERIAL COUNTS OF THE BALTIMORE CITY WATER SUPPLIES BEFORE AND AFTER TREATMENT—JONES FALLS SUPPLY

	IMPOUNDING RESERVOIR EFFLUENT				FIRST STORAGE RESERVOIR						SECOND STORAGE RESERVOIR EFFLUENT		
					INFLUENT			EFFLUENT					
	P. p. m. available chlorine	Turbidity	Bacteria per cc. growing at 37° C.	Bacteria per cc. growing at 20° C.	G. per gal. coagulant added	Bacteria per cc. growing at 37° C.	Bacteria per cc. growing at 20° C.	Turbidity	Bacteria per cc. growing at 37° C.	Bacteria per cc. growing at 20° C.	Turbidity	Bacteria per cc. growing at 37° C.	Bacteria per cc. growing at 20° C.
January	1.50	23	390	10,000	0.617	100	2,800	19	95	6,500	22	100	3,800
February	1.50	11	75	490	0.664	36	36	6	22	12	7	27	15
March	1.50	22	150	2,100	0.585	90	480	21	45	130	21	43	190
April	1.50	40	430	5,000	0.938	240	1,800	60	250	750	34	130	420
May	1.50	30	160	650	0.581	95	150	17	70	140	8	29	55
June	1.35	13	110	470	0.000	65	250	16	140	2,000	7	45	500
July	1.50	17	220	950	0.000	110	1,300	11	170	1,000	7	23	370
August	1.75	22	800	1,100	0.753	80	160	8	180	460	7	28	130
September	2.00	35	850	4,100	0.719	95	95	15	12,000	25,000	7	95	220
October	2.00	29	600	4,200	0.694	55	23	20	600	2,500	6	38	100
November	1.75	12	210	1,800	0.430	50	450	9	50	15,000	4	13	600
December	2.00	15	140	18,000	0.000	35	800	10	43	430,000	6	13	20,000

TABLE III—YEARLY AVERAGES OF BACTERIAL COUNTS AND *B. Coli* TESTS OF THE BALTIMORE CITY WATER SUPPLIES BEFORE AND AFTER TREATMENT

	GUNPOWDER RIVER SUPPLY				JONES FALLS SUPPLY			
	First storage reservoir		Second storage reservoir		Impounding reservoir effluent	First storage reservoir		Second storage reservoir effluent
	Infl.	Effl.	Infl.	Effl.		Infl.	Effl.	
G. per gal. coag.	0.865	...	..	...	...	0.498	..	...
P. p. m. avail. Cl.	...	1.19	..	...	1.65	...	..	...
Turbidity	47	7	..	8	22	...	18	14
Bact. per cc. at 37°	600	85	11	11	350	85	1,100(d)	49
Per cent reduction	...	86	85(b)	85(b)	...	76	..	...
Bact. per cc. at 20°	8,000	3,600(a)	22	5,500(c)	4,000	700	40,000(c)	2,200
Per cent reduction	...	55	99(b)	...	...	83	..	...
B. coli communis	1.638	0.219	..	0.001	0.263	...	0.016	0.008
Per cent reduction	...	86	..	99(b)	...	...	60	98
B. coli communior	5.034	0.389	..	0.009	3.030	...	0.143	0.004
Per cent reduction	...	92	..	98(b)	...	...	96	99
B. lactis aerogenes	5.363	0.467	..	0.010	3.177	...	0.231	0.073
Per cent reduction	...	81	..	98(b)	...	...	93	97
B. acidi lactici	3.181	0.459	..	0.012	1.373	...	0.112	0.048
Per cent reduction	...	85	..	97(b)	...	...	92	97

(a) Eleven months' average, January being excluded on account of after-growths resulting from treatment formerly conducted at the impounding reservoir.

(b) Based upon first storage reservoir effluent, and therefore showing reduction due to hypochlorite.

(c) After-growths during several months.

(d) After-growths during September.

The enumeration of bacteria was made upon standard agar at 37° C. and at 20° C. The ratio of the yearly average of those organisms growing at 37° C. to those growing at the lower temperature was about 1 to 10, with a somewhat higher ratio in the winter months. The organisms growing at 20° C. suffered a greater percentage reduction from the effect of the hypochlorite than those growing at 37° C., which may be due, in part, to the fact that there was a greater number originally present, and because the saphrophytic organisms may be more vulnerable to the treatment. These reductions were 99 per cent and 85 per cent, respectively, in the Gunpowder River supply, and 83 per cent and 76 per cent, respectively, in the Jones Falls supply. On the other hand, the preliminary storage and sedimentation with rather constant use of a coagulant effected a reduction of only 55 per cent of the organisms growing at 20° C., whereas the organisms growing at the higher temperature were reduced by 86 per cent. The four sub-classes of the *B. coli* group were all reduced by nearly an equal amount which varied between 97 per cent and 99 per cent. The *B. lactis aerogenes* and *B. acidi lactici* suffered the least reduction, but the difference is so slight that, although based upon some fifteen hundred isolations, the results do not warrant any conclusion that these types are any less vulnerable to the treatment than the true *B. coli communis* or *B. coli communior*.

During the time when the amount of available chlorine applied exceeded 1.50 parts per million there was frequently observed in the water from the city taps an odor of chlorine, or an odor apparently due to chlorine, and the presence of residual chlorine could be demonstrated by chemical tests; but with the use of 1.50 parts or less few complaints were received, although trouble was still encountered by the ice companies using this water for the manufacture of ice. The odor was most noticeable in the core ice where it becomes segregated as the water freezes, and as distillation of the water before freezing does not remove this odor, it would seem that the chlorine is in some organic combination that passes over with the distillate.

The number of cases of typhoid fever occurring in Baltimore during 1913 was seventeen per cent less than an average of the number of cases occurring during the five years from 1906 to 1910 before the treatment was instituted.

WATER DEPARTMENT, BALTIMORE

A SANITARY SURVEY OF WHITE RIVER[1]

By JOHN C. DIGGS

During the summers of 1908 and 1910 the Water Department of the Indiana State Board of Health made investigations of the sanitary condition of the waters of the southern end of Lake Michigan and of the Calumet River. These surveys disclosed such grossly polluted conditions that it seemed wise to continue similar work on the other streams of the State. In 1911 that portion of the Ohio bordering Indiana was studied and in 1912 attention was given to the Wabash River. These investigations proved both of these streams to be seriously polluted by domestic sewage and manufacturing wastes.

In 1913 the west fork of White River, a stream rising in and traversing its entire course through Indiana, was selected for study. White River is not a large stream, but it is of great importance as a source of water supply for many Indiana cities.

The watershed of the west fork of this stream has an area of 5,034 square miles (one-seventh of the total area of the State). The population of the drainage basin is approximately 638,000. The rural population is 275,000 and the urban 363,000. The average population for the entire basin is 127 per square mile. The highest density, 664 per square mile, is in Marion County, the seat of Indianapolis.

Although the valley of the river is only 275 miles in length, the course of the stream covers 388 miles, due to meanderings and many short curves. Throughout the upper portion, the river is small and very rapid, but from Indianapolis to its mouth it is sluggish and flows in a wide channel.

In the study of the conditions of the stream, attention was given to the following features:

1—General features of drainage basin.
  a—Topography and geology.
  b—Principal tributaries.
  c—Gradient.
  d—River stages and river flow.
  e—Precipitation.
  f—Population of watershed.
2—Water works system.
3—Sewage systems and sewage disposal.
4—Disposal of garbage and night soil.
5—Manufacturing wastes.
6—Oil well wastes.
7—Typhoid fever.
8—General sanitary condition of cities.
9—Sanitary condition of White River.
10—Chemical and bacterial analyses.
  a—From White River, including study of cross river and depth of samples.
  b—Samples from tributaries.
  c—Samples from cities and towns.
    (1) Public: (*a*) surface supplies; (*b*) ground waters.
    (2) Private: (*a*) wells; (*b*) springs; (*c*) cisterns.

The upper portion of the stream was surveyed on foot and by means of a row boat. Samples were collected at frequent intervals from the river and sent to the laboratories of the State Board of Health at Indianapolis for analysis. From Martinsville, a point 43 miles below Indianapolis, to the mouth of the river the work was conducted from a floating laboratory. This was a house boat 40 feet long by 13 feet wide, stern wheel paddle, equipped with room for laboratory, living and sleeping quarters. The surveying party consisted of four to five men made up partially of students taking scientific courses in the State Universities.

Samples were collected at points in the river as the boat moved down stream. Stops of several days were made at towns bordering on the river. At these places samples were collected from public and private water supplies and sanitary surveys of the towns conducted. During the course of the work a total of 779 samples of water were collected and analyzed (391 river samples and 388 from private water supplies, driven wells, dug wells, cisterns and springs); 45 per cent of this number were good, 40 per cent bad and 15 per cent of doubtful quality.

Of the 197 dug wells which were examined, only 50

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[1] Presented at the 49th Meeting of the American Chemical Society, Cincinnati, April 6–10, 1914.

or 25 per cent were good, 58 per cent were bad and 16 per cent classed as doubtful; 11, or 72 per cent, of the 154 driven wells examined, were found to be good, 12 per cent were bad and 16 per cent of doubtful quality. Of 7 springs examined, 3 were good, 3 bad, and 1 doubtful.

At the time of the collection of the samples special notice was given to the sanitary condition of the backyard in which the well or cistern was located. In some places as many as half a dozen wells and a dozen privies (the unsanitary type) occurred within a radius of 100 ft. In most cases the soil was made up largely of gravel, allowing at least a fair filtering material. In one instance, Gosport, Indiana, the wells occurred in a stratum, locally known as Mitchell limestone. This is a very extensively fissured material and quite soluble. Practically all the wells of the town draw their supply from the same vein, or underground stream of water. When one owner cleans out his well, the neighboring wells are muddied. From the analyses of these supplies it was quite evident that this same underground stream served the double duty of water supply and sewerage system.

In carrying on the investigations in towns, coöperation of local health officers was obtained. Many of the unsanitary conditions were remedied and polluted wells abandoned.

This paper can hope to give no more than a mere outline of the work done. Detail of the methods employed will be found in the 1913 report of the Indiana State Board of Health.

From the inspection of local conditions, study of water supply (public and private) and methods of sewage disposal much information has been obtained which will be of great value to the public of the State.

White River is a comparatively small stream, yet it is used as a source of public water supply and sewage disposal for over 300,000 people. It is seriously polluted and in many places a great detriment not only to the health of persons using it as a supply, but in some places to persons living along its banks.

Many private supplies of the State are seriously polluted. This especially applies to dug wells.

This survey shows need of legislative power to be vested in central authority, naturally the State Board of Health, whereby the rivers, our natural resources, can be saved for the future generations. The public is beginning to realize that it is not properly conserving its resources when it permits the streams of its State to be defiled by the refuse of its cities. But public opinion is slow to form and the need of education is decidedly apparent. To collect data regarding the unsanitary conditions of the streams, to determine the tremendous amount of waste which goes into them and to point out to the public the number of deaths and amount of sickness which may be traced back to the polluted water, become the duties of health departments. But education, in many cases, will not cause the packer to cease dumping his offal into the streams. Then it becomes the duty of the health authorities to present to the legislative bodies facts concerning the unsanitary conditions and their causes, that the health of the public may be sought before the financial gain of an individual.

INDIANA STATE BOARD OF HEALTH
INDIANAPOLIS

AN INVESTIGATION INTO THE CHEMISTRY OF LAUNDERING[1]

By W. F. FARAGHER

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The laundry industry is one of a group which are not usually classified as strictly chemical industries, but which, nevertheless, depend in large measure upon the proper control of chemical reactions for their successful operation. The list includes, among others, bakeries, glass factories, brick plants, brass and iron foundries, confectioneries, tanneries and creameries. Although the laundry industry is one of the most important, both in point of the nature of the service it renders modern civilized communities and of the number of employees and the capital invested,[2] it is perhaps the last to avail itself of the benefits to be derived from an extensive adoption of the methods and teachings of chemical and engineering science.

A great deal of ingenuity has been displayed in bringing the processes and machinery employed to their present state, but investigation shows that before the industry may rightfully be classed as an efficient one, much improvement is necessary, especially in the case of the chemical processes which occur either as essential parts of the operation, or as harmful accompanying reactions.

As a result of the study given to the production of high-grade laundry work by the more progressive men engaged in the industry, empirical methods are now quite generally employed in the best plants which leave little to be desired as far as the appearance of the finished articles is concerned. But for the purpose of investigating the possibility of introducing more scientific methods, which would improve conditions by prolonging the period of usefulness of the articles laundered and also by reducing the cost of production of the work, the experiments to be described were carried out.

The work of the laundry is necessarily complex, but may be conveniently divided into a number of parts. Exclusive of the collection and delivery of the bundles, and of the marking and listing of the articles in each bundle to make possible their return to the respective owners, the following operations may be enumerated: sorting, washing, extracting, that is, the removal of excess water by means of centrifugal machines, starching, drying, dampening, ironing, and finally finishing or folding into neat compact form, and sorting into lots to be tied up later into bundles.

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[1] These data represent a part of the work done during the author's tenure of the Alden Speare Fellowship (September, 1907, to December, 1909). The work was carried out under the direction of the late Dr. Robert Kennedy Duncan, to whom the author owes much for valuable advice and encouragement. The author wishes also to express his appreciation for the helpful assistance rendered by Dr. Hamilton P. Cady.

[2] The census of 1910 included power-laundries for the first time. The number of plants reported is 5184. This does not include the laundries in hospitals, public institutions and shirt and collar factories. A careful study of conditions in Chicago indicates an annual volume of business close to $3,000,000.

Obviously, many of these operations have little to do with chemical processes, and it is only with the washing that these experiments are concerned. In fact, it is this part of the process alone which is distinctively chemical, and which seems most largely responsible for the complaints now made against the results obtained in well managed laundries.

On account of the great variety of articles brought to the washroom, it is evident that different treatment must be accorded to the different kinds of fabrics. The only classes which are of great importance are those consisting of articles made from cotton, linen, silk and wool. Greater diversity is caused, however, by the very large list of dyestuffs which are now employed on all of the above groups.

In the case of undyed fabrics of cotton or linen, the treatment employed is, perhaps, the most drastic, and it is largely on account of the too early disintegration of articles of this class that complaints are justly and so frequently made. Since all articles are submitted to the less harmful operations employed in the case of these undyed articles, the experiments were carried out in accordance with the modern practice of handling such articles as are made from cotton and linen only, and which have not been dyed. This seems justifiable, because these articles form the largest part of the work done, and also because the effects produced are necessarily similar in so far as the various operations are duplicated in the case of the other classes of articles. This does not apply to the effect on the dyestuffs, but rather to the weakening of the fabrics. The former problem was not taken into consideration here.

In the sorting room, all articles are separated into lots, according to the kind of fabrics, the nature of the dyestuffs, and finally the extent to which the articles are soiled. Since these different lots are to be washed differently, this separation is preserved throughout the whole course of treatment.

WASHING MACHINES USED IN LAUNDRIES

The machines in which the washing is done consist of two concentric cylinders separated by a space of several inches. The outer cylinder is stationary and is carried on a metal stand for securing the whole machine in position. It is provided with the necessary boxing and gearing for causing the inner cylinder to revolve and to reverse automatically after several revolutions in one direction. It has also pipes for introducing hot and cold water and live steam, and a drain pipe for discharging the liquids after they have done their work. The inner cylinder into which the articles are placed, is perforated so that the liquids may have free access to the fabrics. Both cylinders are provided with suitably hinged doors, so that the articles may be readily introduced and removed. The sizes of the machines vary from small ones, washing fifty shirts, to very large ones, which can handle five hundred shirts at one time. After the articles are placed in the machine they are not removed until they have been cleansed and given the proper color by means of detergents, bleaches and bluing materials. The different solutions are introduced in order and run off after they have performed their respective functions.

The principle upon which the washing is effected is simple. By the revolution of the inner cylinder, the articles are carried part way up the sides, and then fall down into the solutions, causing the latter to be forced through the fabrics, and thus insuring intimate contact between the detergents and the substances to be removed.

LAUNDRY PROCESS IN GENERAL USE

In order to proceed with the problem in hand, the first step was the investigation of the process in general use, in order to determine what parts were defective, and the causes for, as well as the nature of the harmful results produced.

The machine of average size will permit the washing of about one hundred shirts, weighing about seventy-five pounds. The volume of the different solutions used in such a machine is approximately twenty-five gallons. The method of washing is as follows: Cold or luke warm water is admitted and the machine is allowed to run for from five to ten minutes. Very frequently sufficient sodium carbonate, or so-called neutral washing soda,[1] is added to make from $^1/_4$ to 1 per cent solution. The water, or weak alkaline solution, removes some of the starch from starched goods, carries off surface dirt and dissolves stains of an albuminous character, which otherwise might be set by coagulation of the albuminous substances, if hot water were used at once.

Warm water is next admitted and soap added together with some alkaline substance, such as sodium carbonate, neutral washing soda, caustic soda or borax. The first two are the ones most frequently used. The soap is used in from $^1/_4$ to $1^1/_4$ per cent solution, and the alkaline substance in about the same strength. Steam is then admitted and the temperature brought to the boiling point in from ten to twenty minutes. The time of running in this solution is usually from twenty to thirty minutes.

This solution is discharged and another of from $^1/_2$ to $^2/_3$ the strength of the first is added. In some instances a hot rinse is given between the two solutions

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[1] These sodas are mixtures of sodium bicarbonate and sodium carbonate. Analyses which are perhaps typical for articles of this kind are:

Na_2CO_3	46.3	36.1
$NaHCO_3$	37.7	50.0
H_2O and impurities	16.0	13.9
	100.0	100.0

These articles find large sale because they do not yield as strongly alkaline solutions as when sodium carbonate alone is used. The hydrolysis of the sodium carbonate is less extensive in the presence of the bicarbonate than when alone. Theoretically, it is possible to prepare a solution from sodium carbonate which will have the same concentration of hydroxyl ions as is present when a given concentration of these neutral sodas (so-called) is employed. The weight of sodium carbonate is in every case less than that of the neutral soda, and as the price of the two products is nearly the same, a material saving can thus be effected. The difficulty met with in the laundries seems to be attributable to the fact that in replacing a neutral soda by sodium carbonate, the same weight is used, owing to ignorance of the above conditions, and this naturally yields a solution which is too strongly alkaline. Several plants have been induced to decrease the quantity of sodium carbonate to half (or even less) of that used in the case of the neutral sodas, and results have been obtained which are satisfactory in every respect. Summer soda crystals have also been used as a neutral soda ($Na_2CO_3.NaHCO_3.2H_2O$).

in order to carry off the remaining dirty suds. The bleach is also added in this second suds, and the whole run for about the same length of time as the previous one. The bleach used is prepared by adding sufficient sodium carbonate to bleaching powder to convert the calcium salts into the more soluble sodium salts. This has the advantage that none of the soap is decomposed with the formation of lime soap, as would be the case if bleaching powder itself were used. The quantity of bleach used varies from the equivalent of $^1/_4$ to $^3/_4$ of a pound of commercial bleaching powder. The bleach liquor is generally added at the beginning of the run, the steam being admitted so as to bring the temperature to the boiling point in from fifteen to twenty minutes. The boiling is continued, and the whole time of run made from twenty to thirty minutes. From two to four hot rinses follow this suds-bleach treatment.

The next solution is an acid bath. The acids most frequently used are acetic and oxalic. Sufficient acid is added to make the solution about $N/50$ (equivalent). This acid is used for the purpose of neutralizing any alkaline substances which have not been rinsed out, and to cause the aniline blue, which is used subsequently, to produce an even color. If the blue is not added in the acid bath, it is used in the next water. From one to four rinses, sometimes hot, sometimes cold, are given after the bluing.

After the above course of treatment the articles are removed from the machine and placed in the basket of a centrifugal machine, in order to remove the excess of water. Articles which need no starching are usually ironed at once after removing from the centrifugal machine, while the others are sent to the starch room. After starching, all articles are dried by being placed in a drying-room heated to 100° C. by steam coils, and provided with a ventilating fan for removing the moist air. After dampening to the proper degree, the ironing and shaping are next done.

PRELIMINARY EXPERIMENTS ON DIFFERENT PARTS OF ABOVE PROCESS

The first plan adopted for comparing the harmful effects of the different parts of the process outlined above, was to take four series of turnover collars, five to a series, and submit each series to one of the above parts of the washing process, that is, one series to the soap-alkali, one to the bleach, one to the acid and one to water only, in order to have a check on the mechanical effects produced in the washer and in the ironing machines. After each treatment in the laboratory wash machine, under conditions as nearly as possible like those obtaining as an average in general practice, the collars were rinsed (except in the case of the acid series), then taken to a custom laundry to be starched and ironed. The plan was to repeat this treatment in each case until the edges of the collars broke, thus showing the relative harmfulness of the different treatments.

The quantities of soap and soda ash used were 190 grams soap and 95 grams of soda ash per gallon of solution. These quantities are larger than those generally employed, but were chosen rather than quantities below the average. The soap used was a neutral soap made from good red oil or commercial oleic acid, and analyzed as follows:

Water	20.7
Na_2O as soap	9.3
Fatty acid anhydrides	69.5
Soda ash	0.1
NaCl	0.2
Unsaponified	0.1

The soda ash was analyzed and found to be a good commercial product, containing only a small percentage of soluble and insoluble impurities.

The bleach solution was made by taking 12.5 grams of bleaching powder and 8.2 grams of soda ash per gallon of water. It was necessary to add sufficient cloth so that the ratio of the weight of cellulose to the weight of the solution might be comparable to that in practice. The bleaching powder was analyzed and found to contain 26.8 per cent available chlorine. It was a sample obtained from a custom laundry and was of poor grade. The acid used was oxalic and a sufficient amount of it was added to make the solution approximately $N/50$. As has been stated above, no rinse was given after the acid was used, although most laundries now rinse at least once. However, at that time many plants were found which did not rinse subsequently, and this more severe test was made in order to compare its effects with the bleaching which was expected to prove quite harmful. The results obtained were as follows:

Bleach Series: Two broke on 7th time; one on 8th; all on 9th time.

Acid Series: One broke on 5th time; one on 6th; two on 7th; all on 9th time.

Soap and Alkali: All intact 15th time.

Water: All intact 15th time.

The last two series were lost on account of an accident in the laboratory, but they had run sufficiently long to establish the fact that under the conditions of the tests the acid and the bleach are the most destructive chemicals employed. Other series which were comparable to the soap-alkali series were later run as high as twenty-five times before a break occurred, showing that the conclusions drawn above were justified.

THREAD ADOPTED FOR TEST PIECES

The above method was not considered satisfactory for further comparisons, because of the length of time necessary to carry it out and also because of the uncertainty of being able to give all of the collars the same treatment during the starching, ironing and finishing. For this reason the method of determining the breaking strengths of test pieces before and after the various treatments was adopted. On account of the difficulty encountered in attempting to use test pieces in the form of strips of cloth or skeins of yarn, for the reason that it is almost impossible to distribute the strain equally throughout the pieces, the use of single threads as test pieces was decided upon. It was thought that the warp or weft threads of a good grade of muslin or linen cloth might be used, but these were found to be too irregular to make their use advisable. The most suitable material that could be found was a good grade of white thread.

TESTING MACHINE USED

The testing machine used was designed and made in the University Instrument Shop. It is similar in principle to the machines which are in general use for determining the tensile strength of paper. The test piece, about five inches in length, is fastened between two clamps, and the force is applied by causing a weighted arm, to which one end is clamped, to move through an arc by turning a geared wheel which moves a slow-motion screw to which the other clamp is fastened. A scale graduated by means of known weights is placed in front of the weighted arm, and the position of the arm at the time of breaking is marked by a light rider which is caused to move along the scale.

METHOD OF TESTING

Because of the fact that thread is not uniform in cross-section and in the twist, that is, the number of turns per inch due to the spinning, the breaking strengths of pieces from the same spool show large variations. Numerous tests showed that the strength for a No. 20 thread ranged from 1300 to 1900 grams. On account of this great variation it is necessary to employ a large number of test pieces in each series, in order that the mean value may be significant. The thread was sampled by taking every twentieth length of five inches for twenty series of one hundred test pieces each.

Experiments made with a number of these series, after the sizing materials had been removed by boiling the threads for an hour in 1 per cent sodium carbonate solution, showed that the different mean values agreed satisfactorily, usually well within one per cent. With this agreement, the method seems well adapted for making comparisons of the effects of different chemicals, used under various conditions, upon the tensile strengths of cotton thread. It is evident that the breaking strength is closely related to the wearing qualities of threads, and hence of pieces of fabric, under the conditions to which they are subjected in use.

It was found that different spools of thread differed from one another more than the series of threads from one spool differed from each other. For this reason it is necessary to determine the breaking strength for each lot of threads prepared.

COMPARISON OF METHOD WITH PRELIMINARY EXPERIMENTS

Tests were run upon threads, employing solutions of the same kinds and of the same strengths as were used in the experiments on the collars. After each of the processes had been repeated ten times the breaking strengths were determined. The conditions were made as nearly the same as possible, both as regards the times of treatment and ratios of the weights of solutions to the weights of cellulose. The results were as follows:

Original breaking strength, ave.	1724 g. (1722, 1723, 1724, 1726)
Soap-alkali series	1861 g.
Bleach series	181 g.
Oxalic acid series	265 g.

The probable error in the original figured by method of least squares is ±7 grams. These figures confirm the results of the practical tests with collars, and the agreement speaks in favor of the use of the new method which is more rapidly carried out and is more easily controlled.

As has been stated above these results do not permit the drawing of conclusions concerning the actual amount of damage done in the different processes in the best plants. The figures do, however, indicate the parts wherein most care must be exercised and in which improvements are most needed.

The soap-alkali treatment is, perhaps, the least harmful of all the different operations. Experiments showed, however, that if the quantities of alkaline substances were not kept low, the threads were attacked and, although the breaking strength was not affected as greatly as in the bleach and acid series, the appearance suffered, owing to the formation of a woolly coating of loose ends of fibers. The damage done in the acid bath is easily made less than in the case of the tests, for thorough rinsing will remove the acid and prevent its doing damage in the dry room or in the ironing machines.

REACTIONS OF CELLULOSE

Cellulose, which is chemically one of the most inactive of the carbohydrates, is nevertheless extensively attacked by acids, alkalies and bleaches under conditions which often exist in laundries. In the presence of hydrogen ions, cellulose is converted into another substance, hydrocellulose, which differs from the former in many ways. The most important difference for the purpose in hand is that hydrocellulose is a friable substance and, therefore, is valueless under the conditions to which fabrics are subjected in use.

The acid solutions employed in laundry work are relatively dilute, and the extent to which the cellulose is acted upon while in these solutions is small. It is essential, however, that the acid be thoroughly removed because when the articles are placed in the drying room, or are caused to pass over the heated surfaces in the ironing machines, the dilute acid is concentrated and this, together with the high temperature, produces rapid conversion of the cellulose. This practice of rinsing after the acid is discharged is now quite general and is a decided advance in the right direction.

The velocity of this reaction is proportional to the concentration of hydrogen as ion present, and is also greatly accelerated by rise in temperature, in accordance with the general rule for the effect of temperature on chemical reactions.

REAGENTS USED IN TESTS

As has been stated, the soap and soda ash used were of good quality. Very different results have been obtained by others when the soaps and sodas used were adulterated. Dr. Kind[1] has carried out a large number of experiments and has proved conclusively that detergents which contain large percentages of silicate of sodium cause a rapid deterioration in cotton and linen fabrics. Kind attributes this effect to the action of the hydroxyl ions formed by the hydrolysis of the silicate and to the deposition in the fibers of silicic acid, and also of insoluble silicates which are formed when hard water is used. These deposits are shown to be very extensive under some conditions,

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[1] "Die Wirkung der Waschmittel auf Baumwolle und Leinen," A. Ziemsen Verlag, Wittenberg, 1909.

amounting, in one case where a series of test threads were washed thirty times in a 2 per cent solution of 38° Bé. sodium water glass, to 14.2 per cent. The water glass analyzed 27 per cent silicic acid and 0.12 per cent free caustic soda. These threads were brittle owing to the presence of the encrusting substances which did not allow the fibers to yield when subjected to a bending strain, and the threads were also weak on account of the disintegration caused by the loosening up and separation of the fibers composing the thread. Kind's work shows that the action is more severe in the case of linen than of cotton.

In the case of soaps and sodas which contain peroxides and perborates, Leimdoerfer[1] has shown that the harmful effect is also great.

The presence of rosin in soaps has been shown to be objectionable because of the fact that the rosin acids which are formed by hydrolysis of the soap settle in the fibers and produce a decided yellow cast in the finished products. Professor Herbert Jackson[2] has shown that soaps which contain as little as 5 per cent rosin are objectionable for this reason.

Many sodas have been found to contain adulterants: some harmful, as sodium silicate and caustic soda, and some inactive, such as common salt and sodium sulfate. It seems certain from the above tests, however, that if pure soap and pure alkalies are used in quantities no larger than are necessary, the weakening of the fibers treated is not very great.

ACTION OF ALKALI

The following experiments were performed, using solutions of sodium carbonate which are much stronger than those used in practice. The threads were suspended from cords in the boiling solutions and were provided with glass weights to keep them immersed. The boiling was done in open beakers and the water removed by evaporation was replaced at regular short intervals. The times of boiling, strength of solutions and position of the test threads were as indicated.

The reason for exposing some of the series to the action of both the alkaline solutions and the air, was to determine whether or not the weakening produced was greater under these conditions than when oxygen was excluded by complete immersion. Text books describing the manufacture of textile fabrics generally state that cellulose must not be exposed to the air when it is being boiled in alkaline solutions because the oxidation of cellulose which occurs under these conditions will render the fabrics tender.

Original breaking strength, ave.	1696 (1693, 1709, 1696, 1684)
Boiled in 1 per cent Na_2CO_3 5 hrs., one-half exposed to air and one-half immersed in the solution	1711–1666
Same as above, but completely immersed	1634, 1634
Boiled in 2.5 Na_2CO_3, for 3.5 hrs. half immersed	1648
Same as one above but completely immersed	1636
Boiled in 5 per cent Na_2CO_3 for 3.5 hrs., immersed completely	1625, 1622
Same as above, except half immersed	1627, 1610

These results show that even if much stronger solutions than those ordinarily used are employed, the damage done is not excessive. The color, however, is not so clear, and the same roughening of the threads mentioned above is noticed. The formation of lint is also greatly increased when large quantities of alkali are used.

Since the boiling of threads, even in quite strongly alkaline solutions, does not produce great deterioration, it was thought well to determine the effect of alkalies which are not completely rinsed out. The tests were made by dipping the test pieces into a 1 per cent sodium carbonate solution, squeezing dry by hand to about the same extent as would be the case in a centrifugal machine, and then placing in a drying oven heated to 100°. This process was repeated ten times, rinsing with distilled water between each treatment, and the breaking strength determined. Repeated weighing of the dry threads and also of those which had been wrung after dipping into the solutions showed that a weight of the solution about equal to that of the threads was retained. It was possible to get the amount of solution retained to agree to within about two per cent. The result was as follows:

Original strength	1696
After ten treatments	1420

It is, therefore, very necessary that the alkali be removed by rinsing and by the acid bath which is given later, as otherwise both the color of fabrics and their wearing qualities suffer markedly.

RINSING

HOT WATER—The advantage of using hot water for rinsing is obvious, for if cold water is used and soap is present in the hot fabrics in quantities larger than are soluble in the cold water, this soap will be precipitated and will redissolve slowly. All of the substances which are to be removed are more soluble in hot water than in cold, and in addition diffuse more rapidly with rising temperature. Consequently hot water is the more desirable.

HARD WATER—Since hard water forms difficultly soluble calcium and magnesium soaps with the soluble sodium soap remaining after the washing process and as these do not form a suds, rinsing appears to be more quickly and efficiently done with hard water than with soft. In order to test this assumption which is general among launderers, the following experiments were made:

Pieces of cloth of about the same size were weighed under the same atmospheric conditions, when air-dry. These pieces were then dipped into and washed about in the soap solution such as has been used throughout this work. Some of the pieces were then rinsed three times in tap water and some in distilled water, care being taken to give the test pieces the same mechanical treatment. The tap water analyzed 14.5 degrees of hardness. After standing until air-dry the pieces were reweighed under the same atmospheric conditions. The results were as follows:

Weight in grams	No. 1	No. 2
Of cloth after rinsing in soft water	22.074	21.510
Of cloth air-dry at start	21.877	21.396
Of substances retained	0.197	0.114
Of cloth after rinsing in hard water	22.230	21.643
Of cloth air-dry at start	21.895	21.394
Of substances retained	0.335	0.249

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[1] "Wasch-, Bleich-, Blau-, Staerke- und Glanz-mittel," L. Andes, 1909, Hartleben, Wien, p. 14.

[2] Cantor Lectures for 1907, p. 12.

DISTILLED WATER—The last rinse water in the case of the pieces rinsed in distilled water was soapy and considerable suds was formed. However, the weighings show that the rinsing was much more efficient in the case of the distilled water series. This is due to the fact that the insoluble soaps which are formed in the fibers when hard water is used are very difficult to remove.

Upon drying the different pieces in an oven at 100° for thirty minutes, the pieces rinsed in soft water were of much better color than the others. Pieces which were allowed to dry at room temperature showed after several weeks a much yellower color in those rinsed with hard water than in those rinsed with soft water.

That rinsing with soft water is advantageous is shown by the observation that the color of articles laundered in plants where this is the custom is uniformly better than that obtained in other plants.

DEPOSITION OF SALTS IN FIBERS OF FABRICS

A reason for the breaking of threads in fabrics which is thought by launderers to be, perhaps, the most frequent is the deposition in the fibers of calcium carbonate and lime soaps or the crystallization of soluble salts such as sodium chloride or sodium sulfate.

A saturated solution of slaked lime was neutralized with acetic acid. Threads were dipped into this solution, then into a 0.6 per cent solution of sodium carbonate. They were then well rinsed in distilled water and dried for thirty minutes at 100°. This operation was repeated ten times. In one case the calcium carbonate was allowed to accumulate, while in another it was removed after each treatment by means of cold dilute acetic acid followed by rinsing in distilled water.

Original strength	1696
Calcium carbonate accumulated	1656
Calcium carbonate removed each time	1633

Two other series were treated with solutions of sodium sulfate, allowing the salt to crystallize out after removing the excess of solution as was done in the experiments with sodium carbonate. The threads were dried for thirty minutes at 100°, and rinsed well between treatments. Ten treatments were given each series.

Original	1696
5 per cent sodium sulfate	1584
10 per cent sodium sulfate	1614

These tests seem to indicate that this cannot be considered a large factor in the disintegration of laundered articles.

ACTION OF ACIDS

MINERAL ACIDS—Owing to the high price of oxalic and acetic acids it was thought advisable to determine whether or not cheaper acids could be substituted. Sulfuric and hydrochloric acids were chosen as the most desirable ones, and a series of tests was run to compare the harmful effects produced.

The test threads were dipped into *N*/50 (equivalent) solutions, wrung dry, as has been described above, then dried in an oven at 100° for thirty minutes. This was repeated ten times in each case, rinsing with distilled water after each operation to remove the acid left in the threads.

Original strength	1717	Mean of (1706, 1680, 1718, 1716, 1767)
Acetic acid	1611, 1610	
Oxalic acid	682, 676	
Sulfuric acid	Less than 10	
Hydrochloric acid	Less than 10	

The results show clearly that the use of the cheaper acids should not be recommended for general adoption because the wash-room help cannot be depended upon to rinse sufficiently to remove the excess of acid employed. If the rinsing were sufficient, however, these strong acids might be used with entirely satisfactory results, as will be explained below.

USE OF ACID NECESSARY

It would seem that the use of acids might be dispensed with, or at least be made much less objectionable than at present. There are two facts, however, which seem to make the use of some acid indispensable. The small quantity of alkaline substances which is not removed by rinsing would have but little effect in weakening the fabric even if the articles were placed in the dry room or were passed over the heated rolls of an ironing machine. This alkali is objectionable, however, because it forms a bright yellow product with the oxycellulose which is produced by the action of the bleaching solution on the cellulose. Very small quantities of alkali are able to produce an undesirable color in a piece of bleached cloth, as will be shown later. Some acid is necessary, too, for the purpose of removing colored compounds of iron which are present as individual stains or as a general discoloration which results from the use of water or of supplies containing even small quantities of iron salts.

These tests indicate that by the use of acetic acid the damage done may be made almost negligible.

Acetic acid being a weak acid, that is one only slightly dissociated, yields relatively small concentrations of hydrogen as ion, and consequently the conversion of cellulose into hydrocellulose is effected by it less rapidly under corresponding conditions than when the stronger acids are used. The volatility of acetic acid also makes it less harmful than any of the other acids experimented with. It is interesting to note that the order in which the acids attack cellulose and decrease the breaking strength of the threads is the same as that in which they are found to be dissociated into their ions. In many localities, however, oxalic acid is the only substance which will remove the iron compounds sufficiently, and for this reason must be used. The troublesome iron compounds are either oxides or basic salts of iron, which are soluble in the presence of sufficiently large concentrations of hydrogen as ion. Oxalic acid possesses the additional property of forming a complex ion with iron as ion, and consequently is a more efficient solvent for these colored products than is acetic acid. Under these circumstances it has been found possible to effect an improvement by using acetic and oxalic acids together, using only as much oxalic as is required to correct the discoloration, and the acetic for making up the bulk of the acid. Careful rinsing is, of course, necessary in any case.

A series of threads was boiled in $N/10$ sulfuric acid for two and a half hours, and the final breaking strength was found to be 216. It is evident, then, that with the weaker solutions of the weaker acids used, and at the lower temperatures, the damage done while the articles are in the machine is not great.

POSSIBLE SUBSTITUTES FOR ACIDS

Acid sodium sulfate is a cheap substance which might be used for the acid bath. Theoretically, however, it offers little advantage over the use of sulfuric acid itself, because the concentration of hydrogen as ion from acid sodium sulfate is relatively large. This is so because sulfuric acid is a strong dibasic acid, and the bisulfate ion is, therefore, largely dissociated in weak solutions.

An acid sold under a trade name was analyzed and found to be commercial acid sodium sulfate. It was said to be absolutely harmless for laundry use. From the above considerations, this statement seemed very improbable. To test this assertion a series of threads was treated with an $N/50$ solution of the bisulfate in the same way that the experiments were made with the other acid solutions. The results show that the claims for this article were not founded upon fact.

Original breaking strength	1717
After ten treatments with $N/50$ bisulfate	170

The bisulfate is somewhat less harmful than sulfuric acid, owing perhaps to the fact that the salt crystallizes out during the drying process. It is more conveniently handled than sulfuric acid, which is a liquid, but certainly the launderer should know that he is dealing with a very strongly acid substance, and not with some harmless acid, as is often claimed in advertisements.

BLEACHING

Since the bleaching is unquestionably the most harmful of all the parts of the washing process, and it seems impossible to produce a sufficiently white color to satisfy the trade when no bleaching agent is used, a great deal of experimenting was done with a view to improving this operation. The objection to the method now employed is that the hypochlorite solution acts not only on the objectionable colored substances, but also upon the cellulose of the fabric, changing it into the brittle compound, oxycellulose. This formation of oxycellulose not only weakens the fibers to the extent to which they are thus attacked, but the oxycellulose is objectionable for a number of reasons. It is well known that oxycellulose is more readily dyed by basic dyestuffs than is cellulose itself, and for this reason any oxycellulose which is not removed is more deeply colored than the other parts. The behavior of oxycellulose in the presence of alkalies, which has been spoken of, is also a frequent source of trouble.

In order to determine whether or not this behavior is the cause for the yellowing of certain lots of clothes in the laundry and also of those which are stored after having been laundered, the following experiments were performed:

Some pieces of bleached muslin and of cambric were procured on the market and used as the test pieces. Parts of each of these were bleached to the extent of five treatments in the laundry, and parts to the extent of ten such treatments. Test pieces about three inches square were cut and treated as described below. The pieces were dipped into standard solutions of reagents and then the excess of the solution squeezed from them by hand. After standing at room temperature the pieces were examined at intervals to compare their color with that of the original untreated samples. The sizing was removed from all of the cloth by boiling in distilled water.

From these tests it is evident that the yellow color is greatest for a given concentration of the carbonate in the case of the pieces which have been most strongly bleached, that is, which contain most oxycellulose. The presence of even minute quantities of sodium carbonate is able in time to cause a very noticeable yellowing in articles which have been strongly bleached.

EFFECT OF ALKALI ON COLOR

No.	KIND OF CLOTH	Strength of sod. carb. solution used	Time after removing from solution	Condition after treatment
1	Original muslin	$N/10$	3 hrs.	Slightly yellow
2	Muslin, bleached medium (Muslin A)	$N/10$	3 hrs.	Very yellow
3	Muslin, bleached strongly (Muslin B)	$N/10$	3 hrs.	Yellower than 2
4	Muslin B	$N/10$ rinsed 3 times with distilled water	3 hrs.	Yellower than 1
5	Original muslin	$N/10$	3 hrs.	Less yellow than 1
6	Muslin A	$N/10$	3 hrs.	About like 2
7	Muslin B	$N/10$	3 hrs.	About like 3
8	Cambric, medium bleached (Cambric A)	$N/10$	3 hrs.	Yellower than 6
9	Cambric, strongly bleached (Cambric B)	$N/10$	3 hrs.	Yellower than 7
10	Original muslin	$N/50$	16 hrs.	Slightly yellow
11	Muslin A	$N/50$	16 hrs.	Much less yellow than 2
12	Muslin B	$N/50$	16 hrs.	Less than 3
13	Original muslin	$N/100$	72 hrs.	Slightly yellow
14	Muslin A	$N/100$	72 hrs.	Yellower than 1
15	Muslin B?	$N/100$	72 hrs.	Yellower than 4
16	Original cambric	$N/100$	72 hrs.	
17	Cambric A	$N/100$	72 hrs. after 52 days	Yellower than 4 Much yellower than blank
18	Cambric 13	$N/100$	after 72 hrs. after 52 days	Much yellower than blank Much yellower
19	Muslin A	$N/250$	after 52 days	Much yellower than blank
20	Muslin B	$N/250$	after 52 days	Much yellower than blank
21	Original muslin	$N/500$	after 52 days	Same as blank
22	Muslin A	$N/500$	after 52 days	Same as blank
23	Muslin B	$N/500$	after 52 days	Yellower than blank
24	Muslin B	$N/1000$	after 52 days	Very little yellower than blank

Test pieces which were treated with oxalic acid under varying conditions, some of which were boiled in $N/10$ oxalic acid for an hour, did not develop a yellow color even after the expiration of five months. This shows that no colorless compounds were formed by reduction, which subsequently yielded the original colored substances by the oxidizing action of the air. The yellowing of articles on standing has often been attributed to this latter cause.

BLEACHING IN SEPARATE SOLUTION—For the purpose of determining whether or not it would be better to bleach in the second soap solution or in a separate solution after the washing was finished, the following experiments were performed.

A soap-alkali solution of about the strength used in the collar tests was heated to boiling. No cellulose was used in this test. Sufficient bleach solution was added to make the concentration of the hypochlorite the same as that used in the above tests. The boiling was continued after the addition, and the hypochlorite was found to have disappeared after 18 minutes. Another quantity of the bleach solution was diluted so that it had the same concentration as in the soap solution. The proper quantity of cellulose was weighed out and added, so that the ratio of the weights of the cellulose and the solution might be the same as in the previous tests on collars and threads. The boiling was continued and the hypochlorite found to have disappeared in about the same length of time as above—18 to 19 minutes.

A solution of the hypochlorite with no soap or cellulose was evaporated to dryness. Water was then added to redissolve the salts, the volume being made equal to that of the original solution. This process was again carried out and after the third evaporation a strong test for available chlorine was obtained. Lunge[1] has shown that a neutral solution of hypochlorite, or one which is slightly alkaline, can be boiled for two hours with a disappearance of only 24.6 per cent of the available chlorine. It is evident, therefore, that the hypochlorite reacted with the soap and the cellulose in the above tests, and was not decomposed by the high temperature to which it was subjected.

From these tests it was concluded that the soap was attacked by the hypochlorites about as readily as the cellulose, and if this were the case a smaller quantity of bleaching agent than that used with the soap should be able to do the same work if used separately. This was tried both in the laboratory and in several laundries, and besides a saving of from one-half to two-thirds of the bleaching material, better looking work was obtained in every case.

REDUCING AGENTS—On account of the objectionable properties of oxycellulose, it was thought advisable to try the use of reducing agents instead of the oxidizing agents which are generally used. Sodium hydrosulfite was chosen as being the one most likely to give satisfactory results at a reasonable cost. Laboratory experiments showed that this substance when used in quantities chemically equivalent to the ordinary bleach solutions gave results that promised to be satisfactory. The best results were obtained when the hydrosulfite was used after the second suds, although a good color was obtained when the bleach was used along with the soap. Although the cost of the hydrosulfite was high, it was considered possible to produce it at a sufficiently low price to justify its use if it proved satisfactory in other respects.

A test on a series of threads showed that very little decrease in their breaking strength was caused when they were boiled in relatively strong hydrosulfite solutions. The solution was made up 10 grams per gallon, and the boiling continued for two hours, to correspond to ten treatments.

Original strength	1696
Final strength	1685

This process was tried out on a large scale in two custom laundries. After a large number of runs it was found that although a considerable bleaching was effected, the color was not as good as when the old method was used. The quantities of hydrosulfite used for a hundred shirts (75 lbs. of cellulose) in twenty-five gallons of the solution were varied from $^1/_4$ to $1^1/_2$ lbs. The bleaching effected by the smaller quantity was good, but owing to the fact that whiter work could be gotten by the use of hypochlorites the method was abandoned, as it was not thought likely to be generally accepted.

On account of the failure of the reducing agents to produce work that would compare in whiteness with that obtained in practice, attention was again turned to other oxidizing agents. It was hoped that an oxidizing agent might be found which would not attack cellulose as much as do the bleaches now in use, and which would effect the desired whitening of the article to be treated.

MAGNESIUM AND SODIUM HYPOCHLORITES

Magnesium hypochlorite was tried, as was also neutral sodium hypochlorite. Since the oxidation is caused by the hypochlorite ion, and the concentration of this was made the same with each of the hypochlorites, the only chance for a difference in their actions was the possibility that the concentration of hydroxyl ion might influence the reaction between cellulose and the hypochlorite ion. Since magnesium hydroxide is difficultly soluble, it is impossible for the magnesium hypochlorite solution to contain a large concentration of hydroxyl ion.

Many text books contain the statement that magnesium hypochlorite has a much less harmful effect on cotton and linen fabrics than calcium or sodium hypochlorites. A thorough search through the literature showed that this statement is copied from the patent specification submitted by Hermite,[1] concerning his process for preparing magnesium hypochlorite by electrolysis from a solution of magnesium chloride. No data are given in support of this statement in this patent specification, and none have been found in any other place.

Equal weights of threads were used with equal volumes of the different hypochlorites, which were made of equivalent strengths. The conditions of boiling the threads in all cases were the same.

Original strength	1696
Sodium hypochlorite	468, 488
Magnesium hypochlorite	474, 492

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[1] *J. Soc. Chem. Ind.*, **4**, 722; also, "Manufacture of Sulfuric Acid and Alkalies," second edition, Gurney and Johnson, London, 1896, pp. 417 and 419.

[1] English Patent 13,929, *J. Soc. Chem. Ind.*, **4**, 673.

OZONE FOR BLEACHING

Ozone is another oxidizing agent which was experimented with, and it was chosen because the only decomposition product which could be formed is oxygen and this, of course, is not objectionable. Preliminary tests indicated that the bleaching could be done satisfactorily, and if precautions were taken to prevent the simultaneous formation of oxides of nitrogen or to remove them if formed, the strength of threads was not greatly decreased after several successive treatments.

Original strength	1696
Exposed to current of ozone, oxides of nitrogen not removed	less than 5
Oxides of nitrogen removed by tower filled with slaked lime	575
Oxides removed by bubbling ozonized air through water	937

The percentage of ozone by volume was 1.2, and the temperature of the room 22.5° C. The time of passing the current of ozonized air was three and a half hours. The threads were introduced moist, about as they would have come from a laundry centrifugal machine. It could not be decided, however, by the use of the small laboratory apparatus whether the process was sufficiently economical and the bleaching action sufficiently rapid to be practical.

The laboratory ozonizer used was the regular Siemens-Halske apparatus, composed of five cells. By varying the rate of flow of the air it was possible to get a mixture which analyzed from 0.5 to 1.5 per cent by volume of ozone. The quantity of air thus furnished varied from 0.5 to 2 cu. ft. per hour. The concentration of the ozone was determined by titrating the iodine liberated by a known volume of ozonized air from a neutral potassium iodide solution. It was necessary to add acid to decompose any iodates which might have been formed before the titration was made with standard thiosulfate. A gas meter was connected ahead of the ozonizer to show the rate at which the air passed through the apparatus. The air was carefully dried with calcium chloride and concentrated sulfuric acid, in order to reduce the quantity of oxides of nitrogen formed.

The first plan tried was to pass the current of ozonized air into the drying room either before the drying was commenced or while it was in progress. To test this method some starched collars which had not been bleached previously were placed in a large glass desiccator through which the ozonized air was led. After half an hour, the color of the collars was very satisfactory, being better than that obtained in the usual way. When these collars were ironed, however, a very yellow color developed which was due, perhaps, to the fact that part of the starch had been converted into dextrine and this developed a yellow color at the high temperature because of the alkaline substance which had not been removed by rinsing. It was evident that this method could not be used unless the bleaching were done before the articles were starched. As this would necessitate an extra handling of the pieces, and would lengthen the time of treatment, the method was abandoned. The ozone was then used in a different way, which also gave satisfactory results in regard to color. The current of ozonized air was led into the washer while the washing was being done. Tests were run on a series of threads which were boiled for five hours, with the same strength soap-alkali solution as was used in the tests described above, and a strong current of ozonized air passed through continuously. This corresponded to the effect of ten successive treatments such as were to be used in practice.

Original breaking strength	1696
After treatment	1389

In order to test the commercial efficiency of the latter method, a large ozonizer furnished by the Gerard Ozone Process Co. was installed in a custom laundry. The current of ozonized air was led into the washer by means of a perforated brass pipe, and allowed to bubble through the fabrics while they were being run in the machine. This large ozonizer was rated to furnish a current of air containing from 0.5 to 0.7 per cent ozone by volume at a rate of 25 cu. ft. per hour. Tests were run in which the ozone was admitted at all possible times during the regular washing process.

The results obtained when the ozone was passed into the soap-alkali solution were not satisfactory. Fruit and coffee stains were not removed sufficiently well to make the method serviceable. This was thought to be due in part to the fact that the ozone was largely decomposed by the hot water before it came into contact with the stains.

In order to overcome this difficulty, the ozone was used with the clothes in luke-warm water either before or just after the washing with soap was done. The color of the articles was not satisfactory in either case, although the passage of ozone was continued in some cases for forty minutes. Because of the expense of operating the apparatus, and also because of the length of time necessary to do the bleaching, the method was abandoned as not practical.

ACTION OF HYDROGEN PEROXIDE

Some preliminary experiments were performed with hydrogen peroxide, but it was found that even with solutions of considerable strength the action was very slow. Very satisfactory results were obtained with hydrogen peroxide in bleaching woolens, and this method is being extensively used for treating fine woolen articles. The solution is made slightly alkaline with ammonia in the latter case.

DISCUSSION OF USE OF BLEACH

The fact that colored articles last much longer than undyed ones made from the same kind of material, is proof that the use of excessive quantities of alkalies and bleach is responsible for the greater part of the damage done in the wash room. It is general experience that a colored shirt will outlast a white one by considerable, and the reason would seem to be that in the case of the colored shirt alkalies and bleaches must be used very sparingly or not at all.

A great advance would be made if all laundries used much less bleach than they do at present. If bleach is used once on a piece of fabric, it is necessary to use it every time the article is laundered. This is because the oxycellulose formed the first time bleach is used yields the objectionable yellow substance already spoken of when alkalies are used subsequently, and the use of more bleach becomes necessary.

These experiments with bleaching agents seem to show that if excessive damage is to be avoided, some sacrifice in the color of the finished articles will need to be made. This might be accomplished either by using hydrosulfites, or other reducing agents, or by using much smaller quantities than are now considered necessary, of some of the oxidizing agents in use at the present time.

CONCLUSIONS

1—The bleaching and treatment of fabrics with acids are the most harmful parts of the process now in general use in steam laundries. The bleaching not only weakens the fabrics, but also produces oxycellulose, which yields an objectionable yellow substance when treated with even dilute solutions of alkalies. The hydrolysis of cellulose produced by the hydrogen as ion in acid solutions weakens the fibers. Thorough rinsing is essential to remove as much of the acid used as possible. The quantities of bleaching solution and acid used should be kept as small as possible.

2—The use of alkalies in excess affects prejudicially the color and strength of fabrics, and leads to the formation of much lint.

3—Contrary to the common belief of launderers, soft water is superior to hard water for all purposes, rinsing included.

4—The deposition in the fibers of insoluble salts or the crystallization of soluble salts does not greatly affect the wearing qualities of fabrics.

5—The use of mineral acids in the laundry cannot be generally recommended, because of the extent to which they attack cellulose if they are not thoroughly removed by rinsing.

6—One cause for the yellowing of fabrics composed of cellulose on standing is the formation of yellow products by the action of hydroxyl ions on the oxycellulose which is formed during the bleaching process.

7—A saving in the quantity of bleaching solution required and an improvement in the color produced are possible when the bleaching is done as a separate process. The usual practice is to combine washing and bleaching.

8—Hydrosulfites may be used for effecting the bleaching, but the color obtained is not as good as that produced by hypochlorites.

9—Magnesium hypochlorite solutions present no advantages over the slightly alkaline solutions of sodium hypochlorite now employed, as far as their destructive actions are concerned.

10—Ozone produces a satisfactory color when allowed to act on fabrics before or during the drying which is effected in the drying rooms. The fabrics are less attacked than in the present method, but the ozone process is not well received by the trade because it necessitates extra handling of the articles, and increases unduly the length of time necessary to complete the laundering operation.

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A PRACTICAL METHOD FOR THE PREPARATION OF DRY STARCH, SOLUBLE IN COLD WATER, FOR USE AS AN INDICATOR[1]

By Robert M. Chapin

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When, several years ago, the necessity arose for preparing a large quantity of dry starch which should be readily soluble in cold water and appropriate for use as an indicator in iodine titrations, no description of a sufficiently practical method of preparation could be found.

Wroblewski[2] prepared the desired form of starch by running a concentrated solution of soluble starch, in a thin stream, and with vigorous stirring, into a large excess of alcohol, followed by washing with absolute alcohol and ether, and drying *in vacuo*. He stated the resulting product to be soluble in cold water up to about 4 per cent, and to yield a pure blue with iodin. His original soluble starch was prepared by digesting rice starch with 1 per cent caustic potash solution.

In the present work, Wroblewski's method of precipitation, etc., was found effective, but for the preparation of the original soluble starch, Lintner's[3] method of digestion with acid proved more satisfactory. The first preparations, made in 1911, were of good quality, but were obtained through a series of tedious and expensive processes. Since that time, through the repeated preparation of large quantities of the material, the process has become so simplified and standardized that it is believed to be worthy of publication.

Into a 5-liter round flask with a long neck are brought 400 grams potato starch, 2300 cc. distilled water, and lastly, 80 cc. normal hydrochloric acid. The flask is well shaken to wet and distribute the starch thoroughly, and is floated in a kettle of water previously brought to vigorous boiling. The neck of the flask rests conveniently on the side of the kettle at an angle of about 45°, and as soon as the flask is brought into the bath it is smoothly and continuously rotated about its longitudinal axis. As the flask becomes hot the starch forms an evenly distributed uniform jelly, which, in about seven minutes from the time of starting, begins to liquefy and to fall away from the wall of the flask. When this stage is reached the mouth of the flask is loosely closed with an inverted beaker and the flask left in the boiling bath with an occasional rotation until the mobile liquid shows no lumps of gelatinized starch remaining—1 to 1$^1/_2$ hours. The flask is then rapidly cooled in running water until it can be comfortably handled (about 50° C.), then methyl orange is added, followed by concentrated ammonia to alkaline reaction. Next is immediately added 800 cc. of 95 per cent alcohol, and, after thorough mixing and standing for a few minutes to allow air bubbles to separate, the liquid is strained through moderately coarse muslin. The addition of this proportion of alcohol notably reduces the viscosity and increases the permanence of the solution. Starch will separate some time after the solution has become cold, but with proper management ample time remains for the subsequent operations. In fact,

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[1] Printed by permission of the Secretary of Agriculture.

[2] *Ber.*, **30** (1897), 2108.

[3] *J. für prakt. Chem.*, **34** (1886), 378.

after experience has been gained, the amount of water, and in due ratio the total amount of alcohol, may be somewhat reduced. The solution, still at 40 to 45° C., is run through a number of fine jets into four liters of 95 per cent alcohol, with continuous stirring. The whole is left for at least 48 hours with an occasional thorough stirring after which most of the supernatant alcohol is decanted and the rest used to transfer the starch to a two-quart percolator provided with a filter plate which is covered with filter paper or cloth. Here it is percolated with 95 per cent alcohol, being stirred up with a stick at intervals to prevent the formation of clumps or fissures, until alcohol comes through the percolator of a specific gravity indicating a strength of 90 per cent. The starch is then transferred to a Buchner funnel, well drained with suction and spread out to dry in a moderately warm place.

The resulting product is a fine white voluminous powder, more or less compacted to friable lumps which completely disintegrate under slight pressure. In less than a minute, a little of it thrown into cold water dissolves sufficiently to yield a good blue upon the addition of potassium iodide and iodine. Moistened with water or dilute alcohol, it becomes gummy and subsequently dries out to a horny mass, very slowly soluble in cold water. The efficiency of the preparation, therefore, resides largely in its fine state of subdivision and care must be taken during the process of preparation not to expose it to air until after thorough digestion with alcohol of 90 per cent strength. After drying it should be preserved from moist air, though it is not injured by exposure to ordinary atmospheric conditions.

The advantages of the material for iodine titrations made in the field with a portable outfit are sufficiently obvious. It is also a very convenient substance to have about a laboratory, although for highly accurate titrations it is somewhat inferior in sensitiveness and delicacy to a properly prepared fresh solution made from raw starch.

Since the above described process was worked out, Fernbach[1] has described very similar observations; namely, that a dilute starch paste or solution run in a fine stream into a large excess of absolute alcohol or acetone, produces a finely divided precipitate which is soluble in cold water. He apparently attributes the soluble qualities of the resulting product to the dehydrating action of the alcohol or acetone. Inasmuch as the horny form of precipitated starch previously mentioned, and indeed raw starch as well, becomes soluble in cold water when finely ground, the present writer believes that the prime factor which determines the readiness with which precipitated starch dissolves in water is simply the degree of fineness of its mechanical subdivision. It was early found that the more dilute the original starch solution and the greater the excess of alcohol, the finer, more voluminous and more readily soluble in water became the resulting product, but naturally, the less practical became the process.

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[1] *Original Communications, Eighth International Congress of Applied Chemistry*, **13** (1912), 131.

DETERMINATION OF SILVER AND BASE METAL IN PRECIOUS METAL BULLION[1]

By FREDERIC P. DEWEY[2]

Received May 15, 1914

The determination of silver in gold bullion by cupellation methods is such a simple matter and so easily executed that it has long been the standard and almost universally accepted method, but the investigations described in this paper show that it has most serious and incurable defects. In making an assay of gold bullion for base metal, which is the basis for the silver determination, the base metal is not entirely removed from the button, and no means are at present available for insuring the presence of even approximately the same amount of remaining base metals in duplicate buttons. The judgment of the cupeller is the only guide in the matter. The amount of gold and silver absorbed by the cupel may vary greatly in duplicates. The proofs are subject to the same variations as the assays, and it is purely a matter of chance whether they give the proper correction figures or not, and they may fall far short of doing so.

These difficulties are inherent in the work of any one assayer, but when different assayers work upon the same sample, particularly in different laboratories, the opportunities for variation are multiplied; when they work upon different samples of the same bullion, there is no telling how widely they may differ in their reports, even upon apparently docile bullion.

There is urgent need for a better method, but a thoroughly better one is not yet available and undoubtedly the cupellation method will remain in use for many years to come. This paper further describes an attempt to establish a better method by means of fusion with cadmium and titration with sulfocyanate, which, while not entirely successful, is very promising. Comparative tests by cadmium fusion and Gay-Lussac titrations are also described.

During the fiscal year ended June 30, 1912, the Mint service of the United States Treasury purchased 74,179 deposits and redeposits of bullion, most of which contained more or less silver. In the vast majority of cases the fineness of the silver in the bars was not determined directly, but by a method of differences based upon cupellations by which the fineness of gold and base metal present were determined, the difference between these two actual determinations and 1000 being called the silver fineness.

There are two general methods of arriving at the silver result. The actual assaying work in both cases is the same, but the methods of calculating the results differ. In both of them the gold fineness is first determined by a separate assay. Then, in one method of calculating, the combined gold and silver fineness are determined by a second assay and the gold figure subtracted from the combined gold and silver figure to give the silver fineness. In the second method of calculating, the result of the second cupellation is stated as the loss on cupellation, or base metal, and the sum of this determination and the gold determination is subtracted from 1000 to give the silver fineness.

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[1] Published by permission of the Director of the Mint.

[2] Assayer, Bureau of the Mint.

Many of these deposits were purchased at the smaller assay offices of the United States, scattered all over the country, and were subsequently shipped to the larger offices to be refined. These larger offices necessarily treated the smaller ones just as though they were outsiders, making their own weights and assays and often remelting the bullion before accepting the bar. Naturally there are at times differences between purchasing and redeposit offices. Taking the figures of the purchasing offices as a basis, Table I shows the relation between the silver determinations of the purchasing offices and those of the redeposit offices upon 579 redeposits last year which were not remelted at the redeposit offices. It gives the number of times they agreed in their silver determinations and the number of times they differed in fineness by the amount stated.

TABLE I—SILVER ASSAYS ON 579 REDEPOSITS

Redeposit office agreed with purchase office																				59
Redeposit office differed from purchase office																				520
Difference in fineness	1/2	1	1 1/2	2	2 1/2	3	3 1/2	4	4 1/2	5	5 1/2	6	6 1/2	7	8	8 1/2	10	10 1/2	12	
Above	57	56	44	28	32	21	12	11	5	6	6	2	2	4	1	1	4	1	1	294
Below	44	59	43	41	21	7	6	..	4	..	1	..	..	..	..	..	..	..	..	226
Totals	101	115	87	69	53	28	18	11	9	6	7	2	2	4	1	1	4	1	1	520

From Table I it is apparent that the general tendency of the redeposit office is to get higher results on the silver than the purchasing office. It is barely possible that a very few of the results at one redeposit office were not obtained by cupellation.

Of course, some of the differences shown are due to differences in the samples used for the assay work, but the differences are still much too large in many cases and call for improvement in the assaying or for the substitution of some other method for determining the silver.

It is evident that the silver result is naturally open to considerable variation, because its accuracy is dependent upon the accuracy of the two determinations which are actually made. When the net errors of the two actual determinations are opposite it may happen that the silver figure will be close to the truth, but when they are both on the same side the error in the silver determination may be quite large.

I have published two papers[1] dealing with the accuracy of the determination of gold in bullion, showing that the accuracy often claimed for this determination is not generally obtained and that in some bullions the gold determination cannot be depended upon within one fine. In the presence of certain elements, such as arsenic and antimony and in the case of very impure bullion, such as some cyanide bars and some jewelry scrap, the gold assay is subject to much wider variations and is entirely unsatisfactory of itself, to say nothing of its baneful influence upon the silver determinations by cupellation differences.

The cupellation for base metal in gold bullion is a ridiculously simple operation and may be described in a very few words. The assay sample of the bullion is weighed, wrapped in the proper amount of sheet lead and cupelled, accompanied by the proper proofs, to a button of gold and silver, which is cleaned and weighed. The difference between the weight of the button of gold and silver, when corrected by the proof, and the sample taken, is called base metal that has been driven off or absorbed by the cupel. Aside from carelessness, there appear to be but few chances for variation in the operation, but I shall show that some of these chances are exceedingly potent.

It is a fair assumption that the chances of error in weighing the assay sample and the resulting button will be approximately the same as in weighing the sample and cornet in the gold assay. In view of the wide errors that may occur further on in the work it is safe enough to put down the vitiation of the silver determination from this cause as being negligible for the present.

In the actual cupellation in the furnace for removal of the base metal, the first point to attract attention as bearing upon the chances for loss and variation in the result is the possible volatilization of the precious metals during cupellation. Much has been written upon this subject, but most, if not all, of the numerical conclusions announced have been based upon either insufficient data, or upon tests made under conditions which do not at all occur in actual assaying. There is no question that gold and silver are volatile at sufficiently elevated temperatures, but it is an open question how much they do volatilize in actual assaying. It is still more uncertain as to whether it is necessary to carry on the assay work under conditions which produce or even favor the volatilization of the precious metals.

It is by no means an easy matter to obtain the data required to answer this question with any certainty. It is necessary to know the amount of precious metal going into the assay, the amount absorbed by the cupel and the amount actually remaining in the final button as weighed. This last determination requires much careful and painstaking analytical work. As a practical fact, the only way to arrive at this figure is to make wet determinations, with special precautions, of the other metals remaining in the buttons and then call the balance precious metals. I have done considerable work of this character and am in the habit of speaking of it as "hen's-tooth" analysis. I have made several attempts to determine the volatilization loss in the cupellation assay for gold only, but the results obtained are unconvincing and their value seems hardly commensurate with the labor involved. After going through the work, one may get a figure showing a slight loss which may be due to volatilization, but it will be loaded with all the errors of a large amount of analytical work. On the other hand it may easily happen that a slight gain will be shown.

My personal opinion is that in the vast majority of cases and with the exception of bullion high in copper and certain exceptional classes of bullion, such as those containing arsenic and antimony, the volatiliza-

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[1] "The Assay and Valuation of Gold Bullion," *Trans. A. I. M. E.*, **40**, 780. *Ann. Rept., Director of the Mint*, **1908–9**, p. 25. "The Sampling of Gold Bullion," *Trans. A. I. M. E.*, **44**, 853. *Orig. Com., 8th Int. Congr. Appl. Chem.*, **1**, 155.

tion of precious metals in properly conducted base metal assays is insignificant.

The Bureau records contain various cases of excessive loss in base metal proofs which might seem to indicate volatilization of gold and silver during the cupellation, but in the cases where the cupels have been assayed, as far as the records now show, the absorption of precious metals by the cupels has always been more than sufficient to account for the high-proof loss, so that it is by no means necessary to turn to volatilization to explain the excessive loss of the proofs. Specific illustrations of this will be given further along.

It has been known for a very long time that the button obtained in the base-metal assay is by no means pure gold and silver. The work of Tillet (1761–1769) showed that the weight of a silver cupel button added to the weight of silver absorbed by the cupel exceeded the weight of the silver taken in test cases and that the excess was made up of copper and lead retained by the button. It has been stated on the authority of Tillet and D'Arcet that 1000 parts of a silver button may contain 4 parts of foreign metals. As already explained, when treating of volatilization, the accurate determination of the very small amount of copper and lead in a base metal assay button presents unusual difficulty. On one occasion, however, I had an accumulation of base buttons from two laboratories sufficient in amount to work with comfortably. One set was from the assaying of a single sample of standard gold and the other was from assaying three closely related samples of standard gold. I found much more than 4 parts of copper and lead, per 1000 parts of button. In both cases the bullion was only about 2 fine in silver, and 98 fine in copper, so that the work is not strictly comparable with Tillet's. The following results were obtained:

Base Metal Remaining in Cupel Buttons

	Mg. per gram First laboratory	 Second laboratory
Lead	3.09	2.04
Copper	12.62	20.84

On various occasions I have examined the nitrate of silver solutions resulting from parting gold coin assays in sets in the Bureau laboratory. The gold and silver buttons in the gold assays may be treated as quite similar to the base-metal assay buttons, although not strictly the same, and by analyzing the solution from a set of assays there was sufficient lead and copper to work with. It is not possible to state the relation between the lead and copper retained and the weight of the buttons exactly, because neither the parting silver nor the buttons were weighed. In each case, however, the buttons weighed approximately 1450 mg. each. In six cases of regular work the proportion of both lead and copper retained by the buttons was much less in most instances than in the base buttons given above, the average amounts retained per button being as follows:

Lead and Copper Retained by Gold Assay Buttons
Average per Button of Approximately 1450 Mg.

Lead Mg.	Copper Mg.	Lead Mg.	Copper Mg.
0.51	1.43	0.99	1.12
0.84	1.18	1.06	1.73
0.89	1.65	1.63	2.36

In five cases the assays were intentionally run at an unusually low temperature and the retention of lead and copper was greatly increased as shown by the following results:

Lead and Copper Retained by Gold Assay Buttons
Average per Button of Approximately 1450 Mg.

Lead Mg.	Copper Mg.
1.252	6.789
1.511	7.344
1.533	6.98
2.179	7.79
2.626	8.167

In the case of a set of fine gold assays the buttons weighed approximately 1625 mg. each and they averaged to contain 0.38 mg. lead and 2.07 mg. copper.

Since writing the above, Liddell,[1] in comparing bone ash with cement cupels, has uttered a timely warning against assuming the cupel bead to be free from base metals.

When, however, we take up the question of the cupel loss, or absorption, the case becomes quite different. At this point there are opportunities for wide variations which may be readily determined. These variations not only affect the results obtained by different assayers when working upon the same bullion, but they also affect duplicate assays by one worker.

In considering the question of loss of precious metals in the cupel, some sharp distinctions should be drawn, although they cannot yet be rigidly applied. There is a true and actual absorption of these metals into the body of the cupel, which may easily be demonstrated by filing off a portion of the used cupel far away from the button of metal and assaying it. There is an entanglement of one or more individual beads, often plainly visible, upon the surface of the cupel. There may also be a shower of microscopic beads scattered over a portion of the surface of the cupel. In the course of my investigations I have assayed several thousand cupels that have been made and used under most varied conditions, and hope soon to publish the results. At this time I propose to deal with the general aspect of the cupel in a brief manner only, as directly applicable to the base-metal assay.

The true absorption of a cupel depends upon a wide variety of conditions. The entanglement of individual beads may be due to the character and composition of the ash or the manufacture of the cupel or it may be due to imperfections in wrapping the assay sample in the sheet lead in making up the package or packet. A rain of microscopic beads in the cupel may be due either to the composition of the bullion or the temperature of the muffle. It may also possibly be due to the presence of an undue amount of salt in the bone ash.

It is a good plan to form the habit of always examining the used cupels for beads and when there is a wide difference between duplicate assays, such an examination is essential for good work. Whenever beads, either individual or microscopic, appear in a cupel, it must rest in the judgment of the assayer whether he will accept the original result or repeat the work. The amount of the true absorption is not visibly shown

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[1] *Eng. Min. J.*, **96** (1913), 7.

by the cupel and can be determined only by assaying the used cupel. There is seldom sufficient time to do this in a busy commercial laboratory and it is generally assumed that it will be properly corrected by the proof. This, however, is often not even approximately true. Two cupels of identical manufacture standing side by side in the muffle may show wide differences in the amount of gold and silver absorbed when the same bullion is run in them and there are many cases where the proof is only approximately like the bullion being assayed, while such differences may materially affect the relative absorptions. When the cupels are separated in the furnace the differences may be augmented.

Some illustrations to show the effect of cupel absorptions in every-day work may be given. In these the figures stated are intended to represent true absorptions except as noted. Some of the illustrations are taken from actual commercial assaying for the purpose of showing the real conditions. Some of them are from regular work, which was, however, carried out so as to illustrate and investigate some particular point in the routine work, while some few are from specific investigating tests.

In one of the small offices the cupel absorption of gold and silver in duplicate base-metal assays of the A sample were 2.62 and 2.68 mg., but on the B sample they were 1.63 and 1.87 mg.[1] On another bullion the absorptions were 3.75 and 3.95 mg. On a third they were 4.81 and 6.03 mg. This is a most excellent illustration of every-day assaying. There was absolutely no discretion used in selecting the cupels to be assayed. They represent a run of assays on a day when the writer happened to be making an examination of the institution.

The cupels from the base-metal assays of five deposits at another small office were forwarded to the Bureau and assayed there, showing the following absorptions:

CUPEL ABSORPTIONS (MG.) AT SMALL OFFICES

Fineness of bullion	Sample	Gold	Silver	Total
Gold 905.5	A	1.00	1.01	2.01
Silver 92.0	B	0.94	0.97	1.91
Base 2.5	..	..	..	..
Gold 826	A	1.19	1.19	2.38
Silver 119	B	1.11	1.45	2.56
Base 55	..	..	..	..
Gold 786.25	A	1.02	1.42	2.44
Silver 121.5	B	1.16	1.60	2.76
Base 92.25	..	..	..	..
Gold 608	A	0.57	3.35	3.92
Silver 319.5	B	0.50	3.12	3.62
Base 72.5	..	..	..	..
Gold 537.5	A	0.54	4.30	4.84
Silver 440.5	B	0.53	3.99	4.52
Base 22	..	..	..	..

The general conditions in one of the largest laboratories in the service are illustrated by Table II which gives the cupel absorptions in base-metal assays on a wide range of bullions.

TABLE II—CUPEL ABSORPTIONS (MG.) BASE-METAL ASSAYS IN LARGE LABORATORY

Gold	Silver	Total	Gold	Silver	Total
0.97	0.78	1.75	0.81	2.24	3.05
0.75	1.07	1.82	1.02	2.13	3.15
1.13	0.85	1.98	1.65	1.57	3.22
1.58	0.58	2.16	1.75	1.76	3.51
1.17	1.04	2.21	1.64	1.91	3.55
1.06	1.25	2.31	1.70	1.94	3.64
1.34	0.97	2.31	1.51	2.15	3.66
0.91	1.43	2.34	1.05	2.62	3.67
1.01	1.38	2.39	1.81	1.97	3.78
1.09	1.36	2.45	1.58	2.24	3.82
0.28	2.25	2.53	1.95	1.88	3.83
1.03	1.51	2.54	1.63	2.36	3.99
1.23	1.36	2.59	0.42	3.59	4.01
0.90	1.72	2.62	1.93	2.10	4.02
1.08	1.73	2.81	2.10	2.15	4.25
1.12	1.78	2.90	2.24	2.27	4.51
..	..	..	2.49	4.32	6.81

These cupels were made on a power press from bone ash of the following screen composition:

On 40 mesh	4.75 per cent
On 60 mesh	10.75
On 80 mesh	23.0
On 100 mesh	7.5
Through 100 mesh	54.0
	100.00 per cent

A bullion high in copper that was very troublesome to assay and the composition of which is given approximately only at 457 fine in gold and 160 fine in silver yielded the following cupel absorptions in a set of base-metal assays using 10 grams of lead:

CUPEL ABSORPTIONS (MG.) BULLION HIGH IN COPPER

Gold	Silver	Total
3.48	3.49	6.97
3.90	3.68	7.58
5.74	4.17	9.91
6.14	4.29	10.43

As a general illustration of what may occur with a rain of microscopic beads, accompanied in some cases by separate beads, six such cupels that had been used in a purchasing office were assayed at the Bureau with the following results:

METAL RECOVERED (MG.) FROM BEADED CUPELS

Gold	Silver	Total	Gold	Silver	Total
3.55	2.49	6.04	3.28	2.34	5.62
2.98	3.13	6.11	2.81	4.87	7.68
3.45	2.68	6.13	2.16	4.56	6.72

Five base-metal assays each were made on two high-grade bullions, accompanied by two proofs. The cupels were made on a hand-lever machine from the same bone ash as the cupels of Table II. The cupels were arranged in the muffle in three rows of four with the proofs in Nos. 2 and 3 of the middle row. The cupels showed the following absorptions:

CUPEL ABSORPTIONS (MG.)

COMPOSITION	Gold	Silver	Total
No. 1 BULLION:			
Gold 898.5 fine	1.86	1.08	2.94
Silver 89.0 fine	1.97	1.02	2.99
Base 12.5 fine	2.21	1.10	3.31
	2.54	1.19	3.73
	2.48	1.19	3.67
No. 2 BULLION:			
Gold 895.5 fine	2.02	1.03	3.05
Silver 98.5 fine	1.74	1.09	2.83
Base 6 fine	2.12	1.24	3.36
	2.42	1.30	3.72
	2.60	1.29	3.89
PROOFS:			
Gold 450 mg.	2.22	1.06	3.28
Silver 45 mg.	2.36	1.18	3.54

Two somewhat similar bullions from the same office were treated in the same way with the following results:

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[1] For convenience in the Mint service a special set of assay weights is employed, known as "gold weights" and generally designated as "GW," based upon 500 mg. equal to 1000 GW so that 1 mg. equals 2 GW. In general 1000 GW of bullion are used for making a base-metal assay, so that the GW of the button as weighed gives the fineness of the bullion assayed. In a few cases in the paper it is noted that only a half charge, or 500 GW, was employed for the assay. In considering the data in this paper it should be remembered that 1 mg. means 2 in the fineness on a full charge and 4 on the half charge.

CUPEL ABSORPTIONS (MG.)

COMPOSITION	Gold	Silver	Total
1ST BULLION:			
Gold 823.0 fine	1.18	1.48	2.66
Silver 164.25 fine	1.29	1.72	3.01
Base 12.75	1.44	1.69	3.13
	2.01	2.13	4.14
	1.99	1.91	3.90
2ND BULLION:			
Gold 884 fine	1.29	1.12	2.41
Silver 113.5 fine	1.32	1.07	2.39
Base 2.5	1.62	1.27	2.89
	1.99	1.37	3.36
	2.35	1.50	3.85
PROOFS:			
Gold 425 mg.	1.73	1.58	3.31
Silver 70 mg.	1.49	1.60	3.09

The cupels were made on a hand-lever machine from bone ash of the following composition:

On 40 mesh	None
On 60 mesh	10 per cent
On 80 mesh	24
On 100 mesh	6.5
Through 100 mesh	59.5
	100.0

Eight samples of miscellaneous bullion were cupelled in duplicate at one time upon a plate in one of the large offices, the duplicates being widely separated in the furnace. The used cupels were assayed at the Bureau and showed the following absorptions:

TABLE III—MISCELLANEOUS BULLION. CUPEL ABSORPTIONS (MG.) IN ONE SET

COMPOSITION	ASSAY	Gold	Silver	Total
Gold 350	1st	2.09	2.44	4.53
Silver 120	2nd	1.23	1.86	3.09
Base 530	...	..	..	..
Gold 440	1st	1.57	1.94	3.51
Silver 150	2nd	1.41	2.11	3.52
Base 410	...	..	..	..
Gold 520	1st	1.35	1.56	2.91
Silver 140	2nd	1.90	1.74	3.64
Base 340	...	..	..	..
Gold 530	1st	1.09	1.99	3.08
Silver 210	2nd	1.34	2.19	3.53
Base 260	...	..	..	..
Gold 690	1st	1.03	0.96	1.99
Silver 100	2nd	1.69	1.23	2.92
Base 210	...	..	..	..
Gold 800	1st	1.03	0.91	1.94
Silver 120	2nd	1.30	1.05	2.35
Base 80	...	..	..	..
Gold 890	1st	1.94	0.58	2.52
Silver 20	2nd	1.32	0.49	1.81
Base 90	...	..	..	..

Along with these, two samples were run side by side, but the duplicates were cupelled in a different make of cupel, also side by side and separated from the originals on the plate. The used cupels gave the following absorptions:

CUPEL ABSORPTIONS (MG.) BULLION IN DIFFERENT CUPELS

COMPOSITION	CUPEL	Gold	Silver	Total
Silver 190	1st	1.39	2.17	3.56
Base 350	2nd	1.59	2.38	3.97
Gold 440	..	..	..	..
Silver 180	1st	1.40	2.17	3.57
Base 380	2nd	1.59	2.22	3.81
Gold 460	..	..	..	..

Eight base-metal assays were made in duplicate on various samples of a bullion, a proof being placed between each pair of duplicates, and the following absorptions (Group I) of gold and silver were shown by the cupels.

Other samples of the same bullion assayed in a different cupel and slightly hotter part of the muffle yielded the absorptions given as Group II:

GOLD AND SILVER ABSORBED (MG.)

GROUP I			GROUP II		
1st Assay	Proof	2nd Assay	1st Assay	Proof	2nd Assay
1.55	1.71	1.75	2.18	2.26	2.00
1.73	1.88	1.76	2.23	2.36	2.46
1.81	1.82	1.75	2.19	2.41	2.35
1.80	1.88	1.76	2.32	2.44	2.28
2.43	2.47	2.42	2.96	3.11	3.10
2.37	2.66	2.44	3.22	3.26	3.00
2.67	2.66	2.61	3.34	3.28	3.16
2.67	2.62	2.60	3.41	3.60	3.14

This bullion was 757 fine in gold; 196 fine in silver and 47 fine in base. The cupels were made in a hand-lever machine from bone ash of the following screen analysis:

	1st Cupel	2nd Cupel
On 40 mesh	1.0 per cent	1.25 per cent
On 60 mesh	2.5	11.00
On 80 mesh	6.0	21.50
On 100 mesh	7.5	13.75
Through 100 mesh	83.0	52.50
	100.0 per cent	100.00 per cent

Two other comparisons on a different bullion were similar to the last two runs, but the relative positions of the cupels were reversed and in this comparison No. 1 cupel was run slightly hotter than No. 2.

GOLD AND SILVER ABSORBED (MG.)

HOTTER RUNS ON NO. 1 CUPEL			COOLER RUNS ON NO. 2 CUPEL		
1st Assay	Proof	2nd Assay	1st Assay	Proof	2nd Assay
1.98	2.27	1.97	1.97	2.13	1.89
2.16	2.30	2.14	2.00	2.07	2.07
2.33	2.66	2.37	2.21	2.31	2.18
2.72	2.96	2.91	2.46	2.76	2.98
2.84	2.85	2.90	2.60	2.53	2.51
3.07	2.99	3.00	2.66	2.53	2.51
3.17	3.34	3.30	2.76	2.64	2.77
3.27	3.22	3.05	2.86	2.74	2.72

This bullion was 712 fine in gold, 202 fine in silver and 86 fine in base.

Four sets of quadruplicate assays were made on various samples of a bullion, a proof being used between each two assays, making six cupels in each set, arranged in two rows of three in the furnace, and the following absorptions were shown:

GOLD AND SILVER ABSORBED (MG.)

Assays	Proof	Assays	Assays	Proof	Assays
	FIRST SET			THIRD SET	
2.44	2.34	2.44	2.49	2.52	2.38
2.82	2.72	2.67	2.82	2.61	2.22
	SECOND SET			FOURTH SET	
2.36	2.35	2.38	2.55	2.93	2.54
2.72	2.81	2.67	3.04	2.82	2.96

In each set the first row of figures represents the front row of cupels in the furnace. This bullion was 770 gold, 214 silver and 16 base. The cupels were made on a hand-lever machine from bone ash of the following screen composition:

On 40 mesh	1.00 per cent
On 60 mesh	4.25
On 80 mesh	12.75
On 100 mesh	10.0
Through 100 mesh	72.0
	100.00 per cent

Two sets of samples of miscellaneous bullion were run in different cupels, with the following results:

TABLE IV—GOLD AND SILVER ABSORBED (MG.) MISCELLANEOUS BULLION

	1ST CUPEL			2ND CUPEL		
COMPOSITION	Gold	Silver	Total	Gold	Silver	Total
Gold 742.5	0.62	0.90	1.52	0.91	1.23	2.14
Silver 161.5	0.67	0.91	1.58	0.98	1.21	2.19
Base 96	0.71	0.98	1.69	1.03	1.48	2.51
	0.79	1.19	1.98	1.06	1.38	2.44
	0.82	1.05	1.87	..	..	..
	0.94	1.19	2.13	..	..	..
	1.06	1.30	2.36	..	..	..
	1.09	1.28	2.37	..	..	..
Gold 559	0.29	2.12	2.41	0.41	2.31	2.72
Silver 405	0.36	2.53	2.84	0.51	2.67	3.18
Base 36	0.49	2.85	3.34	0.54	2.95	3.49
	0.50	2.90	3.40	0.60	3.00	3.60
	..	..	..	0.72	3.52	4.24
	..	..	..	0.71	3.60	4.31
Gold 486.25	0.27	2.60	2.87	0.28	2.36	2.64
Silver 471.0	0.35	3.01	3.36	0.29	1.98	2.27
Base 42.75	0.56	3.86	4.42	0.41	3.33	3.74
	0.59	3.72	4.31	0.43	3.50	3.93
	..	..	..	0.51	3.74	4.25
	..	..	..	0.51	3.85	4.36
Gold 245	0.10	4.06	4.16	0.15	4.73	4.88
Silver 666	0.11	4.24	4.35	0.17	5.44	5.61
Base 89	0.12	4.75	4.87	0.18	5.22	5.40
	0.17	4.98	5.15	0.19	4.70	4.89
	..	..	..	0.20	3.65	3.85
	..	..	..	0.20	5.16	5.36
Gold 242.75	0.09	3.65	3.74	0.13	4.53	4.66
Silver 675.0	0.10	3.56	3.66	0.14	4.56	4.70
Base 82.25	0.16	4.93	5.09	0.15	3.24	3.39
	..	..	..	0.15	4.96	5.11
	..	..	..	0.16	4.55	4.71
	..	..	..	0.17	5.31	5.48

These cupels were made on a hand-lever machine from bone ash of the following screen composition:

	No. 1 Cupel	No. 2 Cupel
On 40 mesh	1.50 per cent	.. per cent
On 60 mesh	2.75	9.25
On 80 mesh	7.00	22.00
On 100 mesh	8.50	14.00
Through 100 mesh	80.25	54.75
	100.00 per cent	100.00 per cent

A cyanide bullion 884 fine in gold, 6 in silver and 110 base, being mainly zinc and cadmium, with practically no copper, yielded the following absorptions:

TABLE V—GOLD AND SILVER ABSORBED (MG.) CYANIDE BULLION

Gold	Silver	Total	Gold	Silver	Total
0.79	0.07	0.86	0.91	0.09	1.00
0.81	0.06	0.87	0.92	0.11	1.03
0.82	0.09	0.91	0.98	0.07	1.05
0.82	0.09	0.91	1.01	0.08	1.09

This cupel was made on a hand-lever machine from bone ash of the following screen composition:

On 40 mesh	Slight trace
On 60 mesh	6.00 per cent
On 80 mesh	11.75
On 100 mesh	10.0
Through 100 mesh	72.25
	100.00 per cent

A very low-grade bullion, 110 fine in gold, 52 in silver and 838 base, which was mainly lead, yielded the following absorptions in the same cupel as that used in the above cyanide bullion:

TABLE VI—GOLD AND SILVER ABSORBED (MG.)—VERY LEADY BULLION

Gold	Silver	Total
0.28	0.83	1.11
0.29	0.58	0.87
0.33	0.81	1.14
0.37	0.49	0.86

The Mint service does not pay for silver where it is less than 8 fine in the bullion. The cupels used on three such bullions showed the following absorptions:

CUPEL ABSORPTION (MG.)

COMPOSITION			Gold	Silver	Total
No. 1 BULLION:					
Gold 892.25 fine	Proof	A	...	..	2.28
Silver 7.5 fine		B	2.25	0.19	2.44
Base 100.25	..	..	...	..	..
No. 2 BULLION:					
Gold 988.25	987	A	1.80	0.23	2.03
Silver 6.5	13	B	1.91	0.12	2.03
Base 5.25	..	Proof	1.88	0.13	1.94
No. 3 BULLION:					
Gold 985.75	987	A	1.84	0.11	1.95
Silver 7.0	13	B	2.14	0.21	2.35
Base 7.25	..	Proof	2.05	0.15	2.20

A fourth bullion was assayed in three different cupels, but unfortunately I do not know the screen composition of the ashes used. The following absorptions were shown:

CUPEL ABSORPTION

COMPOSITION Bullion		Proof		Gold Mg.	Silver Mg.	Total Mg.
			No. 1 CUPEL			
Gold	987.75	990	A	2.19	0.15	2.34
Silver	6.0	5	B	1.70	0.12	1.82
Base	6.25	5	Proof	2.15	0.09	2.24
			No. 2 CUPEL			
			A	1.38	0.10	1.48
			B	1.42	0.13	1.55
			Proof	1.17(?)	0.29	1.46
			A	1.81	0.09	1.90
			B	2.02	0.12	2.14
			Proof	1.99	0.18	2.17

A special series of synthetic alloys or proofs containing 8 and 10 GW silver and varying amounts of gold and copper were cupelled with varying amounts of lead at one of the mints and the used cupels were assayed at the Bureau. Table VII summarizes the data. The column "Button losses" gives the basis for the corrections that would have been applied to the base metal determinations if these alloys had been used as regular proofs in assaying. This column also illustrates the higher losses to be expected with increasing amounts of copper, accompanied as they must be by more lead and higher temperatures of cupellation.

TABLE VII—SYNTHETIC ALLOYS

Metals taken GW	Lead used Grams	Button losses GW	Cupel absorptions (Mg.) Gold	Silver	Total
All, silver 8					
Gold 980	2.6	12	2.60	0.07	2.67
Copper 10	..	11	2.34	0.07	2.41
Gold 910	3.2	23	2.35	0.17	2.52
Copper 20	..	20	2.32	0.10	2.42
Gold 820	3.9	46	4.50	0.09	4.59
Copper 40	..	45	4.20	0.12	4.32
Gold 700	2.6	8	2.42	0.10	2.52
Copper 5	..	10	3.03	0.07	3.10
Gold 700	6.5	86	5.87	0.13	6.00
Copper 80	..	86	6.20	0.23	6.43
Gold 600	2.6	9	2.58	0.14	2.72
Copper 5	..	11	3.31	0.15	3.46
Gold 500	2.6	10	3.01	0.46	3.47
Copper 5	..	11	3.19	0.22	3.41
All, silver 10					
Gold 600	3.9	54	4.66	0.30	4.96
Copper 50	..	57	6.29	0.45	6.74
Gold 500	7.8	98	5.69	0.29	5.98
Copper 90	..	98	5.91	0.30	6.21
Gold 400	10.4	150	6.17	0.19	6.36
Copper 140	..	148	5.34	0.26	5.60

The surface of several of the cupels was considerably eaten away and some beads were entrained.

From what has gone before it is evident that while there are not many opportunities for variations in the base-metal assay, these opportunities open the way for very large variations in the result. It is generally assumed that the proof assays will correct for these variations, at least approximately, but if the conditions of the work lead to variations in the assay itself, they must do the same for the proofs, and it is quite possible for the proofs to be very misleading. As a matter of fact, the base-metal proof question is an exceedingly troublesome one to deal with and requires the exercise of much thought and caution.

Substantially the same proof may lead to widely differing corrections when the work is performed under supposedly similar conditions in the same laboratory. Under differing conditions in the same laboratory, and still more so under differing conditions of different laboratories, the proofs may give corrections differing astonishingly. Three samples of standard gold, substantially 900 gold and 100 copper, but with a trifle of silver replacing the copper, were cupelled for base-metal in six laboratories. This would seem to be the simplest and easiest kind of a case, and should show a close agreement among the proofs, but it did not turn out so. One laboratory reported the proof conditions as follows:

BASE PROOFS ON STANDARD GOLD. ONE LABORATORY

0.0	2.0+	4.2+
0.2+	2.2+	4.5+
0.3+	2.3+	4.8+
0.5+	3.7+	6.8+
0.6+	3.8+	7.2+
0.9+	4.0+	7.3+

The other five laboratories reported the following proofs:

BASE PROOFS STANDARD GOLD

Laboratories 1 1/2 charge	2 1/2 charge	3	4	5
1 +	1.5—	5 —	1+	5 —
2 +	0	1 —	1+	5 —
4 +	1 +	0	2+	3.9—
5 +	1.5+	0	2+	3.9—
6.5+	1.5+	2.8+	2+	3.9—
6.5+	2 +	2.8+	3+	3.3—
7 +	...	...	...	3.3—
9.5+	...	...	...	3.3—
11.5+	...	...	...	2.5—
..	...	...	...	2.5—
..	...	...	...	1.7—
..	...	...	...	1.7—

The long row of minus proofs from the fifth laboratory is especially noticeable and indicates too high temperature in the cupelling. The sign + shows that the proof button obtained weighed more than the precious metals going into the proof, while — means that it weighed less. In applying the corrections to the assay buttons the signs must be reversed. These three samples were known to differ slightly in silver and it is scarcely profitable to tabulate the silver results reported.

Another sample of standard gold was sent to five of the above laboratories, several times to each. The laboratory individually quoted above refused to commit itself, as to the copper and silver present, upon its cupellation results. The other four laboratories numbered as above, reported the following proofs:

BASE PROOFS STANDARD GOLD

Laboratories			
1 1/2 charge	2 1/2 charge	3	4
4 —	2 —	1 —	4—
3 —	1 —	1 —	3—
1 —	1 —	1 —	1—
0	0	0.8—	1—
0.7+	1.5+	0.6—	0
2 +	...	0	3+

These four laboratories reported 58 determinations of silver and base metal, copper, in this sample, summarized as follows:

TABLE VIII—SILVER AND BASE METAL IN STANDARD GOLD

SILVER		SILVER		BASE METAL		BASE METAL	
Fine	Assays	Fine	Assays	Fine	Assays	Fine	Assays
0.25	8	5.0	6	92.0	2	97.0	4
0.50	1	5.5	4	92.5	1	97.5	3
1.0	1	6.0	2	93.0	5	98.0	6
1.5	1	6.5	1	94.0	1	98.5	1
2.0	2	7.0	4	94.5	2	99.0	2
2.5	5	7.5	2	95.0	9	100.0	9
3.0	4	8.0	1	95.5	1		—
3.5	4	8.5	1	96.0	11		58
4.0	4		—	96.5	1		
4.5	7		58				

In the above case it was a very simple matter for the assayer to make his proof to correspond very closely in composition to the metal being assayed, but the case of miscellaneous and unknown bullion is often further complicated by the fact that the assayer has to rely on his best judgment in making up his proofs. An experienced assayer can generally form a fairly good estimate for the proof from inspection and the preliminary assay, but small amounts of impurities may be present without being properly adjusted in the proofs, and some of these smaller impurities may have undue influence upon the course of the assay. Again, in a busy commercial laboratory it is often necessary to group closely related bullions under one proof composition which may be a cause of further variations.

In comparing the assays of miscellaneous bullion with the proofs, I wish also to illustrate the influence of the relative position of the cupel in the muffle upon both the proof and the assay. In the following table each horizontal line of figures represents a row of cupels as they stood in the furnace and the figures are the gold weights of the buttons resulting from the cupellations. There is no relation between the rows:

ASSAYS AND PROOFS IN SINGLE ROWS

	Assay	Proof	Assay	Proof
No. 1	995.7	997	996	996.5
No. 2	994.6	995	995	995
No. 3	994.3	995	990	993.4
No. 4	633.3	638.3	634.8	636.3

COMPOSITION OF PROOFS

	No. 1	No. 2	No. 3	No. 4
Gold	605	488	488	268
Silver	395	512	512	375
Copper	...	...	...	220
Zinc	...	...	...	100

The high losses on the proofs in Nos. 1, 2 and 3 are especially noticeable.

In five cases quadruple determinations of base metal were made and were run in two rows of four, one immediately behind the other, with varying arrangement for the assays and proofs. In the table the top row of figures in each set represents the front row of cupels and the figures are the button weights in GW. The assays and proofs are indicated by "A" and "P" respectively.

ASSAYS AND PROOFS IN DOUBLE ROWS

No. 1	A 945.0	P 946.1	A 945.3	P 946.7
	A 944.8	P 945.1	A 944.8	P 946.9
No. 2	P 996.9	A 997.0	P 996.0	A 995.2
	A 994.9	P 996.3	A ...	P 996.5
No. 3	P 880.8	A 875.8	P 882.1	A 875.5
	A 871.0	P 880.8	A 874	P 882.0
No. 4	A 961.7	P 962.3	A 964.0	P 963.1
	P 961.3	A 960.3	P 962.4	A 962.0
No. 5	A 827.8	P 831.7	A 827.1	P 832.2
	P 833.0	A 827.0	P 831.5	A 826.3

COMPOSITION OF PROOFS

	No. 1	No. 2	No. 3	No. 4	No. 5
Gold	765	865	675	723	590
Silver	181	135	210	245	245
Copper	54	...	15	32	25
Zinc	...	...	100	...	140

In a sixth set the front and back proof differed slightly.

P 975.8	A 975.4	P 976.0	A 975.3
P 970.8	A 974.2	P 970.0	A 973.8

PROOFS

	Front	Back
Gold	815	815
Silver	165	160

Quadruple base-metal assays were made with two sets of samples from two high-grade bullions. Each set of four assays was run by itself with a proof between each pair of assays. The arrangement of figures in the table represents the arrangement of the cupels in the furnace, the top row representing the front row of cupels in each set. The fineness figures represent the combined gold and silver finenesses shown after correcting the button weights by the proof figures in the middle.

TABLE IX—ASSAYS WITH MIDDLE PROOFS, IN DOUBLE ROWS

1ST BULLION

1ST SAMPLES			2ND SAMPLES		
Gold and silver fineness	Proof	Gold and silver fineness	Gold and silver fineness	Proof	Gold and silver fineness
912.3	2.5 —	912.8	910.4	0.2+	909.3
909.7	1.9 —	911.3	910.2	0.4—	910.3
909.1	2.3 —	908.3	907.5	0.4+	907.1
909.7	2.8 —	909.8	908.6	0	908.3
909.9	2.6 —	911.1	911.8	0.9+	911.5
910.5	3.3 —	912.3	911.5	0.4+	911.5
907.6	2.4 —	913.5	907.7	0.9+	909.0
909.3	2.5 —	909.8	905.9	1.3+	905.4
		2ND BULLION			
953.3	1.69—	957.5	964.0	0.5+	952.2
953.2	2.30—	953.0	952.6	0.2—	952.9
954.0	1.37—	953.9	960.8	0.1+	952.6
954.2	2.25—	954.2	958.8	0.4—	959.2
957.7	1.04—	952.2	947.2	3.9+	953.6
955.3	1.75—	953.6	958.0	0.4—	952.2
958.2	1.19—	957.6	957.7	1.8+	957.2
956.6	2.15—	956.3	947.8	2.1+	953.0

COMPOSITION OF BULLIONS AND PROOFS

	Bullions		Proofs	
	No. 1	No. 2	No. 1	No.2
Gold	713.75	758	714	760
Silver	198.0	196	200	200
Base	88.25	46	Copper	30

These assays were all made in one laboratory by one assayer. The first samples were run at one time and the second at another. A part of the differences shown are undoubtedly due to differences in samples.

This table is worthy of most careful study. It discloses both the remarkable agreement and the utter unreliability of results at times yielded by this method of assay.

Early in the investigation a series of synthetic bullions was prepared for the purpose of elucidating the influence of the composition of the bullion upon the assay results. The samples were distributed to nine laboratories throughout the service and nearly every one was assayed in four laboratories. The results reported, as shown in the next table, indicate that whatever influence the composition may have had on the assaying was masked by other influences in most cases.

TABLE X—BASE AND SILVER IN SYNTHETIC BULLIONS

BULLION NO. 1		BULLION NO. 2		BULLION NO. 3		BULLION NO. 4	
Base	Silver	Base	Silver	Base	Silver	Base	Silver
4.5	105	1.0	387	1.0	508	1.0	123
8.0	105	3.0	387	1.5	509	1.0	128
9.5	105	4.0	389.5	1.5	509.5	2.5	129.5
9.5	105	5.5	390.5	2.0	509.5	4.0	130
10.0	105.5	6.0	392	2.5	511	5.0	131
10.0	106	...	...	...	...	5.0	132
10.5	106	...	...	...	...	7.5	134
10.5	107.5	...	...	...	...	11.0	134
11.0	111	...	...	...	...	Gold	865
Gold	884.75	Gold	607	Gold	489		

BULLION NO. 5		BULLION NO. 6		BULLION NO. 7		BULLION NO. 8	
Base	Silver	Base	Silver	Base	Silver	Base	Silver
19	356	20.5	160	19.5	443.5	30	239
23	356.5	20.5	161.5	23	447	31.5	240
23.5	358	23	162	23	447	32	241
24	358	23.5	162	23	448	35.5	242
24	358	24	162.5	23.5	448	37	244
24	358	24.5	164.5	24	448	37	244.5
26	359	25.5	165	24	448	37	247.5
26	363	..	...	28	452	..	...
Gold	618.25	Gold	814	Gold	529	Gold	722

BULLION NO. 9		BULLION NO. 10		BULLION NO. 11		BULLION NO. 12	
Base	Silver	Base	Silver	Base	Silver	Base	Silver
50	181	152	494	161	240	356	362
50	181.5	158	495.5	167	240	359	362
50.5	181.5	159	498	168	240	360	368
50.5	185	159	499	168	240.5	363	368
52	185	159	499	168	242	364	368
52	186	159.5	499	171	242	364	371
54.5	186	161	500	171	243	368	373
55	187	164	501	171	243	370	376
Gold	763.75	164	507.5	171	249.5	...	...
		Gold	341.5	Gold	590	Gold	268

Bullion No. 4 contained a small amount of arsenic, about 1 fine, No. 8 contained about the same of antimony, No. 9 was nearly saturated with iron, No. 6 contained both antimony and iron and Nos. 11 and 12 were high in zinc.

Two samples containing arsenic are very interesting. One was approximately 785 fine in gold, 107.5 in silver, 100 in copper and 7.5 in arsenic. The gold assays (65) varied from 779.7 to 792.4, a variation of 12.7 in the fineness. The base assays (24) varied from 101 to 117, a variation of 16 in the fineness. The second was approximately 675 fine in gold, 200 in silver, 100 in zinc, 24 in lead and copper and only 1 in arsenic. The gold assays (62) varied from 671.4 to 681.4, a variation of 10 in the fineness, but the base assays (8) varied less than the gold assays. The base assays varied from 120 to 127, showing a variation of only 7 in the fineness. Evidently both of these bullions are hopeless as assaying propositions.

Two special cases will be mentioned here, although they will also be used further along in this paper. The Mint service does not pay for silver in deposits when it is less than 8 fine in the bullion. A deposit 884 fine in gold was cupelled 16 times in 5 laboratories for base metal and 12 of the results gave the silver below 8 fine. The 4 at 8 fine and above were all from one laboratory. Also the Service does not buy bullion over 800 fine in base metal, but a synthetic bullion containing about 838 base, most of which was lead, was cupelled for base 16 times in 4 laboratories and 12 of the results ranged from 840 to 836, while a group of four from one laboratory were from 4 to 7 lower in base than the lowest of the 12. The following tables summarizes the reports:

BASE METAL AND SILVER IN SPECIAL CASES

GOLD 884			GOLD 110		
Base	Assays	Silver	Base	Assays	Silver
111	1	5	840	2	50
110.25	1	5.75	839.5	1	50.5
110	5	6	839	2	51
109.75	2	6.25	838.5	1	51.5
109.50	2	6.50	838	2	52
109	1	7.0	837.75	1	52.25
108	1	8.0	837	1	53
107	3	9	836	2	54
			832	1	58
	16		831	1	59
			830	1	60
			829	1	61
				16	

A few more direct comparisons will be given here, and several others will be found in the sulfocyanate portion of this paper (see September issue).

Various samples of two bullions were assayed for base metal in five laboratories with the following results. Possibly some of the differences shown were due to differences in samples.

1ST BULLION		2ND BULLION	
Assays	Base metal	Assays	Base metal
2	437	1	484
1	438	1	487
1	442	4	488
1	443	1	489
3	444	3	490
2	445	1	492
1	446	1	507
1	448	12	
1	449		
1	453		
14			

A further exceptional illustration is afforded by three bars from each of which two samples were cut and a single assay made on each sample at the purchasing office. These three bars were included in one shipment of redeposits. The redeposit office remelted the bars and reported much more silver, even after allowing for loss of base metal in remelting. The purchasing office samples were then submitted to two other laboratories in the Service and duplicate assays were made on each sample in each laboratory. The results reported were as follows:

	Bar 1		Bar 2		Bar 3		Bar 4	
Samples	A	B	A	B	A	B	A	B
Original	526.25	526	412	412	331	331.5	284.5	284.5
1st Lab.	539.5	539.5	423.5	423	345.5	344.5	286.5	...
	541.5	540	423.25	423	343.5	347	288.5	...
2nd Lab.	537	537	422	424	336	338	286.5	...
	536	536	421	423	338	336	...	...
Gold	303.50		265		215		220.75	

Having shown that the method is often liable to give erratic results, attention should in justice be directed to the large number of satisfactory agreements shown in Table I. This, also, however, raises a most important physiological and psychological question which is approached with some hesitation, but the whole object of the investigations upon which this paper is founded is for the purpose of improving our assaying methods as necessarily carried out under commercial conditions, and before this can be intelligently undertaken or successfully accomplished it is essential to consider all the conditions surrounding our present methods and their application. It becomes, therefore, essential to consider the human aspect of the work, since a large laboratory is liable to contain a variety of personalities. Without going into details, three chief factors may be mentioned under this head: pure carelessness, laziness and the domination of one's own or an outside will or intellect. The first one may cause agreement or disagreement, but the second two may surely be counted on to unify the results.

One of the best assayers I have ever known, who was also big and strong enough to be frank, once said to me: "Why I can *see* any weight at the balance that I want to." The records of the Bureau, particularly the older ones, show far too many cases of remarkable agreement in the reported results to be explained simply upon the general theory of chance.

In one case a sample was sent to an institution on two occasions and assayed in quadruple each time. Everyone of the eight results reported was 0.25 fine in silver. The same sample was sent again and the duplicate results were both given as 4 fine in silver. It was sent again and all four results were stated as 5 fine in silver. In the case of the arsenical bullion already mentioned one laboratory reported the silver at 105, 105, 106 and 107, but on another occasion it was reported by the same laboratory at 106, 109, 110 and 114. In all, 24 determinations of silver were made on this sample in five laboratories and they varied from 101 to 117. Another laboratory shows surprising agreement between duplicates all along the line. A difference of 0.5 in the base-metal duplicates is rare, but when their samples are sent to other institutions for assay, much wider differences are reported, and on one occasion in this laboratory a proof composed of 580 gold, 400 silver and 20 copper lost 20, while a companion proof of the same composition lost only 8. Also a sample of proof gold was once sent to this institution, under the name of fine gold simply, and the report showed 999.5, 999.6, 999.7 and 999.7 fine in gold. Finally in various comparisons the results from this institution form a closely agreeing group of figures at one or the other extreme of all the reports in the comparison. In one instance a docile weigher sitting by the side of a domineering personality turned in many consecutive reports agreeing absolutely with the figures of his associate.

CONCLUSIONS REGARDING THE CUPELLATION METHOD

Determinations by difference are always objectionable since all the errors of the other determinations are thrown upon the final one. This allows a wide margin for differences between duplicates and leaves the question of the actual amount of the estimated material present in doubt.

The mass of data here presented warrants the following conclusions regarding the cupellation for base metal: There are two chief sources of operative error in this determination, the absorption of gold and silver by the cupel and the retention of base metal by the precious metal button. At present we do not have the means of controlling either of these with any certainty, or of readily ascertaining their extent in commercial work. These errors may balance each other, but they often fail to do so. A low cupel absorption may be accompanied by either a high or a low button retention, or a high cupel absorption by either kind of button retention, and the relations may be reversed in the duplicates. A third defect arises from the fact that the proofs are subject to the same uncontrollable errors as the assays, and the proof corrections may be fallacious.

Notwithstanding the defects pointed out in this paper, which render the method unsatisfactory, the simplicity and ease of execution of the cupellation method commend its use and undoubtedly it will be extensively employed for many years to come. It is also evident that the defects are inherent and that there is no apparent way of overcoming them in the present state of our knowledge. It, therefore, becomes necessary to seek for a better method, and preferably a direct determination of the silver.

Moreover, aside from the ordinary errors of manipulation, the presence in a bullion of members of the platinum group of metals, which are soluble in nitric acid when alloyed with silver, further complicates the determination of the silver by cupellation. Such bullions are not uncommon in Mint work, although much of the platinum occurs in scrap material purchased.

(To be concluded)

THE DETERMINATION OF CHROMIUM AND MANGANESE IN IRON AND STEEL

By Fred C. T. Daniels

Received May 6, 1914

In steel furnace operations it is frequently necessary to include chromium among elements to be determined in the preliminary analysis. The following 20-minute method has been worked out to fill this necessity. It has been in constant use for the past two years and is sufficiently accurate to be used as a daily routine method, and it occupies but little of the chemist's actual working time.

The method for chromium is an adaptation of the persulfate method for the manganese determination in iron and steel.

The method for manganese is the persulfate method except that the sum of the manganese and chromium is obtained in this titration and the manganese calculated by difference, using the results from the chromium determination. The objection to the usual persulfate method for manganese, in the presence of chromium, is that a varying quantity of the chromium is reduced along with the manganese by the ferrous ammonium sulfate or sodium arsenite. If determined colorimetrically, the chromium gives the solution a different shade, which is difficult to compare. This may be overcome by using for a standard a steel containing approximately the same amount of chromium as the sample. A still more convenient way is to add the chromium as potassium bichromate, using a standard solution, so that 1 cc. would equal 0.0005 gram of chromium, *i. e.*, 0.25 per cent chromium for a 0.20 gram charge of the sample. This solution is added to the standard after the solutions have been transferred to the color comparison tubes.

CHROMIUM—Weigh 1 gram of the sample into a 300 cc. Erlenmeyer flask (Jena glass), add 100 cc. nitric acid (1.135 specific gravity), place on the hot plate, and when solution is complete, boil off all nitrous fumes. (The volume of the solution should not be less than 75 cc. It is unnecessary to filter off the silicon and graphite residue if the solution is complete. When the sample is high in combined carbon, it is well to add a few crystals of ammonium persulfate when the solution is complete and boil a moment longer to destroy the combined carbon.) Remove the flask from the hot plate, add 75 cc. silver nitrate solution (2.00 grams per liter), and immediately 5 grams of ammonium persulfate crystals. Replace flask on the hot plate and bring gently to boiling. Boil vigorously for a minute, and while still boiling add dilute hydrochloric acid, drop by drop, until the permanganate color is completely destroyed. Continue the boiling for one minute and then cool the flask immediately in water. Titrate by adding an excess of tenth-normal ferrous ammonium sulfate solution above that required to reduce the chromium, and titrate back with tenth-normal potassium permanganate solution. The number of cubic centimeters of the ferrous ammonium sulfate oxidized by the chromate, multiplied by 0.00174, gives the weight of chromium in the sample.

MANGANESE IN THE PRESENCE OF CHROMIUM—Proceed according to the above directions for the determination of chromium except that after the ammonium persulfate is added, only heat until the solution just comes to boiling, then cool immediately and titrate as before, this time adding enough ferrous ammonium sulfate to reduce both the manganese and chromium. The number of cubic centimeters of ferrous ammonium sulfate used, minus the number used in the chromium determination, multiplied by 0.0055, equals the weight of manganese in the sample.

The ultimate value of the solutions may be used in calculations as above. In this case it is advisable to carry along a blank with a sample containing no chromium and subtracting the blank. The standardization of the solutions against a standard steel is the most satisfactory procedure.

WHEELING MOLD & FOUNDRY CO.
WHEELING, WEST VIRGINIA

PRINTING INKS AND THEIR ANALYSIS[1]

By J. B. TUTTLE AND W. H. SMITH

Received April 16, 1914

There will be published shortly by the Bureau of Standards, two papers on the subject of printing inks: one, a technologic paper on "The Analysis of Printing Inks," and the other a circular of general information on this subject. The length of these papers is such as to make it unwise to attempt to present either of them in full at this time, but it is desired to give some idea of their scope.

The first paper treats the subject from an analytical point of view. Four types of ink have been investigated: web press, flat-bed, job, and half-tone inks. These included a number of colored as well as the more common black inks. The method of analysis has been in use for several years for the testing of supplies delivered to the Government Printing Office, and has been found very satisfactory for this purpose.

Using as the solvent a mixture of benzene and ethyl ether, the oil is separated from the pigment by means of a centrifuge. In some cases petroleum ether may be used as the solvent. This method gives an effective separation, and the pigment may be determined with a fair degree of accuracy.

The oil fraction, after evaporating off the solvent, is analyzed for unsaponifiable oils (rosin and mineral oils), rosin, hard gums and linseed oil.

In the black inks, the pigment is ignited and the ash tested for driers and ferric oxide, the latter being the residue left on the ignition of Prussian blue. A qualitative test for Prussian blue is given, which will detect less than one per cent of this material in the pigment. If aniline dyes are present, they may be determined by extraction by means of alcohol, unless preliminary examination shows that the dye is insoluble in this solvent. In the latter event, a suitable solvent must be found.

The colored inks require a preliminary examination to determine the nature of the pigment used, and the method of attack depends largely upon the results of these tests. Some of the mineral pigments, such as vermilion (mercuric sulfide) and chrome green (*i. e.*, the material known commercially as Brunswick or Milori Green), may be determined quantitatively according to the procedure outlined in the original article. If the coloring matter consists of aniline dyes or lakes, it will usually be found sufficient to determine whether or not these colors are fast to light. Two methods for this test are given.

A table is given showing how closely one may expect duplicate determinations on the same sample to check. These figures are the result of testing several hundred samples of ink by at least half a dozen analysts, so that they may reasonably be taken as a fair measure of the accuracy of the method.

The paper also includes a brief discussion of the relation of these laboratory tests to the practical tests which may be made by the printer. It is not the intention that the latter shall be supplanted by the former, but that the two shall supplement each other in order to obtain the grade of ink which is the most suitable for the purpose.

The second paper is the circular of information on the general subject of printing inks. It gives a brief description of some of the materials used in the manufacture of ink, and also treats broadly some of the problems concerning the relation between the ink

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[1] Published by permission of the Director of the Bureau of Standards.

and the paper. While the first paper will probably be of more particular interest to chemists, this circular, it is hoped, will appeal to all those who may desire some general information on the subject. It will include at first, only the same classes of ink covered by the technologic paper, but it is proposed to revise this circular from time to time, adding to it other classes of ink as rapidly as accurate and reliable information about them can be obtained.

Anyone who is interested in the subject of printing inks, may obtain either one, or both of these publications, on application to the Bureau of Standards, Washington, D. C.

Bureau of Standards, Washington

THE OCCURRENCE OF MANGANESE IN KENTUCKY SOILS AND ITS POSSIBLE SIGNIFICANCE

By O. M. Shedd

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HISTORICAL

Although manganese is not generally regarded as one of the essential elements of plant food, nevertheless numerous experiments have shown that its compounds are invariably present in soils and in a large variety of plants and animals which necessarily derive their sustenance from the soil. The fact having been generally proven that it is universally present in plants has caused considerable work and discussion as to what function it performs and whether or not the application of some manganese salts will prove beneficial to plant growth.

In the analysis of 23 Italian soils of various kinds (sandy, volcanic, clay and calcareous), Contino[1] found that manganese was always present in amounts varying from a trace to as much as 0.48 per cent Mn_3O_4, the average being 0.17 per cent Mn_3O_4.

De Sornay[2] has shown in the analyses of 37 Mauritius soils that the manganese varies from 0.03 to 0.41 per cent, the average being from 0.15 to 0.20 per cent. He also found that some plants contain considerable manganese in their ash, the proportion in the natural plants being usually less than 0.01 per cent but is universally present indicating that plants assimilate it naturally. These results have been confirmed by Boname[3] who found as much as 1.26 per cent of manganese in arrowroot grown in Mauritius soils.

In this country, Sullivan and Robinson[4] have found that of 26 American soils recently analyzed, all contain manganese (MnO) in proportions ranging from 0.01 to 0.51 per cent. The average content is 0.20 per cent, or about 8000 pounds per acre foot.

Gortner and Rost[5] have found in a few Nebraska soils that the average manganese content is about 0.11 per cent MnO.

Jadin and Astruc[6] give the results of analyses of about 65 species of plants in which it is shown that this element is widely distributed in the plant kingdom. The amount present was found to vary with the different organs of the plant examined. The manganese content of different plants belonging to the same family could not be taken as indicative of the average content to be expected in other members of the order. The chlorophyll portions were, as a rule, richer in this element than the subterranean parts and the percentage was greater in the older leaves, especially when the fresh weight is taken, but often the reverse if the ash weight is considered.

McHargue[1] has determined the manganese in a variety of plants and his results confirm those of Jadin, Astruc and others who might be mentioned, that this element varies considerably in the different organs of the same plant and of course in different plants.

Furthermore, Bertrand and Medigreceneau[2] have found traces of this element in about 60 species of wild and domestic animals and it is therefore thought that its presence has some physiological significance and is not merely accidental as is commonly supposed.

Experience has shown that the presence of excessive manganese compounds in the soil are very injurious to vegetation as they act directly on the chlorophyll and cause bleaching or yellowing of the leaves. For instance, Kelley[3] has found, in Hawaii, that certain black lands on which pineapples did not grow well, showed the presence of from 2.43 to 9.74 per cent Mn_3O_4 and indicated a close relation between the manganese content of the soils and the general appearance and growth of the pineapples. Other areas in close proximity in which they thrived, contained considerably less manganese; otherwise the soils were the same. Moreover, it was found that when an attempt was made to grow other plants in these soils, there invariably occurred a yellowing of the leaves and premature falling of the lower ones. His conclusions were that soils that contain over 4 per cent of manganese are not suitable for the growth of pineapples.

Guthrie and Cohen[4] also found that bare patches of grass soil showed 0.254 per cent Mn_2O_3, while other portions of the soil in which the grass was growing well, contained much less. No other differences were found. They suggest that the element was present originally in innocuous form which became toxic by oxidation. It is interesting to note in both cases that the application of soluble phosphates had a tendency to correct these toxic conditions and in the case of the grass, restored its growth.

Ewell[5] gives another illustration in reporting the results of an examination of a soil which failed to grow legumes and which was found to contain considerable amounts of manganese compounds soluble in water, more in fact than of lime.

It has been claimed that manganese serves no useful purpose in plants but that it is merely taken from the

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[1] *Staz. Sper. Agar. Ital.*, **44** (1911), 51–55; *J. Chem. Soc.* (London), **1911**, Aii, p. 649.

[2] *J. Chem. Soc.* (London), **1912**, Aii, p. 1089.

[3] *Exper. Sta. Rec.*, **21** (1909), 717.

[4] *U. S. D. A., Bur. Soils, Circ.* **75**, p. 3; *Exper. Sta. Rec.*, **28** (1913), 523.

[5] This Journal, **4** (1912), 522.

[6] *Compt. rend. Acad. Sci.* (Paris), **156** (1913), 26, 2023–24; *Exper. Sta. Rec.*, **29** (1913), 28, 628.

[1] *Ky. Agr. Exper. Sta.*

[2] *Compt. rend. Acad. Sci.* (Paris), **154** (1912), 15, 941–3; 22, 1450–52; *Exper. Sta. Rec.*, **27** (1912), 670.

[3] Hawaii Sta., *Press Bull.* **23**, 14; *Repl.*, **1909**, pp. 58–63; **1910**, pp. 14–16, 41–43, 45–50.

[4] *Agr. Gaz. N. S. Wales*, **1910**, 21, 219–222; **1911**, 22, 1, 70; *J. Chem. Soc.* (London), **1910**, Aii, 444; *Exper. Sta. Rec.*, **25**, 122.

[5] *Science*, N. Ser., **16** (1912), 339, 291; *Exper. Sta. Rec.*, **14**, 231.

soil as are some other non-essential elements, and from plants finds its way into the animal organism. This view has led a number of investigators to conduct experiments to determine if manganese compounds would have any practical use in agriculture and the opinion of the majority is that under certain conditions they may have a decided value.

From their work with water, sand and soil cultures, Salomone,[1] Stoklasa,[2] Leidreiter,[3] Katayama,[4] Loew[5] and Aso[6] have come to the conclusion that small amounts of manganese are decidedly beneficial to some plants, while large amounts are toxic. In these experiments, the manganese salts used included the phosphate, carbonate, nitrate, sulfate and others and were tried on a variety of plants such as oats, wheat, potatoes, sugar beets, rice and a large number of vegetables.

In pot and field experiments on different crops, using manganese salts, very favorable results have been obtained provided the right quantities are used, but here as in the above trials, it has again been demonstrated that large quantities are injurious.

Bertrand[7] has made experiments on a clay soil containing 0.057 per cent of manganese soluble in hydrochloric acid and 0.02 per cent soluble in boiling acetic acid. Oats were grown on 2 plots of 20 acres, both of which had the usual manures and one pure manganese sulfate at the rate of 44 pounds per acre. The manganese salt resulted in a gain of 17 per cent of grain and 26 per cent of straw. The grain from both plots contained the same amount of the element.

In plot tests with grain, using different manganese compounds, Stranipelli[8] obtained increased yields due to their effect, the greatest increase resulting from the use of the sulfate.

Ray and Pradier[9] have found that the use of manganese sulfate on apricots produced a more luxuriant vegetation and increased the size of the fruits.

Stoklasa[10] increased the yield of sugar beets from 30 to 50 per cent by adding about 8 pounds of manganese and 4 pounds of aluminum per acre, in the form of sulfates, to a complete basal fertilizer. The assimilable aluminum salt apparently corrected the toxic action and promoted the stimulating effect of the manganese.

Very good results have been obtained by Boullanger[11] with manganese fertilizers on potatoes, oats, peas, clover and some truck crops.

Extending its use somewhat further, Sanning and Tosatti[12] report results indicating that manganese sulfate tends to increase the yield of grapes considerably while McCallum[1] has obtained remarkable results in the growth of potatoes by preliminary treatment of the tubers with manganese chloride. Seed potatoes thus treated, while showing no difference in the growth of foliage, exhibited a most pronounced acceleration in the formation of tubers.

Loew and others referred to above, who are connected with the Tokyo Imperial University, have for a number of years made numerous experiments in Japan on the effect of manganese salts on various crops. They have obtained some very favorable and interesting results, especially with rice.

Others might be mentioned who have experimented with manganese fertilizers and while the results of some are indifferent or negative, still those of the majority are favorable. This of course is to be expected in work of this character, which, being only in its experimental stage, involves many unknown factors such as the amount and kind of material used, the character and location of the soil and the crop grown on it.

While the experiments have covered a wide field and included a large number of investigators, it is interesting to note that identical conclusions regarding the use and function of manganese compounds in plants have been independently agreed upon by several of the workers. Briefly stated, these conclusions are as follows:

1—Small applications of manganese compounds are in many cases beneficial, while large applications are invariably toxic.

2—The presence of manganese plays a very important part in the formation of chlorophyll in the leaf and hence performs an important function in carbon assimilation by promoting rapid photosynthesis in the chlorophyll apparatus.

3—When small amounts of manganese compounds occur in natural soils, it is believed that a two-fold function in plant growth is performed. One is that they act catalytically, increasing the oxidation in the soil and accelerating auto-oxidation in plants, and furthermore, they tend to modify the absorption of lime and magnesia by partially replacing them from insoluble combinations and to exert a direct effect on the osmotic absorption of both.

4—That manganese is invariably associated with the oxidases in plants and stimulates their action has been proven by Bertrand and others, while Loew considers it probable that very fertile soils are characterized by the presence of readily available compounds of this element.

EXPERIMENTAL

As a considerable number of carefully selected soils had been used by the writer in some former work in comparing the amount of total sulfur in continuously cultivated soils and subsoils with the corresponding virgin samples, it was thought that it might prove of interest to use these for total manganese determinations, in order to find out what effect continuous cultivation might have on this element. A description of the locality where the samples were taken, the ro-

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[1] *Chem. Zentr.*, **1906**, ii, 532; *J. Chem. Soc.*, (London) **1906**, Aii, 792.

[2] *Compt. rend.*, **152** (1911), 1340–42; *J. Chem. Soc.* (London), **1911**, Aii, 643.

[3] *Bied. Zentr.*, **40** (1911), 531–35; *J. Chem. Soc.*, **1911**, Aii, 923.

[4] *Bull. Coll. Agr. Tokyo Imp. Univ.*, **7** (1906), 91–93.

[5] *Ibid.*, **5** (1902), 161–172.

[6] *Ibid.*, **5** (1902), 177–185.

[7] *Compt. rend. Acad. Sci.* (Paris), **141** (1905), 26, 1255–57; *Exper. Sta. Rec.*, **17**, 954.

[8] *Atti. 6 Cong. Inter. Chem. Appl.*, **4** (1906), 14–17.

[9] *Exper. Sta. Rec.*, **22** (1910), 718.

[10] *Ibid.*, **26** (1912), 225.

[11] *Ibid.*, **29** (1913), 838.

[12] *Ibid.*, **29** (1913), 838.

[1] *Ariz. Sta. Rept.*, **1909**, pp. 584–86.

tation and number of years of cultivation, together with the yields of crops usually produced on the old and new land were given in a former publication.[1] It is not necessary to repeat these data here, except it might be stated that in a large majority of instances the soils had been continuously cultivated for a considerable number of years and no stable manure or commercial fertilizer had been used.

The procedure used for the determination of total manganese was practically the same as that employed by Gortner and Rost in their work referred to above and consisted of what is commonly known as the sodium bismuthate method. They have shown that their method which consists in fusing the soil with sodium carbonate to obtain the manganese in solution and its subsequent oxidation to permanganic acid with sodium bismuthate gives higher and more concordant results on Nebraska soils than Walters' method in which ammonium persulfate is employed as the oxidizing agent. The Walters method[2] had, until this time, been regarded as the most accurate method, either gravimetric or volumetric, known for this purpose and was adopted by Hillebrand[3] and Washington[4] for the determination of total manganese in rocks.

It is only necessary to examine the results obtained by Gortner and Rost to be convinced that their method is simpler and more accurate than that of Walters; in fact Blair[5] and Brinton[6] have recognized the superiority of the sodium bismuthate oxidation by stating that "for samples containing not over 2 per cent of manganese, the bismuthate is the most accurate method known."

The method as used in this work is as follows: One gram of soil is intimately mixed with 4 grams of manganese-free, dry, sodium carbonate and fused in a 20 cc. platinum crucible over a blast lamp until the melt is quiet or for about ten minutes. The liquid mass is then poured into a 100 cc. platinum dish and the dish rotated in order to obtain the melt in a thin film, thus providing for more rapid solution. The melt and crucible are then treated with about 100 cc. of distilled water and heated on the water bath until the fused product is completely disintegrated, which requires about an hour or two. The crucible is then removed from the dish, any adhering solution washed off, and the mixture acidified with 130 cc. of 35 per cent (by weight) sulfuric acid and diluted to 250 cc. Should there be a heavy precipitate of silica at this point it is advisable to filter, using a Buchner funnel and filtering by suction. This is seldom necessary, however, for in most cases the silica does not precipitate to any extent, but merely produces a slight opalescence which does not interfere with the permanganate readings. One hundred cc. of this solution are then placed in an Erlenmeyer flask, the contents brought to boiling, cooled, and 0.50 gram Baker's C. P. sodium bismuthate added. The amount of bismuthate to be added, of course, depends on the quantity of manganese present and might vary from 0.25 gram to 1 gram. It is advisable not to add any large excess so that the bismuth salts will remain in solution. It has been found that 0.25 gram of bismuthate is sufficient where the manganese content does not exceed 0.20 per cent. The oxidation mixture is then heated just to boiling and continued only until the liquid has the true permanganate color, which requires only a minute or two. The solution at this point may have a slight foreign red color but this will disappear on cooling. Excessive heating of the solution is to be avoided as this tends to destroy the permanganate color and gives low results. After cooling, the solution is made to its original volume, or 100 cc., shaken thoroughly and if any bismuthate salts precipitate, it is allowed to stand for some minutes in the dark until these settle. If it is found necessary in order to obtain a clear solution, it can be filtered through properly prepared asbestos, but as soon as possible the solution is read in a colorimeter or Nessler's glasses against a standard solution of permanganic acid which has been prepared by reducing a solution of potassium permanganate in 20 per cent (by weight) sulfuric acid by the cautious addition of sulfurous acid, and reoxidizing with bismuthate. The standard solution should contain about 0.2 mg. of MnO per 10 cc. From the ratios thus obtained, the quantity of manganese in the original sample is calculated.

The writer in this work used a Duboscq colorimeter and the standard was prepared as described above and compared every day with a freshly prepared potassium permanganate solution, 10 cc. of which = 0.2 mg. MnO. The standard permanganic acid solution was found to deteriorate gradually in strength and as a potassium permanganate solution of the same manganese strength was found to have the same color, a factor could be used on the true standard. The potassium permanganate standard could just as well be used as a standard but as it was thought best to have both the standard and unknown solution prepared in the same manner, the permanganic acid standard was employed throughout the work.

It might also be mentioned here that a potassium permanganate solution of this weak strength gradually deteriorates, so the plan followed was to make the permanganate solution daily, by the proper dilution of a *N*/10 solution, and the permanganic acid standard, every four or five days. In both, boiled distilled water was used to which a few drops of weak permanganate were added until just faintly colored.

Gortner and Rost used the permanganate reduced with sulfurous acid as a stock solution which they found to be stable and from which they made their standard as needed, but the writer prefers the other plan since the exact strength of the standard can be determined with very little trouble.

The method has given very good duplicate results on independent fusions while it might be mentioned that blank determinations showed no manganese present in the chemicals used.

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[1] *Ky. Agr. Exper. Sta. Bull.*, **174**.

[2] *Chem. News*, **83** (1901), 76; **84** (1901), 239.

[3] *Bull.*, **422**, 116, U. S. Geol. Survey.

[4] "The Chemical Analysis of Rocks," Wiley & Sons, N. Y., 1910.

[5] "Chemical Analysis of Iron," 7th ed., p. 121; *J. Amer. Chem. Soc.*, **26**, 793.

[6] THIS JOURNAL, **3** (1911), 237.

In the following tables, the samples in which the results are strictly comparable, both in the surface and subsoil of the virgin and cultivated areas, are given in the same horizontal line. In computing the percentages of manganese to pounds per acre, the calculations were made by assuming the surface, or first 6$6^1/_2$ to 7 inches of soil as weighing 2,000,000 pounds, and the second 6 inches or subsoil, as weighing the same. The pounds per acre of manganese given for the subsoils approximately represent the second 6 inches, or from $6^1/_2$ to $12^1/_2$ inches, although the subsoil samples were usually taken from 6 to 18 inches in depth. This of course assumes that the second and third 6 inches of soil will have about the same manganese content and they probably will be close enough so that the differences which are shown in the tables between the surface soils and subsoils, taken to these depths, will not be materially changed.

The soils, with the amount of manganese reported as the element, have been arranged according to the geological areas to which they belong and all the areas found in this state are more or less represented in Tables I and II.

TABLE I—TOTAL MANGANESE IN KENTUCKY SOILS RESULTS IN PERCENTAGES AND POUNDS PER ACRE

		SURFACE SOIL				SUBSOIL			
		Virgin		Cultivated		Virgin		Cultivated	
No.	COUNTY	%	Lbs.	%	Lbs.	%	Lbs.	%	Lbs.
EASTERN COAL FIELDS AREA									
669–72.......	Wolfe	0.152	3040	0.072	1440	0.122	2440	0.054	1080
700– 1.......	Magoffin	...	..	0.077	1540	...	..	0.051	1020
702– 3.......	Johnson	...	..	0.050	1000	...	..	0.031	620
704– 5.......	Johnson	...	..	0.068	1360	...	..	0.076	1520
763– 4.......	Johnson	0.050	1000	...	..	0.009	180	...	..
706	Floyd	0.148	2960	...	..	...	..	...	..
707–10.......	Perry	0.078	1560	0.067	1340	0.063	1260	0.036	720
715–18.......	Lawrence	0.060	1200	0.027	540	0.037	740	0.009	180
731– 4.......	Pike	0.125	2500	0.078	1560	0.095	1900	0.063	1260
AVERAGE............		0.102	2043	0.063	1254	0.065	1304	0.046	914
ST. LOUIS—CHESTER AREA									
681– 2.......	Lyon	...	..	0.026	520	...	..	0.022	440
683– 4.......	Metcalfe	...	..	0.050	1000	...	..	0.018	360
685	Adair	0.101	2020	...	..	...	..	...	..
759–60.......	Lincoln	0.134	2680	...	..	...	..	...	..
806– 9.......	Warren	0.065	1300	0.033	660	0.063	1260	0.031	620
813– 4.......	Metcalfe	In first 18 inches			..	0.192	3840	0.089	1780
815– 6.......	Metcalfe	In first 18 inches			..	0.080	1600	0.094	1880
AVERAGE............		0.100	2000	0.036	727	0.063	1260	0.024	473
CINCINNATIAN AREA									
757– 8.......	Henry	0.094	1880	0.053	1060	...	..	...	..
769–70(*a*)....	Washington	0.320	6400	0.159	3180	...	..	...	..
771	Washington	...	..	0.204	4080	...	..	...	..
772	Washington	...	..	0.136	2720	...	..	...	..
773(*b*).......	Mason	...	..	0.215	4300	...	..	...	..
775(*b*).......	Mason	...	..	0.215	4300	...	..	...	..
774(*b*).......	Mason	...	..	0.248	4960	...	..	...	..
AVERAGE............		0.207	4140	0.176	3514	...	..	...	..
WESTERN COAL FIELDS AREA									
692– 5.......	Webster	0.027	540	0.017	340	0.024	480	0.015	300
821– 4.......	Henderson	0.099	1980	0.076	1520	0.036	720	0.031	620
841– 4.......	Muhlenberg	0.308	6160	0.205	4100	0.116	2320	0.062	1240
AVERAGE............		0.145	2893	0.099	1987	0.059	1173	0.036	720
KEOKUK-WAVERLY AREA									
686	Adair	...	..	0.031	620	...	..	...	..
723– 6.......	Adair	0.005	100	0.019	380	0.002	40	0.015	300
688–91.......	Rockcastle	0.011	220	0.029	580	0.010	200	0.012	240
696– 9.......	Green	0.177	3540	0.166	3320	0.132	2640	0.115	2300
AVERAGE............		0.064	1287	0.061	1225	0.048	960	0.047	947
QUATERNARY AREA									
719–22.......	Graves	0.246	4920	0.216	4320	0.072	1440	0.024	480
845– 8.......	McCracken	0.148	2960	0.225	4500	0.046	920	0.091	1820
AVERAGE............		0.197	3940	0.221	4410	0.059	1180	0.058	1150
TRENTON AREA									
749– 3 750– 4	Clark	0.258	5160	0.182	3640	0.264	5280	0.160	3200
751– 2.......	Clark(*c*)	...	..	0.245	4900	...	..	0.198	3960
755– 6.......	Fayette	0.228	4560	0.215	4300	...	..	...	..
765– 8.......	Woodford	0.273	5460	0.225	4500	0.254	5080	0.225	4500
837–40.......	Madison	0.252	5040	0.227	4540	0.227	4540	0.139	2780
AVERAGE............		0.253	5055	0.219	4376	0.248	4967	0.181	3610
DEVONIAN AREA									
727– 8.......	Clark	0.147	2940	0.142	2840	...	..	...	..
761– 2.......	Marion	0.047	940	0.065	1300	...	..	...	..
833– 6.......	Madison	0.012	240	0.007	140	0.003	60	0.002	40
AVERAGE............		0.069	1373	0.071	1427	0.003	60	0.002	40
SILURIAN AREA									
817–20.......	Jefferson	0.166	3320	0.194	3880	0.107	2140	0.136	2720
829–32.......	Madison	0.022	440	0.022	440	0.018	360	0.015	300
AVERAGE............		0.094	1880	0.108	2160	0.063	1250	0.076	1510
RIVER ALLUVIAL AREA									
676– 7.......	Daviess	0.218	4360	0.163	3260	...	..	...	..
678–80.......	Daviess	0.166	3320	0.131	2620	...	..	...	..
679	Daviess(*d*)	...	..	0.031	620	...	..	...	..
711–14.......	Jefferson	0.331	6620	0.215	4300	0.163	3260	0.105	2100
825– 8.......	Henderson	0.038	760	0.038	760	0.032	640	0.022	440
AVERAGE............		0.188	3765	0.137	2735	0.098	1950	0.064	1270

(*a*) Nos. 769 to 772 were taken on the same farm but Nos. 771 and 772 had been cultivated for a longer time.

(*b*) All on the same farm but the number of years that each had been in cultivation was as follows: No. 773, 62 years; No. 775, 33 years; and No. 774, 9 years.

(*c*) Taken from the same field as the one just above it. In this particular area the tobacco was a failure while in the remainder of the field it was growing well. No material differences in the chief plant food elements which might account for it were found from a chemical analysis.

(*d*) Omitted from the average. This soil is of a peaty character and the river overflows it three or four times a year.

TABLE II—AVERAGE NUMBER OF POUNDS PER ACRE OF MANGANESE IN THE GEOLOGICAL AREAS OF KENTUCKY AND PERCENTAGE LOSS DUE TO CULTIVATION

	SURFACE			SUBSOIL		
AREA	Virgin Lbs.	Cult. Lbs.	Loss %	Virgin	Cult.	Loss %
Eastern coal fields.........	2043	1254	39	1304	914	30
St. Louis-Chester..........	2000	727	64	1260	473	62
Cincinnatian...............	4140	3514	15	..	..	..
Western coal fields........	2893	1987	31	1173	720	39
Keokuk-Waverly..........	1287	1225	5	960	947	1
Quaternary................	3940	4410	12(*a*)	1180	1150	3
Trenton....................	5055	4376	13	4967	3610	27
Devonian..................	1373	1427	4(*a*)	60	40	33
Silurian	1880	2160	15(*a*)	1250	1510	21(*a*)
River Alluvial............	3765	2735	27	1950	1270	35

(*a*) Increase.

DISCUSSION

The various amounts of manganese found in the different samples disclose some very interesting facts when the known fertility of the areas is considered, the chief of which is that the best agricultural areas contain the largest amounts of this element, as they do of some of the essential elements of plant food.

The geological areas in Tables I and II are arranged according to their size, the Eastern Coal Field occupying the greatest territory. If a comparison now be made of the areas containing from the largest to the smallest number of pounds per acre of sulfur and phosphorus found in these soils, in the earlier work, with the amount of manganese, there is seen to be an interesting relation existing between these three elements. To illustrate this Table III is given, the areas in which are abbreviated, and commencing at the top of the column, under each element, the area is first given which was found to have the largest number of pounds per acre of that element and so on down the column for the other areas in regular order according to the diminishing amounts found. In this connection it might be mentioned that of the three elements, sulfur was usually found in the smallest and manganese in the largest amounts in these soils.

From the standpoint of the store of fertility in the soils of the different areas and their agricultural value, the Trenton undoubtedly occupies first place and the Cincinnatian second. The approximate order of importance of the remainder might be classified as follows: River Alluvial, Devonian, St. Louis-Chester, Silurian,

Table III—Relation Existing between the Sulfur, Phosphorus and Manganese in the Geological Areas of Kentucky

Virgin Surface			Cultivated Surface			Virgin Subsoil			Cultivated Subsoil		
Sulfur	Phosphorus	Manganese	Sulfur	Phosphorus	Manganese	Sulfur	Phosphorus	Manganese	Sulfur	Phosphorus	Manganese
D	T	T	T	T	Q	St L-C	T	T	T	T	T
C	D	C	R A	C	T	R A	R A	R A	St L-C	R A	S
T	C	Q	D	D	C	T	E C F	E C F	R A	E C F	R A
S	R A	R A	C	R A	R A	S	S	St L-C	S	S	Q
R A	E C F	W C F	S	E C F	S	E C F	W C F	S	W C F	Q	K-W
E C F	S	E C F	W C F	S	W C F	W C F	Q	Q	E C F	W C F	E C F
W C F	Q	St L-C	St L-C	Q	D	Q	St L-C	W C F	D	St L-C	W C F
Q	W C F	S	E C F	W C F	E C F	D	K-W	K-W	K-W	K-W	St L-C
St L-C	St L-C	D	K-W	K-W	K-W	K-W	D	D	Q	D	D
K-W	K-W	K-W	Q	St L-C	St L-C						

Quaternary, Eastern and Western Coal Fields and finally the Keokuk-Waverly, which is generally regarded as the poorest of all.

In a majority of the samples, the cultivated surface as well as the subsoils show considerable losses of manganese when compared with the corresponding virgin. Furthermore, the surface soils of both generally contain more of this element than their respective subsoils.

The counties in which the soils were collected for this work were Wolfe, Graves, Warren, Henderson and Madison; also Nos. 813 to 820 from Metcalfe and Jefferson, or a total of forty samples. The above holds true in all with respect to the manganese content of the surface compared with its subsoil, while in three instances the virgin surface contained less and in two the same amounts of manganese as the cultivated samples.

The remainder of the samples were generally selected from those sent in by the residents of the state for chemical analysis and as it is sometimes difficult to obtain the accurate history of a field for several years past, since in certain sections much of the land is rented to tenants, it would have been better to collect all for this work, but this would have caused considerable delay.

In the Keokuk-Waverly area, commercial fertilizers were used while in some of the others it is very probable that commercial fertilizers or manure had been used in former years. This may partly account for the fact that the manganese content has been maintained in the soils of this area as well as in some of the others.

The large losses of manganese in some of the cultivated soils are hardly to be explained as due to the amounts removed by the different crops grown on them for the accumulated analyses show that the ordinary crops do not contain sufficient amounts of this element to justify this conclusion. It may be that cultivation converts the manganese compounds into soluble forms which are readily leached out and thus lost in the drainage water. This is a matter that needs further investigation, and the writer desires, as soon as an opportunity affords, to examine some of the surface and deeper drainage waters of the different areas in order to determine to what extent this element is present.

SUMMARY

I—It has been proven by different observers that manganese is universally present in soils, plants and many animals.

II—The majority of the experiments show that the application of certain manganese compounds, particularly the sulfate, to some crops, is decidedly beneficial. These experiments have further shown that while small applications are in many cases beneficial to plants, large applications are generally harmful.

III—In a large majority of the soils examined, the writer found considerably less manganese in the cultivated surface than in the corresponding virgin samples. The same holds true for the subsoils.

IV—In practically every case, the surface soils of the virgin and cultivated areas contain larger amounts of this element than their respective subsoils.

V—When some former work on these samples is considered, it is found that a majority of the soils contain considerably more manganese than phosphorus, but many samples have much less, while the losses of manganese in the cultivated areas are usually greater than of phosphorus.

VI—There are large differences in the manganese content of the soils of the different geological areas and sometimes in those from the same area. The amounts found in the surface soils vary from 0.005 to 0.331 per cent, and in the subsoils from 0.002 to 0.264 per cent.

VII—As a rule, the better agricultural areas contain much larger amounts of manganese than the inferior areas.

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ON THE COMPOSITION AND VALUE OF BAT GUANO

By C. F. Miller

Received April 20, 1914

At various points in this country, especially in the warmer regions, caves exist which are frequented by bats in such numbers that their excrement or "bat guano" has accumulated in amounts sufficient to give it some commercial importance as a fertilizer.

Generally, the amount of guano is rather limited in any one deposit and in the aggregate, the entire quantity now in sight, or probably to be discovered in this country, is not sufficient to appreciably affect the fertilizer industry. On the other hand, such a deposit may represent a considerable fortune to the individual discoverer or owner, and the frequency with which these small deposits occur, justifies a short discussion of their composition and value.

The following table containing the results of analyses of bat guano samples sent to this Bureau from time to time, shows their composition as well as the locality from which they were taken.

Bat Guano Analyses

Results in percentages, based on air-dry sample

Location	N(*a*)	P_2O_5	K_2O	Volatile	Analyst
Near Carlsbad, N. M.	4.24	2.31	1.28	..	J. A. Cullen
Guadeloupe Mts., N. M.	1.77	2.68	0.41	40.0	C. F. Miller
Torreon, N. M.	10.82	1.08	1.01	..	W. H. Waggaman
Oregon Co., Mo.	8.10	2.06	0.58	..	B. E. Brown
San Juan, Porto Rico(*b*)	1.00	3.40	0.21	..	W. H. Waggaman
San Juan, Porto Rico(*b*)	0.50	2.40	0.29	..	W. H. Waggaman
El Fondo, Santo Domingo, Haiti	11.84	4.80	1.61	90.0	C. F. Miller

(*a*) Determined by Mr. T. C. Trescott, of the Bureau of Chemistry.
(*b*) Both of these samples contained considerable calcium carbonate.

Both potash (K_2O) and phosphoric acid (P_2O_5) were determined by the official method for fertilizers, the former by treatment with concentrated sulfuric acid, ignition and extraction with dilute hydrochloric acid; the latter by treatment with a solution of magnesium nitrate, evaporation, ignition and a similar extraction.

A glance at the table shows that a wide variation exists, not only in the percentages of the fertilizer constituents present, but also in the ratios of nitrogen to phosphoric acid, nitrogen to potash or phosphoric acid to potash. This large variation is attributable to either one, or both of two things: (1) The presence of considerable extraneous matter such as rock débris, etc., or (2) the removal of some of the more available constituents by leaching, or, in the case of nitrogen, by decomposition of the material and subsequent volatilization as ammonia.

It may be said in this connection, that in the more recent deposits, nitrogen is the most valuable constituent, phosphoric acid and potash following in the order given; but on "aging," the nitrogen content decreases very rapidly since most of it is present in an available form.[1]

The writer wishes to place particular stress on the sample from Haiti as it represents uncontaminated and practically undecomposed bat guano which is very likely of recent origin, since thousands of bats[2] spend their days in the cave at the present time. As received in the laboratory, it consists of a dry, dark brown powder, in which the wings and other parts of insects can be seen by the naked eye.[3]

Over 90 per cent of the phosphoric acid present is water-soluble as is also the greater part of the potash; and if the high percentage of nitrogen, together with the large amount of organic matter (as shown by the volatile determination), are reckoned with these facts, it is evident that the substance is very valuable.

It has been calculated from data concerning the Haitian cave (which had not been fully explored at the time) that it contains approximately seven hundred tons of bat guano. Based on the market prices of 20 cents per pound for nitrogen,[4] and 5 cents per pound for phosphoric acid and potash, the material is worth (not considering the organic matter, which is a big factor) very close to $40 per ton, or approximately $30,000 for the entire deposit. Whether or not this is a representative example is a matter for conjecture, but very likely it is above the average in quantity and it certainly is in quality.

No specific data on the extent of the American deposits already discovered, are available. In several instances, however, they were reported as being of considerable size.

The facts given in this paper warrant the suggestion that a further search for bat guano be made, since there is a possibility, or even a probability, of the existence of other valuable, and as yet undiscovered deposits in this country.

BUREAU OF SOILS
U. S. DEPARTMENT OF AGRICULTURE
WASHINGTON

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[1] Thompstone, E., "Bat Guano in Burma," *Agr. J. India*, **4** (1909), 379–81.

[2] It has been reported that the "flight of the bats on leaving the cave; in rope-like formation, as large in diameter as an ordinary street car, requires over an hour, by actual timing."

[3] For further description see, Tod, W., "Ueber Fledermausguano," *Landw. vers. Station*, **1** (1859), 264–268.

[4] "Quotation on Nitrogen of Bat Guano," *Bull. Texas Exp. Station*, **160**, July, 1913, p. 10.

STUDIES IN SYNTHETIC DRUG ANALYSIS—I. ESTIMATION OF ACETANILIDE AND PHENACETIN IN ADMIXTURE

By W. O. EMERY[1]

Received April 30, 1914

INTRODUCTION

During the past few years, more particularly since the inception of both federal and State drug enactments, attention has been directed repeatedly to the dearth of adequately tested methods for detecting and estimating medicinal agents. The need of these methods was most keenly felt in connection with certain inhibited substances of synthetic character like acetanilide and its derivatives, antipyrin, cocaine, codeine, heroin and other similarly potent drugs, which find extended application in many of our proprietary medicines.

Aside from these considerations, however, there existed in the case of acetanilide and phenacetin (acetphenetidin) additional cause, on the part of drug analysts at least, for desiring quantitative methods. The relatively low cost of acetanilide, taken in connection with its pronounced physical resemblance to phenacetin, has already suggested to the unscrupulous the possibility of partial or even complete substitution of the former drug for the latter, and indeed several flagrant instances of such practice are on record. Accordingly, much time and effort have been expended in various quarters in the hope of devising a quantitative separation, though hitherto apparently without marked success. It is evident, however, that any procedure, calculated to determine even approximately the relative proportions of acetanilide and phenacetin in admixture, thus blocking the ways of the sophisticator, must prove welcome to officials and chemists engaged in drug control.

Ordinarily, the preliminary or gross separation of these two drugs from complex mixtures presents no unusual difficulties, being easily effected by extraction with chloroform. It is in the subsequent quantitative partition of the mixture thus isolated where the real problem begins, since no purely physical method, involving, for example, water or any of the commonly available organic solvents, lends itself to a sharp separation. A partial separation may indeed be effected according to Will[2] with water about as follows: If 1 gram of a mixture of equal parts of acetanilide and phenacetin be shaken with 200 cc. of water, all of the acetanilide goes into solution together with 0.13 g. of phenacetin, the remainder being unaffected. This latter portion is then filtered and weighed. Its weight, corrected by the addition of 0.13, represents the phenacetin originally present in this particular

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[1] Chief, Synthetic Products Laboratory.

[2] *Pharm. J.*, [3] **21**, (1890), 377.

mixture. In two similar experiments, but involving slightly different proportions of the two constituents, it was found that the weight of the undissolved phenacetin augmented by 0.13 corresponded to the quantity of this drug present in the mixture. It is quite evident, however, that such a procedure, while having a legitimate place in proximate determinations, could hardly form the basis for the quantitative separation of unknown mixtures.

In the method presently to be described, advantage is taken of the fact that, when an aqueous solution of phenacetin is added to a solution of iodine and potassium iodide containing a mineral acid, an iodine addition product or periodide separates, at first in an apparently emulsified condition, later assuming with greater or less rapidity—depending on temperature, concentration, and other undetermined factors—the form of brilliant bronze-colored leaflets, practically insoluble in the resulting menstruum, and having the composition[1] $(C_2H_5O.C_6H_4NH.COCH_3)_2.HI.I_4$.

Acetanilide under like treatment yields no insoluble periodide, though there may be and doubtless is present in the resulting solution an iodine addition product of corresponding form,[2] $(C_6H_5NH.COCH_3)_2.HI.I_4$. If, therefore, the precipitation of the periodide is effected in a measured volume of standard iodine and the insoluble addition product then removed by filtration, it readily becomes possible to determine volumetrically the quantity of iodine thus withdrawn from solution and, by means of appropriate factors, calculate the phenacetin present in the mixture. The phenacetin may also be determined gravimetrically after liberation from its periodide and subsequent extraction with chloroform. The acetanilide is estimated in an aliquot of the filtrate from the insoluble periodide by extraction with chloroform—the free iodine having been first discharged with a sulfite—followed by hydrolysis with dilute sulfuric acid and final titration of the resulting aniline sulfate with standard potassium bromide-bromate.

EXPERIMENTAL

In practice, the mixture of acetanilide and phenacetin dissolved in very dilute acetic acid is added to standard iodine contained in a graduated glass-stoppered flask, in preference to the reverse operation, the resulting liquid being then acidified with hydrochloric acid. This order of procedure is the outcome of results obtained in a variety of experiments and based on the following considerations:

The chemical and physical properties of the periodide are such that the determination to be quantitative must be made in a relatively restricted volume, that is, in rather concentrated solution, but on the other hand, owing to the very slight solubility of phenacetin in aqueous media, the transfer of this substance in solution to that of iodine in the graduated flask, as also its retention therein in dissolved condition, is a matter requiring very nice manipulation, since any premature separation of phenacetin as such from the resulting menstruum would necessarily lead to a corresponding loss in periodide formation and thus vititate the determination. The small quantity of acetic acid employed not only facilitates solution of both phenacetin and acetanilide, but also inhibits latent hydrolytic tendencies affecting the acetyl group. Now it so happens that phenacetin yields with iodine and hydriodic acid not only the periodide,

$$(C_{10}H_{13}NO_2)_2.HI.I_4 \qquad (1)$$

on the formation of which the separation of acetanilide and phenacetin is based, but under certain conditions also a less insoluble addition product, containing one-half as much iodine,

$$(C_{10}H_{13}NO_2)_2.HI.I_2 \qquad (2)$$

While the former of these two periodides represents the optimum in iodine addition, constituting as it does the sole or major portion of the addition product as ordinarily obtained, the more the iodine content of the reacting medium is reduced by the separation of the favored type (1), the greater the tendency for the formation of type (2). Furthermore, since the separation of any periodide of the phenacetin type is conditioned on the presence of free hydriodic acid (or what amounts to the same thing, potassium iodide and hydrochloric acid), it is quite evident that a maximum homogeneity in the precipitated product can result only by first bringing the phenacetin, iodine and potassium iodide into such uniform distribution and intimate relationship that, on the rapid addition of hydrochloric acid, an immediate liberation of hydriodic acid required to complete the combination will take place simultaneously throughout the entire mass. With due regard, therefore, for the conditions set forth above, as also for errors naturally inherent in iodometric operations, it becomes possible to reduce to a minimum certain of these disturbing elements which might otherwise seriously impair the efficiency of the method.

In order to determine experimentally the most favorable conditions under which to operate, in any analytical procedure, it became necessary to carry through several hundred estimations, both singly and in series, a few of which appear below. With exception of Series 2, in which 25, 30, and 35 cc. of standard iodine were, respectively, used in the three determinations, 25 cc. of iodine were invariably employed.

Series 1

No.	Phenacetin Gram	Glacial AcOH Cc.	Conc. HCl	Iodin Excess Cc.	Iodin Expended Cc.	Phenacetin recovery Gram	Phenacetin recovery Per cent
1..........	0.2000	1.00	3 cc.	19.23	21.84	0.1959	97.95
2..........	0.2000	0.75	3 cc.	19.20	21.90	0.1964	98.20
3..........	0.2000	0.50	3 cc.	19.20	21.90	0.1964	98.20
4..........	0.2000	1.00	H_2SO_4 2 cc.	19.15	22.00	0.1973	98.65
5..........	0.2000	1.00	H_3PO_4 2 cc.	19.45	21.40	0.1932	96.60

Series 2

No.	Phenacetin Gram	Acetanilide Gram	Glacial AcOH Cc.	Conc. HCl Cc.	Iodin Excess Cc.	Iodin Expended Cc.	Phenacetin recovery Gram	Phenacetin recovery Per cent	Acetanilide recovery Gram	Acetanilide recovery Per cent
1....	0.1200	0.0960	3	5	20.90	11.25	0.1197	99.75	0.0940	97.92
2....	0.1200	0.0960	3	5	25.81	11.08	0.1179	98.25	0.0944	98.33
3....	0.1200	0.0960	3	5	31.02	11.11	0.1182	98.50	0.0952	99.17

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[1] A more detailed description of the properties of this addition product —which was first described, though incorrectly interpreted, by Scholvien, *Pharm. Zentralhalle*, **32** (1891), 311—will appear shortly in a paper entitled "Periodides of Phenacetin, Methacetin and Triphenin."

[2] Wheeler and Walden, *Am. Chem. J.*, **18**, 89.

	Phenacetin Gram	Acetanilide Gram	Ratio	Glacial AcOH Cc.	Conc. HCl Cc.	Phenacetin recovery		Acetanilide recovery	
						Gram	Per cent	Gram	Per cent
Series 3									
1.....	0.2000	..	..	1	3	19.02	21.83	0.1976	98.83
2.....	0.2000	..	..	5	3	19.25	21.37	0.1934	96.70
3.....	0.2000	0.0500	4 : 1	5	3	19.18	21.51	0.1947	97.35
4.....	0.2000	0.1000	2 : 1	5	3	19.10	21.67	0.1961	98.50
5.....	0.2000	0.1500	4 : 3	5	3	18.98	21.91	0.1983	99.15
6.....	0.2000	0.2000	1 : 1	5	3	18.90	22.07	0.1994	99.70
7.....	0.1500	0.2000	3 : 4	5	3	21.76	16.35	0.1480	98.67
8.....	0.1000	0.2000	1 : 2	5	3	24.50	10.87	0.0984	98.40
9.....	0.0500	0.2000	1 : 4	5	3	27.60	4.67	0.0423	84.60
Series 4									
1.....	0.2000	..	..	1	3	19.00	21.87	0.1977	98.85
2.....	0.2000	..	..	4	3	19.25	21.37	0.1932	96.60
3.....	0.2000	0.0400	5 : 1	4	3	19.06	21.75	0.1966	98.30
4.....	0.2000	0.0500	4 : 1	4	3	19.05	21.77	0.1968	98.40
5.....	0.2000	0.0667	3 : 1	4	3	19.06	21.75	0.1966	98.30
6.....	0.2000	0.1000	2 : 1	4	3	18.94	21.99	0.1988	99.40
7.....	0.2000	0.2000	1 : 1	4	3	18.70	22.47	0.2028	101.40
8.....	0.1000	0.2000	1 : 2	4	3	24.38	11.11	0.1004	100.43
9.....	0.0667	0.2000	1 : 3	4	3	26.42	7.03	0.0636	95.30
10.....	0.0500	0.2000	1 : 4	4	3	27.36	5.15	0.0466	93.20
11.....	0.0400	0.2000	1 : 5	4	3	28.13	3.61	0.0326	81.50
Series 5									
1.....	0.2000	..	..	1	3	19.01	21.85	0.1975	98.75
2.....	0.2000	..	..	3	3	19.22	21.43	0.1937	96.86
3.....	0.2000	0.0400	5 : 1	3	3	19.10	21.67	0.1959	97.95
4.....	0.2000	0.0500	4 : 1	3	3	19.02	21.83	0.1973	98.67
5.....	0.2000	0.0667	3 : 1	3	3	19.02	21.83	0.1973	98.67
6.....	0.2000	0.1000	2 : 1	3	3	18.91	22.05	0.1993	99.67
7.....	0.2000	0.2000	1 : 1	3	3	18.75	22.37	0.2022	101.11
8.....	0.1000	0.2000	1 : 2	3	3	24.32	11.23	0.1015	101.52
9.....	0.0500	0.2000	1 : 4	3	3	27.40	5.07	0.0458	91.55
Series 6									
1.....	0.2000	..	..	1	3	19.02	21.83	0.1973	98.67
2.....	0.2000	..	..	2	3	19.15	21.57	0.1950	97.50
3.....	0.2000	0.0200	10 : 1	2	3	19.10	21.67	0.1959	97.95
4.....	0.2000	0.0400	5 : 1	2	3	18.98	21.91	0.1981	99.05
5.....	0.2000	0.0500	4 : 1	2	3	18.95	21.97	0.1986	99.30
6.....	0.2000	0.0667	3 : 1	2	3	18.90	22.07	0.1995	99.75
7.....	0.2000	0.1000	2 : 1	2	3	18.76	22.35	0.2020	101.02
8.....	0.2000	0.2000	1 : 1	2	3	18.60	22.67	0.2049	102.46
9.....	0.1500	0.2000	3 : 4	2	3	21.25	17.37	0.1570	104.67
10.....	0.1000	0.2000	1 : 2	2	3	24.25	11.37	0.1028	102.78
11.....	0.0500	0.2000	1 : 4	2	3	27.60	4.67	0.0422	84.43
Series 7									
1.....	0.2000	..	..	1	3	16.12	19.26	0.1978	98.90
2.....	0.2000	..	..	2	3	16.22	19.06	0.1957	97.85
3.....	0.1800	0.0200	9 : 1	2	3	17.08	17.34	0.1781	98.93
4.....	0.1600	0.0400	4 : 1	2	3	18.02	15.46	0.1588	99.23
5.....	0.1400	0.0600	7 : 3	2	3	18.94	13.62	0.1399	99.93
6.....	0.1200	0.0800	3 : 2	2	3	19.93	11.64	0.1195	99.62
7.....	0.1000	0.1000	1 : 1	2	3	20.90	9.70	0.0996	99.62
8.....	0.0800	0.1200	2 : 3	2	3	21.80	7.90	0.0811	101.41
9.....	0.0600	0.1400	3 : 7	2	3	22.80	5.90	0.0606	100.99
10.....	0.0400	0.1600	1 : 4	2	3	24.02	3.46	0.0355	88.83
11.....	0.0200	0.1800	1 : 9	2	3	25.32	0.86	0.0088	44.16
Series 8									
1.....	0.2000	..	..	2	2	16.30	18.90	0.1941	97.05
2.....	0.2000	..	..	2	1	16.40	18.70	0.1921	96.05
3.....	0.1800	0.0200	9 : 1	2	2	17.15	17.20	0.1766	98.13
4.....	0.1800	0.0200	9 : 1	2	1	17.30	16.90	0.1756	97.53
5.....	0.1600	0.0400	4 : 1	2	2	18.12	15.26	0.1567	97.95
6.....	0.1600	0.0400	4 : 1	2	1	18.20	15.10	0.1551	96.92
7.....	0.1400	0.0600	7 : 3	2	2	18.93	13.64	0.1401	100.06
8.....	0.1400	0.0600	7 : 3	2	1	19.12	13.26	0.1362	97.27
9.....	0.1200	0.0800	3 : 2	2	2	19.93	11.64	0.1195	99.62
10.....	0.1200	0.0800	3 : 2	2	1	20.02	11.46	0.1177	98.08
11.....	0.1000	0.1000	1 : 1	2	2	20.98	9.54	0.0980	97.98
12.....	0.1000	0.1000	1 : 1	2	1	21.00	9.50	0.0976	97.57
13.....	0.0800	0.1200	2 : 3	2	2	21.90	7.70	0.0791	98.85
14.....	0.0800	0.1200	2 : 3	2	1	22.05	7.40	0.0760	94.99
15.....	0.0600	0.1400	3 : 7	2	2	22.95	5.60	0.0575	95.85
16.....	0.0600	0.1400	3 : 7	2	1	23.04	5.42	0.0557	92.77
Series 9									
1.....	0.2000	..	..	1	3	16.20	19.10	0.1962	98.10
2.....	0.2000	..	..	1	3	16.22	19.06	0.1957	97.85
3.....	0.1800	0.0200	9 : 1	2	1	17.30	16.90	0.1736	96.42
4.....	0.1800	0.0200	9 : 1	2	3	17.05	17.40	0.1787	99.28
5.....	0.1600	0.0400	4 : 1	2	1	18.18	15.14	0.1555	97.17
6.....	0.1600	0.0400	4 : 1	2	3	17.98	15.54	0.1596	99.75
7.....	0.1400	0.0600	7 : 3	2	1	19.17	13.16	0.1352	96.54
8.....	0.1400	0.0600	7 : 3	2	3	18.96	13.58	0.1395	99.62
9.....	0.1200	0.0800	3 : 2	2	1	20.00	11.50	0.1181	98.42
10.....	0.1200	0.0800	3 : 2	2	3	19.90	11.70	0.1202	100.13
11.....	0.1000	0.1000	1 : 1	2	1	20.92	9.66	0.0992	99.21
12.....	0.1000	0.1000	1 : 1	2	3	20.90	9.70	0.0996	99.62
13.....	0.0800	0.1200	2 : 3	2	1	22.12	7.26	0.0746	93.20
14.....	0.0800	0.1200	2 : 3	2	3	21.90	7.70	0.0791	98.85
15.....	0.0600	0.1400	3 : 7	2	1	23.00	5.50	0.0566	94.14
16.....	0.0600	0.1400	3 : 7	2	3	22.90	5.70	0.0585	97.56
17.....	0.0400	0.1600	1 : 4	2	1	24.85	1.80	0.0185	46.21
18.....	0.0400	0.1600	1 : 4	2	3	24.22	3.06	0.0314	78.56

INTERPRETATION OF RESULTS

As the title of this paper implies, the procedure comprehends in its entirety not only the separation but the estimation as well of both acetanilide and phenacetin. Accordingly, several of the mixtures examined were treated with this object in view, namely, the recovery of both ingredients, as embodied in Series 2. As a rule, however, analysis ended with the recovery of phenacetin, since this was believed to represent the more important phase of the problem under investigation. Examination of the data presented in the several series, as also that of other series not here shown, leads to the following conclusions:

Any mineral acid unaffected by iodine or hydriodic acid under the conditions of the experiment can apparently be employed, although hydrochloric acid is perhaps, on account of its physical properties, the one best suited to the purpose in hand. It will be noted that an increase of this acid within reasonable limits operates favorably on phenacetin recovery. In the estimation of this substance alone, not more than 200 mg. should be taken for every 25 cc. of standard iodine of specified strength, while the amount of acetic acid used in each determination should not exceed 1 cc., in which event the recovery will fall within 3 to 5 mg. of the quantity taken or actually present. In admixture with acetanilide, however, the total amount of both ingredients taken for analysis should likewise not exceed 200 mg., but more acetic acid may be advantageously employed, since such increase tends to counteract an apparent tendency on the part of acetanilide to augment unduly the quantity of phenacetin recovered. Whatever the cause of such excess recovery, whether due to occlusion or adsorption of iodine as such or in form of acetanilide periodide on the part of phenacetin periodide, the limit of usefulness of the method appears to lie between the ratios 1 : 3 and 1 : 4 of phenacetin to acetanilide. In order to observe what influence, if any, freshly boiled distilled water might have on phenacetin recovery, all estimations recorded in Series 9, with the exception of No. 1, were made with water thus treated. A comparison of recoveries noted under estimations Nos. 1 and 2 reveals a slight difference, it is true, apparently in favor of ordinary distilled water, that is, that from which the air had not been expelled, but such difference, conceivably due to the action of dissolved atmospheric oxygen or hydriodic acid, may have been the result of entirely different influences.

METHOD

PHENACETIN—Into a small (50 cc.) lipped Erlenmeyer introduce 0.2 g. of the phenacetin-acetanilide mixture, add 2 cc. of glacial acetic acid, heat gently over wire gauze to complete solution, then dilute with 40 cc. water previously warmed to 70°. Transfer the clear acetous liquid by pouring and careful washing of flask with two 10 cc. portions of warm (40°) water to a glass-stoppered, graduated 100 cc. flask, into which have been previously run from a burette 25 cc. of standard iodine, of a strength slightly above 0.2 *N*, and warmed to 40°. Rotate the resulting menstruum to uniformity, the flask being closed meanwhile, then add 3 cc. of concentrated hydrochloric acid, close flask anew and continue rotation until copious crystallization is apparent, then set the product aside to cool. If the ratio of phenacetin to acetanilide is equal to or greater than 1, the formation of crystalline scales will be almost immediate on the addition of acid. As the proportion of acetanilide increases, however, the periodide is not only more inclined to maintain the liquid state, with the result that crystallization becomes proportionately slower, but its separation also from the menstruum itself is in a measure apparently retarded. In such cases, gentle agitation of the liquid or rotation of the flask in water warmed to 40° or less tends to promote the formation of crystals. When the contents of the flask have assumed the room temperature, fill with water to within 2 to 3 cc. of the mark, rotate to uniformity and allow to stand overnight. Fill to mark with water, mix thoroughly, then after standing one-half hour withdraw a 50 cc. aliquot of clear liquid by passing through a small (5.5 cm.) dry, closely-fitted filter into a graduated 50 cc. flask, rejecting, however, about 15 cc. of the first runnings, the latter being received in any convenient container for eventual later use, along with additional filtrate, for the recovery of acetanilide. Transfer the 50 cc. aliquot by pouring and washing to a 200 cc. Erlenmeyer and titrate with 0.1 *N* sodium thiosulfate.

If reference is had to the composition of the insoluble addition product, constituting the basis for the foregoing separation,

$$(C_2H_5O.C_6H_4NH.COCH_3)_2.HI.I_4,$$

it will be noted that, for every molecule of phenacetin involved, two atoms of iodine are required, hence from a titrimetric standpoint one atom of iodine is equivalent to one-half molecule of phenacetin. If, therefore, the quantity of iodine expended in the formation of insoluble periodide is ascertained as the result of such titration, the quantity of phenacetin thereby involved is readily calculated from the expression,

$$\text{phenacetin} = I(0.008890 \times N),$$

in which 0.008890 represents the quantity of phenacetin in 1 cc. of a 0.1 *N* solution of this substance, *N* the normality of standard thiosulfate employed, while I represents the number of cubic centimeters of such thiosulfate corresponding to the iodine entering into combination with phenacetin isolated as periodide.

The gravimetric determination of phenacetin may, if desired, be effected substantially as follows: In the operation of filtering off the periodide, the latter is collected on the filter and washed with 10 to 15 cc. of standard iodine solution, preferably by suction, then transferred together with filter (likewise any particles of precipitate eventually remaining in the graduated flask) to a separatory funnel, using for the purpose not over 50 cc. of water. After discharging both free and added iodine with a few small crystals of sodium sulfite, the liquid is extracted with three 50 cc. portions of chloroform, each portion being subsequently washed in a second separatory funnel with 5 cc. of water. After washing and clearing, withdraw solvent through a small (5.5 cm.) dry filter into a 200 cc. Erlenmeyer, distill off most of the chloroform, transferring the residual 5 to 10 cc. by pouring and washing with fresh solvent to a small tared beaker or crystallizing dish. Evaporate to dryness on steam bath, cool, and weigh.

ACETANILIDE—Should the combined weight of the phenacetin-acetanilide mixture be known, that of the latter constituent can be determined by difference, or, if necessary, estimated directly from a second aliquot of filtrate from the phenacetin periodide.

To this end, transfer to a separatory funnel by means of a pipette 25 to 30 cc. of the clear liquid, decolorize with sufficient solid sodium sulfite, add solid sodium bicarbonate in slight excess, follow with 1 to 2 drops of acetic anhydride, then extract with three 60 cc. portions of chloroform, passing solvent when cleared through a small, dry filter into a 200 cc. Erlenmeyer, from which the chloroform is distilled by the aid of gentle heat down to about 20 cc. Now add 10 cc. of dilute sulfuric acid (1 cc. of concentrated acid to 10 cc. of water) and digest product on steam bath until the aqueous residue has been reduced one-half, add 20 cc. of water and continue digestion one hour, add a second 20 cc. portion of water and 10 cc. of concentrated hydrochloric acid, then titrate very slowly, drop by drop, with standard potassium bromide-bromate (1 cc. of which is equivalent to 5 to 10 mg. of acetanilide), until a faint yellow coloration persists. While adding this reagent, the flask should be rotated sufficiently to agglomerate the precipitated tribromoaniline and thus clarify the supernatant liquid. The number of cubic centimeters of standard bromide solution required to complete the precipitation, multiplied by the value of 1 cc. in terms of acetanilide, will give the quantity of this substance present in the aliquot taken.

COMMENT AND SUGGESTIONS

The preliminary or gross separation of phenacetin and acetanilide from complex mixtures is materially lengthened, if the preparation contains, in addition to those substances, caffeine or antipyrin or both, in which event it would be necessary first to subject the mixture of four ingredients to hot digestion with dilute sulfuric acid in order to convert phenacetin and acetanilide to phenetidine and aniline sulfates, respectively, from which caffeine and antipyrin may be easily separated by means of chloroform, after which operation phenacetin and acetanilide should be regenerated by treating the aqueous-acid solution of the corresponding sulfates with solid sodium bicarbonate in slight excess, thereupon with a few drops of acetic anhydride, followed by extraction with chloroform.[1]

In the operation of transferring the acetous solution of phenacetin-acetanilide mixture to the graduated flask containing standard iodine, great care must be exercised to the end that none of the dissolved substances crystallize out as such during or after the transfer, either in the liquid or about the neck of the Erlenmeyer, since any undissolved phenacetin introduced into the iodine reagent would fail in obtaining its full complement of iodine, thus vitiating the determination. The necessary transfer is most conveniently effected, and indeed without loss, by the use of an Erlenmeyer provided with a lip, a form easily

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[1] *Proc. A. O. A. C.*, U. S. Dept. Agr., Bur. Chem., *Bull.* **162** (1912), 197.

made in the laboratory from the ordinary type by heating the neck of flask in a moderate blast flame, then by the aid of a file or other suitable instrument pulling down the rim to the desired pitch. Thus modified, the flask delivers aqueous solutions with little or no tendency to run down on the outside of neck.

The standard solution of iodine employed in the foregoing separation and the one giving the best results has a strength slightly above 0.2 *N*, that is, a solution containing 30 g. of iodine and 40 g. of potassium iodide to the liter. To prepare, dissolve the potassium iodide in the least possible quantity of water, add the iodine and after complete solution, dilute to 1 liter. Twenty-five cc. of this reagent, the volume taken for each determination, are standardized with a solution of sodium thiosulfate containing 30 g. to the liter, the value of which has in turn been ascertained by titration with very carefully purified iodine. The end point is best observed by adding to the liquid toward the close of titration 1 to 2 drops of freshly prepared starch solution. In measuring off the standard iodine, make readings by the aid of transmitted light. This is easily done by holding an electric bulb just back of the burette, thus bringing into sharp relief the lower meniscus.

For this and similar iodometric operations, very pure iodine was prepared by dissolving the commercial resublimed product in concentrated aqueous potassium iodide, pouring the clear liquid into a large volume of water, filtering and washing the finely precipitated iodine on a porous plate several times with water, then drying first in the air and finally in a desiccator over sulfuric acid, where it is kept for future use in a glass-stoppered weighing tube. To standardize the sodium thiosulfate, weigh out in a small glass capsule (about $^{1}/_{2}''$ high and $^{5}/_{8}''$ diameter), provided with a closely-fitting glass cap or stopper, about 0.3 g. of pure iodine, which together with capsule and cover are transferred to a 200 cc. Erlenmeyer, containing 0.5 g. of potassium iodide dissolved in 10 cc. of water. After complete solution, titrate the iodine with sodium thiosulfate, using 1 to 2 drops of starch solution as indicator.

In the qualitative examination of preparations or mixtures, of which phenacetin alone is a known or declared ingredient, suitable tests should be applied in order to verify the presence or absence of acetanilide, such as are prescribed in the U. S. Pharmacopoeia or described in Allen's "Commercial Organic Analysis." For the identification of phenacetin, either alone or in admixture with acetanilide, the following test in addition to those ordinarily employed for this substance will be found of value: To 1 to 2 mg. of sample in a test tube add a drop of acetic acid, 0.5 cc. of water and 1 cc. of 0.1 *N* iodine, warm mixture to about 40°, then add a drop of concentrated hydrochloric acid. Almost immediately if phenacetin alone is present, or on cooling and agitating the liquid if sample consists in large part of acetanilide, the iodine addition product of phenacetin separates in the form of reddish brown leaflets or needle-like crystals. In the presence of considerable acetanilide, the periodide first separates as minute oily globules, which on vigorous shaking gradually become crystalline aggregates. This test is so delicate that as little as 0.5 mg. of phenacetin may, if alone, be detected in form of its characteristic periodide.

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COMMERCIAL PAPAIN AND ITS ASSAY

By H. M. Adams

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A recent article by William Mansfield[1] gives a clear idea of the cultivation, preparation and adulteration of the commodity papain. The adulteration from the commercial standpoint is especially interesting, in view of the fact that about 50 per cent of the samples received were found to possess so little digestive power that they are practically worthless. It has long been noticed in this laboratory that the dark, lumpy samples invariably give the best digestive strength. It seemed that the darker, the more crude the appearance, the better they were. Occasionally a comparatively light colored sample would show a fair degree of activity, but such an occurrence was very rare indeed. This led to an investigation, with the result that in the poor samples starch was always found to be present in very marked quantities, while good samples showed no perceptible trace. Mansfield corroborates this with his statement that a large portion of the papain on the market is adulterated by adding wheat or rye bread crumbs or by pouring the papain juice over the breads and then grinding.

This discovery of starch instituted a preliminary test, which was applied to every sample of papain received. A small portion of the finely ground sample was placed on a white porcelain surface and a few drops of a weak solution of iodine added. The presence of starch was thus immediately noted by the appearance of a blue color and, with a little experience, a rough estimate could be made, by the intensity of this color, as to the digestive value of the sample.

To further illustrate this, a few experiments were carried out, showing the digestive strength of the papain and the amount of starch present. In these experiments a high-grade papain was used as a standard and called 100 per cent. The others are given in terms of this standard. The digestion was carried on at 55° C., with frequent shaking for five hours. Finely ground beefsteak was used as the material to be digested and distilled water as a medium.

SAMPLE	Cc. of residue standing 1 hour	Percentage as compared with standard	Percentage starch
Standard	5.25	100	..
1	15	35	57.4
2	12.5	42	57.1
3	13	40	58.7
4	13	40	58.3
5	13	40	55
6	6	85.7	20
7	5.25	100	..

It was observed in the above experiments that when large amounts of starch were present, the lower portion of the residue was white in color instead of having a greenish tinge as in the good samples.

Besides starch, pepsin is sometimes used as an adul-

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[1] *J. Am. Pharm. Assoc.*, **1914**, p. 169.

terant and is rather more difficult to detect. When tested in an acid solution a small amount of pepsin apparently greatly increases the strength of the papain; however, if a neutral or slightly alkaline solution is used, the action of the pepsin is inhibited or checked completely and the true digestive value of the papain is thus obtained. This point is shown by the following experiments, in which a high-standard papain was used and known quantities of pepsin added. The digestion was carried on as stated before.

Sample 0.325 gram papain	Pepsin added (1 : 3000) Gram	Medium	Residue standing 1 hour Cc
1	...	Neutral	$5\frac{1}{2}$
2	0.1	Neutral	$5\frac{1}{2}$
3	...	0.2% HCl	24
4	0.1	0.2% HCl	13

There appear in the late literature but two methods for the assay of papain, one by H. Graber[1] and the other by Rippetoe.[2]

Graber's method differs from the one used by the author in only one point. He uses a 0.3 per cent solution of hydrochloric acid as a medium, instead of a neutral solution. This, however, proves to be a decided difference, for as shown by all the following experiments, no very satisfactory results were obtained in an acid medium. It is true there is some digestion, but the residue is large and seems to hang in suspension throughout the tube in such a way that it makes the readings rather indistinct. The residue settles very slowly and has a decidedly different appearance than in either neutral or alkaline solution, having a dark brown color instead of having a greenish tinge as in the others.

Rippetoe supports this inhibitory action of an acid solution in his article, and Martin in 1883 states that hydrochloric acid above 0.05 per cent destroys the digestive activity completely. This latter statement, however, is, in the opinion of the author, much too severe, for, as the following experiments will show, there appears to be considerable digestion in a 0.1 per cent acid solution, which, however, decreases as the strength of the acid is increased. In these experiments both meat and whites of eggs were used as the material to be digested.

10 grams of	Papain used Gram	100 cc. medium	Residue 1 hour Cc.	Residue overnight Cc.
Beef	None	0.3% HCl	33	31
Beef	0.325	0.3% HCl	28 indistinct	30
Beef	0.325	0.3% HCl	26 indistinct	30
Beef	0.325	Neutral	$6\frac{1}{2}$	$5\frac{1}{4}$
Egg	None	0.3% HCl	34	33
Egg	0.325	0.3% HCl	33	$29\frac{1}{2}$
Egg	0.325	0.2% HCl	30	$28\frac{1}{2}$
Egg	0.325	0.1% HCl	28	26
Egg	0.325	Neutral	15	14

Rippetoe used in his method the whites of eggs prepared as for the pepsin assay in the U. S. P. He also uses 40 cc. of a 0.1 per cent caustic soda solution as a medium. There appear to be no serious objections to this method except that it seems to be a large amount of unnecessary work and gives no better results. The residues are larger than with meat and the readings indistinct even after an hour's standing. In fact the author obtained more definite, clearer results, with egg, if a medium of distilled water was used instead of an alkaline solution.

The following experiments were made to illustrate this and also the advisability of using 40 cc. of solution as a medium instead of 100 cc. It is shown that with meat 40 cc. has a deleterious effect but with egg it is slightly advantageous.

0.325 gram of papain used

10 grams of	Medium	Medium Cc.	Residue after 1 hour Cc.	Residue overnight Cc.
Beef	Neutral	100	$6\frac{1}{2}$	$5\frac{3}{4}$
Beef	Neutral	40	15	$9\frac{1}{2}$
Egg	Neutral	100	15	14
Egg	Neutral	40	14	13
Egg	0.1% NaOH	100	24 indistinct	$17\frac{1}{2}$
Egg	0.1% NaOH	40	15	13

The method found to be suitable to all samples and which has proved itself satisfactory by a great many trials, is outlined as follows:

Add 0.325 gram of the powdered sample of papain to 10 grams of fresh, lean, raw beef, which has been finely chopped or passed through a sausage grinder and placed in a 6-ounce wide mouth bottle. Now add 100 cc. of distilled water, stopper, and shake the bottle with contents thoroughly until the meat is entirely disintegrated. Place in a water bath at 50–55° C., for 5 hours, shaking gently 1 minute every 15 minutes. Pour the contents of the bottle into a long, graduated tube and allow the residue to settle.

Due to various changes in the conditions in carrying on this digestion (such as a different lot of meat or a fluctuation of the temperature of the bath) the same sample on different days was found to give a variable residue of from 5 to 7 cc. Therefore a papain shown to possess a high digestive strength was chosen as standard and two bottles containing the required amounts of this standard were placed in the bath with the samples to be tested and thus definite results could be obtained, the unknowns being reported in terms of the standard, as for instance, if the standard gave a residue of 6.3 cc. and the prospective sample 7 cc., it was reported as 90 per cent papain.

Below are given comparative results of the three methods discussed, Graber's, Rippetoe's and the above method.

0.325 gram of papain used—6 hours digestion

METHOD	SOLUTIONS	Cc. SOLUTION	SUBSTANCE DIGESTED	Residue 1 hour Cc.	Residue overnight Cc.
Graber's	0.3% HCl	100	Beef	30 26	32 30
Rippetoe's	0.1% NaOH	40	White of egg	14 14.5	12 13
X	Neutral	100	Beef	6 6.25	6.5 6.5

SUMMARY AND CONCLUSIONS

Commercial papain is sometimes adulterated with starch or pepsin. The presence of starch is shown with iodine solution and the pepsin by digestion of meat in a weak acid solution.

Neutral solutions give the most satisfactory results with either meat or whites of eggs.

Meat appears to be the best material to be digested on account of its easy preparation and also because of the small residue left after digestion.

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[1] THIS JOURNAL, 3 (1911), 120.

[2] *Ibid.*, 4 (1912), 517.

A METHOD FOR THE ESTIMATION OF PODOPHYLLUM RESIN

By W. M. Jenkins

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It seems to be a generally acknowledged fact that the therapeutic activity of Podophyllum is due to the resin which it contains. While this resin is recognized in the United States Pharmacopoeia, and its properties and solubilities are well described, it must be remembered that the resin is not a simple substance, but a mixture of substances, the most important of which is a crystalline body called Podophyllotoxin. From a therapeutic standpoint, however, Podophyllum Resin, U. S. P., is a well known substance and the dose is well defined. It would seem therefore that any attempts at assaying or standardizing the drug should be in terms of Podophyllum Resin, U. S. P. It was with this idea in view that the work described in this paper was undertaken.

All previous methods for the determination of Podophyllum Resin have been based on the idea that the resin is insoluble in water, and that by pouring an alcoholic solution of the resin into a large volume of acidulated water the resin[1] would be completely precipitated and could be collected and weighed. Through long experience with this precipitation method, however, it has been found that the results are very unreliable and greatly affected by the conditions of the method, *viz.*, the volume and temperature of the acidulated water, the amount of alcohol used and the amount of sample taken. The only way to get results which were at all concordant was to adhere strictly to the same amounts of alcohol, water, acid and sample; the results were thus purely arbitrary.

The reason for these variable results was later found to be the fact that Podophyllum Resin is slightly soluble in water and that this solubility is increased by small percentages of alcohol, and hence the recovery of the full amount of resin by the precipitation method is impossible. Thus it was found that by dissolving 0.4 gram of U. S. P. Podophyllum Resin in 10 cc. of alcohol and precipitating the resin in 600 cc. of water acidulated with 10 cc. of hydrochloric acid, only 75 per cent of the resin was recovered.

Podophyllum Resin is only partly soluble in chloroform but is readily soluble in a mixture of 1 part of alcohol and 2 parts of chloroform. Hence it was thought that a mixture of alcohol and chloroform might be used for extracting the resin quantitatively from an alcohol solution which had been diluted with water.

When equal volumes of alcohol, chloroform and water are mixed, this mixture separates, on standing, into two layers. The upper portion consisting approximately of one part of alcohol and two parts of water, and the lower layer of one part of alcohol and two parts of chloroform.

By keeping the proportions of alcohol, chloroform and water constant, it was found that over 99 per cent of resin was recovered by three extractions with the alcohol chloroform mixture when working with U. S. P. Podophyllum Resin.

When this method was applied to the fluidextract, however, and the resulting resin compared with the U. S. P. Podophyllum Resin, it was found to be darker, more hygroscopic, less soluble in alcohol and more soluble in water. Thus it was necessary to modify the method in some way in order to obtain a resin identical with the official resin. This was accomplished by washing the alcohol chloroform extract with acidulated water. The resin obtained by this modification was found to conform to the United States Pharmacopoeia requirements for Podophyllum Resin, *viz.:*

Soluble in alcohol in all proportions.
86.4 per cent soluble in ether.
69.1 per cent soluble in chloroform.
21.3 per cent soluble in boiling water.
0.1 per cent ash.

By this procedure from 0.4 gram Podophyllum Resin U. S. P. dissolved in alcohol, 0.394 gram was recovered, corresponding to 98.4 per cent.

Accordingly the following method for estimating the amount of Podophyllum Resin in Fluidextract Podophyllum is suggested.

Measure 5 cc. of Fluidextract Podophyllum into a separatory funnel, add 5 cc. of alcohol, 10 cc. of chloroform and 10 cc. of acidulated water containing 0.6 per cent hydrochloric acid (2 cc. HCl in 100 cc. water). Shake and allow the mixture to separate. Draw off the lower layer into another separatory funnel; repeat the extraction twice, using 15 cc. of a mixture of one part of alcohol and two parts of chloroform, each time, and add these extractions to the first. Shake the combined extractions with 10 cc. of the acidulated water and allow the mixture to separate. Draw off the lower layer into a tared flask, and repeat the extraction twice, using 15 cc. of the alcohol chloroform mixture each time. Evaporate the combined extractions and dry the residue to constant weight at 100° C.

For comparison a number of fluidextracts were assayed by this method, and by the usual precipitation method with the following results:

RESIN IN FLUIDEXTRACTS

	Precipitation method		Shake-out method	
	G. in 10 cc.	Per cent	G. in 5 cc.	Per cent
1	0.424	4.2	0.3480	6.9
2	0.420	4.2	0.3130	6.2
3	0.420	4.2	0.2895	5.7
4	0.458	4.5	0.3430	6.8

In assaying the drug, 10 grams in a No. 60 powder are placed in an Erlenmeyer flask, and 25 cc. of alcohol are added. The flask is then fitted with a stopper through which is inserted a glass tube about two feet long for a condenser and left on a sand bath at 80° C. for three hours.

The contents of the flask are then transferred to a small percolator and washed with alcohol until about 50 cc. of percolate are obtained. When cooled to room temperature, the solution is made up to exactly 50 cc. Of this solution, 10 cc., representing 2 grams of the drug, are used for assay, which is carried out in exactly the same way as described for the fluidextract, with the exception of the addition of the 5 cc. of alcohol, which is omitted.

It was found that it required at least 48 hours macer-

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[1] *J. Chem. Soc. (Trans.)*, **1898**, p. 209.

ation with cold alcohol to exhaust the drug, and hence the hot maceration is advisable.

Six different samples of Podophyllum were assayed by this method, and from the same samples fluidextracts were made according to the directions in the United States Pharmacopoeia, and were also assayed. The results are given below:

	Grams resin in 100 grams drug	Grams resin in 100 cc. fluidextract
1	5.03	4.96
2	5.24	5.16
3	4.65	4.66
4	4.92	4.89
5	4.73	4.83
6	6.82	6.71

These results show that the method gives very concordant results on the assay of the drug and fluidextract and much higher results than the precipitation method. If the method gives equally good results in the hands of other workers, then it would be advisable that fluidextract of Podophyllum, U. S. P., be assayed and standardized. As good lots of Podophyllum drug contain 5 per cent of resin, a standard of 5 per cent resin for the fluidextract is suggested.

The method can also be applied to the assay of solid and powdered extracts of Podophyllum by dissolving weighed quantities of the extracts in sufficient alcohol to render the solutions of about the same strength as fluidextract.

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LABORATORY AND PLANT

STUDIES ON FILTRATION[1]

By J. W. BAIN AND A. E. WIGLE

In connection with factory operation quite recently, one of the authors had to form an estimate, in advance, of the amount of moisture which would be retained by a finely divided solid on a vacuum filter. A search among the usual sources of information yielded no serviceable data. When the filters were in actual operation, their performance in this respect was very much better than had been anticipated, and had this fact been known in advance some economy in construction might have been effected.

With a view to gaining information on this point, the authors investigated the literature at their disposal, and with the exception of the interesting and valuable paper by Hatschek,[2] they were unable to find any useful data. When the experimental work had progressed to a certain extent, an accident drew our attention to the exhaustive monograph of King and Slichter, "Principles and Conditions of the Movements of Ground Waters,"[3] from which we have drawn freely in this discussion.

In the problem which is here under investigation, the solid is assumed to be bathed by a liquid in which it is insoluble, such as, for instance, the mother liquor of a crystalline magma. It is proposed, therefore, to investigate the amount of liquid retained by a mass of finely divided solid when filtration is carried out under atmospheric or other pressure and also in the centrifuge.

The experimental work was considerably simplified by the condition laid down above, which permitted the use of a solid insoluble in water. A quantity of pure well-rounded lake sand was carefully sieved, and the grains which were retained on the 40 mesh screen but which passed the 30 mesh, are referred to throughout as 40 mesh sand. The screens used were not of very good quality in the regularity of the mesh opening, as will be seen from the data given later, but this point is of no particular significance in this investigation.

The rate of flow of a given liquid under a constant head through a filter-mass of a finely divided solid will obviously be dependent upon the amount of space which is not occupied by the grains, *i. e.*, what is commonly called the "pore space." On first consideration, it would appear that the pore space would vary a good deal according to the size of the grains composing the mass, and the results of computation and experiment are an astonishing contradiction to this idea. The pore space is almost independent of the size of the grains, and the arrangement of the latter is of chief importance. By considering a number of small spheres of uniform diameter packed as closely as possible in a given space, it is possible to arrive at a mathematical formula from which the pore space may readily be calculated.

Slichter[1] has shown that if the spheres are so arranged that their centers lie at the corners of a cube, the pore space will be 47.64 per cent; while if the centers of the spheres lie at the corners of a rhombohedron which permits the closest possible packing, the pore space is 25.95 per cent. Between these limits we may expect to find the porosities of all ordinary materials.

With actual materials, in the case where the grains are of approximately equal size, the pore space and also the diameter of the particles may be readily determined by counting a number of the grains, determining their combined weight and the specific gravity of the material; the total volume may be ascertained by adding the sand in small quantities to a cylinder, tapping gently with a flat-faced pestle until no further decrease in volume takes place. The results of this procedure on our sands are presented in Table I.

TABLE I

Mesh screen	No. of grains	Total wt. grm.	One grain grm. × 10^{-5}	Sp. gravity	Pore space per cent	Diam. Mm.
30	300	0.0307	10.23	2.74	35.4	0.420
	300	0.0316	10.36			
40	400	0.0251	6.3	2.68	34.1	0.354
	400	0.0253	6.3			
50	400	0.0182	4.55	2.73	36.4	0.318
	500	0.0246	4.92			
60	800	0.0238	2.97	2.82	36.8	0.269
	600	0.0172	2.87			
80	800	0.0202	2.52	2.85	37.7	0.257
	600	0.0156	2.60			

The comparatively slight variation in pore space

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[1] Presented at the 6th Semi-annual Meeting of the American Institute of Chemical Engineers, Troy, New York, June 17–20, 1914.

[2] *J. Soc. Chem. Ind.*, **1908**, p. 538.

[3] *Nineteenth Ann. Report*, U. S. Geol. Survey.

[1] *Loc. cit.*, p. 309.

is worthy of note; and it may be added at this point that mixtures of small and large grains show a surprising similarity in their porosity to that of either taken alone. For all practical purposes, the pore space of masses of crystals, such as are commonly produced by rapid cooling, may be placed at 37 per cent of the total volume occupied.

FILTRATION UNDER ATMOSPHERIC PRESSURE

This part of the subject has been so carefully worked out by King[1] that it suffices to reproduce some of the results, slightly modified to suit the present purpose. Cylinders 8 feet long, 5 inches in diameter, were filled with special, sorted sands, wire gauze being used as a support at the bottom. Water was introduced from below, and when the tubes were full, percolation was allowed to commence, and the water which drained away was collected and weighed at intervals.

TABLE II

Effective size of grains Mm.	Pore space Per cent	Water retained—per cent of dry sand	
		After 1 hour	After 9 days
0.4745	38.86	11.23	4.24
0.1848	40.06	12.72	5.05
0.1551	40.76	14.73	7.25
0.1183	40.57	19.30	9.41
0.0826	39.77	20.15	11.82

FILTRATION WITH VACUUM

Experiments were carried out by the authors with the idea of approximating to factory conditions.

The sand was poured into a Buchner funnel provided with a piece of wire gauze, and gently tamped down with a flat-faced pestle; the depth of the layer was 1$^1/_4$ inches. The top of the funnel was closed by a glass plate ground to fit and provided with a central aperture through which air could be admitted. To avoid the error of surface evaporation during filtration, this air was drawn through a tower, down which water trickled slowly. The funnel was placed in a suction flask and a simple gauge enabled the vacuum to be read. When the sand had been under vacuum for a given period, it was thoroughly mixed and a sample removed; water was once more poured on and the vacuum was maintained for a longer period. The results are given in Table III.

TABLE III

Mesh screen	Moisture at the end of			Vacuum In. mercury
	5 min.	15 min.	30 min.	
30	7.20	5.69	4.75	1.5
40	8.20	6.84	5.19	1.75
50	8.65	7.50	6.41	0.75
60	8.42	7.38	6.90	2.0
80	9.15	7.52	7.37	2.25

It is seen from these results that the moisture content increases inversely as the diameter of the grains of sand. In each experiment the water pump was worked at full capacity, and as might be predicted, the vacuum increases slightly as the size of the grains decreases.

By way of comparison, a single experiment with sand of mesh 50 may be quoted. Water was poured on the layer and no vacuum was used; after 15 minutes' standing, the moisture content was found to be 27.4 per cent against the 7.50 per cent under vacuum.

The amount of liquid retained by different portions of a mass of grains in a filter, becomes important when the question of washing away an impure mother liquor has to be considered. A series of experiments was performed with the object of ascertaining the amount of water retained in the sands at different levels while under vacuum.

To carry this out, a tube about 80 cm. long and provided with side tubes closed with corks at 10 cm. intervals, was filled with each sand, and connected as has been described in the case of the Buchner funnel. A powerful water pump was run to full capacity and the pressure, as before, varied with the size of the grain. The results are given in Tables IV and V.

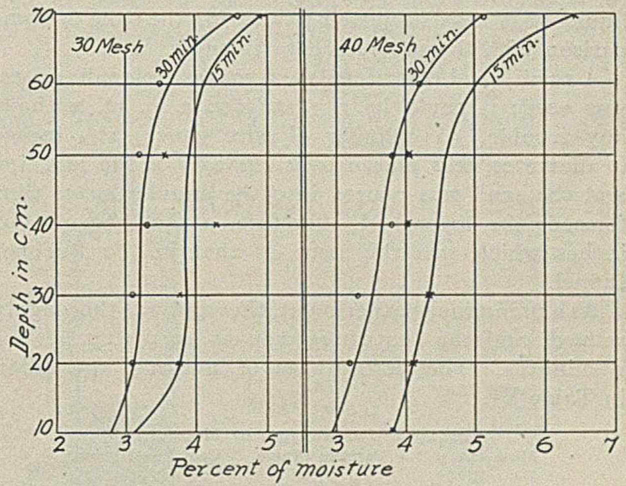


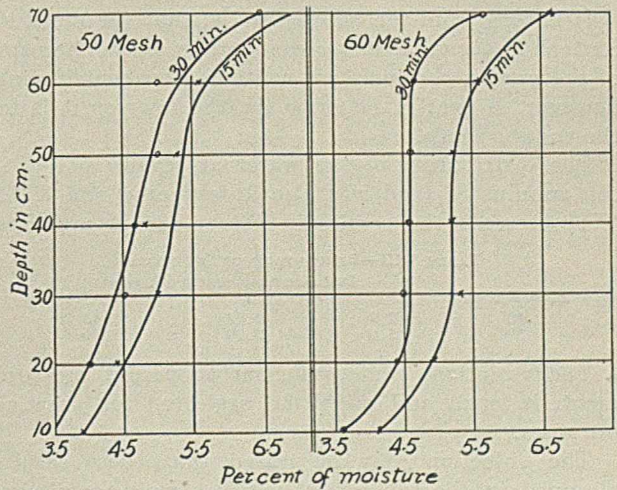
TABLE IV—PERCENTAGE MOISTURE AT END OF 15 MINUTES

Mesh screen	Pressure In. mercury	Depth of sample from top in cm.							Mean per cent moisture
		10	20	30	40	50	60	70	
30	4.5	3.13	3.78	3.77	4.28	3.56	4.13	4.90	3.97
40	4.0	3.82	4.10	4.33	4.08	4.08	5.08	6.45	4.60
50	6.5	3.90	4.40	5.00	4.80	5.30	5.60	7.60	5.30
60	7.0	4.14	4.95	5.32	5.20	5.20	5.63	6.60	5.30

TABLE V—PERCENTAGE MOISTURE AT END OF 30 MINUTES

Mesh screen	Pressure In. mercury	10	20	30	40	50	60	70	Mean per cent moisture
30	4.5	2.84	3.08	3.10	3.31	3.19	3.51	4.56	3.35
40	5.0	3.03	3.24	3.30	3.76	3.83	4.20	5.13	3.85
50	6.5	3.40	4.00	4.50	4.65	4.95	5.00	6.50	4.70
60	7.0	3.58	4.37	4.56	4.60	4.60	4.65	5.75	4.70

These results were plotted and curves were drawn as shown in the accompanying illustrations. The individual points were sometimes decidedly off the curves, but although the experiments were repeated in these cases, no better agreement could be obtained;



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[1] *Loc. cit.*

the accurate determination of small amounts of moisture in these sands proved to be difficult, probably owing to sampling. The average per cent of moisture was determined by measuring the areas under the curve, and dividing this by the height which gave the width of the rectangle of equal area.

FILTRATION WITH CENTRIFUGE

This well-known method of separating solids from liquids was next subjected to test for the sake of comparison with the previous experiments.

A small hand centrifugal, $4\frac{1}{4}$ inches inside diameter, was used; it could be run at 5000 r. p. m. without any trouble. A cylinder of wire gauze, $1\frac{3}{4}$ inches in diameter, was placed over the axis of the machine and the sand was poured into the annular space thus formed; the layer had, therefore, a thickness of $1\frac{1}{4}$ inches which was the same as that in the Buchner funnel.

As a preliminary experiment, the sand was thoroughly wetted, and the centrifugal run at 2000 r. p. m. for 2 minutes. The percentages of moisture are given in Table VI.

TABLE VI—PERCENTAGES OF MOISTURE

Mesh screen	Vacuum 15 min.	Centrifugal 2 min.
50	7.50	2.56
60	7.38	2.55

The marked efficiency of the centrifugal is noteworthy and the method of procedure was altered to show this more forcibly.

Sand was placed in the Buchner funnel, wetted and vacuum applied for 5 minutes. After sampling, the sand was placed while still moist, in the centrifugal which was then run for 2 minutes at 2000 r. p. m. Table VII shows the percentages of moisture.

TABLE VII—PERCENTAGES OF MOISTURE

Mesh screen	Vacuum 5 min.	Centrifugal 2 min.
30	7.25	2.26
	7.12	2.20
40	7.50	1.93
	7.60	2.30
50	8.70	2.56
	8.60	2.80
60	9.35	2.36
	8.40	2.65
80	9.70	2.49
	9.56	2.46

It is seen from the above results, that the moisture content under vacuum varies inversely as the diameter of the grains; the moisture content after centrifuging, however, is nearly the same for the finer as it is for the coarser sands.

The distribution of the water at several points in the annulus of sand was also investigated and Table VIII presents the results in percentage of moisture.

TABLE VIII—PERCENTAGE OF MOISTURE

	Distance from center of basket		
Mesh screen	$\frac{1}{2}''$	$1''$	$1\frac{1}{2}''$
40	2.9	2.72	2.43
50	3.0	2.90	2.76

The variation, while sufficient to permit measurement, is small and might be neglected for practical purposes.

The objection may be raised that these results, obtained in the laboratory with a small centrifugal, are of little value for comparison with the larger machines used in the factory. While with the hand centrifugal, the diameter is small, the speed is high, and we have calculated that a weight of 1 lb. revolving at a 2 inch radius at 2000 r. p. m. is subjected to practically the same centrifugal force as a weight of 1 lb. revolving at a radius of 12 inches at 600 r. p. m. The comparison is, therefore, justifiable and a good idea of the behavior of a moist mass when centrifuged in the factory, may be obtained beforehand in the laboratory.

Using the formula given by Griscom,[1] we have calculated the pressure as the periphery of the $4\frac{1}{4}$ inch centrifugal running at 2000 r. p. m. and find it to be 7.66 lbs. per sq. in.

THEORETICAL CONSIDERATION

Hatschek[2] has discussed the behavior of very finely divided substances on the filter, and has pointed out the value of a microscopic examination in this connection. The probable arrangement of the particles, with respect to the pores of the septum, are pointed out, and the influence of the flexibility of the latter is taken into consideration.

The retention of small quantities of liquid in the mass of fine grains is due, undoubtedly, to capillarity. The extraordinary difficulty in removing the last few per cent is well known and is again set forth above. In considering the reasons for this, it seemed to be worth while to calculate what would be the thickness of the film, if all the residual water were assumed to be distributed uniformly over the superficies of the grains. For this purpose, sand of 30 mesh with 6 per cent moisture was selected; the thickness of the film of water on each grain was found to be 0.0116 mm.

It would be interesting to calculate what stress must be applied to a grain thus coated, to overcome the surface tension of the liquid in so far as to allow the removal of at least part of the water; such a computation, if it could be effected, might furnish a scientific basis for the prediction of the behavior of finely divided solids on centrifuging. The authors have been unable to find time to carry this out, but hope to do so in the future.

The above discussion assumes that all the water is present on the superficies of the grains, but the capillary action of the small spaces between the grains is undoubtedly of great importance. In the case of the sand just quoted, which has a pore space of 35.4 per cent, the moisture present would fill 30 per cent of this; that is, 70 per cent of the pore space is filled only with air. This gives some idea of the comparatively poor performance of the ordinary filter and of the vacuum filter; in each case, air channels form and the downward pressure on the water-filled pores is thus relieved. In the case of the centrifugal, each particle of water experiences practically the same stress, and only the capillarity of the finest pores and the surface tension of the films on the grains are sufficient to resist its action.

SUMMARY

1—The pore space in a mass of fine grains averages about 37 per cent of the total volume.

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[1] *Metal. and Chem. Eng.*, April, **1913**.

[2] *Loc. cit.*

2—The amount of water retained when an ordinary filter is used varies from 11 per cent, with 20 mesh material, to 20 per cent with 100 mesh material, one hour being allowed for drainage.

3—The amount of water retained on a filter with 2 in. vacuum averages 7 per cent after 15 minutes for material varying from 30 to 80 mesh.

4—In a layer of material 70 cm. deep on a filter, with 5 in. vacuum, the top layer will average, after 15 minutes, 4 per cent moisture, and the bottom 6.5 per cent; the size of the grains is not of importance within the limits discussed. If the vacuum be maintained for 15 minutes longer, the above figures will be reduced by another half per cent.

5—By the use of a centrifugal, the percentage of moisture, in all the materials employed, may be reduced to an average of 2.5 per cent.

6—In the case of a sand of 30 mesh with 6 per cent moisture, if all the water be distributed over the surface of the particles, each grain would have a film 0.0116 mm. thick; or the water would fill 30 per cent of the pore space.

Faculty of Applied Science
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SCRUBBER FOR CHEMICAL LABORATORY VACUUM SYSTEM[1]

By Charles Baskerville

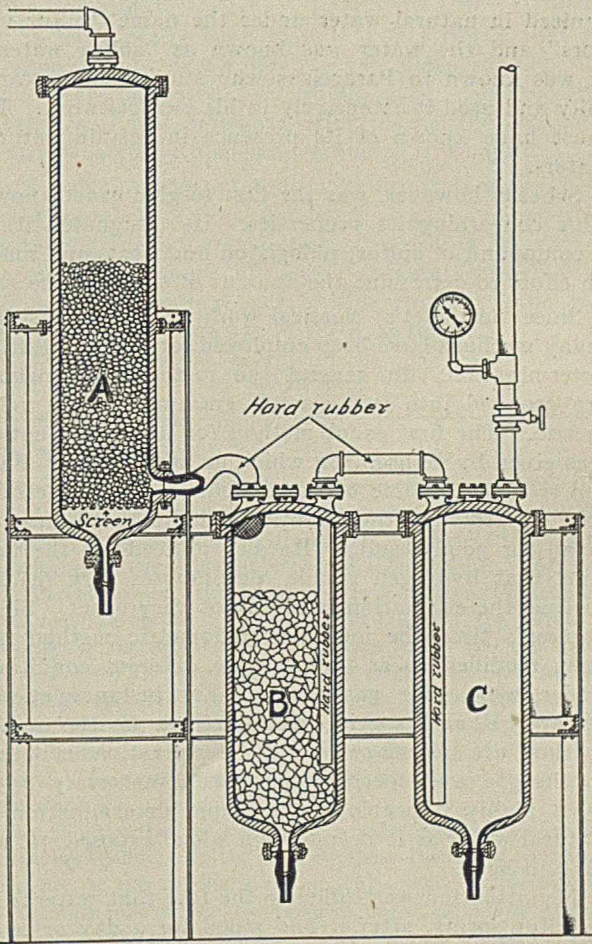
In order to protect the vacuum pump of our laboratory from the corrosive action of the gases drawn therein, I devised the installation described herewith. The pump—an improved Packard Vacuum Pump, 2 cylinder, 12 in. diam., motor-belt driven—has been in more or less continuous service for seven years without any expenditure thereon for repairs, as a result of this protection. It seemed safe, therefore, to present an account of it.

The installation is an application of the simple principles usually applied on a small scale with glass apparatus in the laboratory.

The towers are made of cast iron, porcelain-lined, and set into the system with a by-pass, which we have used only during the short time necessary for recharging. The towers are connected by hard rubber pipes (2 in. internal diameter). At the bottom of each tower is a hard rubber drain cock, bolted to a flange. At the top of *B* and *C* are plates bolted to flanges, which may easily be removed. The opening is of sufficient size to admit dropping a strung incandescent bulb for inspection.

Tower *B* is three-quarters filled with pumice stone in egg-size pieces. The pumice is thoroughly saturated with concentrated sulfuric acid. I believe lead pipe would be better in this cylinder as the hard rubber softened on contact with the acid. So far, however, the weight of the pumice and acid has not been sufficient to cause the hard rubber pipe to collapse. The decomposition of the rubber compound became so pronounced with the drain cock in a short while that it was replaced by a lead plate, which has proven satisfactory. Incidentally, it may be stated that all efforts to get the hard rubber people to provide a material which would stand up against cold concentrated sulfuric acid have been futile. Hence, it may be well to warn others as to their claims in this respect. A pear-shaped screen of copper gauze was placed in the opening of Tower *B* leading to Tower *A* to prevent clogging, in the event a rushing action of the pump sucked pieces of the pumice. We draw off and replenish the acid once or twice a year.

Tower *A* is half filled with angular pieces of commercial caustic soda, in size from a hazel nut to an egg. The mass rests upon a copper wire gauze screen supported on and by the tapering bottom of the tower. The drain cock admits of drawing off any liquefied caustic which may accumulate. A metal pipe leads from the top to the pump.



Scrubber for Chemical Laboratory Vacuum System—Scale, 1 in.=2 ft.
A—Caustic Soda; B—Sulfuric Acid and Pumice; C—Trap

Tower *C* is a safety reservoir to catch the fluid from *B* in the event of a leak beyond or other cause for increase in pressure on the pump side in the line. So far, no indication of its real need has been apparent, as the maximum and minimum contacts of the automatic regulator of the motor have never failed.

A gauge in the system beyond the scrubber serves, by comparison with the gauge on the pump, to show leaks in the scrubber. None was observed until the hard rubber drain cock on Tower *B* failed, and none

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[1] Presented at the 6th Semi-annual Meeting of the American Institute of Chemical Engineers, Troy, New York, June 17–20, 1914.

has been noted since the change described above, over six years ago.

The whole installation is supported on angle iron, painted with a rust-proof paint and may be inspected by members of the Institute any time.

College of the City of New York

NEW APPARATUS FOR DETERMINATION OF HYDROGEN SULFIDE IN WATER—PART I

By Geo. B. Frankforter

Received May 18, 1914

Hydrogen sulfide has been known with absolute certainty since the 15th century. It was first recognized in natural water under the name "sulfur vapors" and the water was known as "sulfur water." It was known to Paracelsus who studied sulfur carefully and used it extensively in his medical work. He must have known of its presence in certain natural waters.

Scheele, however, was the first to give exact knowledge concerning its properties. He designated it as a compound of sulfur, phlogiston and heat, and made an effort to determine the amount of sulfur in the gas.

Since Bertholet's[1] classical work on its composition many methods have been employed for its quantitative determination. In general the methods of analysis are grouped into two classes, gravimetric and volumetric. The first exact method for its determination was given by Bunsen,[2] in which he used iodine. Bunsen recognized some of the difficulties in the method, for he states that the quantity of iodine used must be small for good results. He also noticed for the first time that hydrogen sulfide decomposes very readily so that the estimation is often not very exact. Since Bunsen's time the iodine or iodometric method has been modified so as to meet the different conditions under which the gas occurs. For instance, special apparatus and special modifications in the iodine method are necessary for its determination in illuminating gas, and special apparatus is necessary or at least highly desirable for its rapid determination in natural water as it decomposes when exposed to the air and light.

My attention was called to the fact that water from a sulfur spring, after it had stood for a day or so in a clear glass bottle—whether directly exposed to air and light or not—showed but a trace of gas, although it was present in the water in appreciable quantities when the sample was taken. I was aware that the gas, when dissolved in water containing air, readily decomposes liberating free sulfur, but I could hardly believe that the sulfur water hermetically sealed would change very rapidly if the water contained dissolved air.

In the case of a spring water containing approximately 1 cc. per liter, the gas was entirely dissociated in six hours after the sample had been taken from the spring. So rapid was the dissociation in this particular spring that it was quite impossible to obtain concordant results without making the analysis right at the spring.

In order to do this, however, it was found necessary to carry considerable apparatus along, making the whole method quite unsatisfactory. I therefore experimented with a number of different forms of apparatus which could be carried around without difficulty, and which would simplify the process in such a way that it might be used for field service. After trying out a number of forms the two following were found to give perfectly satisfactory results.

Figure I consists of a flask, "A", which holds exactly 500 cc. of water when filled to "G". "C" is a burette with a stopper, "D," connected with flask "A" by means of a three-way cock, "B". "F" is a funnel tube also connected with "A" by means of a three-way cock "E".

Manipulation is as follows: The three-way cock "E" is turned so that the opening in the end of the cock is directly connected with "A." "B" is likewise turned so that the opening in the end of the cock is connected with "A." The flask is then thrust into the water to be examined. Water enters "E" forcing the air out through "B" until the flask is full. On removing the flask, "E" acts as a siphon allowing the water to run out to the level "G." By this means exactly 500 cc. of water can be measured. Cock "E" is now turned a quarter way around, connecting funnel "F" with "A." One cc. of starch solution is introduced, "E" is closed and the water is titrated with standard iodine solution from burette "C." From the amount of iodine solution used the quantity of hydrogen sulfide may be calculated according to the following equation:

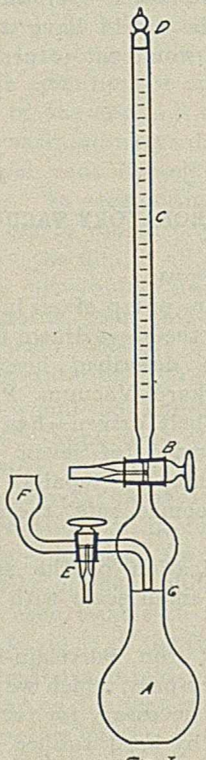

Fig. I

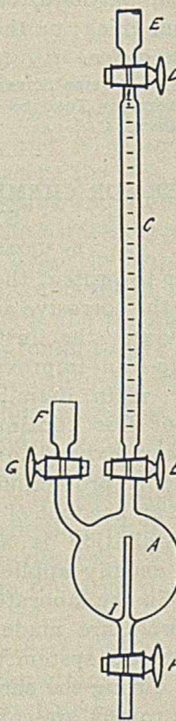

Fig II

$$H_2S + I_2 = 2\ HI + S$$

In rapid work, and especially in field work, it is very

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[1] *Ann. chim.*, **1791.**

[2] *Ann. Chem. Pharm.*, **86**, 265.

essential that the quantity of gas be read off directly without calculations. In working out this method, therefore, a standard solution was so prepared that 1 cc. of the iodine solution would be equivalent to exactly 1 cc. of hydrogen sulfide gas, under normal conditions.

Figure II is the form which was finally adopted as giving most satisfactory results. It consists of a bulb, "A," which acts as the receiver, and which is connected at the bottom with a tube, "I," which extends up into the bulb so that when cock "H" is open bulb "A" will hold a definite quantity of water. The quantity which "A" will hold when exactly perpendicular is quite constant, at least enough for all ordinary purposes.

"B" is a stopcock connecting "A" with burette "C." "F" is an outlet necessary for filling the flask and for introducing starch solution as an indicator. "D" is a stopcock on the upper end of the burette connected with a funnel tube, "E." The latter is necessary for filling the burette and also for enclosing the standard iodine solution so that the apparatus may be shaken or even turned upside down without losing any of the solution.

The manipulation is as follows: Cocks "H" and "G" are opened, the apparatus is grasped by the burette and "A" is thrust into the water to be examined and held there until the bulb is full. It is then withdrawn, held perpendicular until the water is on a level with the top of the tube "I." The quantity of water is therefore automatically measured, the tube being so adjusted that it measures 250 cc. Stopcock "H" is then closed and 1 cc. of starch solution introduced through "F." "G" is then closed and the water titrated with standard iodine solution from burette "C".

Calculations were made in the same manner as was described above for Fig. I.

With either of these forms, a sample of water may be taken directly from the spring or source of supply and a determination of hydrogen sulfide made in less than one minute.

As has already been stated, it was found that hydrogen sulfide decomposed much more readily than had been supposed. In some cases decomposition began in a few moments after taking the sample, as was indicated by opalescence due to free sulfur.

In order to test out the above forms of apparatus a great number of analyses were made. In addition to testing the apparatus, data concerning the rate of decomposition were obtained. Several series of experiments extending over a wide range I hope may appear in THIS JOURNAL in the near future.

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ADDRESSES

THE PRESENT PATENT SITUATION[1]

By Maximilian Toch

On February 1, 1913, the new rules for procedure in patent litigation became effective, and after fifteen months a calm review of the benefits derived from the new rules is opportune. To those who are unacquainted with these new rules let me state briefly that the old custom of patent litigation was in taking of testimony before a Master in the office of either the defendant's or the plaintiff's attorney, and this Master came in to swear in each new witness, but never remained, and even if he did remain he had no authority to decide upon the propriety of the questions asked. The testimony was taken down invariably in long-hand. The costs were appalling, for the fees of a patent attorney are from $50 to $100 per day, the fees of the experts are the same, the cost of printing or typewriting is very great, and although it has often been said that no poor man can litigate a patent I know that no man in medium circumstances can fight one either, for in six months $20,000 can disappear faster than ice under the midsummer sun.

The new rules in themselves are excellent. They provide that the testimony shall be taken in open court before a judge; they provide that the testimony shall be taken in shorthand, and a very important case can be finished in nineteen working days and even less; and if a Judge is not overwhelmed nor overburdened with work he can render a decision within a month thereafter. An excellent feature of the new rules is that upon petition the opposing experts will be required, within a certain number of days after the case has been put at issue, to file their expert opinions in the form of an affidavit, so that each side will have these affidavits before them as a basis for preparing for cross-examination of the expert witnesses in open court, and to enable them to see each other's positions, as far as these affidavits will disclose them, in order to enable them to produce such fact witnesses as they may deem it necessary to produce to meet the attacks which the affidavits may indicate will arise. This, to a considerable extent, relieves the new practice from the surprises that may be sprung at the trial, and which, the nature of surprises in the expert side of the case would make it almost impossible for the opposing party to meet, since such matters frequently require experimentation. The affidavit of the complainant's expert witness, of course, is required to be put in first, and a certain number of days afterwards, that of defendant's expert. The cross-examination of the experts is conducted in open court.

My plaint is that we are suffering under the régime of a parsimonious republic. In the great Southern District of New York there are, at this writing, but four judges who are available for patent work: one of them has resigned, one of them is on leave in Europe, and the other two are staggering under a mass of litigation. Nor is it to be assumed by any means that a Federal Judge is a patent Judge only, for in one day I have heard motions on questions of immigration, bankruptcy, interstate business relations, injunctions in matters already decided, trademarks, copyrights, and patents; so that a Judge must needs be keen of eye and ear, clear of mind, and in the finest physical and mental condition possible to withstand the terrific onslaughts that are made upon what should be otherwise a man of mental equipoise.

In the parsimony of our republic the Attorney-General of the United States has decided that the vacancy which exists in this district shall not be filled with a new Judge, for the $7500 meagre and insignificant salary can be saved if a Judge from some other district will occasionally come down and sit in the place of the one who resigned. In the meantime, infringements go on, injustice is meted out right and left, decisions cannot be had on cases pending on account of the overwhelming amount of work which crowds the dockets—all because our parsimonious, and,

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[1] Presented at the 6th Semi-annual Meeting of the American Institute of Chemical Engineers, Troy, New York, June 17–20, 1914.

in this instance, penurious Government seeks to save a sum so insignificant in the business affairs of this Government, that it is hardly worth mentioning. If it were a real saving, nobody could criticize it, but it is not even a saving—it is a hardship, and has a destructive influence on the intellectual property of this country. I do not advise the building of one battleship less per year, but the building of only one battleship less for all time would give a fund sufficiently great to give us a new patent office building, which is so sorely needed, even though the money is at present available, and the interest on the balance at four per cent between the cost of this building and the cost of a battleship and its equipment, and the saving in the cost of maintenance of such a battleship, would give us fifty more Judges throughout the United States at a decent living wage, and place this country in the position that it should have been placed in years and years ago.

It is absurd that the United States Government should issue a patent for a consideration after making its usual objections and a more or less thorough search, and then repudiate its own action; but after spending a fortune and getting a decision it will cover only ONE circuit in the United States. Even the man who has recovered a decision on appeal could only sing, "*One-ninth of my country 'tis of thee, sweet land of liberty*," for such a man stands in danger of having a Judge in another circuit overthrow what was done in the one; and where the philosophy, the justice, the reason, the sense and the equity come in, I fail to see, for if the United States Government is a sponsor for a patent it should be a sponsor for the entire United States, for it was so incorporated in the bond that was made between the fathers of this country and the people who sought their freedom and independence that each man shall have the right to pursue in peace his trade, and the exclusive right for a limited time shall be given to every inventor.

All that inventors want is the same protection that is given to real property or other personal property. If you buy a piece of real property in the United States, a search is made and title passed, and once you have it it is almost impossible for any one to deprive you of your ownership. In the purchase of other personal property the title is implied, for you are accustomed to buy from reputable people, and only in the case of stolen goods can the dispute of ownership be had; but when a man makes a new and useful invention it costs him almost all that he has to prove that the invention is his, and even after he has proved it he cannot collect damages excepting by due process of law. Let us hope that within a reasonable time the ownership of a patent will be the equivalent to the ownership of real property or other personal property.

It is puerile for any one to say the whole trouble with the patent situation today is the fault of President Wilson or Mr. Oldfield, or ex-President Taft. As a matter of fact, it is no one man's fault. Ex-President Taft sat in judgment on many a patent case when he was a Supreme Court Judge of the State of Ohio, and he, better than any one else, was aware of the shortcomings of the patent situation; and under his administration I believe it was largely by reason of his personal interest and experience on the bench, that the new equity rules were promulgated. Inasmuch as this is not a one-man Government it is not within the province of any one to make any personal criticisms. It is as much your fault as it is mine. What we are trying to do is to amend the situation by showing up the weaknesses that exist.

In closing, I recognize that my wail for the present is, more Judges. Some other battle-scarred veteran of the patent court wants the German system of six months publicity; a third man wants a Patent Commission; and so it goes on, but let me say that if every one of us had his wish, and that were the only improvement and remedy for the present, it would help a great deal, but just as long as the Constitution provides that Congress shall make these laws so long will our voices fall on the desert air.

320 Fifth Avenue, New York

SOME ECONOMIC ASPECTS OF INDUSTRIAL CHEMISTRY[1]

By Bernhard C. Hesse

In considering this subject the difficulty lies not in a scarcity of material, but principally in keeping the discussion of the voluminous matter within a small compass.

The expression "industrial chemistry" has no universally accepted meaning and the reason seems to lie in the fact that, while a process may be essentially dependent upon a chemical reaction, yet the proportion of attention given or required of the chemist is small when compared with the other details of manufacture and control. For example, metallurgical operations require a chemical change in the ore before it yields the metal in its commercial form, yet few, if any, consider metallurgy a branch of industrial chemistry. It forms a distinct subject by itself, most likely because the mechanical and engineering requirements and details absorb more attention than the chemicals which have been worked out to what may be considered for our purposes as their final form, while the handling of material and the other mechanical problems call for constant supervision and scrutiny.

INDUSTRIAL CHEMISTRY IN THE U. S. CENSUS

Taking the thirteenth census of the United States as a guide in ascertaining what is regarded by the Census as industrial chemistry, it will be found that in the division of chemical and allied products, metals and all metallurgical operations are excluded, as well as the production of refined petroleum, and a host of other large industries such as glass, soap, pottery, sugar, starch and the fermentation industries which depend upon chemical reactions and chemical control for their successful execution.

The Census of the United States includes under chemicals and allied products nine principal divisions:

1—Paint and varnish.
2—Chemicals.
3—Fertilizers.
4—Explosives.
5—Dyestuffs and extracts.
6—Sulfuric, nitric and mixed acids.
7—Wood distillation (not including rosin and turpentine).
8—Essential oils.
9—Bone, carbon and lampblack.

For the present, these nine divisions of the Census will be considered. Having arrived at a tentative conclusion as to the scope of the subject matter, this subject matter will be considered from the two following aspects:

I—The relationship of these industries to the manufacturing industry of the United States as a whole.

II—The position of the United States in those respects as a buying and selling nation.

The volume and distribution of foreign trade of the United States in the fiscal year of 1913 is given by the Department of Commerce as follows:

Exports	$2,428,506,358
Imports	1,812,978,234
Total	4,241,484,592
Excess of exports	615,528,124

In order to obtain a conception of the relationship of these nine branches of chemical industry to the manufacturing industries of the United States as a whole, Table I will be helpful.

The story told by Column D is encouraging in some respects, and is not so encouraging in others. Compared with other manufacturing industries, the chemical and allied industries do not so easily lend themselves to small units. It takes 3.3 times as much capital for the average chemical plant as for the average manufacturing plant. This is the discouraging feature from the individual point of view.

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[1] Lecture delivered at the College of the City of New York, May 1, 1914.

TABLE I—COMPARISON OF CHEMICAL AND GENERAL MANUFACTURING IN CONTINENTAL U. S.

		Manufacturing establishments				
	Items	A Total	B Chemical and allied products	C Percentage of A in B	D(a) Average chem. plant. / Av. general manuf. plant	E(b) Average in chemical plants for $1 investment
1	Number of establishments	268,491	2,140	0.79	..	0.30
2	Persons engaged in manufactures	7,678,578	88,097	1.15	1.44	0.44
3	Proprietors and firm members	273,265	1,155	0.42	0.53	0.16
4	Salaried employees	790,267	16,516	2.09	2.64	0.80
5	Wage earners (average No.)	6,615,046	70,426	1.06	1.34	0.40
6	Primary horsepower	18,680,776	398,880	2.14	2.71	0.82
7	Capital	$18,428,270,000	$483,729,410	2.62	3.31	..
8	Expenses	18,453,080,000	359,425,126	1.95	2.46	0.74
9	Services	4,365,613,000	62,700,767	1.44	1.82	0.55
10	Salaries	938,575,000	24,042,566	2.56	3.24	0.98
11	Wages	3,427,038,000	38,658,201	1.13	1.43	0.43
12	Materials	12,141,791,000	258,115,975	2.13	2.69	0.81
13	Miscellaneous	1,945,676,000	38,608,384	1.98	2.51	0.76
14	Value of products	20,672,052,000	425,084,540	2.06	2.61	0.79
15	Value added by manufacture (value of products less cost of materials)	8,530,261,000	166,968,565	1.96	2.48	0.75

(a) Values obtained by dividing separate items in C by Item 1 in C. (b) Values obtained by dividing separate items in C by Item 7 in C.

From the broader point of view, Column D, however, is very encouraging. The average chemical plant requires 50 per cent more help than the average manufacturing plant; it employs over two and a half times as many salaried employees as does the average manufacturing plant, but unfortunately only 34 per cent more than the average number of wage-earners. The average chemical plant bears much more than its proportionate share of expenses, whether in the shape of salaries, wages, materials, or miscellaneous expenditures; in the value of the product produced per unit of chemical plant the average chemical plant produces 161 per cent more than its average share.

TABLE II—ANALYSIS OF CHEMICAL AND ALLIED PRODUCTS BY DIVISIONS

	VALUE IN DOLLARS	PERCENTAGE OF TOTAL DIVISION
PAINT AND VARNISH INDUSTRY		
Pigments	16,985,588	13.6
Paints in oil	56,763,296	45.4
Varnishes and Japans	31,262,535	25.0
Fillers	3,126,271	2.5
Water paints and kalsomine	1,979,007	1.6
Linseed oil	1,912,594	1.5
Bleached shellac	578,650	0.5
All other products	12,281,481	9.8
Total	124,889,422	
CHEMICALS		
Acids	11,926,389	10.1
Sodas	21,417,982	18.1
Potashes	88,940	0.7
Alums	2,578,842	2.2
Coal tar products	2,675,327	2.3
Cyanides	1,941,893	1.6
Bleaching material	1,635,046	1.4
Chemical products made by the aid of electricity	17,968,277	15.2
Plastics	7,180,172	6.1
Compressed and liquefied gases	4,969,805	4.2
Fine chemicals	10,956,666	9.3
Chemicals not elsewhere specified	34,349,548	29.1
Total	117,688,422	
FERTILIZERS		
Fertilizers	92,369,631	88.8
Superphosphates	13,318,529	(12.8)
Ammoniated fertilizers	10,061,193	(9.7)
Concentrated phosphate fertilizers	3,638,210	(3.5)
Complete fertilizers	57,243,899	(55.0)
Other fertilizers	8,107,800	(7.8)
Sulfuric acid for sale (as 50° Bé. acid)	923,492	0.9
Other acids for sale	611,288	0.6
All other products	10,055,802	9.7
Total	103,960,213	
EXPLOSIVES		
Dynamite	18,699,746	46.6
Permissible explosives	863,209	2.2
Nitroglycerin	3,162,434	7.9
Blasting powder	9,608,265	24.9
Gunpowder	1,736,427	4.3
Other explosives	3,913,787	9.7
Materials not elsewhere specified	2,155,793	5.4
Total	40,139,661	

	VALUE IN DOLLARS	PERCENTAGE OF TOTAL DIVISION
DYESTUFFS AND EXTRACTS		
Artificial dyestuffs	3,462,436	21.6
Extracts for dyeing	991,974	6.2
Extracts for tanning	6,449,105	40.4
Other tanning materials	625,401	4.0
Mordants	99,797	0.6
Sizes and finishes	2,418,652	15.0
Ground and chipped woods, etc.	344,761	2.2
All other products	1,562,448	9.7
Total	15,954,574	
SULFURIC, NITRIC AND MIXED ACIDS		
Sulfuric acid	5,629,496	57.0
Nitric acid	499,303	5.1
Mixed acid	1,438,475	14.6
All other products	2,316,783	23.5
Total	9,884,057	
WOOD DISTILLATION (not including rosin and turpentine)		
Wood alcohol:		
Crude	1,627,878	16.7
Refined	2,901,709	29.8
Acetate of lime	1,981,220	20.3
Charcoal	2,351,644	24.0
Turpentine	249,526	2.6
All other wood distillation products	357,290	3.7
All other products	267,731	2.8
Total	9,736,998	
BONE, CARBON AND LAMPBLACK		
Bone black	1,070,333	50.0
Carbon black	625,514	29.3
Lampblack	439,707	20.6
Total	2,135,554	
ESSENTIAL OILS		
Oil, peppermint	519,079	29.8
Oil, black birch	102,045	5.9
Oil, spearmint	83,283	4.8
Oil, wintergreen	68,983	3.9
Other oils	335,213	19.3
Witch-hazel extract	412,322	23.7
All other products	216,309	12.4
Total	1,737,234	

If the principal object of manufacture be the enhancement of value of the outgoing material over the incoming material, then the fact that the average chemical plant enhances its raw material 148 per cent more than its average share is a matter for congratulation and of encouragement.

Turning now to the question of productive power of capital invested in chemical industry, it will be found on inspecting Column E that a dollar is not so productive in the chemical and allied industries, average against average, as in the other branches of manufacturing endeavor. The disbursements for salaries, materials, power, value of product and expenses of miscellaneous nature are each about three-quarters of the average of the same items for the other branches of manufacture, and the enhancement in value is only 75 per cent of the average enhancement produced by unit capital investment in the other branches of manufacture. The dollar so invested employs fewer wage earners, salaried or otherwise, than a dollar otherwise invested in manufacturing enterprise. This, of course, is merely a natural consequence of the high initial cost of plant, the large size unit of plant required and the close markets.

Turning to the value of products in Column B, it is to be noted that the percentage participation of each of the nine divisions in that title is as follows:

Paint and varnish	29.4	Sulfuric, nitric and mixed acids	2.3
Chemicals	27.4	Wood distillation	2.3
Fertilizers	24.5	Essential oils	0.3
Explosives	9.4	Bone, carbon and lampblack	0.4
Dyestuffs and extracts	3.8		

The thirteenth census of the United States has distributed the participation of these nine divisions in this amount of product with considerable detail, which does not lend itself very well to discussion. The not specifically described items amount to $73,563,059 or 17 per cent of the total. For the purpose of obtaining a better understanding of the relationship of the various principal items under each of these nine divisions, Table II has been prepared.

Within the nine divisions given, the United States is in a large measure self-sustaining, although it is necessary for it to obtain much of the raw material from abroad. In the division of dyestuffs and extracts, and particularly that portion of it dealing with artificial dyestuffs, it is to be noted that during 1913, the total importation into the United States of artificial dyestuffs, exclusive of alizarine dyes and indigo, amounted to $7,105,284; during the census year of 1910, this country manufactured $3,462,436 worth of such artificial dyestuffs which amounts roughly to 32 per cent of this country's entire consumption of the so-called coal-tar dyes; no doubt, since the census year 1910, the domestic production of coal-tar dyes has increased. However, much of the coal-tar raw material used in such manufacture comes to us from abroad, particularly from Germany and England.

In the fertilizer division we are, of course, dependent, for our potash requirements, upon Germany, and these amount in round numbers to $1,000,000 per month. In the same division, we are dependent upon Europe for much of the ammonia entering into the fertilizers, amounting in 1910 to over $4,000,000. It will probably not be long before most of our ammonia requirement is supplied by our own by-product coke-ovens.

INDUSTRIAL CHEMISTRY IN ITS BROAD ASPECT

However, industrial chemistry or chemical industry is much broader in scope than is indicated in the thirteenth Census of the United States on chemicals and allied products. From the point of view of the person with chemical training, every industrial operation which calls for chemical control is a branch of industrial chemistry or of chemical industry, the two terms being used interchangeably.

In Germany the official classification of material connected with chemical industry is as follows:

1—Malt, oil fruits, plants, etc.
2—Industrial or medicinal vegetable products.
3—Tanning extracts.
4—Resins, gums and adhesives.
5—Caoutchouc and camphor.
6—Animal and vegetable fats and oils.
7—Animal products.
8—Starch and sugar.
9—Alcohol, acetic acid, mineral waters.
10—Mineral and fossil raw materials.
11—Ores, iron and slags.
12—Fossil fuels.
13—Mineral oils and like fossil raw materials.
14—Coal-tar oils and products.
15—Waxes.
16—Soap and fat products.
17—Chemical and pharmaceutical products.
18—Miscellaneous chemical and pharmaceutical products.
19—Dyes and dye materials.
20—Ethers and alcohols.
21—Volatile oils, synthetic perfumes, toilet articles.
22—Artificial fertilizers.
23—Explosives and combustibles.
24—Wood fiber and chemical paper.
25—Metals.

These twenty-five large classes or divisions comprise four hundred and forty-two sub-classes.

An examination of the records of imports and exports into and from the United States during the fiscal year 1913, discloses a total business of $4,241,484,592; of this, not less than $1,302,274,994 or 30 per cent deal with products of chemical industry or materials used in the products of chemical industry, and of these $759,193,688, or 18 per cent of the total represent imports and $543,081,306, or 12 per cent of the total represent exports, leaving a balance of trade against the United States, $216,112,382.

LARGE ITEMS IN CHEMICAL TRADE OF THE U. S. FOR 1913.

IMPORTS		EXPORTS	
Sugar	$204,212,581	Refined petroleum and its products	$139,882,905
Hides and skins	117,386,174	Copper as metal	120,605,914
Unmanufactured India rubber	101,333,158	Beef and hog products	82,890,777
		Leather	42,384,199
Paper and paperstock	27,706,697	Naval stores	26,471,492
		Fertilizer material	11,400,888
Potash compounds	14,408,124	Cement industry	5,822,107
	$465,046,734		$429,458,282

Information as to the distribution of the exports and imports just given as to countries of destination and countries of origin is not readily accessible, since it would be a never ending task for the officials of the Department of Commerce to rearrange all of this vast information from the various points of view possible.

MOVEMENT OF CHEMICAL PRODUCTS BETWEEN GERMANY AND THE UNITED STATES

However, fragmentary information is accessible with respect to the relationship between the United States and Germany as regards the interchange of chemical products between the two countries. This information is based upon German official publications.

From the point of view of values, information[1] is at hand for only the year 1904. In that year Germany sent to the United States $16,993,200 worth, and the United States sent to Germany during that time $38,194,240, or an excess in favor of the United States of $21,201,040, which means about $1,800,000 per month.

With regard to the tonnage movement between those two countries, information for the year 1913 is at hand,[2] and it shows that during that period a total of 3,430,564 metric tons of commodities of the chemical industry passed between the two countries, of which 1,917,430 metric tons passed from the United States to Germany, and 1,513,134 metric tons passed from Germany into the United States; that is, the United States sent to Germany an excess of 404,000 tons over what it took from Germany in 1913.

FREIGHT MOVEMENTS IN THE UNITED STATES

In 1911 the total freight movement over the railroads of the United States amounted to 967,233,991 tons; of these about 14 per cent comprised manufactured goods, and about 28,000,000 tons of the total freight moved was composed of products of chemical industry, that is, about 3 per cent of the total freight movement of this country is represented by products of chemical industry. The three and a half million tons gross above referred to between the United States and Germany, therefore, represent about 12 per cent of the probable total freight movement of products of chemical industry in this country.

EFFICIENCY OF AMERICAN INDUSTRIAL CHEMISTRY

An examination of the relative exports and imports of products of chemical industry from and into the United States shows that there is little, if any, ground for criticism of American chemists in not utilizing their opportunities. It is safe to say that the American chemical industry is developing its own natural resources with a degree of foresight and success very favorably

[1] THIS JOURNAL, **6**, 2.

[2] *Ibid.*, **6**, 274.

comparable with that accomplished by chemists in other lands. Much is heard in criticism of American chemists for not developing a coal-tar chemical industry, but I do not believe such criticism to warrant a wholesale belief in the backwardness of American chemists. There can be no question that the chemical work involved as well as the engineering work involved in the production of a useful and usable illuminating oil, or a medicinal preparation from crude petroleum, compares very favorably with the chemistry involved and the engineering involved, in the production of the majority of so-called coal-tar dyes. The relative economic value of the two products is, of course, in favor of the products of petroleum. It will be sufficient to say Germany is supreme in the coal-tar dye industry, because (1) Germany was the home of the industry; (2) the industry itself is so dependent upon interlocking chemicals and the growth of this interlocking dependence has been as fast as economic development warrants and has now reached such a stage of complexity and interdependence that it is difficult of transplantation as a whole; (3) there are relatively few so-called staple articles among the coal-tar dyes—by staple is meant those which are consumed in quantities to be measured by tons—many of those few are so interlocked with subsidiary or by-products that the transplantation of the work out of Germany would be economically unprofitable. Wherever it has been profitably transplantable to this country, the manufacturing of such staples has been done, and with considerable success even though the raw material supply is still provided by Europe.

THEORY AND PRACTICE

The chemical industry, probably more than any other industry, is dependent upon the application of much theoretical work, *i. e.*, scientific work to every-day conditions, and in order that the chemical industry may grow, it is necessary that there should be brought to bear upon the manufacture of each and all of the products the highest chemical training available under the circumstances. The beneficial interaction of practice upon theory and theory upon practice, is evident in almost every branch of industrial chemistry. It has been brought to its highest efficiency, however, in the organic division, and more particularly that dealing with coal-tar dyes and synthetic medicinals and pharmaceuticals. However, the chemist can, with profit, follow Mr. Kerr's excellent advice to engineers when a difficulty is encountered: "Go as far as you can see and then see how far you can go."

The simplification brought about in organic chemistry through the creation of the Kekulé conception of the structure of benzol, made the development of the coal-tar dye industry in its early stages possible, or at any rate immeasurably facilitated it. In return, the coal-tar dye industry has enriched scientific or theoretical organic chemistry with a wealth of information and facts with respect, not only to benzol, but to naphthalene, anthracene and the higher aromatic hydrocarbons; the two working together have developed a very large number of new classes of organic compounds, for example: the azines, oxazines, numerous classes of azo compounds, and the wealth of oxy and oxyamido derivatives in all the classes. New methods of sulfonation, chlorination and nitration have been developed almost without number, and in turn, theoretical organic chemistry has supplied the industry with many useful methods of the same kind.

To contemplate the results of this interaction is to view one of the greatest of intellectual triumphs. It is this very fact that has misled so many to ascribe to the coal-tar dye industry an economic effect far beyond its actual and to belittle the economic effect of the so-called inorganic industry. It is perfectly safe to say that the money value of the inorganic exceeds the money value of the dye industry by at least 15 to 1.

From 1877 down to the close of 1912 there were taken out in Germany 5,675 German patents, or 158 per year, dealing with the utilization of coal-tar hydrocarbons and their by-products; it has been estimated that not more than one out of every hundred has secured financial returns for its owners. During the years 1895 to 1903, 382 German patents, or at the rate of 48 per year, were taken out in the inorganic chemical industries.

It would be an interesting subject for speculation to consider the intellectual effort involved in the 5,675 coal-tar patents as compared with the intellectual effort required for the 382 inorganic patents. It would also be of interest to consider the difficulties, financial and otherwise, in the way of creating those respective patents. A far-reaching experiment can be made in the coal-tar industry for a very little expenditure of material and labor, but in the inorganic industry the expenditure of material and labor is inordinately greater. You can make a coal-tar dyestuff and determine whether there are any probabilities of its having commercial utility at an infinitely slighter expense than you can determine whether certain alterations in the construction of a bleach-chamber in the production of bleaching powder will or will not be profitable; on the other hand, as you approach the more highly developed and almost completed manufacturing phase of coal-tar dye chemistry, you immediately come into about the same difficulties and embarrassments that you do in the inorganic field, and for precisely the same reason, namely, that in both cases you are endeavoring to develop refinements, and refinements are much more difficult of detection, elaboration and application than is the question of determining whether you have, or have not, a new and probably useful dyestuff.

By way of illustration, there are probably fewer than 35,000 compounds listed in Beilstein, but it will be no difficulty whatever to find a dozen different patents on coal-tar dyes, each and every one of which covers several million, even several hundreds of millions of different and distinct dyestuffs. Of course, to discover a new type of a dyestuff is almost as difficult as it is to discover a refinement in the almost fully developed inorganic industry, but once the type is given, there is no difficulty in creating a new dyestuff under that type.

THE FUNCTION OF THE CHEMIST AS AN INDIVIDUAL

Now, the function of the chemist in the production of things is twofold. Take the apparently most humble position, namely, that of analyst. Upon his accuracy of manipulation depends, in a large measure, the profitableness of the undertaking. If an analyst makes a mistake of 1 per cent in determining copper, on the $120,000,000 worth that we export annually, that would mean a loss of $100,000 per month. Therefore, analytical control, in order to be of value, must be accurate, since inaccuracies can easily run into large sums of money.

But the chemist's contribution does not stop merely with control; he does create a great many new uses for old things, and he does create new things and find uses for them. To be able to do these things to the best advantage, he must be thoroughly versed in what has been done, must know what tools are at his command, must be able to use those tools and to tell when they shall be used, must possess also the merchant's instinct of values, if he desires to rise to the highest efficiency in industrial chemistry. Of course, he must know how to handle men, and how to get results with what is at his command, as must anyone who attempts to conduct any business enterprise.

He must be alert, and he must overcome any disdain that he may naturally have for small things, for in industrial chemistry, perhaps oftener than in any other, it is the small thing that has pointed the way to achievement and success.

It is an old story how the production of benzol from coal gas was brought about by a mistaken notion that oxalic acid could be made from coal gas and nitric acid. An alert and very observant chemist in repeating this attempted synthesis found not only that oxalic acid was not formed, but that nitrobenzol was produced with benzol dissolved therein. That was the beginning of the recovery of benzol from coal gas, and the addition to the sources of benzol of a source much greater and more dependable than any theretofore available.

The neglect of a laboratory boy to maintain the temperature he was directed to keep in a certain vessel, taught that laboratory boy nothing, but the chemist in charge following up this result, finally ended up with a method of substituting sulfuric acid for bromine, thereby reducing the cost of production by over 50 per cent. In both of these cases, it is very doubtful if a man having no training beyond that required in the production of the things with which he was directly concerned, would ever have made those discoveries. The attempt to make oxalic acid would have resulted in failure, and would have been so reported, the result of the laboratory boy's negligence would have been dumped into the sewer, and a new start made along the original lines.

CONCLUSION

I have shown how, in a national sense, the chemical industry contributes a very substantial portion to our national welfare and the useful part it plays in this work-a-day world, in the employment of persons, materials and of capital; how in a broader sense it touches almost every field of human activity; how it is interwoven with the means required for the gratification of all our personal needs and desires.

It needs merely to be mentioned in order to bring about a full appreciation of the importance of the chemical industry to refer to the important part it plays with respect to agricultural chemistry. The chemical methods of investigation and research applied to agricultural problems indicate the requirement of certain materials by the soil, and these materials are supplied by the chemical industry. In that way the chemical industry contributes to the activity of the soil and the increased output per unit area of agricultural products.

Conversely, as in the case of alizarin and indigo, hundreds upon hundreds of square miles of the earth's surface were devoted to the cultivation of the plants necessary to produce these articles. This very large area is no longer required for that purpose, and it is safe to say that in the chemical factories now producing these things the combined working area is under four square miles. Right or wrong, I have always personally felt that had the botanist devoted the necessary attention to the growth and cultivation of indigo plant when the first synthesis of indigo was announced in 1880, the displacement of vegetable indigo between 1897 and 1900 by synthetic indigo would not have taken place, or at any rate, it would not have been accomplished after so brief a struggle. The botanist has assisted wonderfully in increasing the alkaloidal content of cinchona barks, and in the discovery of a large number of new plants capable of producing a latex suitable for India rubber production and he has also contributed greatly to the development of plantations, wherein the yield per unit area is much increased.

While at the present day it may not be commercially profitable to produce synthetic rubber, or synthetic camphor, or synthetic nitric acid, or synthetic ammonia, yet it is perfectly true that the very existence of these possible synthetic sources of these materials renders it less and less likely that there will be any undue advance in the cost to the consumer of these articles; at any rate, the cost will not be advanced beyond a figure where the synthetic process can achieve a reasonable profit.

Chemical industry, therefore, not only provides for our present needs, but acts as safety device against famine, shortage or undue monopolization of a number of vegetable and mineral products.

90 William St., New York

CHEMICAL STUDIES OF THE POLLUTION OF THE OHIO RIVER[1]

By Earle B. Phelps

The extensive investigation of the Ohio river now being undertaken by the U. S. Public Health Service under the direction of Passed Assistant Surgeon Wade H. Prost has a twofold object. It is desired to learn primarily the extent and character of the pollution now entering the Ohio river, the capacity of that river to receive and dispose of pollution, and the effect of such pollution upon the waters of the river and upon the health and comfort of the riparian dwellers. Secondarily, and possibly of equal ultimate importance, it is hoped to establish certain basic data necessary to a general discussion of the principles of the self-purification of streams.

No such comprehensive investigation of a great river system has ever been made. In addition to chemical, biological and bacteriological, and hydrographic studies of the river itself and of the polluting waters, the investigation will include sanitary surveys and epidemiological studies of the bordering communities and engineering studies of water supplies and sewerage systems.

River pollution may be regarded from the point of view of the river itself or of the health of the people dwelling upon its banks. The sanitary qualities of a drinking water, and the effect of pollution upon riparian dwellers is essentially a biological question to be studied by biological methods, supplemented at times by chemical methods. The question of nuisance in a stream, although it deals with biological agencies, is essentially chemical and necessitates chemical or biochemical studies.

The present paper deals solely with the chemical part of this investigation, as applied to the pollution and self-purification of the stream. It will be pertinent, therefore, to present first, a general statement of the problem as it appears in the light of modern sanitary chemistry.

The self-purification of streams is in no way a unique or remarkable process. It is essentially like the oxidation and destruction of organic matter by the soil. In the case of a polluted stream, however, purification by oxidation is assisted by other factors, such as dilution and sedimentation, which together with the ideal conditions for oxidation which may exist, combine to produce such improvement that the phenomenon has ever been regarded as one peculiar to itself.

The reactions involved in this process are biochemical reactions. For their occurrence it is necessary to bring together oxidizable organic matter, oxygen and oxidizing bacteria. The first and last are necessarily present in polluted waters. The questions of stream purification and prevention of nuisance, therefore, reduce to one of oxygen supply.

The ultimate source of the oxygen available for this work is the atmosphere. Under normal atmospheric conditions and at any given temperature, water dissolves a specified quantity of oxygen which, unfortunately, is known as the saturation value. This incorrect usage has resulted in serious misconceptions of the true solubility relations of oxygen. Since the solubility of any gas is proportional to the partial pressure of that gas in the atmosphere above, it follows that the solubility of oxygen in water is approximately five times as great under an atmosphere of pure oxygen as it is under a normal atmosphere. Hence "supersaturation" is readily obtainable. It is of frequent occurrence in nature in the neighborhood of green plant life where the oxygen content of the immediate atmosphere, or of the gases rising through the water, is greater than in the normal atmosphere. It would be eminently desirable to refer the solubility of oxygen to a pure oxygen atmosphere in which case the accepted saturation value would be reduced to approximately 20 per cent; but usage has sanctioned the present method which makes it necessary for us to deal with "supersaturation."

A saturated water will obviously dissolve no more oxygen. Atmospheric oxygen tends to re-enter the water in proportion as the oxygen content of the water is lowered by the oxidation of organic matter. The intensity of the driving force of re-

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[1] Presented at the 49th Meeting of the American Chemical Society, Cincinnati, April 6–10, 1914.

aeration is a direct function of the lowering of this oxygen content. It is at a maximum in a completely deoxygenated water and this is the condition of maximum oxidizing work in any stream. This condition, however, is also one of maximum nuisance and is not to be tolerated. Such an anaerobic stream gives off foul odors and is black and unsightly in appearance.

It becomes a matter of some importance, therefore, to determine the miminum value which the dissolved oxygen of the stream may reach before conditions approach the nuisance stage. This point practically fixes the capacity of the stream in question to care for pollution. The lower the permissible oxygen concentration the greater the proportion of the initial dissolved oxygen of the water available for the oxidizing reaction, and the greater the capacity of the stream to reabsorb oxygen from the atmosphere.

Upon this question of permissible oxygen reduction there are many diverse opinions and very little real knowledge. It has even been held that any oxygen whatever will prevent conditions of serious nuisance. The present writer's experience has not tended to confirm this view. That condition of nuisance, for example, which makes a river undesirable for canoeing on a quiet summer evening by reason of sewage odors emanating therefrom has been found to result from a reduction to fifty per cent of saturation. Extremely offensive conditions, with foul odors and black appearance, have been found to be associated with 38 per cent of saturation. On the other hand certain streams which have ranged from 60 to 75 per cent of saturation have given to the senses no direct evidences of pollution. This point needs further study and discussion. It is merely desired to draw attention at this time to its importance as one of the fundamental factors of the problem.

The second and most important factor is the re-aeration. The rate of re-aeration of water depends not only upon the oxygen concentration existing at the time but upon the vertical distribution of that concentration. Assume, for example, that the water is uniformly mixed and quiescent. Absorption at the surface leads to a downward diffusion which in time establishes a gradient ranging from essential saturation in the upper film to the initial concentration at some point below. The diffusion process becomes slower as the curve of distribution of oxygen becomes flatter. In practice, quiescent water, even though it start with zero oxygen concentration at all points, will, except in shallow layers, come to a condition of practical equilibrium with very low average oxygen concentration. Beyond this point the diffusion process is so exceedingly slow as to be quite negligible. Mixing of the water, after such a condition has become established, reestablishes the even distribution and allows the absorption to proceed toward a new condition of equilibrium. It is apparent, therefore, that, as conditions depart more and more from the condition of complete quiescence, the rate of re-aeration is increased accordingly. The departures from quiescence may be definitely stated, and are more easily conceived, as the average time between uniform mixings. This form of expression is used, not only because it gives a workable statement of the degree of agitation in a stream, but because such a time factor appears in any formula for re-aeration derived from the laws of solubility and of diffusion. Such a formula was developed by William M. Black, Colonel, Corps of Engineers, U. S. A., and the writer in an investigation of the pollution of New York Harbor.[1] In that case it was possible to determine the average time between mixings from a study of the mixing effect of winds, vessels and tidal currents. The re-aeration calculated from this theoretical formula, using the determined time factors, was in close agreement with the actual values found during the subsequent year and thus gave satisfactory confirmation of the accuracy of the method. With the deep and relatively quiescent waters of New York harbor re-aeration was found to be almost a negligible factor. The capacity of such a body of water to oxidize pollution is practically limited by the amount of available oxygen brought in from the ocean with each tide.

Under river conditions matters are directly reversed. The initial volume of available oxygen is small compared with the total capacity of the stream to oxidize pollution. Re-aeration in rivers is the chief factor. The time between mixings, instead of being measured in hours, is probably measured in minutes, so that its actual determination from direct observations cannot be made with even workable precision. It becomes necessary, therefore, to reverse our process of reasoning, to learn by suitable methods the actual extent of re-aeration, and, from those data, to derive the time factor in the original aeration formula. This factor will vary with the depth, character of the river bed, and rapidity of flow. It will differ, therefore, for various rivers and for various sections of each river but should be similar for similar types of stream. If it can be determined for a sufficiently large number of typical stream stretches, it may be possible to deduce general formulas which will be applicable to other streams of similar type. This, then, is the second important factor to be investigated in our stream studies and if it can be satisfactorily determined it should be possible to estimate the capacity of a given river to dispose of pollution without objectionable results, or, conversely, the effect of any stated pollution upon a river of given type.

The actual rate of re-aeration in a polluted stream cannot, unfortunately, be determined directly. In spite of re-aeration a stream at any given point may be losing oxygen, or it may be in oxygen equilibrium, since at all times the biochemical reaction tending to reduce the oxygen is opposed to the actual re-aeration. It is necessary therefore to develop suitable chemical methods for the separation of these opposing tendencies.

Consider first an ideal situation with two sampling stations on the stream between which stations there is no increment either to the pollution or to the volume of the stream. These conditions cannot, as a rule, be obtained and it is necessary to make suitable correction for the interference of additional pollution or additional dilution. The oxidizing reaction has been studied in the laboratory sufficiently to show that it follows a fairly definite course and like all biochemical reactions is essentially monomolecular in its order. This means that it proceeds at a constant rate or velocity so that the concentration of oxidizable material decreases as a logarithmic function of the time. A sample of the water from the upper station is submitted to study for the determination of three things: (1) The available oxygen which it contains; (2) the total amount of oxygen which will be required for the completion of the oxidizing reaction, known as the oxygen demand; (3) and the velocity with which that reaction proceeds. The sample from the lower station is submitted to the same examination. Since any loss of available oxygen by oxidation must give rise to an equivalent loss in the oxygen demand, the difference of these two terms would remain constant throughout the course of the reaction, in the absence of re-aeration. Any increase in dissolved oxygen at the lower station over the value calculated from the results of examinations at the upper station is therefore due to aeration. Correction for additional pollution or dilution between the stations is next made by means of the velocity of reaction determinations. From the determination at the upper station and the known time required for water to pass from one station to the other, the concentration of reacting substance at the lower station is calculated. With increasing dilution the concentration is decreased, while with increasing pollution it is increased. Any change in the concentration, calculated from an assumed constant velocity of reaction indicates an equivalent change in dilution or pollution between these stations. It is obvious that

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[1] Report of Colonel William M. Black, U. S. A., and Earle B. Phelps, on the "Discharge of Sewage into New York Harbor," March, 1911.

these two factors are opposed to one another in a plus and minus sense and that if the added water were of the same character relative to its pollution as the water under investigation, the correction factor would disappear. In brief, from the known constant velocity of reaction, stated in terms of physical chemistry, are determined changes in the concentration of the reacting substance, namely, pollution.

The actual laboratory technique of these determinations is simple. The usual dissolved oxygen determinations are made upon a freshly collected sample; a second sample is incubated at 20° C. and a dissolved oxygen determination made upon it at the end of any convenient period, usually 24 or 48 hours. The difference between these two results is the oxidation that has taken place in the interval. Knowing the form of the reaction curve one computes from this, first, the velocity coefficient of the reaction and then, by extrapolation to a very long time, the total oxygen demand of the polluting organic matter. These two determinations at each station furnish the required data, but there are many points that require special attention. It is necessary in the first place to secure an adequate sample of the entire cross section of the stream. This involves the careful selection of sample stations and the sampling of a stream at various points in the cross section both vertically and horizontally. It is desirable in the second place to select stretches involving a minimum correction for additional pollution or dilution and it is quite necessary finally to consider the effect of sedimentation. This can be arrived at only by a study of the surface of the river bottom. A special apparatus is necessary for the withdrawal of the surface deposit from a given area of bottom and it is necessary to make a careful survey of the river bottom between stations from time to time. A new reaction velocity must be determined for this deposited material and suitable correction made to the average findings in the water above for the period between the two bottom mud surveys. Finally the temperature of the river is not that at which the incubations are made. The temperature coefficient of the reaction must be known and suitable correction applied.

It will perhaps be noticed that no attention has been given in the foregoing discussion to the supposed relation between concentration of sewage in water and probable nuisance. This factor has heretofore been the chief theme in any discussion of stream pollution and self-purification. Recognized authorities have variously estimated stream flows of from 2.5 to 3.5 cubic feet per second per thousand persons contributing, as the danger line. A still less correct statement is often made in that sewage dilutions of from 1 in 16 to 1 in 23 will undoubtedly produce nuisance. A little consideration of the true factors of self-purification will show that any such form of statement is entirely incompatible with the facts. A deep quiescent swimming pool may become putrescent even with the slight amount of organic pollution which it receives. A one per cent dilution of sewage in water will often putresce under laboratory conditions. Deep and slow-moving bodies of water such as are found in canals or in rivers behind dams, especially if they be protected against wind action, have very little capacity for re-aeration and are in consequence much more affected by sewage than rapidly running and relatively shallow streams. The maximum oxidizing work occurs under conditions of minimum depth and maximum agitation. Any discussion, therefore, of permissible concentration of sewage in water without reference to the character of the stream in question is futile and misleading.

It is proposed to study by the methods outlined the rate of reaeration of the Ohio river at a great many points, but particularly below the three points of greatest pollution, namely, Pittsburg, Cincinnati and Louisville. In none of these cases are the conditions ideal and it will be necessary to do a large amount of work to obtain results of satisfactory precision. As an additional check upon results it is also proposed to make as thorough a study as practicable of the actual polluting material entering the river at these three points. The total oxygen demand and the velocity of the oxidizing reaction will be determined upon this initial pollution in a manner similar to that which has been described. In case of concentrated organic matter, the methods are modified by first diluting in suitable proportions with aerated water. Further checks upon the work involve similar studies upon the tributaries and upon pollution from smaller communities between stations. Moreover, instead of the two stations which have been used in illustration, the work will actually comprise a chain of stations for regular study. In addition, connecting data will be obtained by means of house boat laboratories. The three regions of maximum pollution are fortunately of three distinct types. The river below Pittsburg is a series of short pools separated by shallow water flowage. Below Cincinnati there is a long quiescent stretch in which sedimentation will be an important factor. At Louisville there are rapids giving a minimum of sedimentation and a maximum of aeration. Certain special minor points such as the effect of low temperature upon aeration and the effect of long quiescent stretches upon sedimentation will also receive special study.

It is anticipated as a net result of this chemical portion of the Ohio river investigation that sanitarians will be in a position to discuss with much more assurance than at present the general principles which underlie the phenomenon of the self-purification of streams.

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THE APPLICATION OF PHYSICAL CHEMISTRY TO INDUSTRIAL PROCESSES[1]

By Walter F. Rittman

The luxury of today is the necessity of tomorrow; likewise the theory of today is the practice of tomorrow. Gayley's process of drying air for a steel furnace, the various nitrogen-from-air processes, the contact process of manufacturing sulfuric acid, synthetic indigo, synthetic tanning materials—all were in the field of abstract theory but a few years ago. Today they are practical realities. Similarly, many of the theoretical principles and processes of today will, in all probability, be realities a few years hence.

The invasion of chemistry by physics, and the production of what is known as physical chemistry, promises to be a most important basis for progress in the field of applied chemistry. Whereas physical chemistry is often looked upon as one of our most theoretical subjects, it will be found to be one of our most practical as well. Its principles are useful regardless of the materials involved in the reactions, whether copper, steel, soap, glass, cement, gas, textile, or any other chemical product. Physical chemistry is described as that branch of chemistry which has for its object the study of the laws governing chemical phenomena. When these laws and their application to a reaction or process are once understood it is a relatively easy matter to select the most favorable physical conditions. The task of the chemical engineer is to produce these most favorable working conditions in an apparatus which operates on an industrial scale. A further advantage of a knowledge of theoretical principles and perhaps one to be more frequently applied is the aid such knowledge gives in avoiding fantastic so-called improvements.

The chemical engineer rarely creates new products; he deals with processes and machinery which produce quantities economically. Obviously his problems often differ from those of the laboratory chemist. The fact that a reaction is slightly exothermic or endothermic is of secondary consequence in laboratory experiments, but in applied engineering this fact at once de-

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[1] Presented at the 6th Semi-annual Meeting of the American Institute of Chemical Engineers, Troy, New York, June 17–20, 1914.

termines whether the reaction should be carried out in a cooled or in a heated apparatus. The amount of heat given off in a reaction, such as the hydrogenation of a vegetable oil, is of no serious consequence in laboratory experiments, but where tons are handled the accumulated heat is sufficient to ruin any process which does not provide for its disposal. Latent heat of fusion or of evaporation is not important in the laboratory where there is always an excess of heat or cold, but in many cases this heat of fusion or of evaporation becomes all important in its influence on the cost of an industrial operation. The cost of the heat absorbed by an endothermic reaction seldom concerns the laboratory chemist; but it is profit or loss to the chemical engineer. The percentage of yield, and the cost per unit, are the vital questions to the engineer; they are usually not vital to the laboratory chemist, however valuable and constructive his work may be.

It sometimes seems as if the inertia of years has limited the temperature imagination of many engineers and some chemists. Theoretical considerations might suggest the broad field which comprises the several thousand available degrees above the boiling point, as well as the 273 degrees below the freezing point of water. Likewise, we are prone to overlook the great advantages which sometimes may be derived from the application of pressures greater or less than the one atmosphere which surrounds us and with which we are so familiar.

Because of the numerous possibilities in the application of physical chemistry to industrial processes, I must greatly restrict myself in dealing with the subject. Some of the most interesting parts deal with equilibrium relationships, phase rule applications, radioactivity, energy considerations and electrolytic reactions. Excellent examples illustrating the successful application of each can be found, but today I shall deal in some detail only with the one mentioned first, *i. e.*, equilibrium relationships.

I shall not attempt to deal with every branch of modern production which involves the equilibrium relations of physical chemistry, nor shall I attempt to advance speculations as to future applications of equilibrium relations in industry. The attempt will be confined to successful present-day applications, by way of examples. However familiar these processes may be, I hope that there will be at least something interesting, if not new, in pointing out that these familiar processes have a purely theoretical aspect. In fact, dealing with them historically indicates that they have all developed out of the most abstract theoretical reasoning into the practical machinery of economical production.

OXIDATION OF NITROGEN FROM AIR

It is known that at room temperature there is no perceptible union of the nitrogen and oxygen of air; it is known that at temperatures as high as 3000° C. only a partial union takes place; it is known that the amount which does unite is a function of the temperature; that is, at each temperature there is a definite percentage of nitric oxide formed, and equilibrium exists between the combined and uncombined constituents. In other words, the tendency of the uncombined constituents to combine at any particular temperature is exactly counterbalanced by the tendency of the combined constituents to separate at that temperature. There is a true equilibrium. Experiment has proven that when air analyzing 79.1 per cent N_2 and 20.9 per cent O_2 is brought to equilibrium at 2400° C. the resultant mixture analyzes 2.23 per cent NO, 77.98 per cent N_2 and 19.78 per cent O_2;[1] *i. e.*, 1.116 per cent of an atmosphere each of nitrogen and oxygen have disappeared in the formation of nitric oxide. Further, let it be clear that this 2.23 per cent of NO obtained at 2400° C. is not an accidental figure; it will always be the same when air of the above composition is brought to equilibrium at 2400° C. This fact makes it possible to calculate the equilibrium constant for nitrogen, oxygen and nitric oxide at 2400° C.

$$N_2 + O_2 \rightleftarrows 2NO - 43200 \text{ cal}$$

$$K_{2400° \text{ C.}} = \frac{p^2_{NO}}{p_{N_2}p_{O_2}} = \frac{(0.0223)^2}{(0.7798)(0.1978)} = 0.0032$$

where p represents the partial pressures of each of the three constituents; *i. e.*, the part of the whole pressure exerted by each. The constant K which joins these partial pressures has a definite numerical value for each definite temperature. The square of the partial pressure of NO, divided by the product of the partial pressure of N_2 multiplied by the partial pressure of O_2, for any mixture of these three constituents in equilibrium at 2400° C. will be equal to 0.0032. Through the application of thermodynamic principles,[1] it is possible to calculate the value of K' for any other temperature from the above experimentally determined value of K for 2400° C. From this value of K' for any other temperature, as 3000° C., for example, it becomes a simple matter to calculate the yield of NO which will be obtained from any initial mixture of nitrogen and oxygen brought to equilibrium at that temperature. Percentages of N_2, O_2, and NO which satisfy the equilibrium relationship for any temperature will always be obtained when these constituents are brought to equilibrium at that temperature. Further, the reaction is reversible, and reaches the same results from either direction. A number of values for equilibrium constants of this reaction at different temperatures have been calculated. From these values the percentage yield of NO from air has been calculated, and the calculations have been checked, as follows:[2]

TABLE I—COMPARISON OF CALCULATED AND OBSERVED VALUES OF EQUILIBRIUM CONSTANTS FOR THE $N_2 + O_2 \rightleftarrows 2NO$ REACTION

Temperature ° C.	NO (calculated from values of K) Per cent	NO (observed) Per cent
1538	0.35	0.37
1604	0.43	0.42
1760	0.67	0.64
1922	0.98	0.97
2307	2.02	2.05
2402	2.35	2.23
3060	5.00	..

It is observed that until 3000° C. is exceeded the yield of NO is below 5 per cent. The above clearly indicates how theoretical considerations show the limits of a reaction as well as the most favorable conditions for its industrial application. The oxidation-of-nitrogen process obviously is limited in practical application to localities where large quantities of cheap electric power are available.

CONTACT PROCESS OF MANUFACTURING SULFURIC ACID

The contact process of manufacturing sulfuric acid, considered from the equilibrium view point, can be expressed by the equations:

$$SO_2 + {}^1/_2O_2 \rightleftarrows SO_3 + 22600 \text{ cal.}$$

$$K = \frac{p_{SO_3}}{p_{SO_2}\, p_{O_2}{}^{1/2}}$$

A few values of K follow:[3]

TABLE II—CONSTANTS FOR CONTACT PROCESS OF MANUFACTURING SULFURIC ACID

Temperature ° C.	K_p (experimental)	
400	580	(calculated)
450	188	
515	65.4	
600	14.9	
800	1.81	
900	0.57	

Upon calculating the maximum yields of SO_3 obtainable at the different temperatures from the various values of K, it is

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[1] Nernst-Finckh, *Z. anorg. Chem.*, **1905**, p. 116; *Ibid.*, **1906**, pp. 212, 229.

[1] Nernst, "Theoretical Chemistry," 7th German edition, pp. 575–6; Morgan, "Elements of Physical Chemistry," 5th edition in press.

[2] Nernst, *Z. anorg. Chem.*, **1906**, pp. 213–228; *Z. f. Elektroch.*, **1906**, pp. 257, 529; Jellinek, *Z. anorg. Chem.*, **1906**, pp. 229–276; Nernst-Finckh, *Z. anorg. Chem.*, **1905**, p. 116.

[3] Knietsch, *Ber.*, **1901**, p. 4069; Bodländer, u. Köppen *Z. f. Elektrochem.*, **1903**, p. 787; Bodenstein u. Pohl, *Ibid.*, **1905**, p. 373.

observed that the yield rapidly decreases as the temperature increases. This is in contrast to the nitric oxide illustration where the yield of NO from N_2 and O_2 increases with the temperature. As the temperature increases in the $SO_2 + O_2$ reaction the values of the equilibrium constants decrease rapidly. At temperatures below 400° C., however, the union of SO_2 and O_2 is too slow for an industrial process. At this temperature there is but a slight sacrifice of the percentage of SO_2 and O_2 combination.

Temperature, however, is not the only thing which influences a reaction of this nature. Without entering into a mathematical discussion of the influence of pressure we can recall LeChatelier's principle: that pressure stimulates those reactions involving contraction, while vacuum encourages those reactions involving expansion.

Further, temperature and pressure do not complete the factors influencing chemical reactions where equilibriums are involved. The third and important factor is the relative concentration of the various reacting elements. The SO_3 reaction furnishes an excellent example showing the influence of the concentration of the combining reagents. Observing the mathematical expression for the equilibrium relationship,

$$K = \frac{p_{SO_3}}{p_{SO_2}\ p_{O_2}^{1/2}} \quad \text{or} \quad \frac{p_{SO_3}}{p_{SO_2}} = K\sqrt{p_{O_2}}$$

it becomes evident that the relative yield of SO_3, with respect to SO_2, increases as the partial pressure of oxygen increases, since the value of K for any given temperature does not change. This can best be observed by giving K the arbitrary value 200, and assigning to O_2 the partial pressures 0.25, 0.50, 1.00 and 2.00: Then

$$\frac{SO_3}{SO_2} = 200\sqrt{\text{partial pressure } O_2}$$

and the ratios desired are given below:

TABLE III—EFFECT OF CHANGING THE CONCENTRATION OF ONE OF THE CONSTITUENTS IN AN EQUILIBRIUM

Partial pressure of oxygen	Ratio of SO_3 to SO_2
0.25	100
0.50	141
1.00	200
2.00	282

This influence of an excess of oxygen is of practical value and is used in the commercial manufacture of SO_3.

SYNTHESIS OF AMMONIA FROM HYDROGEN AND NITROGEN

Another illustration of the factors entering into chemical equilibriums involving temperature, pressure, and concentration is the Haber method of manufacturing ammonia from nitrogen and hydrogen.[1] The synthesis of ammonia from nitrogen and hydrogen depends upon the equilibrium represented by the expression,

$$\underbrace{{}^1/_2N_2 + {}^3/_2H_2}_{\text{2 volumes}} \rightleftarrows \underbrace{NH_3}_{\text{1 volume}} + 1300 \text{ cal.}$$

$$K = \frac{p_{NH_3}}{p_{N_2}^{1/2}\ p_{H_2}^{3/2}}$$

A few investigated values for K follow:[2]

TABLE IV—EQUILIBRIUM CONSTANTS FOR THE AMMONIA SYNTHESIS

Temperature ° C.	K (experimental)	K (calculated)
700	....	0.00068
800	0.00033	0.00036
1000	0.000148	0.000145

Haber[3] found that as the temperature rises above 500° C., the yield of NH_3 is low, while below 500° C., the rate of reaction is too slow. He eventually so perfected his experimental apparatus that his yields of NH_3 permitted him to calculate K from experimental data and compare the same with theoretical values. The close correspondence of the theoretical and actual values indicates how experiment reinforced by theory will often show what can be expected in practice better than imperfect experimental results without theory. Without theory, in fact, Haber would never have known whether his experimental work was perfect, imperfect, or worthless.

In this ammonia reaction, equilibrium relations are such that when the reaction is practiced under atmospheric pressure the maximum yield is not sufficient to warrant industrial application. A yield of less than one-quarter of one per cent is of little more than scientific interest. Through the introduction of increased pressures, however, the contraction from two volumes to one volume is greatly favored and the process yielding twelve per cent at once becomes of decided commercial interest. In the oxidation-of-nitrogen process, on the other hand, there is no change in the number of volumes, and pressure is without influence on the reaction. This pressure influence in connection with equilibrium relations is strikingly shown in Table IV.[1]

TABLE V—PERCENTAGE OF NH_3 IN THE EQUILIBRIUM OF THE REACTION $N_2 + 3H_2 \rightleftarrows 2NH_3$

Pressure in atmospheres	Temperature ° C.				
	550	650	750	850	950
1	0.0769	0.0321	0.0159	0.0089	0.0055
100	6.70	3.02	1.54	0.874	0.542
200	11.9	5.71	2.99	1.68	1.07

OTHER APPLICATIONS OF EQUILIBRIUM RELATIONS

The equilibrium relationship between reacting agents persists throughout all chemical phenomena. The relative amount of CO_2 to CO issuing from a furnace is primarily a function of temperature and pressure, and is influenced by the machine only in so far as the machine influences these variables. The equilibrium between CO_2 and CO in the presence of carbon for any temperature is reached regardless of whether one starts with CO or with CO_2, or with any mixture of the two.

$$CO_2 + C \rightleftarrows 2CO$$

$$K = \frac{p_{CO}^2}{p_{CO_2}}$$

TABLE VI[1]—EQUILIBRIUM RELATIONS BETWEEN CO AND CO_2 IN PRESENCE OF CARBON

Temperature ° C.	Per cent by volume	
	CO	CO_2
450	2	98
750	76	24
1050	99.6	0.4

Typical examples of this relationship are found in the kitchen stove, the factory boiler, the blast furnace, the gas machine or the open hearth furnace. Doubling the size of the blast furnace changes the relative amounts of CO_2 and CO only so far as doubling the size of the furnace influences the temperature in the various reacting zones. With increasing temperature the percentage of CO increases, with decreasing temperature the percentage of CO_2 increases. In the blast furnace, for instance, not only are the CO and CO_2 in equilibrium, but the various oxides of iron are likewise in equilibrium with carbon, CO and CO_2, as well as with one another. Consider the blast furnace reactions:

$$\begin{aligned} 2CO &\rightleftarrows C + CO_2 \\ Fe_2O_3 + CO &\rightleftarrows Fe_3O_4 + CO_2 \\ Fe_3O_4 + CO &\rightleftarrows 3FeO + CO_2 \\ FeO + CO &\rightleftarrows Fe + CO_2 \end{aligned}$$

from the equilibrium point of view; there is found to be a vital relationship between them. On first sight a series of equations of such a nature looks very complex, but on the application of equilibrium relationships, formulated by means of the phase rule diagram, it is found to be relatively simple and clear. Experimental work[2] has been done on these relationships, from which it is possible to plot the diagram of equilibriums.

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[1] *Zeitsch. f. Elek.*, **1913**, p. 53.

[2] F. Haber, "Thermodynamics of Technical Gas Reactions."

[3] F. Haber, THIS JOURNAL, **6** (1914), 325.

[1] J. Mellor, "Modern Inorganic Chemistry," p. 713.

[2] Baur und Glaessner, *Z. physik. Chem.*, **1903**, p. 354.

All of the reactions are reversible, their direction is entirely a function of temperature. From the diagram, the fields of stability of Fe, FeO and Fe_3O_4 in the presence of CO and CO_2 for the temperatures shown can be observed. It can be noted for example, that FeO at 650° C. is not stable in the presence of more than 65 per cent or less than 43 per cent CO_2. It becomes evident that in the reduction of FeO to Fe a maximum of CO_2 in the flue gases is obtained when the reaction takes place at about 675° C., and that this percentage of CO_2 decreases as the temperature increases. The diagram indicates that most of the reduction takes place in the cooler part of the furnace.

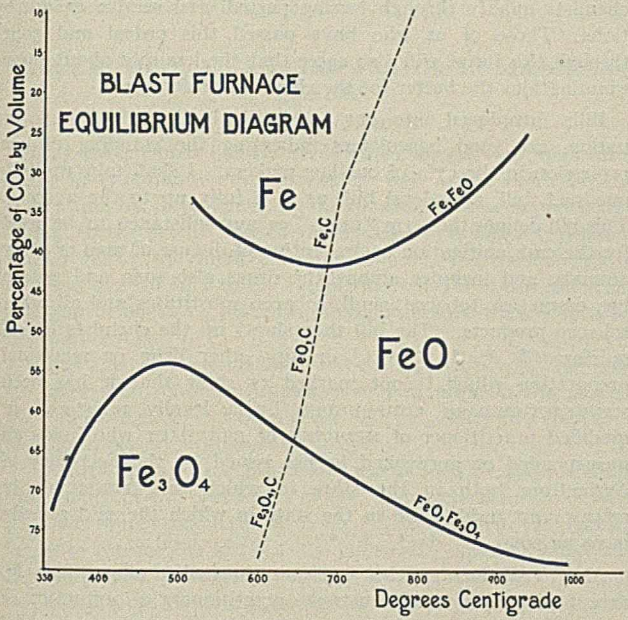

FIG. I.—BLAST FURNACE EQUILIBRIUM DIAGRAM, SHOWING RELATIONS BETWEEN C, CO, CO_2, FE, FEO, AND FE_3O_4

COEFFICIENT OF PARTITION OR DISTRIBUTION

Equilibrium conditions also prevail in the more purely physical world as well as in chemistry. A solute which divides itself between two immiscible solvents will always be found in a definite concentration in both solvents, and there will always be a definite ratio between the concentration in each. This ratio is known as the partition or distribution coefficient. I will cite first the laboratory example dealing with iodine, water and carbon disulfide. Iodine is slightly soluble in water and much more soluble in carbon disulfide, while water and carbon disulfide are practically insoluble in each other. Suppose we have both water and carbon disulfide in one vessel and add some iodine. It has been observed from experiments that the concentration of iodine in the carbon disulfide is 588 times the concentration of iodine in water. In other words,

$$K_{\text{Iodine}} = \frac{C_{CS_2}}{C_{H_2O}} = 588$$

In similar manner, iodine divides itself between ether and water so that the concentration of iodine in the ether is 200 times the concentration of iodine in the water.

$$K_{\text{Iodine}} = \frac{C_{\text{ether}}}{C_{\text{water}}} = 200$$

Similar examples can be found in the distribution of acetic acid between benzene and water, benzoic acid in benzene and water, succinic acid in ether and water, acetic acid in chloroform and water, saccharin in ether and water, acetanilid in ether and water, vanillin in ether and water, or acetanilid in chloroform and water. This aspect of equilibrium is finding application in analytical chemistry, more especially in that branch dealing with alkaloids.[1] Through its application the haphazard washing out process in alkaloid work is replaced by one of mathematical precision. Technical application can be found in Parke's process for extracting silver from lead. Silver is very much more soluble in zinc than in lead, whereas lead and zinc are only slightly soluble in each other. The lead containing silver is melted and thoroughly mixed with a small proportion of zinc. The zinc floats to the top, carrying with it in solution practically all of the silver, and on cooling solidifies while the lead is still molten. The zinc containing the silver is then skimmed off, and these two constituents separated.

Lack of time forbids the consideration of the equilibrium relationships existing in the ionization of acids, bases and salts. Their application in analytical chemical methods is today a reality; their technical application promises much.

EQUILIBRIUM RELATIONS ARE OF GENERAL APPLICATION

The equilibrium or kinetic relationship is accepted and used by theoretical chemists, and is believed to prevail in practically all fields of chemistry. When considered in mathematical units it changes qualitative suggestion into quantitative information. Equilibriums deal with yields in terms of percentages or weights, they deal with temperature, pressure and concentration in numerical terms. When so applied, they are concrete and cease to be more theoretical than any other mathematical statement.

Equilibriums exist between reacting agents in solution; between reacting liquids; between liquids and vapors; solids and liquids; solids and gases; between gases which react chemically; between the concentrations of a solute divided between two immiscible solvents; in the ionization of acids, bases and salts, in hydrolysis and saponification; in fact in all the chemical and physical phenomena with which the chemist or the chemical engineer deals. The industrial development and application of physical chemistry, including this equilibrium principle, is only partially realized today; its further development and application seem to depend largely upon competition and necessity, and the stimulus they offer to the inventive faculties of chemical engineers as the leading specialists in this most promising field of our science.

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STANDARDS OF FOOD AND DRUG CHEMISTS[1]

By EDWARD GUDEMAN

The Food and Drug chemists are those who today are and should be vitally interested and concerned with the health and well-being of the inhabitants of communities, state and nation. What is the standing of the chemists in the United States, not as we see ourselves but as others see us? In fact do we as a profession exist at all? Have we any rights or standing and if so, where, what are they, how do we get them and what do they amount to, outside of our own family circle?

I broached this matter before our local Chicago Section and was told that my remarks were funny, which recalled to me what a great German poet and philosopher said—"Die Sache wäre lächerlich, wäre sie nicht so fürchterlich," freely translated as—"The matter would be laughable, were it not so terrible."

Have you recognized that every great discovery or advancement, made within the last decade or two, that directly affects the health and well-being of the human race, depends directly on chemistry and its application?[1] All advances and progress in biology, physiology, medicine, pharmacy, dentistry, veterinary practice, sanitation and health protection of the individual or community is directly based on a chemical foundation. Let me illustrate with a recent publication, *Science*, March 27, 1914, "Action on Vital Stains, Etc," by Evans and Schulemann,

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[1] J. W. Marden, THIS JOURNAL, 6 (1914), 315.

[1] Presented at the 49th Meeting of the American Chemical Society, Cincinnati, April 6–10, 1914.

giving the results of biological, physiological, medical research work affecting the human body, based directly on the most modern branch of chemistry, that of the colloids. Not alone internal medicine, but surgery of today uses chemical substances to act on the nerves or nerve centers to overcome "shock." Are we not today, in the chemical laboratories, separating and manufacturing the substances that cause toxic and anti-toxic effects? Do we not know today that digestion is not due to "organs" or a "vital" force, but that it is a direct analytical or synthetic chemical process? Do we not produce today outside of the animal body the exact products that are produced in the body? I am certain that many diseases will, within a reasonable time, be greatly benefited by direct chemical treatment. As a special example I wish to cite the use of sulfurous acid fumes and chemical anti-toxic serums in the treatment of the early stages of tuberculosis.

We use many descriptive adjectives in connection with our profession, such as medical, biological, physical, electrical, pharmaceutical, sanitary and XYZ chemistry, making our profession the handmaid to the other professions. Let us see where the agricultural, food or drug chemist stands today compared with other professions, such as the medical, pharmaceutical, veterinary and legal professions. Is it not true that to practice any of these professions in most states or communities, a diploma from a recognized institute of learning is required, besides a special license or permission to practice? Is not such license issued only by some board or commission or committee, on whom is conferred, often by legislative act, the right to issue such permit? The granting of such license, with or without special examination, carries with it the legal right to kill or cure, the right of depriving you of your liberty for a greater or lesser time. All these professions have conferred on them the legal or public right to render their verdict of "to be or not to be." Where does the chemist come in? We do not even get the leavings. "There ain't no core" for us, as the other professions are individually or collectively the whole thing, and we chemists are the bung-hole of the barrel, a perfect nothing.

It is true that a limited number of chemists have some "recognized" standing. I refer to the so-called "official" chemists. Who are they as a body, and what makes them "official," and what does the designation "official" mean? Anybody or any concern, any school, college or university, private or incorporated, can attach to itself a chemist and immediately such chemist becomes the "official" chemist of the party, concern or institution, and remains such official chemist as long as he remains on the payroll; with the loss of the position goes the "official" standing. I am not against the "official" chemist as I have to admit that I am one myself.

Now what standing has an "official" chemist? Many of you may agree or disagree with me, that as soon as one qualifies in court as an "official" chemist, more weight is given to the testimony, than to that of the non-official chemist, without due consideration to the ability or capability of the chemists involved. Often the qualification as an "EX Official" gives extra weight to the testimony. Often official chemists from the same laboratory testify on collaboration work, thereby getting the double advantage of that due to the "official" standing and the preponderance of testimony. It is unfortunate that the courts often hold the testimony of the "official" chemist as being neutral and unprejudiced, and the testimony of the non-official chemist as that of a partisan. This applies more especially to official chemists connected with city, state or national bodies. My own observation has been that there are as many non-partisan non-official chemists as there are partisan official chemists, and I have also found that change from "official" to "non-official" chemist often carries with it a quick and radical reversal of opinion.

The chemical profession is not recognized as it should be, since we have no legal or legislative standing, such as have the other professions mentioned. It is a fact that in the State of Illinois, you cannot run an automobile or an engine, nor a barber-shop, nor can you be a boot-black, nor an undertaker, without having a special city or state license to practice these professions, and in many cases a special examination is required to obtain the license. I am perfectly aware that many "official" chemists qualify through having passed civil service examinations. Those of us who have passed this ordeal and gone through this farce, will also agree that the less said about these examinations the better for the chemical profession.

Bills introduced into our legislative bodies, city, state or nation, are good barometers indicating the standing of our profession in the eyes of our law makers. I shall take up only one such bill, a Federal bill, as it is fully up to the average. This bill defines the term "DRUG" as any substance to be used for the cure, mitigation or prevention of disease of man or other animals, and includes among the drugs also soda and potash lye, cosmetics, tobacco, snuff, tobacco substitutes and all other tobacco products. The bill then shows up the chemists by requiring "* * * * * * or any other drug or medicinal preparation which is not marked to show that it has been MANUFACTURED or COMPOUNDED by a legally registered or qualified practitioner of MEDICINE or PHARMACY who holds an unsuspended or unrevoked license issued by the Secretary of Agriculture both in the state in which said PHYSICIAN or PHARMACIST resides and in the state in which the said remedy IS TO BE SOLD * * * * *"

Also: "All these articles or preparations when offered for sale, except prescriptions of LICENSED practitioners of MEDICINE or DENTAL-SURGERY or VETERINARY SURGEONS in the course of their personal practice shall bear a label containing not only the name by which they are known but also the names of the parent substances from which they are derived."

This bill creates a monopoly for the medical man and the pharmacists in the manufacture of food and drug products. There are some very good points in the bill, as tobacco, snuff and other tobacco products must come up to a fixed standard. You must be sure that you do not handle any smoking, chewing or snuffing tobacco that: "consists in whole or in part of filthy, decomposed or putrid animal or vegetable matter." It may be on account of the animal matter in tobacco that the bill recognizes the veterinary profession. The exclusion of some kinds of vegetable matter from tobacco may help reduce the high cost of living, by forcing back into its natural food channel—cabbage. Another excellent point in this bill is that it does away with the misunderstanding as to "like substances" found in the Food and Drugs Act of June 1906. This new bill does not recognize that term and replaced it with the easily understood term of "similar substances."

As I do not want to start any discussion on State Rights, I have selected a bill introduced into Congress by a member from Illinois.

Does it not strike you as peculiar, to use a very mild expression, to find legislative acts, enumerating a large number of drugs and chemical products, or derivatives of parent chemical products, pure chemicals and synthetic products of the chemical laboratories, all full-fledged children of chemistry, not even half-orphans, and the chemists, the natural parents or guardians of their offsprings, ABSOLUTELY IGNORED, and the manufacture and sale directly placed under the supervision of only distant relatives, those belonging to the MEDICAL, PHARMACEUTICAL or VETERINARY professions? What is the reason? Is it due or partly due to the fact that anybody can call himself a chemist in the UNITED STATES and get away with it? Is it because the standard or quality of any food or drug can be passed on by anybody? Is it not time for the chemists, especially those who are interested in the health and welfare of their fellow beings, to do something, to get the recognition due them and to place the profession on the high plane which it should occupy? In Illinois the only two SCIENTIFIC professions that can be followed by anyone without license, or permit, or qualification to practice, are those of COOKS and CHEMISTS. What shall we do and what is the cure, remedy or prevention? Is it not time for the CHEMIST to take a stand for a standard of the CHEMIST?

POSTAL TELEGRAPH BUILDING, CHICAGO

THE CHEMIST, A GROWING FACTOR IN MERCHANDIZING[1]

By A. V. H. MORY

That the chemist has for some time been a very important factor in manufacture is everywhere well recognized. On the other hand, his employment by the consumer has been practically limited to the extent that the manufacturer is also a consumer. Until recently the small consumer has enjoyed the benefits of chemical control only to the extent that control of raw materials and improvement of processes of manufacture work indirectly to his advantage.

Under the old trade maxim, "Let the buyer beware," the need for more than off-hand inspection of purchases on the part of the small consumer has been great, but his ability to afford such inspection plainly negligible.

At an early day little protection was needed by the consumer since many of the necessities of life, and such luxuries as were afforded, were produced at home. Later, when the factory began to replace the kitchen, the churn, the spinning wheel and the loom, and powdering, mixing, coating, coloring, flavoring and preserving frequently made the original raw material well-nigh unrecognizable, sophistication became increasingly difficult of detection. With the introduction of package goods and the necessary label came also the opportunity and temptation to misrepresent.

It is well to remember in this connection, however, that the beginnings of adulteration and misbranding were certainly the work of only a relatively small class in the community—the unfair minority—though it must be admitted that with unfair competition thus set up, the relatively honest majority too often felt the necessity of meeting such competition in kind.

The introduction of these abuses was naturally a gradual process, as was also the development of resentment on the part of the consumer, but the latter finally began to feel that under our form of government, in which the majority is at least entitled to rule, the interest of the consumer, who is in the vast majority, is certainly the matter of first consideration. This awakening public sentiment has caused the enactment of commodity laws, which though designed originally to protect the consumer, are bound to result through the elimination of unfair competition in great good to the majority of producers and distributors as well.

This "business honesty" legislation began with laws governing the character and description of commodities related in part to the matter of public health, *viz.*, foods and drugs, but has already been supplemented by laws regulating the character and description of other commodities and is rapidly spreading in its application to the whole business fabric. The public sentiment that is bringing this about is no doubt being influenced by the fact that the enforcement of these food and drug laws has uncovered more of simple fraud than of injury to health. As greatly to be desired, therefore, as is the protection of the health of the people, still, where health is not involved, there is no logic in requiring a higher standard of honesty for one class of commodities than for another. As there can be no doubt of the permanency of these initial laws, we may expect the future to give us laws designed to eliminate fraud not only from foods and drugs but from commodities in general. A beginning made in the case of insecticides, paints, and honest weights and measures, is destined soon to be extended to include textiles, metals and other commodities whose off-hand valuation is difficult or impossible.

Again since the individual consumer has little or no opportunity to protect himself when off-hand inspection is inadequate, we are coming to recognize that, as representing the vast majority of the people, he is entitled to the protection that comes from placing the responsibility as to quality and description upon the producer and distributor. And so it is that the old rule of trade, "Let the buyer beware," is giving place to the more logical and fair requirement, "Let the seller beware," a principle which finds its natural expression in the commodity law.

Though this new rule of trade is coming in through the demand of the buyer, still the far-sighted seller is beginning to look upon it as more of an asset than a liability. He knows that permanent success must rest on the continued satisfaction of the buyer, and that this satisfaction may be depended on to continue only so long as he, the seller, is willing to take upon himself the obligation of seeing that the quality, as well as the price, is right. Furthermore, he knows that the degree of the buyer's satisfaction depends not entirely on value, since the buyer may not be a good judge of values, but depends rather on the ratio between realization and expectation—a fact suggesting the disadvantage of extravagant advertising. Accordingly, the merchant is coming to believe that the only permanent basis of successful merchandizing, at least in this day and age, lies in the sale of none but dependable goods, and that through a medium of advertising that is both truthful and accurate.

The notion that the merchant's obligation is fulfilled when he sells his wares simply for what they are represented to him to be is rapidly passing, along with the fallacy that the press has no responsibility for the character of its advertising matter. Likewise the merchant who hides behind the excuse that he has no way of knowing whether or not his goods are what they are represented to him to be, is going to have to give way to the merchant who acquires means of finding out.

It is here that the chemist makes his entrance. His is the work of appraising value when off-hand inspection proves inadequate—the work of finding the small percentage of cotton in the "all wool" suit, an adulterant which the touch of the expert might fail to reveal; of finding the same cheaper fiber that may lessen the value of the linen table cloth and the silk dress; of determining whether or not the filled gold watch is indeed worthy of the name; whether the linseed oil is true to name and the turpentine not obtained in part from mother earth or from another cheap source. Indeed the merchandise chemist's problems may well be many, if he turn his attention to all that might be improved through his criticism. If his work lie in the field of foods, drugs, insecticides, or in any other covered by inspection laws, he has the added responsibility of protecting his employer from the bad advertising that even being the distributor of illegal goods is likely to entail. The guaranty of the seller may be depended on to forestall prosecution, but ignorance as an explanation of the possession of contraband goods cannot be expected to satisfy the customer. There is therefore a growing suspicion that the safe course lies in criticizing one's own product more severely than any public official would have the heart to.

Possibly some may be thinking of our merchandise chemist as an analyst, pure and simple, but he must be more than this. To be sure, analysis must precede criticism, but criticism, which is the interpretation of analysis—the rendering of an opinion as to value—is the service really required.

As value is a purely relative matter, no opinion worth while is possible without a standard for comparison. The selection of

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[1] Presented at the 49th Meeting of the American Chemical Society, Cincinnati, April 6–10, 1914.

suitable standards is a work of first importance, therefore, and one of no little difficulty. Much along this line has been and is being done by various organizations, but a much greater part remains to be done. With the advent of commodity laws has naturally come greater attention to standards as a necessary basis of criticism of both product and label, and much of value is to be expected from this source.

We turn aside to observe, in this connection, that these commodity laws can scarcely serve the consuming public better than through the establishment of standards specifying properties and constituents, and even origin and method of production when necessary, since the general adoption of such standards will tend in the long run not only to improve quality but to reduce the cost to the consumer. We hear much of the advantage by way of uniformity of quality, that is associated with proprietorship and the "coined name," but this advantage too often costs the public much more than it is worth. The justice of rewarding the author of a new and useful idea, as voiced in our patent laws, is easily granted, but the collection of tribute through the employment of secrecy and much advertising is quite another matter. When superiority is measured largely or entirely in terms of printer's ink, the consumer pays the printer and gets little or nothing but misinformation for his added expenditure. The remedy for such abuses must come, in part at least, through the adoption of commodity standards.

In this work of the preparation of standards, in fact, wherever opportunity offers, the merchandise chemist may logically join hands with those engaged in the enforcement of commodity laws, since such laws are now generally acknowledged to give expression to the principles underlying permanent success in his own field. He must furthermore keep in close touch with all the laws that affect his goods, for he must conform to the letter as well as to the spirit of the law.

It is plainly this necessity of meeting the requirements of commodity laws, present and to come, that is largely responsible for the growing demand for the chemist in the field of merchandizing. It is important to note in this connection that though our present commodity laws have come through the demand of the consumer, our future laws of this sort are likely to be welcomed (as is the continuance of our present laws desired) by the business world, which is coming to look upon success as something to be attained through service rather than through exploitation, and is tending to be guided by an enlightened self-interest that welcomes the law that commands strict obedience to basic principles of honesty, since thereby comes the elimination of unfair competition.

That we are destined to have general commodity laws in the not distant future appears certain. Even without the necessity of law obedience a broad merchandizing policy is already finding much need for the chemist. With the coming of general commodity laws there will be added many new fields in which the importance of the chemist's work will amount to a necessity.

CHICAGO

CURRENT INDUSTRIAL NEWS

By M. L. HAMLIN

CHEMICAL INDUSTRY AND TRADE IN AMERICA IN 1913

In an article in *Chemie*, June 6, 1914, a large amount of statistical data concerning chemical trade in this country appear. It is as yet too early to gain from these data any precise information as to the permanent effect of the new tariff on this branch of foreign trade, but it is stated that the imports of chemicals, drugs, dyes and medicines in November and December of last year were about five million dollars less than in the same months of the previous year, while the value of these articles imported during the whole of 1913 was in round numbers $101,000,000 as compared with $87,000,000 in 1912. Of these materials, goods to the value of $67,000,000 came in duty-free. The exports of these classes of articles amounted to $27,000,000 in 1913 and $26,000,000 in 1912.

In general, chemical technology is not as advanced in this country as in Europe, and it is those things that are manufactured by comparatively simple methods, such as sulfuric acid, soap, cement, petroleum products, and vegetable oils that form the bulk of American chemical manufactures. While the manufacture of complicated organic products like artificial perfumes has increased greatly in the last few years, the inorganic and electro-chemical fields are the most highly developed.

The petroleum trade in its relation to Germany is shown in the following table:

OIL EXPORTS TO GERMANY

	1911	1912	1913
Light oils	$5,510,000	$5,502,000	$4,526,000
Lubricating and heavy paraffin oils	2,628,000	3,284,000	3,661,000

Exports of gasoline have increased enormously but the amount sent to Germany is not given in the statistics. In 1913, Belgium imported $276,000 and Holland $905,000 worth, while to the rest of Europe the United States sent $4,600,00 worth.

The chemical and related imports into and exports from the United States in 1913 were as follows:

IMPORTS

CHEMICALS	1912	1913
Arsenic and arsenic sulfide	$ 247,000	$ 276,000
Calcium chloride	597,000	510,000
Calcium nitrate	689,000	500.000
Iodine	737,000	521,000
Magnesite	1,266,000	1,669,000
Acids:		
Carbolic	706,000	558,000
Acetic	51,000	....
Oxalic	372,000	365,000
Other acids, duty free	404,000	383,000
Other acids, dutiable	217,000	533,000
POTASSIUM SALTS		
Potassium carbonate	$658,000	$653,000
Caustic potash	366,000	246,000
Caustic potash, not less than 15 per cent caustic soda	....	89,000
Potassium cyanide	170,000	105,000
Potassium chloride	7,229,000	7,120,000
Potassium sulfate	1,770,000	1,633,000
Saltpeter, crude	216,000	263,000
Other salts	317,000	555,000
SODIUM SALTS		
Sodium nitrate	$16,554,000	$21,631,000
Other salts	302,000	325,000
AMMONIUM SALTS		
Ammonium chloride	$ 553,000	$ 466,000
Ammonium sulfate	3,447,000	3,957,000
Sulfur	495,000	278,000
Iron pyrites	3,861,000	3.611,000
Tartar, crude	2,526,000	2,779,000
MEDICINES, DRUGS, ETC.		
Opium (at least 9 per cent morphine)	$2,220,000	$2,391,000
Opium from England	489,000	269,000
Opium from Turkey	1,614,000	1,910,000
China bark	310,000	367,000
Quinine, all forms	482,000	562,000
Medicinal preparations	1,642,000	1,430,000
Amyl alcohol	1,336,000	1,087,000
Hops	2,592,000	2,946,000
Licorice	1,806,000	1,775,000
Vanilla beans	2,528,000	2,530,000
Mineral water	967,000	993,000
FERTILIZERS		
Guano	$ 336,000	$ 538,000
Bone meal	847,000	837,000
Kainite	2,386,000	2,207,000
Salts	1,795,000	2,150,000
Other fertilizers	3,528,000	4,996,000

OILS, WAXES, ETC.	1912	1913
Ethereal oils:		
Lemon oil	$ 511,000	$ 721,000
Other ethereal oils, duty-free	2,542,000	2,804,000
Other ethereal oils, dutiable	1,064,000	1,196,000
Plant oils:		
Cocoa butter	1,238,000	1,223,000
Cocoanut oil, crude	3,865,000	6,258,000
Linseed oil	193,000	87,000
Cottonseed oil	117,000	724,000
Peanut oil	670,000	1,038,000
Chinese nut oil	2,829,000	2,370,000
Olive oil, technical	469,000	369,000
Olive oil, table oil	7,147,000	6,777,000
Rapeseed oil	698,000	712,000
Palm oil	3,443,000	3,631,000
Palm oil, from seed	2,139,000	2,445,000
Soya bean oil	1,361,000	693,000
Fish and codliver oil	882,000	834,000
Mineral oils, crude	4,656,000	10,945,000
Benzine, gasoline, naphtha	1,218,000	1,472,000
Other oils	159,000	580,000
Wax, mineral	489,000	555,000
Wax, vegetable	1,088,000	1,146,000
Glycerine, crude	3,655,000	4,695,000
Olive oil residue	925,000	717,000
Other fats and oils	706,000	439,000
Gelatin	129,000	624,000
DYES AND TANNING MATERIALS		
Alizarine and alizarine dyes	$1,504,000	$1,493,000
Coal tar dyes	7,317,000	7,111,000
From Germany	6,001,000	5,778,000
From England	222,000	239,000
From Switzerland	835,000	839,000
From other countries	258,000	256,000
Aniline salts	354,000	324,000
Indigo, natural and synthetic	1,212,000	1,138,000
Paints, pigments, varnishes	512,000	469,000
Logwood	512,000	469,000
Dye woods	44,000	86,000
Mangrove bark	395,000	245,000
Quebracho wood	1,039,000	990,000
Sumach	380,000	218,000
Dye and tanning extracts	1,789,000	2,221,000
Other tanning materials	339,000	401,000
Pencils and pencil leads	535,000	599,000
GUMS AND RESINS		
Camphor, crude and natural	$ 747,000	$1,118,000
Camphor, refined and artificial	84,000	211,000
Chicle	3,646,000	5,120,000
Copal, Kauri and Dammer	2,081,000	3,193,000
Gambir	876,000	658,000
Shellac	2,472,000	3,058,000
Other resins, duty-free	2,204,000	1,615,000
Other resins, dutiable	188,000	269,000
RUBBER AND RUBBER SUBSTITUTES		
Balata	$ 668,000	$ 792,000
Guahule	5,625,000	2,130,000
Guttajulatong	2,215,000	1,766,000
Gutta-percha	157,000	200,000
Caoutchouc	99,567,000	76,821,000
Caoutchouc, waste	2,973,000	3,193,000
Caoutchouc substitutes	92,000	97,000
Origin of caoutchouc imports:		
Belgium	6,091,000	4,983,000
Germany	7,073,000	4,270,000
England	35,358,000	31,754,000
France	3,398,000	1,690,000
Portugal	1,102,000	239,000
Brazil	32,133,000	19,867,000
East Indies	9,040,000	11,004,000
Mexico	1,734,000	921,000
MISCELLANEOUS IMPORTS		
Asbestos	$1,456,000	$1,929,000
Asbestos goods	364,000	390,000
Graphite	1,709,000	2,110,000
Mica	745,000	981,000
Platinum, crude	1,717,000	1,979,000
Platinum, in blocks, sheets, etc.	2,618,000	2,969,000
Platinum, laboratory apparatus	160,000	105,000
Coal tar preparations not otherwise listed, duty-free	1,004,000	1,035,000
Coal tar preparations, dutiable	661,000	782,000
Creosote oil	2,908,000	4,081,000
Glue	171,000	907,000
Glue, crude	1,733,000	1,852,000
Perfumes and toilet articles	1,810,000	2,044,000
Soap, Marseilles	408,000	348,000
Other soaps	411,000	402,000
Photographic paper	1,147,000	1,275,000
Photographic plates and films	621,000	1,056,000
Explosives	614,000	723,000
Matches	649,000	758,000
Artificial silk	1,869,000	2,877,000
Cement	94,000	134,000
EXPORTS		
CHEMICALS, DRUGS, ETC.		
Calcium carbide	$ 960,000	$ 946,000
Calcium acetate	1,891,000	2,158,000
Sulfuric acid	94,000	104,000
Other acids	372,000	381,000
Copper sulfate	325,000	212,000
Sulfur	1,076,000	1,600,000
Methyl alcohol	594,000	827,000
Dyes	335,000	357,000
Tan bark extract	494,000	508,000
Baking powder	784,000	866,000
Washing powder	409,000	506,000
Vaseline, etc.	247,000	635,000
Ginseng	1,606,000	1,480,000
Roots, herbs, barks, etc.	447,000	476,000
Patent medicines	7,608,000	6,966,000
PAINTS, VARNISHES, ETC.	1912	1913
Zinc oxide	1,248,000	1,136,000
White lead	481,000	905,000
Lamp-black	659,000	470,000
Ready mixed paints	589,000	1,167,000
Lacquers and varnishes	1,230,000	1,107,000
Other related articles	2,822,000	1,819,000
Printer's ink	424,000	435,000
Other inks	214,000	197,000
Blacking	775,000	698,000
Pencils	292,000	611,000
NAVAL STORES		
Turpentine	9,372,000	8,158,000
Rosin	16,376,000	13,563,000
Tar, pitch, etc.	217,000	529,000
OILS		
Vegetable oils:		
Cottonseed oil	21,928,000	17,991,000
Exported to Germany	1,150,000	889,000
Corn oil	1,428,000	1,219,000
Linseed oil	279,000	784,000
Other like oils	353,000	418,000
Animal oils, total	1,339,000	1,250,000
Fish oil (not codliver oil)	330,000	319,000
Mineral oils and crude oil	6,770,000	8,448,000
Illuminating oil	62,084,000	72,042,000
Lubricating and paraffine oils	28,297,000	29,609,000
Naphtha and other light distillates:		
Gasoline	$4,672,000	$17,419,000
Other light oils	15,788,000	10,674,000
Gas and fuel oil	4,111,000	9,990,000
Other like oils	2,488,000	1,134,000
Paraffine	9,603,000	8,177,000
SOAPS AND TOILET ARTICLES		
Toilet soaps	2,006,000	2,185,000
Other soaps	2,635,000	2,672,000
Perfumes, etc.	1,280,000	1,575,000
Raw materials for soap manufacture	4,619,000	5,117,000
EXPLOSIVES		
Cartridges	2,507,000	3,015,000
Dynamite	1,301,000	1,498,000
Gunpowder	352,000	360,000
Other explosives	904,000	652,000
MISCELLANEOUS EXPORTS		
Mercury	13,000	44,000
Celluloid	1,880,000	1,317,000
Waste rubber	869,000	768,000
Graphite	343,000	392,000
Cellulose	543,000	738,000
Glue	289,000	260,000
Candles	257,000	253,000
Coke	3,003,000	3,310,000
Cement	6,160,000	4,271,000

CANADA'S FOREIGN TRADE IN CHEMICAL AND RELATED PRODUCTS

Not strictly comparable with the figures of the previous article, but similar enough for a restricted comparison are the data of Canada's chemical exports and imports during the "Rechnungsjahr," 1912–1913, which appeared in an article in *Chemiker Zeitung*, 38 (1914), 643. During this period the total imports into Canada rose 23 per cent from $547,500,000 in the previous year to $675,500,000; of this amount Germany sent $14,200,000 worth, an increase of $11,100,000.

The value of imports classified as drugs, dyes, chemicals and medicines in the year 1912–1913 amounted to $17,029,000 as compared with $12,360,000 in the previous year; $788,000 worth of this came from Germany as compared with the previous years' $512,000, an increase of 54 per cent. The imports in this class from the United States amounted to $8,997,000.

In the above mentioned class of imports the most important are the following:

IMPORTS	1911–1912	1912–1913
Potassium salts (total)	$ 333,000	$ 428,000
Caustic potash	30,000	30,000
Potassium chlorate	42,000	57,000
Potassium chloride and sulfate (crude)	117,000	195,000
Potassium bichromate	21,000	26,000
Potassium ferro- and ferricyanides	13,000	21,000
Saltpeter	109,000	88,000
Sodium salts (total)	1,917,000	2,834,000
Caustic soda	274,000	303,000
Sodium carbonate	390,000	458,000
Sodium bicarbonate	52,000	62,000
Sodium chlorate	55,000	20,000
Sodium sulfate (crude)	91,000	108,000
Sodium silicate (solid and dissolved)	63,000	77,000
Chili saltpeter	857,000	1,642,000
Acids (total)	292,000	441,000
Tartaric acid (crystalline)	60,000	75,000
Alum	122,000	176,000
Ammonium sulfate	11,000	16,000
Ammonium nitrate	40,000	102,000

Imports	1911–1912	1912–1913
Salammoniac	$ 39,000	$ 56,000
Borax	122,000	113,000
Chloride of lime	122,000	107,000
Tartar (crystalline)	275,000	276,000
Cyanides	96,000	155,000
Mercury	61,000	78,000
Sulfur (crude)	466,000	760,000
Copper sulfate	88,000	132,000
Drugs (crude)	130,000	126,000
Gelatin	133,000	145,000
Glycerine (for explosives)	943,000	906,000
Glycerine (raw)	129,000	159,000
Glycerine (not classified)	46,000	23,000
Gums and resins	434,000	534,000
Chicle gum	2,005,000	3,052,000
Gambir	110,000	136,000
Medicines and chemical preparations (dry)	923,000	1,105,000
Medicines and chemical preparations (non-alcoholic)	61,000	103,000
Medicines and chemical preparations (all others)	132,000	145,000
Linaments, etc	155,000	198,000
Disinfectants (non-alcoholic)	59,000	74,000
Bacteriological preparations	96,000	128,000
Aniline and coal tar dyes (total)	467,000	555,000
From Germany	187,000	228,000
From the United States	....	209,000
From Great Britain	....	77,000
From Switzerland	....	28,000
Indigo (paste and extract)	18,000	16,000
Extracts of logwood, quebracho, etc	683,000	977,000
Dyes and tanning materials (crude)	162,000	171,000

The following imports were not included in the above classification but are of a similar character:

	1911–1912	1912–1913
Fertilizers (total)	$ 620,000	$ 663,000
Artificial fertilizers	445,000	540,000
Bone meal, ash, etc	103,000	123,000
Kainite and other German potash (salts)	7,000	300
Phosphates	1,767,000	1,997,000
Paints and pigments (total)	1,767,000	1,997,000
Lead paints	219,000	260,000
Zinc white	341,000	465,000
Lampblack	80,000	93,000
Paris green	101,000	131,000
Pigments (not classified)	248,000	308,000
Metal pigments—cobalt, copper and zinc oxide	118,000	138,000
Liquid fillers, protective paints, etc	407,000	497,000
Inks (including printer's ink)	148,000	160,000
Varnishes, lacquers, etc	163,000	190,000
Turpentine	629,000	576,000
Waxes	262,000	263,000
Soap (total)	1,121,000	1,333,000
Laundry soap	339,000	386,000
Castile soap	191,000	176,000
Pearline and other soap powders	109,000	138,000
Sapolio and sand soaps	128,000	197,000
Toilet soaps	351,000	416,000
Perfumes and toilet articles	547,000	667,000
Ethereal oils	261,000	350,000
Celluloid, xylenite, etc	225,000	246,000
Guttapercha, caoutchouc and manufactured articles of rubber	8,103,000	11,153,000
Coke	1,637,000	2,023,000
Glue, paste, etc	284,000	363,000
Explosives	1,681,000	1,230,000
Cement	945,000	1,955,000
Sugar, molasses, etc	18,152,000	19,226,000

The total exports from Canada amounted to $393,200,000 in the year 1912–1913 and $315,300,000 in 1911–1912, an increase of 25 per cent. In these two years the exports of "Chemicals and Drugs" amounted, respectively, to $4,968,000 and $4,034,000, of which Canada's own products amounted, respectively, to $1,447,000 and $1,677,000.

In the following list are given the amounts exported of the more important home products of chemical or related industries.

Exports	1911–1912	1912–1913
Calcium acetate	$ 218,000	$ 311,000
Calcium carbide	200,000	199,000
Lye	33,000	39,000
Phosphorus	91,000	63,000
Dyes	5,000	14,000
Chicle gum	17,000	....
Hemlock bark extract	36,000	24,000
Hops	....	42,000
Senega root	74,000	143,000
Casein	38,000	15,000
All other drugs, etc	965,000	991,000
Fertilizers	945,000	1,678,000
Creosote oil	....	74,000
Paints, etc. (total)	109,000	156,000
Mineral pigments	35,000	27,000
Varnishes, etc	....	129,000
Explosives	188,000	101,000
Minerals and mineral products:		
Arsenic	82,000	108,000
Asbestos	2,098,000	2,487,000
Corundum	131,000	196,000
Mica	258,000	319,000
Graphite	66,000	79,000
Graphite products	$ 27,000	$ 52,000
Pyrites	110,000	7,000
Coke	66,000	269,000
Gypsum (crude)	423,000	439,000
Wood pulp (chemically treated)	1,588,000	2,101,000
Wood pulp (mechanically ground)	3,507,000	3,409,000
Press cake	659,000	1,075,000
Matches	11,000	1,000
Sugar and sugar products (total)	171,000	151,000
Maple sugar	110,000	104,000

RECENT INCREASE IN PRODUCTION OF LIME NITROGEN

The following are interesting figures from the report in Carbid and Acetylene of a lecture on artificial fertilizer materials and their significance to agriculture, by Conrad Kubierschky, of Eisenach, before a recent meeting of the Society of German Chemists at Breslau.

The Cyanamid produced from the beginning of the industry is as follows:

Year	Tons
1906	500
1907	2,200
1908	8,300
1909	16,000
1910	30,300
1911	52,000
1912	95,000
1913	97,000 (estimated)
1914	208,000 (estimated)

The increase in production of fertilizer materials within the last few years is as follows:

	Years	Average annual per cent increase
Cyanamid	1907–1912	212.0
Norway saltpeter	1903–1911	170.0
Ozeanien phosphate	1901–1911	28.0
Tunis phosphate	1901–1911	24.0
Florida phosphate	1901–1911	17.4
Potash	1901–1911	11.0
Ammonium sulfate	1901–1911	10.5
Potash	1891–1900	10.0
Thomas phosphate	1900–1910	8.0
Superphosphate	1900–1910	7.8
Crude phosphate	1901–1911	7.5
Chili saltpeter	1901–1911	6.8
Guano	1901–1911	3.7
Algerian phosphate	1901–1911	2.0

FURTHER HYDRO-ELECTRIC POWER UNDERTAKINGS IN NORWAY

The exploitation of water-power in Norway has recently received a tremendous impetus; reports of new companies organized to control and develop water-power rights appear with unusual frequency. An account of this development and comment on its probable outcome form the subject of an editorial article in *Engineering* (London), 98 (1914), 18.

Among the most important projects is a large power-station with a capacity of some 50,000 horse-power which is being laid out at the Folla River, an auxiliary to the Surna, in the Surendal. It will be necessary to construct a tunnel 3 km. long through the Sande mountain, whereby a satisfactory fall will be obtained. The station will be located at a place with good harbor accommodation and sites for new industries. In the absence of a natural reservoir it will be necessary to construct a dam across a flat valley, between the steep mountains of the Troldheimen, and the wall across the Folla Valley is to be 20 meters high. This large undertaking is controlled by the owner of the water-power of the Heane River, in the Southern Drontheim district, which, duly exploited, will represent some 15,000 horse-power, and this, it is understood, will be applied to electric ore-smelting. At Folla there are large deposits of limestone which have been secured.

The building of another hydro-electric power-station has just been decided upon, the cost of exploitation and transmission amounting to about $975,000. The power will be derived from the Högfos Falls, and will amount to some 25,000 horse-power, which is to be transmitted to the town of Risör, a distance of some thirty miles. The fact that the power can be utilized in an existing town, instead of works and dwellings having to be built in an entirely desolate country, as is the case with so many large power-stations, means a very material saving. The Akershus district has just purchased the Raanaasfos Fall; the price for the waterfall is $275,000.

The Arendal Water-Power Company, which is already in operation, is to be greatly extended, at an outlay of some $1,200,000, and the Bjölvo waterfall is to be exploited.

A Norwegian journal of some standing has recently given expression to some apprehension as regards an over-production of hydro-electric power-stations, more especially as far as the electro-chemical industry is concerned. Only a few years ago it was difficult to find uses for capacities of 5000 to 10,000 horsepower in this industry, but such capacities no longer count for anything. Now the installations and projected schemes comprise capacities of 50,000 and 100,000, or even several hundred thousand horse-power, in Norway, Italy, Spain, Savoy, Canada, and even in Iceland. As far as Norway goes, not only are the installations already in operation at Rjukan, Tysse, Arendal, etc., being extended on a large scale, but schemes are being advanced at Sande, Matre, Tyin, Aura, Take, Lysefjord, Bölve, Höjangen, Osa, Glomfjord, etc. If only half of the projects just enumerated are completed within the first few years, the question presents itself as to how all this power shall be applied.

It is a well known fact that the old electro-chemical products, aluminum, carbide, ferro-alloys, all have very limited areas of consumption, which no doubt grow every year, but even a small overproduction leads immediately to a decline of prices and to crises. Such have already arisen twice during the comparatively short span of fifteen to twenty years which has passed since these manufactures commenced, and experts are already prophesying a third crisis, with ruinous prices below the cost of production, as being near at hand. It will be remembered that during the former crisis at least two Norwegian carbide manufactories had to stop; the losses were heavy, as the factories had to be sold for a song.

On the other hand, the opinion is often expressed that the new electro-technical nitrogen industries have an unlimited scope for the sale of their products. But this view must assuredly be accepted with considerable reserve. In the market for artificial fertilizers the consequences of overproduction are already felt. The quotation for Chili saltpeter has dropped from 10.50 marks in the beginning of March to 9.55 marks in the beginning of May, the market having been unable to receive the offered quantities of Chili saltpeter and artificial fertilizers. Nor does the position of sulfate of ammonia offer any encouragement, as German reports show. Also the demand for cyanide shows signs of falling off.

In addition to all this, new methods have been discovered by which nitrogenous fertilizers can be manufactured chemically, without the aid of electricity (as, for instance, the Haber system) so there seems every reason not to embark too light-heartedly on the wholesale exploitation of water-power.

HYDROGENATED FATS AS FOODSTUFFS

A series of experiments on fats hardened by hydrogenation (peanut oil, sesame oil and cottonseed oil) has been carried out by Professor Lehmann of the Institute of Hygiene of the University of Würzburg, to determine, first, the amounts of nickel present (from the hydrogenation in contact with nickel) and whether these amounts are harmful; second, whether the fats are easily assimilable. Analysis showed that the fats contained a maximum of 6 mg. and a minimum of a little less than 0.1 mg. per kilogram [*Chem. Ztg.*, 38 (1914), 708]. Since the author's previous experiments have shown that much larger amounts—at least 100 mg. per day—have never been known to be harmful to human beings, and that in animal experiments 6–10 mg. per kilogram of body weight have caused no ill effects, toxic action from this source in hydrogenated fats is not to be feared.

In animal experiments, too, the fats proved easily assimilable and in household tests of from two to six months no unpleasant effects of any kind were observed.

AMMONIUM SULFATE AND SODIUM NITRATE IN 1913

The figures for the ammonium sulfate exports of Germany and England in the last two years were published in THIS JOURNAL, 6 (1914), 597. The whole situation is commented on in *Engineering* (London), 97 (1914), 760. The international market for ammonium sulfate and Chili saltpeter was, in 1913, unfavorably influenced by the conditions of the preceding autumn. Although the spring of 1913 encouraged, on the whole, the use of fertilizers, the demand fell off in the latter part of the year, and more material remained finally stored than had been on hand at the beginning of this year. This is true both of ammonium sulfate and sodium nitrate and its substitutes. The world's production of ammonium sulfate is steadily on the increase, and had, in 1913, risen to 1,365,700 tons, against 1,214,400 tons in 1912. Germany leads in this production with 549,000 tons in 1913; the United Kingdom comes next with 420,000 tons; then follow the United States with 177,000 tons, and France with 75,400 tons. We take these figures, which do not include British India, from the report of the German Ammoniak Verkaufs-Vereinigung for 1913. As regards consumption the lead of Germany is still more striking, the figures being for 1913: Germany 460,000 tons, United States 335,000 tons, Japan 115,000 tons, England 97,000 tons. Thus German consumption is much higher, especially for agricultural purposes, than that of any other country; but the United States is rapidly following that country, both as regards production and demand. This is, of course, an important factor in the international market. One feels some doubt about the future of the nitrolim and the synthetic ammonia processes, considering that the recovery of ammonia from coal-gas, the demand for which is not likely to decrease, is becoming more and more perfect. The manufacture of synthetic ammonia passed into the practical stage last year; some 50,000 tons of nitrolim and about 30,000 tons of Nor saltpeter were supplied last year. But the experiments on the oxidation of nitrogen by long electric arcs, which seemed so promising, have been given up, and whether the other electric oxidation processes will be able to stand the competition of the old-established products seems doubtful, though the further development of electric-power application and distribution may turn the scale in favor of electric processes. The production of Chili saltpeter, for the first time almost since 1885, decreased last year from 2,552,770 tons in 1912 to 2,450,000 tons.

AMERICAN COKE

The United States Geological Survey reports that all records in American coke production were broken last year, the output of the twelve months having been 46,311,369 tons, valued at $128,951,430. This was an increase over the 1912 output of 2,327,770 tons in quantity and $17,146,317 in value.

LABOR CONDITIONS IN GERMANY

According to the *Reichsarbeitsblatt* the number of workmen applicants in Germany per hundred vacancies amounted in March last to 173, as against 218 in February, and 234 in January. The figure for March of last year was 168. The figures for the current year point to an improvement. The situation has slightly improved in the building trades, leading to better conditions in the brick and tile industries and in wood-working. The same could be said for the textile industry, although cotton-spinning and weaving firms complained of lack of orders. There was a slackening in the activity in coal and lignite mining, as also in that of the iron and steel industry and engineering, except in the case of special machinery. The electrical and chemical trades continued to be satisfactorily employed.

A SUBSTITUTE FOR GALVANIZED IRON

It is a well known fact that the purer iron is, the less liable it is to pitting and corrosion, chemically pure iron being practically rustless. A new process, described in *Engineering* (London), 97 (1914), 828, has just been brought out, termed "ferro-zincing" or "ironizing;" it turns this fact to account by coating the steel surface with almost pure iron, the only impurity of any significance being hydrogen. The addition of hydrogen is an advantage, for the reason that it makes the iron slightly more electro-positive to the underlying steel than it would otherwise be, so that it forms a better protective coating.

Another advantage of the coating of electrolytic iron is that the coating is homogeneous, and is not under unequal strain caused by mechanical operations such as drawing or hammering, and has not been subjected to any heat or mechanical treatment which of necessity causes impurities to be absorbed by the metal so treated.

It is found in practice that it is advantageous to coat the electrolytic iron surface with zinc, as a zinc coating with an intermediate layer of pure iron hydrogen alloy gives a greatly increased life to an ordinary steel tube or plate for the reasons already given.

The inventor of the process, Mr. S. Cowper-Coles, has granted a license to the British Mannesmann Tube Company for the protection of boiler tubes, and is applying the process to a number of other purposes.

OPEN-HEARTH AND BESSEMER RAILS IN AMERICA

In *Engineering*, 84, 688, it was pointed out how the gradual working out of the good Bessemer ores in this country had led to the production of rails dangerously high in phosphorus. It was also then suggested that the future would see a considerable change over from Bessemer to open-hearth rails for this reason. Figures quoted at the time showed that, in 1905, of 3,375,929 tons of rails rolled in the United States, only 183,264 tons were of open-hearth steel, the remainder being Bessemer. The figures, recently available, for 1913 [*Loc. cit.*, 97 (1914), 786] are a confirmation of the forecast. Last year 3,502,780 tons of rails were rolled in the United States, of which no less than 2,527,710 tons were open-hearth, the Bessemer production having, of course, fallen off in proportion.

COMBUSTION ON GOLD AND SILVER SURFACES

Among the papers presented or reported at the 51st Annual Meeting of the Institution of Gas Engineers at Liverpool, the proceedings of which are reported in full in the *Jour. Gas Lighting and Water Sup.*, 126 (1914), 879 ff., is one on "The Electrical Condition of Gold and Silver Surfaces during the Absorption of Gases and Their Catalytic Combustion," by H. Hartley. The results of the investigation (*loc. cit.*, p. 912) may be summarized in the following conclusions:

1—A gold surface acquires a negative charge during the catalytic combustion of gases in contact with it.

2—This electrical effect is probably antecedent to the actual combustion, and is primarily due to "occlusion" phenomena.

3—The metal becomes negatively charged during the occlusion of the combustible gas (hydrogen or carbon monoxide), and positively charged during the occlusion of oxygen.

4—Such electrical effects are probably due to occluded gas which is leaving (rather than entering) the metal. Any cause, such as a sudden lowering of temperature, or a sudden increase in pressure, which would momentarily check the outflow of occluded gas, will likewise diminish the intensity of the charge, or may even momentarily stop it altogether. Conversely, a sudden diminution in the outside gaseous pressure in the vicinity of the metal, which would increase the rate of outflow of the occluded gas from the metal, will temporarily increase the intensity of the electrical effect.

5—Such temporary disturbances in the intensities of the electrical effects as are described in (4) are probably due to the fact that a change in either temperature or pressure of the system is accompanied by a change in the dynamic equilibrium between the in-going and out-flowing gas at the surface system, which change lags behind the exciting cause.

The investigation of the subject is being extended to other surfaces by Professor Bone, in the new Department of Chemical Technology at the Imperial College of Science and Technology, London.

NOTES AND CORRESPONDENCE

RELATION OF COMPOSITION OF ASH IN COAL TO ITS FUSING TEMPERATURE

Editor of the Journal of Industrial and Engineering Chemistry:

Your April number contains an article by Mr. Oscar W. Palmenberg on "The Relation of Composition of Ash in Coal to Its Fusing Temperature." The Engineering Department of the Crucible Steel Company has had this subject under consideration for some time, and has made some investigations, but as they are not yet so numerous as Mr. Palmenberg's, we are glad to get the information contained in his article and have given it a great deal of study, but draw somewhat different conclusions.

The substance of the article may be best stated by quoting the two following extracts:

"To show that there is no relation between the clinkering quality of a coal and the sulfur or iron content, the writer has made this investigation."

"Therefore a chemical analysis is of no value to arrive at a conclusion regarding the clinkering quality of a coal. It may be noted that although coals having an ash with a very low iron content seem to give the highest fusing ash, no definite fusing temperature fits a definite percentage and when the iron content goes beyond 10 per cent the fusing temperature cannot be judged at all. That the sulfur content of the coal has no bearing whatsoever upon the fusibility of the ash is also apparent."

The two accompanying charts have been prepared from Mr. Palmenberg's tables, and an examination of them will show at least that there is reason for questioning the finality of his conclusions.

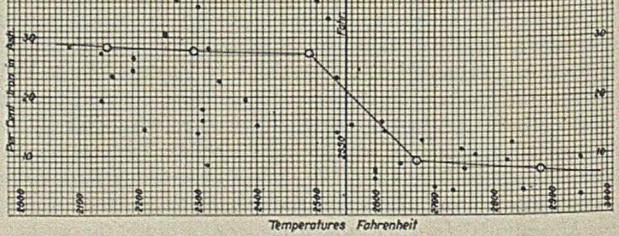

Chart I

CHART I—In Chart I the abscissae are based on the temperature Fahrenheit at which the ash fused, and the ordinates on the iron content. This chart shows that an ash containing less than 10 per cent of iron does not fuse at a temperature lower than 2550° F., and that when the iron content exceeds 20 per cent the fusing temperature is never higher than 2550° F. Between 10 per cent and 20 per cent of iron the fusing temperature varies over a wide range.

A chart based on the sulfur content of the coal was made from the same tables and was found to give identically the same results as stated above, substituting 1 per cent and 2 per cent of sulfur content for 10 per cent and 20 per cent of iron. There were no exceptions. This chart is not reproduced.

CHART II goes a step further and shows a combination made by adding the sulfur to the iron—having first reduced the iron to its percentage as referred to the coal instead of to the ash. From this it will be noticed that under 3 per cent of sulfur plus iron the fusing temperature is above 2550° F., and over 3 per cent it is below that point. To this there are only three exceptions out of forty-five observations; and all three lie close to the 3 per cent line.

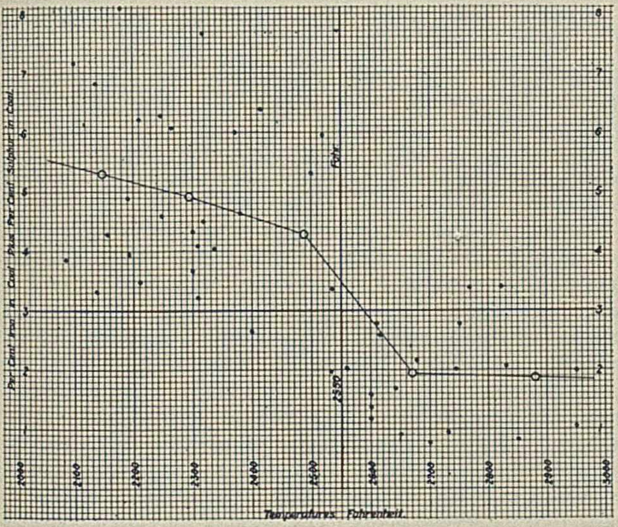

CHART II

It is true, as Mr. Palmenberg says, that "no definite fusing temperature fits a definite percentage," but if the correctness of Chart II is not successfully attacked, it has considerable value, inasmuch as it indicates that the ash of coals containing more than 3 per cent of sulfur plus iron will fuse at a temperature less than 2550° F. This is a point below which it may be said in general that it is undesirable, and—with even moderately hard driving—impossible to keep the heat of a boiler furnace.

JOHN H. K. BURGWIN

PITTSBURGH, May 29, 1914

THE EFFECTS OF THE ENSILAGE PROCESS ON THE SOLUBILITY AND METABOLISM OF FLOATS

The letter by E. B. Forbes, published in THIS JOURNAL, 6, 605, contains a statement which we find difficult to reconcile with the idea gained by us from a careful perusal of his original article. Mr. Forbes says, "In order to correct an impression given by Professor Mooers' article we would state that our especial interest in the subject was as applying to animal feeding........" The opening paragraphs, however, of their original article read as follows: "One of the standard methods of adding floats to the soil is through its addition to manure, and the effect of the fermentation of manure on the solubility of floats has been the subject of discussion and experiment."

"It has occurred to the writers that perhaps we might profitably add a part of the floats to the plant-food two steps further from the soil by introducing it into the silo with the fodder corn, thus gaining two opportunities for increasing the solubility of the floats, first in the ensilage process, and second in the digestive tract of the animal; and further, giving to the animal such benefit as it might be able to get from the rock phosphate in its passage through the body. We do not mean to suggest, however, that all of the floats which one might desire to add to the soil could in this way be passed through the silo and the animal."

These paragraphs are the only ones preceding the experimental data and the reader can easily come to an opinion as to whether or not we were justified in the impression that the main object was plant-food rather than animal feeding. Furthermore, while data were presented as to the effect of the ensilage process upon the solubility of rock phosphate no data were given by them in regard to the acceptance of livestock of treated ensilage as food.

We stand corrected for overlooking the composition of the phosphate rock, the total phosphorus in which we find reported in the article by Forbes and Fritz.

Mr. Forbes continues, "We do not follow........" the "conclusion that in the process of animal digestion there was reversion of the P_2O_5 made soluble by the ensilage process." Our position was briefly this: if all the phosphorus eaten was voided in the dung then the relative availability of the phosphate which had passed through the animal could be determined by means of a weak acid solvent. As the availability when determined in this way proved decidedly less than that obtained by Forbes and Fritz in their ensilage work, we stated that reversion during the process of digestion was "*indicated*" and by no means did we draw the *conclusion* that such was certainly the case. Far more extensive investigations would be required in order to get conclusive evidence.

In regard to another part of our work, Mr. Forbes states, "It is also assumed that the rations involved in the comparison differed only in regard to the presence of rock phosphate, but the data submitted show marked differences in the proportionate amounts of the other components." The table shows that the animals of each group were given the same amount of cotton-seed meal and that there were placed before them the amounts of ensilage that they had in a preliminary trial been found to eat without waste. The amounts were practically the same for each group per 1000 pounds of live weight. Of course the refusal of the animals to eat all of the phosphated silage was unavoidable, and might give rise to minor differences in the analytical results. However, with the marked differences—amounting to more than 500 per cent on the average—between the P_2O_5 content of the manure from the animals fed plain ensilage and those fed phosphated ensilage no great error would be expected. Further proof of this is supplied by the facts that the increase of the soluble P_2O_5 per 100 pounds of rock phosphate was calculated to be 1.17 lb. for the heifer, which ate about 84 per cent of her full silage ration, and 0.93 lb. for the cow, which ate only about 61 per cent of her silage ration.

In conclusion, Mr. Forbes asks this question, "Is it not more likely that the cows absorbed and assimilated the soluble phosphate than that it 'reverted'?"

In reply we would say that since both of the animals which ate the phosphated ensilage lost in weight—as was shown in a table of our article—we considered the probability to be against the retention of any of the added phosphate.

C. A. MOOERS

DEPARTMENT OF CHEMISTRY AND AGRONOMY
TENNESSEE AGRICULTURAL EXPERIMENT STATION
KNOXVILLE, July 13, 1914

ON ANALYSIS OF COPPER, TIN AND SILICON ALLOYS

We recently had occasion to analyze several alloys of copper, tin and silicon, and found that the usual methods of procedure would not answer. The reasons were quite obvious, and besides the alloys were insoluble in nitric acid. The following scheme of procedure was worked out and found to give entirely satisfactory results. The method is given in detail below. No claim is made for originality other than adaptation to the work in hand:

SILICON—Weigh out 0.5 gram of alloy into a 400 cc. Erlenmeyer flask and cover with 20 cc. of water; add 15 cc. HCl and 5 cc. HNO_3. Boil until completely decomposed. Carefully add 20 cc. concentrated H_2SO_4 and boil until sulfuric anhydride fumes are freely evolved. The silica is now completely separated and is dehydrated. Cool and carefully add 75 cc. of water. Boil until all sulfates are in solution and filter, catching the filtrate in a 200 cc. volumetric flask. Wash with hot water nearly to mark and place the flask in ice-water to cool, being careful to have the contents near the temperature of calibration of the flask, when it is finally made to the mark. Ignite, weigh the residue as SiO_2 and calculate to silicon.

TIN—When the flask has cooled make up to the mark with water, and transfer 100 cc. to a 400 cc. Erlenmeyer flask, add 0.15 gram of finely powdered metallic antimony, dissolved in 5 cc. concentrated H_2SO_4, 35 cc. of concentrated HCl, and 1 gram of iron filings. Boil until the iron is nearly all in solution and then connect the flask by means of a three-hole rubber stopper which carries a right angle tube dipping into the liquid, to a carbon dioxide generator. The second hole in the stopper is fitted with an exit tube which connects to a small flask holding a saturated solution of sodium bicarbonate which acts as a seal. The third hole is fitted with a glass plug and serves to admit the burette tip during titration. The flask is now heated to boiling while CO_2 is passing until all iron is in solution and reduction is complete: 20 to 30 minutes are usually sufficient. The flask is now removed from the flame and set in cold water to cool as rapidly as possible. The glass plug is now removed, a small funnel inserted, about 5 cc. starch solution poured in, and the plug replaced. When the contents of the flask are below 40° C., the generator is shut off, the flask detached, and the tin rapidly titrated with $N/10$ iodine solution which has been standardized against pure tin. Air must not enter the flask and the flask with the bicarbonate seal remains in place during the titration.

COPPER—The other 100 cc. portion is made alkaline with ammonia, then acid with nitric acid and allowed to digest on the hot plate for an hour. The stannic acid, which should now be white, is filtered off and washed well. To the filtrate 5 cc. H_2SO_4 are added and it is boiled down to fumes, cooled, diluted with water, neutralized with ammonia, made acid with 7 cc. of a mixture of 2 parts 50 per cent nitric acid and one part 50 per cent sulfuric acid, washed into a 150 cc. beaker and the copper determined by electrolysis.

E. D. KOEPPING

THE ELECTRIC SMELTING AND ALUMINUM CO.
LOCKPORT, N. Y., May 9, 1914

ON THE RAPID DETERMINATION OF COPPER IN OPEN HEARTH AND ALLOY STEEL OR IN CAST IRON

The prevailing method of determining copper in steel by precipitation with hydrogen sulfide with subsequent incineration in porcelain, digestion with nitric acid and transfer of the solution to platinum, where it is again evaporated with hydrofluoric and sulfuric acids to remove silica, and re-solution in sulfuric acid is tedious and becomes even more so in the presence of molybdenum.

The following modification of Low's method will be found to give entire satisfaction, and is much more rapid and convenient where many samples are to be run than the well known method outlined above or any modification which involves electrolysis.

METHOD—From 3 to 10 grams of steel are dissolved in 35 cc. of 1:1 HCl or 1:5 H_2SO_4 and then diluted with 35 cc. of water. A strip of sheet aluminum,[1] with the corners bent up so that it will not lie flat on the bottom of the beaker, is then dropped in and the solution boiled vigorously for 20 minutes.

Remove from the hot plate and wash down the cover glass and the sides of the beaker with hot water. Filter through a 11 cm. S. & S. filter and wash thoroughly with hot water. Puncture the filter and wash the precipitated copper into a 300 cc. Erlenmeyer flask. Over the strip of aluminum in the beaker pour 3 cc. HNO_3 and 7 cc. water, warm and pour through the paper, giving the beaker and paper a final wash with hot water.

The volume of the solution in the beaker should now be about 30 cc. Boil 15 minutes to remove any nitrous fumes. Add 7 cc. NH_4OH and boil until the deep blue fades to a very light blue and the odor of ammonia is faint. Add 10 cc. of 80 per cent acetic acid and boil one minute. Cool, add 10 cc. of 30 per cent KI solution and titrate with standard thiosulfate solution, using starch indicator.

THIOSULFATE SOLUTION—About 5 grams of the pure crystallized salt to one liter of water gives a solution, 1 cc. of which = 0.00125 gram of copper, approximately.

The solution should be standardized against a bichromate solution of known iron value, or against pure copper foil or a standard copper solution, the copper content of which has been accurately determined by electrolysis. A better method than any of the foregoing, to the writer's mind, is the use of a standard steel from the Bureau of Standards.

STARCH INDICATOR[2]—The starch solution is prepared by allowing raw starch to soak in 0.1 per cent hydrochloric acid for 24 hours. The acid is then poured off and the starch washed with cold water until free of acid. The starch is then dried at 32°, occasionally stirring to break up the pieces, and finally drying at 100° for several hours. One gram of the starch prepared in this way boiled in 100 cc. of water and filtered will give a clear solution which will keep indefinitely and will give a brilliant transparent blue.

E. D. KOEPPING

ELECTRIC SMELTING AND ALUMINUM CO.
LOCKPORT, N. Y., May 9, 1914

TIN PLATE AND STEEL MILL OPERATIONS IN JULY

During July the tin plate mills ran at between 85 and 90% of capacity, one or two interests being to about 50%, while the others ran full. The Jones and Laughlin Steel Company operated thirty-two tin mills at its Woodlawn, Pa., plant having added eight mills to this plant in the record period of two months. The Woodlawn plant is now the largest in the United States, having during the week of July 13th wrested the honor from the Shenango plant at New Castle, Pa., which held first place for more than fifteen years. The third largest plant is the American, at Elwood, Ind., with twenty-eight mills, while the fourth in output is the National at Monessen, Pa., with twenty-five mills.

In July, steel mill operations in the Pittsburg District averaged between 65 and 70% of the full capacity, while the average for the country at large was close to 65% of capacity. The production is somewhat larger than in the late part of May and this showing is looked upon as a favorable one by experts because ordinarily the production is much reduced in July. A slight improvement was noted in the demand for wire products.

W. A. HAMOR

PLATINUM IN WESTPHALIA

A report of a general meeting of the Deutscher Platinwerke, held recently in Düsseldorf, given in the London *Mining Journal*, says that a platinum ingot of about 500 grams, obtained from the ore occurrences near Wenden in Westphalia, was shown. Dr. W. Hommel, of the Clausthal Mining Academy, made an interesting report on the ore deposits, in which he laid stress on the statement that the metal occurs with lead, zinc, antimony and nickel.

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[1] The use of cast pieces is to be avoided as they usually contain some copper.

[2] *Chem. Abs.*, 4, 2617.

A sensation was caused when Dr. Hommel exhibited a lump of pure platinum, which was obtained, he stated, by smelting 1 ton of concentrates obtained from 25 tons of crude ore. In addition to the platinum, the concentrates gave about 10 to 12 per cent nickel. The cost of production including mining would be about $4.76 per ton, and ores containing no more than 5 grams platinum would be payable.

CHEAPER PIG IRON

The Interstate Commerce Commission handed down on July 7th a decision of great importance to the pig iron business of the country.

The decision put into effect a substantial reduction on the freight rates on pig iron from Alabama, Tennessee and other Southern points to all Northern and Eastern consuming points. This will enable the Southern producers to effectively compete with the big pig iron producers of Ohio, Pennsylvania, Michigan and Illinois. In substance the commission has cut the rate approximately 35 cents a ton on all rail and something like 45 cents on rail and water hauls. The commission's order goes into effect on Octobor 1st, 1914.

The protestants stated that the decision would force a general readjustment of prices on pig iron. Ohio and Pennsylvania furnace operators will be compelled to cut the price of their product in order to meet the new competition.

The decision was handed down on a complaint brought by the Sloss-Sheffield Steel and Iron Company and others in the Birmingham and Tennessee districts. After it was filed, foundries and other users of Southern pig iron located in the North, East and West intervened on behalf of the complainants. Furnace operators in Ohio, Pennsylvania, Illinois, Michigan, Wisconsin and Minnesota made an organized effort to have the present rates maintained. The case has been pending for more than a year and the commission made an exhaustive investigation.

W. A. Hamor

PERSONAL NOTES

Dr. Arthur H. Elliott received the honorary degree of Master of Science on the occasion of the 50th anniversary of the founding of the School of Mines, Columbia University, May 29th. Dr. Elliott is at present abroad and is representing the American Gas Institute at various gas association meetings advancing the interests of the International Gas Congress.

Dr. Edward Dyer Peters, Gordon McKay Professor of Metallurgy at Harvard University, has received the honorary degree of Doctor in Engineering from the Royal School of Mines, Freiberg, Saxony. The degree was conferred upon Professor Peters in recognition of his academic and practical services and writings on the metallurgy of copper.

A license agreement has been made between the Pittsburgh Iron and Steel Foundry Company of Midland, Pa., and the United Engineering and Foundry Company of Pittsburgh, Pa., by which the latter concern will be permitted to manufacture "adamite" steel rolls for rolling mills. "Adamite" is a patented alloy which has been owned by the former corporation for several years.

At its recent commencement Wesleyan University conferred the degree of Doctor of Science on Dr. Walter P. Bradley, who has this year retired from the professorship of chemistry which he had held since 1893.

Dr. Jokichi Takamine entertained, on July 8th at the Nippon Club, a number of friends at a Japanese dinner given in honor of Dr. L. H. Baekeland on the eve of his departure for Japan. Dr. Takamine officiated as toastmaster. Ellwood Hendrick directed to the guest of honor a characteristic and brilliant poem on the catalysis of friendship and good fellowship. The other speakers at the dinner were Charles F. McKenna, Charles Baskerville, Dr. H. Noguchi, M. C. Whitaker and H. S. May.

The U. S. District Court at Buffalo, Judge Hazel presiding, sustained Patent No. 939,757 of the Williams Patent Crusher & Pulverizer Co., in their suit against the Kinsey Manufacturing Co.

Dr. Hans Goldschmidt, the inventor of the Thermit Process and President of the Goldschmidt Thermit Co., is now paying his annual visit to the United States in order to keep in touch with his numerous interests in this country.

Dr. William L. Dudley, Dean of the Medical Department and Director of the chemical laboratories of Vanderbilt University, Nashville, Tenn., had conferred upon him the degree of LL.D. by the University of Cincinnati at its recent commencement.

The Pittsburgh Iron and Steel Foundry Company is erecting additional open-hearth furnaces and plans to make other important extensions to their plant at Midland, Pa.

Dr. Jerome Alexander is convalescing from a serious illness which has confined him to his home for the past two months.

Keuffel & Esser announce the removal of their Chicago headquarters to a new seven-story building which they have purchased, at 516–520 South Dearborn Street, Chicago. The main portion of the building, which is centrally located near the Buren "loop" between Van Buren and Harrison Streets, will be occupied by their stockrooms and offices.

Dr. Ross A. Gortner, since 1909 resident investigator in biological chemistry at the station for experimental evolution of the Carnegie Institution of Washington, has been appointed associate professor of soil chemistry in the University of Minnesota.

President Francis P. Venable has retired from the presidency of the University of North Carolina and has assumed the chair of the Francis Preston Venable Professorship of Chemistry in the University of North Carolina.

The Tagliabue Manufacturing Company have announced the issue of a Codex giving full information about industrial thermometers.

Ralph W. Perry, Ph.B. announces that he has severed his connection with the Michigan Central Railroad as Chemist and Engineer of Tests, in which capacity he has served them during the construction of the Detroit River Tunnel, the New Station and subsequent improvements to their terminal in the City of Detroit. Mr. Perry has leased the laboratory used in the above work for a general Chemical, Inspecting and Testing business to be known as the "Perry Testing Laboratory."

Professor J. Miller Thomson, F.R.S., is retiring at the end of this session from his position as Vice-principal of King's College, London and head of the chemical department of the college, after a service of forty-three years.

J. U. N. Dorr was given the honorary degree of Mining Engineer at the recent commencement of Rutgers College, New Brunswick, N. J., in recognition of his contributions to gold and silver metallurgy.

Archibald F. Law, Vice-President and General Manager of the Temple Iron Company, which controls furnaces at Temple, Pa., died at Scranton, Pa., on July 19, 1914, aged 58 years. Mr. Law's grandfather, Charles Law, introduced underground (shaft) mining in Pennsylvania.

Mr. C. M. Means, Electrical Engineer, of Pittsburgh, Pa., has been appointed Consulting Electrical Engineer with the U. S. Bureau of Mines.

Mr. Wm. W. Clark has resigned as Chief Chemist for the American Vanadium Co., and has accepted the position of Metallurgist with the Seymour Manufacturing Co., Seymour, Conn.

Joseph Soisson, aged 85, the pioneer manufacturer of firebrick used in the construction of coke ovens, died at his home in Connellsville, Pa., on July 19, 1914. Mr. Soisson began the manufacture of firebrick sixty-five years ago, and at the time of his death was the president of the Soisson Fire Brick Company.

The manufacturing plant of the Leicester Rubber Co., at Catasauqua, Pa., was totally destroyed by fire on July 19, 1914, with a loss of $75,000. The principal stockholders of the company reside at Trenton, N. J.

Plans are maturing at Sebring, Ohio, for the erection of a new pottery plant. There are five potteries in operation there now, having a combined capacity of 42 kilns. The new pottery will be of either six or nine kilns, and will add about $12,000 to the monthly pay-roll of Sebring.

GOVERNMENT PUBLICATIONS

By R. S. McBride, Bureau of Standards, Washington

NOTICE—Publications for which price is indicated can be purchased from the Superintendent of Documents, Government Printing Office, Washington, D. C. Other publications can usually be supplied from the Bureau or Department from which they originate. Consular Reports are received by all large libraries and may be consulted there, or single numbers can be secured by application to the Bureau of Foreign and Domestic Commerce, Department of Commerce, Washington. The regular subscription rate for these Consular Reports mailed daily is $2.50 per year, payable in advance, to the Superintendent of Documents.

HOUSE OF REPRESENTATIVES

Utilization of Alaskan Coal. The Naval appropriation act of Aug. 22, 1912, provided for a survey and testing of coal from the Alaskan fields with a view to its availability for use by the ships of the U. S. Navy. The report resulting has been printed as House document 876, 63rd Congress. It is unfavorable to the use of Alaskan coal under existing conditions. The elaborate report fills a pamphlet of 123 pages illustrated by many plates and maps.

PUBLIC HEALTH SERVICE

The Pollution of Tidal Water. By Hugh S. Cumming. Reprint 181 from the Public Health Reports. This is an address given before the Maryland Conservation Association, February 25, 1914. It discusses the bearing of tidal water pollution upon health and the importance to the State of its control. The subject is developed primarily from the hygienic standpoint, but is of interest also in connection with sewage disposal, water supply, and the shell-fish industry.

DEPARTMENT OF AGRICULTURE

Identification of Commercial Fertilizer Materials. By William H. Fry. Department Bulletin 97. 13 pages. Paper, 5 cents. This bulletin, which is contributed from the Bureau of Soils, "gives methods for identifying the carriers of the various fertilizing ingredients, and is intended to serve as a laboratory guide to those studying this phase of the fertilizer question."

Arsenate of Lead as an Insecticide against the Tobacco Horn-worms in the Dark-Tobacco District. By A. C. Morgan and D. C. Parman. Farmers' Bulletin 595. 8 pages. This bulletin from the Bureau of Entomology is primarily of interest in the tobacco growing industry of Kentucky and Tennessee. It indicates, however, a probable outlet for the chemical product suggested.

Economic Waste from Soil Erosion. By R. O. E. Davis. Separate 624. 18 pages. 5 cuts. This pamphlet is an excerpt from the 1913 yearbook; it is a contribution from the Bureau of Soils.

Hemp. By Lyster H. Dewey. Separate 628. 63 pages. 15 cents. This excerpt from the 1913 yearbook gives an extended report which is developed largely from the standpoint of the fiber-plant investigator.

BUREAU OF FISHERIES

Fishery Industries. By Fred M. Chamberlain and Ward T. Bower. This article is included as one of the special papers in the report of the commissioner of fisheries for the year ending June 30, 1913. It is of interest as giving a general summary of this industry.

BUREAU OF FOREIGN AND DOMESTIC COMMERCE

Cottonseed Products and their Competitors in Northern Europe. By Erwin W. Thompson. Special Agents' Series 84. 93 pages. Paper, 10 cents. Part 1 of this report is already issued; it deals with cake and meal. Part 2, which is to follow shortly, will deal with oils.

Utilization of Potatoes in Europe. By Robert P. Skinner and other Consular Officers. Special Consular Report 64. 44 pages. 10 cents. This report is of interest in connection with the starch and alcohol industries as the statistics given indicate the consumption of potatoes in the various European districts not only as food and feeding material, but also in their industrial application.

BUREAU OF STANDARDS

Standard Analyzed Samples—General Information. Supplement to accompany Circular 25. 5 pages. In this pamphlet are given the certificate analyses for the standard samples of iron, steel, ores, calorimetric materials, etc., which are issued by the Bureau of Standards.

United States Specification for Portland Cement. Second edition of Circular No. 33. 28 pages. The revised edition of this Circular includes only minor changes and additions from the 1st edition which was issued in July, 1913.

Flame Standards in Photometry. By E. B. Rosa and E. C. Crittenden. Scientific Paper 222. 40 pages. This paper is a revision of one published in 1910 (Transactions of the Illuminating Engineering Society, 5, 753–78), entitled Report of Progress on Flame Standards. Further experiments are reported, but these have not materially changed the conclusions previously stated and many of the tables stand as in the original. The effect of atmospheric conditions upon several types of standard lamp is fully discussed and certain suggestions made as to the development of a primary standard for photometry.

Special Studies in Electrolysis Mitigation.—No. 2. Electrolysis from Electric Railway Currents and Its Prevention; an Experimental Test on a System of Insulated Negative Feeders in St. Louis. By E. B. Rosa, Burton McCollum and K. H. Logan. Technologic Paper 32. 34 pages. This paper gives experimental data obtained during the practical working out of a system in St. Louis. In general no chemical factors are considered, the problem being treated from the electrical engineering viewpoint.

Combustion Method for the Direct Determination of Rubber. By L. G. Wesson. Technologic Paper 35. 11 pages. This paper was printed in full in This Journal, 6, pages 459–62.

GEOLOGICAL SURVEY

Useful Minerals of the United States. Compiled by Samuel Sanford and Ralph W. Stone. Bulletin 585. 250 pages. Paper, 20 cents. This bulletin contains first, a list of the occurrences for all commercially important deposits of minerals arranged alphabetically under each State; second, a glossary of over 400 names. This glossary includes in addition to the definitions, a list of the states in which the mineral occurs; it is, therefore, virtually an index to the first part. A general statement of the occurrences of the minerals is given with the idea of making this publication useful to the manufacturer, miner, or student of economic conditions rather than to the professional mineralogist. The more extensive deposits of some common mineral products such as clay, coal, and iron ore are mentioned only in general terms. This is the first publication of the Government giving a general summary of the mineral resources since 1887. However, Geological Survey Bulletin 507, "The Mining Districts of the Western United States," and one chapter of the 1912, "Mineral Resources," give limited information of similar character and these two sources are of interest in connection with the present bulletin.

Production of Copper in the United States in 1913. By B. S. Butler. This advance statement gives the first full summary of statistics prepared for the comprehensive report on the copper industry. The full report will be published later by the Geological Survey as a part of the general review of the industries of gold, silver, lead, zinc, and copper. The following data appear in this advance statement:

Production of Primary Copper in 1913

	Domestic		Foreign
Primary production:			
Electrolytic	1,022,497,601		378,243,869
Lake	155,715,286		....
Casting	22,606,040		....
Pig	36,004,986		....
	1,236,823,913		378,243,869
Total primary		1,615,067,782	
Secondary production:			
Electrolytic		14,862,577	
Casting		22,360,182	
Total secondary		37,222,759	
Total output		1,652,290,541 lbs.	

From the above statistics and the stock of copper on hand at the beginning and end of the year and the export of copper, the apparent consumption of new refined copper and secondary copper and copper in alloys is found to be 1,085,000,000 pounds.

SUPERVISING ARCHITECT, TREASURY DEPARTMENT

Specification for Lubricating Oils. As a part of the information given to bidders proposing to furnish cylinder, engine, and motor oils for use in buildings under the control of the Treasury Department the following specification is included:

"Quality—The oils furnished must be of a suitable quality to give proper lubrication without the use of excessive quantities. They must be free from mineral acids and must not contain such an amount of organic acid as to indicate improper refining or inferior stock. Cylinder oil must flow at a temperature of 50° F. The custodian of the building for which the oil is ordered shall be the judge as to whether it gives proper lubrication."

CONSULAR REPORTS, JUNE

Large **soap factories** are in operation in Hong-Kong and Shanghai, using **cocoanut oil** from Manila, **soda** from Germany and Great Britain, and **rosin** from the United States. (P. 1212.)

Asphalt-paper pipes are being used in Austria as it is claimed that they can replace **clay** and **iron pipes** for most purposes. (P. 1213.)

Petroleum has been struck in Venezuela, on the eastern coast of Lake Maracaibo. (P. 1214.)

The **magnesite** deposits of Greece are mostly found in serpentine rocks. Much of it is calcined directly at the mines; large amounts of **magnesia** and **magnesite brick** are exported from Greece to the United States, where the only commercial supply is located in California. (P. 1239–41.)

Soap makers of Venezuela are endeavoring to have the import duty on **cottonseed oil** reduced, so that this oil can be profitably used. (P. 1255.)

A very active **radium** spring has been discovered at Gollitz, Bohemia. (P. 1257.)

The International Association of Silk Dyers at Lyons, France, has increased the price of **dyeing silk** owing to increase in cost of materials and labor. No responsibility is assumed for dyeing previously weighted silks. (Pp. 1258–9.)

A German inventor, Johannes Marschall, has patented a furnace containing a series of thermopiles, from which he claims to produce **electricity directly from coal** at a cost below regular practice. (P. 1278.)

The Greek government has just signed a contract with the Standard Oil Company of New York for 93,000 cases of **petroleum oil**. (P. 1294.)

The Belgian **cement industry**, especially exports, shows a decline. (P. 1295.)

A new **plate glass** factory is to be established at Jorda, Hungary, using **natural gas**. (P. 1359.)

The production and use of **kelp** in the United Kingdom for **fertilizer** and for **iodine** are described. (Pp. 1402–5.)

A large **beet-sugar** factory is to be built at Winnipeg, Canada. (P. 1409.)

Asphalt of good quality has been discovered in the Philippines. (P. 1422.)

A factory for **briquetting** slack coal is to be erected at Nanaimo, near Victoria, Canada. (P. 1426.)

Statistics of the World's production of **raw silk** are given. (P. 1434.)

The mineral products of the Philippine Islands include **iron, silver, gold, coal, clay products, lime, sand, stone, salt,** and **mineral water**. (P. 1456.)

The **dry-milk industry** of Norway is in a transition stage, but soon new processes will be installed in which the milk will be dried as a film instead of by spraying. (Pp. 1480–1.)

Methyl alcohol to be used in the manufacture of **formaldehyde** is exempted from the manufacturing tax in Italy, if denatured by the addition of formaldehyde. (P. 1516.)

Birmingham, England, conducts four **municipal industries**, *viz.*, **water, gas, electricity** and **street railways**. The average cost of gas for 1913 was given as 38.8 cents per 1000 cubic feet. (P. 1539.)

Water hyacinth is being investigated in Judo, China, as a source of fiber. This fiber has about the same quality as **jute**; it dyes readily and is strong. (P. 1543.)

The output of **mineral products** in Chili has increased, especially **sodium nitrate, copper, coal, borax** and **phosphate**. (P. 1582.)

A new **oil-bearing nut** has been found in the Philippines, from a tree supposed to belong to the genus Amoora or Dysoxylum. The nut contains 45 per cent of a new edible oil which has been found useful in the manufacture of **soap**, but not as a drying oil. (P. 1615.)

Mills in Judo, China, for the production of **paper pulp** from bamboo have not been very successful, but are being reorganized. (P. 1627.)

A new high-power **explosive, sabulite,** to be manufactured at Coquitlam, British Columbia, for blasting is claimed to be three times as efficient as **dynamite**, to be safe in handling, not to be effected by temperatures from —75° F. to +258° F., and to evolve no poisonous fumes on explosion. (P. 1641.)

A committee of experts has been appointed in Sweden to investigate the possibilities of the production of **mineral oil** and **sulfur** from Swedish deposits of **"alum shale"** or **"alum slate"** which is a mixture of **pyrite, aluminum silicate** and **bituminous matter**. (P. 1707.)

The Hong-Kong Exporters Association is endeavoring, to establish **standards of quality** for their exports, especially **wood oil, cassia,** and **cassia oil**. (P. 1710.)

A cargo of Spanish **sugar-beet pulp** has been shipped to Boston and New Orleans for feeding cattle. (P. 1711.)

The **turpentine** industry in India is being increased. (P. 1712.)

The production of **petroleum** in the Caucasus has decreased in the last decade. (P. 1717.)

The **petroleum** output of Peru is largely used as **fuel oil,** especially in Diesel motors. (P. 1729.)

By-product coke ovens, mostly of the Coppe, Carway and Otto types, are largely replacing the bee-hive type in Russia. (Pp. 1732–3.)

The peppermint industry in Japan is increasing, the principal products being **peppermint oil** and **menthol.** (P. 1738.)

The statistics of the areas planted in **sugar beets** in Europe show an increase. (P. 1773.)

The conditions of the following industries in France are discussed, *viz.*, **brewing, phosphates, coal, iron and steel, artificial silk, sugar,** and **alcohol.** (Pp. 1841–5.)

Efforts are being made to develop a large **cottonseed-oil industry** in India, the second largest cotton-producing country in the world. (Pp. 1866–7.)

Experiments at Croydon, England, indicate that the addition of one seven-hundredths grain of **radium** per ton of soil, causes marked increase in the rate of plant growth. Radium residues may be used as the source of radium. (P. 1871.)

Gunpowder for the Swedish government is made in a government factory, the principal explosives used being **nitroglycerine,** and **nitrocellulose,** with smaller amounts of **trinitrotoluol.** (P. 1890.)

Soya bean oil is being refined in Germany to be used in the manufacture of **artificial butter** and **lard,** and as **salad oil.** (P. 1908.)

The manufacture of **aluminum ware** in India is increasing, and the possibility of producing the metal is being considered. (P. 1924.)

The **oil of the cohune nut** is in great demand in Europe as a hardening ingredient in **margarin.** Great difficulty is experienced in cracking the nuts by machine without damaging the kernels. (Pp. 1930–1.)

Discovery of **petroleum** in Calgary, Canada, has caused considerable prospecting. (P. 1957.)

The **sea-weed industry** of France includes its use for **fertilizer** and for the manufacture of **iodine** and **potash** (Pp. 1988–90.)

The **sisal** produced in Bahamas is mostly shipped to the United States. (P. 1994.)

Removal of the duty on **charcoal** has made possible the importation of charcoal from China to the United States. (P. 1997.)

Statistics and other **information regarding exports** from various localities **to the United States** will be found as follows:

Belfast—Fusel oil, hides, paper stock, tow, and whiskey. (P. 1209.)

Florence—Hemp, marble, porcelain, hides, raw silk, terra cotta, and wine. (P. 1285.)

Cuba—Hides, copper, molasses, sugar, wax, alcohol, and asphalt. (P. 1289.)

Rouen, France—Tanning liquor, fusel oil, rubber substitute, lubricating oil and paper stock. (P. 1308.)

Aleppo, Turkey—Gum tragacanth, licorice root, and hides. (P. 1334.)

Jaffa, Turkey—Hides, sesame seeds and oil, olive oil, and wines. (P. 1345.)

Smyrna—Chrome ore, emery, gum mastic, gum tragacanth, laurel, licorice root, olive and sesame oil, opium, and hides. (P. 1373.)

Singapore—Benzine, copra, cubebs, gambier, gums, gutta jelutong, gutta percha, hides, spices, cocoanut oil, wood oil, patchouli leaves, rubber, stick lac, tin, and paraffin. (P. 1396.)

Valencia, Spain—Coal, mineral phosphate, and petroleum.

Moscow—Drugs, furs, hides, mineral oils, spirits, and wines. (P. 1466.)

Bombay—Beeswax. (P. 1468.)

Munich—Beer, chemicals, glue, metal, paper, pumice, rennet, scientific apparatus, and skins. (P. 1474.)

Hongkong—Aniseed oil, cassia and cassia oil, tin, and peanuts. (P. 1483 and 1786.)

Carlsbad—Beer, uranium, color, chemical glassware, glue, kaolin, lenses, lupuline, mineral water, rennet, mineral salts, artificial silk, and zinc oxide. (P. 1495.)

Prague and Reichenberg—Beer, potassium carbonate, barium chloride, zinc oxide, potassium permanganate, coffee substitute, gelatin, glue, graphite, paraffin, sod oil, and tool steel. (Pp. 1500–5.)

Calgary, Canada—Fertilizer, glycerine, hides, and oil cake. (P. 1511.)

Dundee and Aberdeen, Scotland—Flax, hemp, jute, gauge glass, paper stock, spirits, horn, and iron grit. (Pp. 1528–32.)

Leghorn and Carrara, Italy—Alabaster, argols, beeswax, boracic acid, glass bottles, glue stock, glycerine, hemp, hides, juniper berries, marble, mercury, olive oil, pumice stone, sienna, soap stock, talc, umber, and wine. (Pp. 1536–7.)

Valparaiso—Beeswax, coal, copper and copper ore, skins, gold, sodium nitrate, quillaja bark (soap bark), and silver. (P. 1589.)

Riga and Liban, Russia—Drugs, flax, hemp, glue stock, hides, linseed, mineral oil, rennet, wood pulp, fusel oil, and turpentine. (P. 1632.)

New Zealand—Hides and kauri gum. (P. 1647.)

Barcelona—Antimony oxide, argols, bones, cork, glycerine, licorice, olive oil, fusel oil, oleo stearin, saffron, sugar beet pulp, skins, mineral water, and wine. (P. 1658.)

Brunswick, Germany—Asphalt, paints, optical glass, scientific instruments, potash, quinine, and sugar. (P. 1670.)

Rosario, Argentine—Bones, hides, copper ore, linseed and quebracho. (P. 1686.)

Batum, Russia—Licorice, manganese ore, potassium carbonate, and hides. (P. 1717.)

Southampton—Scientific instruments, metals, skins, spirits, cocoa, drugs, gum, gutta percha, mica, and rubber. (Pp. 1728–9.)

Guayaquil, Ecuador—Gold, hides, ivory, nuts, kapok, and rubber. (P. 1755.)

Costa Rica—Gold, rubber, silver, and sugar. (P. 1759.)

Ontario—Artificial abrasive, beet pulp, beet sugar residue, bones, gold, silver, carbons, ammonia, arsenic, glycerine, cyanide, sulfuric acid, coal, coal tar, coke, diamonds, gas liquor, glue stock, grease, gum chicle, hides, lime juice, milk powder, feldspar, graphite, mica, silica, talc, cottonseed, creosote, fusel and petroleum oils, ores of cobalt, copper, nickel, corundum, gold, iron, pyrite, and silver; paper stock, rubber, flaxseed, soap stock, steel, tallow, tan bark, paraffin, and whiskey. (P. 1885.)

Stettin, Germany—Amber, cellulose, drugs, dextrin, ceramics, glycerine, palm oil, rapeseed oil, potash and wood pulp. (P. 1911.)

Newcastle-on-Tyne—Antimony, asphalt, barium carbonate, coal, coke, paint materials, copper matte, hides, ceramics, fluorspar, pig iron, silica ware, steel, and ammonium sulfate. (P. 1950.)

West Hartlepool, England—Diamond grit, ferromanganese, fertilizer, pig iron, linoleum, salt, slag blocks, spiegeleisen, and steel. (P. 1952.)

Uruguay—Bones, casein, fertilizer, glue stock, guano, and hides. (P. 1954.)

Nagasaki—Coal, graphite, and vegetable wax. (P. 1976.)

BOOK REVIEWS

Welding and Cutting of Metals: Oxyacetylene Process. Published by the Vulcan Process Company, Minneapolis. 86 pages. Cloth-bound. Price, $1.00.

This little book contains drawings and descriptions of the various appliances used in the oxyacetylene welding operations, together with a description of the methods of application. It also contains a number of illustrations of successful welds and tabular data covering the range of application. The book will be useful to anyone interested in construction and repair work coming within the range of this process.

M. C. WHITAKER

The Synthetic Use of Metals in Organic Chemistry. BY ARTHUR J. HALE, B.Sc. (Lond.), A.I.C. Pp. xii + 169. P. Blakiston's Son & Co., Philadelphia. 1914. Price, $1.50.

Many reactions and syntheses of organic chemistry in which metals and their compounds take part are presented in this book. The chapters include reactions involving sodium and potassium, copper and silver, magnesium, calcium and barium, zinc and mercury, aluminum, tin and lead, iron, nickel and platinum, followed by six appendices containing experiments exemplifying a number of the methods mentioned in the text.

This work is based upon a course of lectures to advanced students, and, to judge from the text, presupposes a rather thorough knowledge of elementary organic chemistry. The number of reactions taken up is surprisingly large for a book of this size. A detailed discussion of any one of them is therefore obviously impossible. The weakness of the presentation lies in the lack of a systematic classification of the material. A systematization of the reactions as a whole, at which at least an attempt might have been made, would have added greatly to the value of the book, especially in connection with reactions of inorganic chemistry. As a further result of the concise treatment, the student is left in doubt as to the value of the reactions from a practical standpoint except in the case of those for which experimental details are given in the appendices.

In a book of this nature, some slips are inevitable, but on the whole fewer are apparent than would ordinarily have been expected. Some of the reactions, such as the preparation of triphenyl methyl, etc., for example, might have been brought more up to date. While other minor criticisms might be made, this book should prove of value to those chemists who wish a summary of the reactions of organic chemistry in which metals or metallic compounds take part.

K. G. FALK

Modern Steel Analysis. A Selection of Practical Methods for the Chemical Analysis of Steel. BY J. A. PICKARD, B.Sc., A.R.C.Sc., A.I.C., Carnegie Research Scholar of the Iron and Steel Institute, Fellow of the Chemical Society of London. Pp. viii + 128. Illustrated. 12mo. Cloth, $1.25, post-paid. P. Blakiston's Son & Co., publishers, Philadelphia.

The author states in the Preface that he has "endeavored to condense into a small space practical methods for the exact estimation of all those constituents of steel which are of fairly common occurrence. No attempt has been made to give a comprehensive description of all the processes used in the analysis of steel, but the methods detailed have been selected for their practical utility.

The first section of the book is on General Procedure. This is an admirable feature of the book, wherein the author gives practical suggestions relative to weighing, precipitation, filtration, evaporation and baking, absolute value of results, arrangement of work, sampling, and useful apparatus. Under weighing precipitates the following is given as an example of a very practical suggestion: "A good many precipitates, such as silica, barium sulfate, aluminum oxide, are most conveniently weighed by brushing out of the crucible, into the balance scoop, taking precautions against loss by performing the operation over smooth paper. * * * * * This procedure is to be recommended not only on the ground of speed and convenience, but also for its accuracy."

Methods for the following elements in steel are given in their alphabetical order: Aluminum, Arsenic, Carbon, Chromium, Cobalt, Copper, Hydrogen, Manganese, Molybdenum, Nickel, Nitrogen, Oxygen, Phosphorus, Silicon, Sulfur, Titanium, Tungsten, Uranium and Vanadium. This is followed by Appendix I, Solutions; Appendix II, Analysis of Different Steels and Alloys.

The methods given are, in general, those in practice in iron and steel laboratories. We note with regret the absence of Dr. Drown's well-known method for the determination of silicon in steel; that "SiO_2 contains 46.93 per cent Si," and that the author uses the word "estimation" throughout the book as a heading before giving the method.

WILLIAM BRADY

Underground Waters for Commercial Purposes. BY FRANK L. RECTOR. 98 pp. 8 figs. John Wiley & Sons, New York. 1913. Price, $1.00.

The first thirty-one pages of this book reviews for us our "Physical Geography" lesson on "Water and Its Occurrence." We learn that, " . . thermal springs and geysers exist in widely separated parts of the universe;" that, "its (water's) specific gravity is 1 at 15° C.," etc., etc. Then follow two very interesting chapters. The one, on "Watershed" (8 pages), more especially concerned with the relation of the watershed to epidemics; the other, on "Mineral Water" (9 pages), gives us ten definitions of the term by as many different authorities and cites various classifications of mineral waters. Just as we are becoming interested in "Underground Waters" we find that the author has grown weary of his task and has filled out his book with a compilation of analytical methods and tables. The analytical methods are given too briefly to be of assistance to the analyst and too technically for the lay reader.

A. M. BUSWELL

Sugars and their Simple Derivatives. BY JOHN E. MACKENZIE. J. B. Lippincott Co., Philadelphia. 1914. xvi + 242 pp. Price, $2.25, net.

This book is based on a course of lectures given by the author to a class of students, some in pure chemistry and others interested in medicine, brewing, distilling, the manufacture of sugar, etc. The more important physical and chemical properties of most of the simple carbohydrates are given, and considerable space is devoted to a description of methods for the determination of their structural formulae and stereochemical configurations. Special chapters on subjects like the manufacture of cane sugar, fermentation, and the metabolism of the sugars are presented in a brief way.

The form of the book does not lend itself very well to connected reading and it probably will be most used as a companion to works on physiological and analytical chemistry and brewing, where no very complete references on the subject are necessary.

Since E. F. Armstrong's "The Simple Carbohydrates and the Glucosides" has already appeared, there seems to be little reason why a second book so similar in character should have been published.

J. M. NELSON

NEW PUBLICATIONS

By D. D. Berolzheimer, Librarian The Chemists' Club, New York

Alumina, The Manufacture of. By A. Berge. 8vo. 70 pp. Price, $1.25. Wilhelm Knapp, Halle. (German.)

Analysis, Blowpipe. By Nicholas Knight. 5th Ed. 8vo. Cornell College, Mt. Vernon, Iowa.

Coke, Fundamentals of the Chemistry of. By O. Simmersbach. 2nd Ed. L. 8vo. 314 pp. Price, $2.50. Julius Springer, Berlin. (German.)

Color Chemistry, Textbook of. By Hans Th. Bucherer. 8vo. 537 pp. Price, $5.50. Otto Spamer, Leipzig. (German.)

Constants, Selection of Physical. By H. Abraham and P. Sacerdote. 8vo. 753 pp. Gauthier-Villars, Paris. (French.)

Copper, Metallurgy of. By H. O. Hofman. 8vo. 556 pp. Price, $5.00. McGraw-Hill Book Co, New York.

Explosives, The Production of. A. Voigt. 8vo. Price, $1.75. Wilhelm Knapp, Halle. (German.)

Inorganic Chemistry, Fundamentals of. By C. Oppenheimer. 8th Ed. 8vo. 246 pp. Price, $0.90. G. Thieme, Leipzig. (German.)

Invention and Imitation. By Richard Wirth. 8vo. 265 pp. Price, $1.25. Julius Springer, Berlin. (German.)

Matter, Study of the Conditions of. By P. P. von Weimarn. Vol. 2. 8vo. Price, $2.25. Theodor Steinkopf, Dresden. (German.)

Nitrocelluloses, The. By C. Haeussermann. 8vo. 34 pp. Friedrich Vieweg & Sohn, Brunswick. (German.)

Nitrogen, The Fixation of Atmospheric. By Joseph Knox. 8vo. 110 pp. Price, $0.50. Gurney and Jackson, London.

Organic Chemistry; Principles of Analysis and Synthesis in. By M. Hanriot, P. Carré, *et al.* 8vo. Ch. Béranger, Paris. (French.)

Photographic Chemistry, Treatise on. By L. Mathet. Vol. 2. 3rd Ed. 8vo. Price, $4.00. Ch. Mendel, Paris. (French.)

Photography, by Means of Artificial Light. By A. Londe. 18mo. Price, $1.00. Doin et Fils, Paris. (French.)

Physical Chemistry, A Manual of Practical. By Francis W. Gray. 8vo. Macmillan Co., New York.

Physical Chemistry, Textbook of Vol. I. By Karl Jellinék. Vol. 4. L. 8vo. 732 pp. Price, $6.75. Ferdinand Enke, Stuttgart. (German.)

Steel Analysis, Modern. By J. A. Pickard. 8vo. J. & A. Churchill, London.

Steel Foundry, The. By John Howe Hall. 8vo. 271 pp. Price, $3.00. McGraw-Hill Book Co., New York.

Stereochemistry. By E. Wedekind. 2nd Ed. 8vo. G. J. Goeschen, Berlin. (German.)

Terpenes and Camphor. By O. Wallach. 2nd ed. L. 8vo. 580 pp. Price, $6.75. Veit & Co., Leipzig. (German.)

Triphenylmethyl. By J. Schmidlin. 8vo. Price, $2.20. Ferdinand Enke, Stuttgart. (German.)

RECENT JOURNAL ARTICLES

Alkali, Electrolytic Production of, in Bell and Diaphragm Cells. Anonymous. *Chemical Engineering and the Works Chemist*, Vol. 4, 1914, No. 37, pp. 129–136.

Alloys, Commercial Copper, The Approximate Melting Points of. By H. W. Gillett and A. B. Norton. *Transactions of the American Institute of Metals*, Vol. 7, for 1913, pp. 335–343.

Alloys, Nomenclature of Non-Ferrous. By G. K. Burgess and C. P. Karr. *Transactions of the American Institute of Metals.* Vol. 7, 1913, pp. 141–160.

Alloys: Three-Metal Bronzes. By Allmand M. Blow. *Metallurgical and Chemical Engineering*, Vol. 12, 1914, No. 7, pp. 461–467.

Anthraquinon, The Present Status of the Chemistry of. By Robert E. Schmidt. *Bulletin de la Société Chimique de France*, Vol. 15, 1914, No. 12, pp. I–XL.

Carbolic Acid, Separation of, from the Oils of Coal-tar Distillation. By William Mason. *Chemiker Zeitung*, Vol. 38, 1914, No. 69, pp. 732.

Chromium Determination, Methods of. By L. Balderston. *Journal of the American Leather Chemists' Association*, Vol. 9, 1914, No. 6, pp. 255–258.

Cloth, A New Process for Testing the Solidity of. By A. Kertess. *Chemiker Zeitung*, Vol. 38, 1914, No. 70, pp. 752–754.

Coal, Products of the Carbonization of. By C. Earl Little. *Gas Age*, Vol. 33, 1914, No. 11, pp. 513–515.

Color Analysis, Modern Methods of. By Richard Weiss. *Textil American*, Vol. 22, 1914, No. 1, pp. 23 and 44.

Dyeing Industry, Glycollic Acid in the. By William H. Redfern. *Textile Colorist*, Vol. 36, 1914, No. 426, pp. 185–186.

Fats, Hardening (Hydrogenating). By A. Bergius. *Zeitschrift fuer angewandte Chemie*, Vol. 27/I, 1914, No. 46, pp. 322–323.

Gas Analyses by Fractional Distillation at Low Temperatures. By G. A. Burrell and F. M. Seibert. *Journal of the American Chemical Society*, Vol. 36, 1914, No. 7, pp. 1537–1548.

Gas, Coal, Modern Practice. By W. E. Hartman. *American Gas Light Journal*, Vol. 100, 1914, No. 26, pp. 404–406.

Gas Dissociation, The Theory of. By Otto Stern. *Annalen der Physik*, Series 4, Vol. 44, 1914, No. 12, pp. 497–524.

Gas, Producer, The Application of, to Brass Foundries. By E. F. Bulmahn. *Transactions of the American Institute of Metals*, Vol. 7, 1913, pp. 288–312.

Heat Economy in the Tar and Petroleum Industry. By P. W. Uhlmann. *Chemische Apparatur*, Vol. 1, 1914, No. 12, pp. 177–179.

Hydrogenation, Catalytic, of Liquids under the Influence of Common Metals and at Moderate Temperatures and Pressures. By Andre Brochet. *Bulletin de la Société Chimique de France*, Vol. 15, 1914, No. 12, pp. 554–564.

Iodin, Determination of: Particularly in Organic Substances. By R. Gruetzner. *Chemiker Zeitung*, Vol. 38, 1914, No. 72, pp. 769–770.

Iron, Permanganate Determination of, in the Presence of Chlorides. By O. L. Barnebey. *Journal of the American Chemical Society*, Vol. 36, 1914, No. 7, pp. 1429–1448.

Linen, Production of Waterproof, and of its Raw Materials. By Johann Arns. *Kunststoffe*, Vol. 4, 1914, No. 11, pp. 201–203.

Lubricant, Tallow as a. By Friedrich Thalberg. *Chemiker Zeitung*, Vol. 38, 1914, No. 67, pp. 711–712.

Metals, The Boiling of. By Joseph W. Richards. *Transactions of the American Institute of Metals*, Vol. 7, 1913, pp. 237–244.

Mill Wastes, Clay in the Purification of. Anon. *Pulp and Paper Magazine of Canada*, Vol. 12, 1914, No. 12, pp. 367–368.

Natural Gas Problems, Notes on (Chemistry of Natural Gas). By George A. Burrell and Frank M. Seibert. *Chemical Engineer*, Vol. 19, 1914, No. 6, pp. 227–232.

Nickel, Determination of, by Means of Dimethylglyoxim. By O. Brunck. *Zeitschrift fuer angewandte Chemie*, Vol. 27/I, 1914, No. 44, pp. 315–318.

Oil, Pine, The Chemistry of. By Maximilian Toch. *Journal of the Society of Chemical Industry*, Vol. 33, 1914, No. 11, pp. 576–578.

Paper Pulp, Suitability of Longleaf Pine for. By Henry E. Surface and Robert E. Cooper. *Pulp and Paper Magazine of Canada*, Vol. 12, 1914, No. 12, pp. 369–372.

Poisons, Industrial. By Rambousek. *Seifenfabrikant*, Vol. 34, 1914, No. 25, pp. 675–676.

Refrigeration, Mechanical, Chemical and Industrial Applications of. By H. J. Macintire. *Metallurgical and Chemical Engineering*, Vol. 12, 1914, No. 7, pp. 447–448.

Rubber Substitutes. By Rudolf Ditmar. *Seifenfabrikant*, Vol. 34, 1914, No. 23, pp. 613–615.

Silicic Acids, Determination of the. By G. Tschermak. *Zeitschrift fuer anorganische Chemie*, Vol. 87, 1914, No. 3, pp. 300–318.

Soda Recovery in Soda-Cellulose Factories, Apparatus for. By Hugo Schroeder. *Chemische Apparatur*, Vol. 1, 1914, No. 11, pp. 161–168.

Steel: A Proposed New Converter and the Application of the Bessemerizing Process to the Smelting of Ores. By Herbert Haas. *Bulletin of the American Institute of Mining Engineers*, 1914, No. 90, pp. 1071–1127.

Stirring Machine, Construction of a New. By Ludwig Wickop. *Zeitschrift fuer angewandte Chemie*, Vol. 27/I, 1914, No. 44, pp. 318–320.

Sulfurous Acid, Free, Titrimetric Determination of. By E. Kedesdy. *Chemiker Zeitung*, Vol. 38, 1914, No. 57, pp. 601–602.

Tar Oil as a Fuel, The Use of. Anonymous. *Practical Engineer*, Vol. 18, 1914, No. 13, pp. 682–685.

Temperatures, High, in a Vacuum, Special Working Method for the Production of, and the Behavior of Metals, Oxids and Carbids in Same. By Erich Thiede and Erich Bernbraewer. *Zeitschrift fuer anorganische Chemie*, Vol. 87, 1914, No. 2, pp. 129–168.

Terpenes and Oils, Ethereal, Progress in the Field of, in 1912 and 1913. By A. Reclaire. *Chemiker Zeitung*, Vol. 38, 1914, No. 69, pp. 729–731, 770–771 and 783–784.

Water: Apparatus for the Automatic Measuring and Injection of Chemicals. By R. C. Parsons. *Journal of the Society of Chemical Industry*, Vol. 33, 1914, No. 10, pp. 515–521.

Waters, Fluorin in Mineral. By Armand Gautier and P. Clausmann. *Comptes rendus de l'Academie des Sciences*, Vol. 158, 1914, No. 22, pp. 1631–1640.

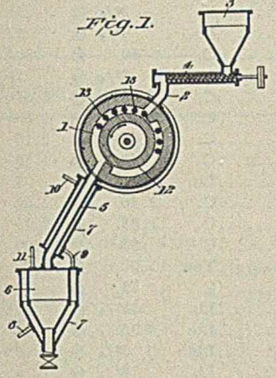
Wool Dyeing, Theory of. By K. Gebhard. *Zeitschrift fuer angewandte Chemie*, Vol. 27/I, 1914, No. 42, pp. 297–307.

Zinc, Physico-Chemical Studies on. By Ernst Cohen and W. D. Helderman. *Zeitschrift fuer physikalische Chemie*, Vol. 87, 1914, No. 4, pp. 426–430.

Zirconium Dioxid, Production of Refractory Objects of. By Otto Ruff, H. Seiferheld and O. Bruschke. *Zeitschrift fuer anorganische Chemie*, Vol. 86, 1914, No. 4, pp. 389–400.

RECENT INVENTIONS

By C. L. Parker, Solicitor of Chemical Patents, McGill Building, Washington, D. C.



Manufacturing Nitrogen Compounds. T. Fujiyama, March 17, 1914. U. S. Pat. 1,090,391. This apparatus is designed for producing nitrogen compounds from carbids by the action of nitrogen. In the chamber 1 is mounted roller 12 made of fire-proof material. Carbon rods 13 capable of producing electric arcs or carbon resistors are arranged in an annular series for heating the chamber. The material is brought on to roller 12 from pipe 2 and is said to absorb nitrogen while moving to the discharge pipe 5 which is water-jacketed to prevent decomposition of the nitrogen compounds produced.

Synthetic Caoutchouc. C. K. F. L. Gross, March 24, 1914. U. S. Pat. 1,090,847. Isoprene is heated in contact with trioxymethylene until a viscous mass is obtained.

Potash from Feldspar. H. P. Bassett, March 24, 1914. U. S. Pat. 1,091,034. Feldspar is mixed with sodium acid sulfate, sodium chlorid, and a reducing agent, the reducing agent being employed in such quantity as to reduce only a part of the sulfate to sulfid. The mixture is heated to a bright red heat for from one to two hours and the water-soluble portion of the remaining mass is separated and the potash recovered from it.

Treating Metals. E. G. Gilson, March 24, 1914. U. S. Pat. 1,091,057. Metals are heated in a non-oxidizing atmosphere in contact with aluminum, aluminum oxid and a chlorid in order to render them inoxidizable.

Extracting Potassium and Sodium Compounds from Silicates which Contain Alkalis. A. Messerschmitt, March 24, 1914. U. S. Pat. 1,091,230. Soluble sodium and potassium compounds are produced from feldspar and similar materials by finely dividing such material and mixing it with a slime containing undried precipitated calcium carbonate resulting from a soda manufacturing process. The mixture is heated to a decomposing temperature and lixiviated.

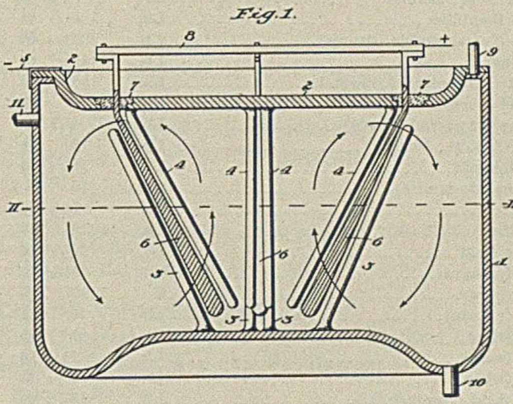
Sulfur Dioxid. H. K. Moore and R. B. Wolf, March 31, 1914. U. S. Pat. 1,091,689. Sulfur-bearing materials are burned and the products of combustion passed through a circulating body of refrigerated solvent for the sulfur dioxid gas such as an aqueous calcium chlorid solution maintained at a temperature of approximately 32° F. The sulfur dioxid gas is extracted *in vacuo* from the solvent and refrigerated *in vacuo* to liquefy it.

Ammonia Production. S. Peacock, April 7, 1914. U. S. Pat. 1,092,167. Ammonia is produced from a higher iron hydrid in the presence of free nitrogen by causing the iron hydrid to split off a portion of its hydrogen at a temperature suitable for the nascent hydrogen thus produced to combine with the free nitrogen to form ammonia. Free hydrogen is simultaneously fed to the mass to reform the higher iron hydrid as fast as the ammonia is produced.

Making Catalyzers. C. Ellis, April 7, 1914. U. S. Pat. 1,092,206. An arc is formed between nickel electrodes in the presence of water and the finely divided nickel containing precipitate resulting from the eroding action of the arc is collected.

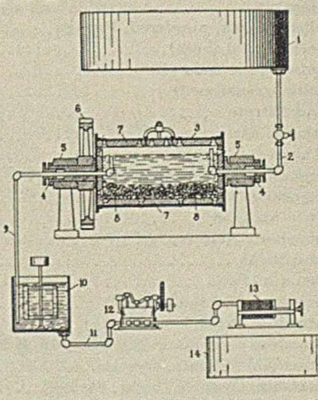
Process of Making Chlorates. G. Kolsky, April 7, 1914. U. S. Pat. 1,092,369. Chlorates are produced by passing an electric current through a suitable electrolyte between electrode surfaces separated only by the electrolyte. Such evolution of gas at the electrodes is maintained as will suffice to induce an active circulation of the electrolyte past the electrodes and effect depolarization, the lines of flow of the electrolyte passing electrodes of opposite polarity in rapid succession.

In the use of the apparatus illustrated for the manufacture of potassium chlorate, a considerable body of liquid is subjected to electrolytic action for several hours or until the percentage of chlorate has risen to a desired degree, whereupon the liquid is withdrawn and replaced by fresh electrolyte. There is no continuous flow of electrolyte into and from the apparatus, the circulation of liquid being due solely to the evolution of hydrogen at the electrodes.



Composition for Use in Matches. H. Staier, April 7, 1914. U. S. Pat. 1,092,408. A substitute for yellow phosphorus in the manufacture of match compositions is produced by thoroughly mixing red phosphorus, a metallic sulfid and sulfur in the proportions by weight of six parts of red phosphorus, two parts of metallic sulfid and three parts of sulfur. The mixture is heated to a temperature of about 500° F., washed with water at a high temperature and dried.

Precipitation of Metals from Cyanid Solutions. C. Butters, April 7, 1914. U. S. Pat. 1,092,765. Precious metals have been precipitated from cyanid solutions by the action of aluminum in the form of dust. To avoid the expense of reducing aluminum to dust form, the patentee employs aluminum in granular form, disposed within a rotating mill through which the cyanid solution is conducted. The attrition to which the granular pieces are continually subjected prevents the formation upon their surfaces of a deposit which would arrest the chemical action.



Hardening or Treatment of Steel. A. W. Machlet, April 14, 1914. U. S. Pat. 1,092,925. The iron or steel under treatment is heated to at least a red heat in an atmosphere of ammonia which has been passed or filtered through kerosene and then in an atmosphere of ammonia alone.

MARKET REPORT

AVERAGE WHOLESALE PRICES OF STANDARD CHEMICALS, ETC., FOR THE MONTH OF JULY, 1914

ORGANIC CHEMICALS

Acetanilid	Lb.	21½	@	22
Acetic Acid (28 per cent)	C.	1.50	@	1.65
Acetone (drums)	Lb.	10½	@	11
Alcohol, denatured (180 proof)	Gal.	33	@	35
Alcohol, grain (188 proof)	Gal.	2.48	@	2.50
Alcohol, wood (95 per cent)	Gal.	45	@	47
Amyl Acetate	Gal.	1.55	@	1.60
Aniline Oil	Lb.	10½	@	10¾
Benzoic Acid	Lb.	23	@	27
Benzol (90 per cent)	Gal.	23	to	25
Camphor (refined in bulk)	Lb.	—	@	44½
Carbolic Acid (drums)	Lb.	7½	@	9
Carbon Bisulfide	Lb.	6½	@	8
Carbon Tetrachloride (drums)	Lb.	7⅜	@	7¾
Chloroform	Lb.	19	@	24
Citric Acid (domestic), crystals	Lb.	53	@	54
Dextrine (corn)	C.	2.77	@	3.02
Dextrine (imported potato)	Lb.	4¾	@	5
Ether (U. S. P., 1900)	Lb.	18	@	24
Formaldehyde	Lb.	8½	@	9½
Glycerine (dynamite)	Lb.	19	@	19½
Oxalic Acid	Lb.	7¼	@	7½
Pyrogallic Acid (bulk)	Lb.	1.20	@	1.40
Salicylic Acid	Lb.	22½	@	25
Starch (cassava)	Lb.	3¼	@	4
Starch (corn)	C.	1.99	@	2.10
Starch (potato)	Lb.	4	@	4¼
Starch (rice)	Lb.	7	@	8
Starch (sago)	Lb.	2¼	@	2¾
Starch (wheat)	Lb.	4¾	@	5¼
Tannic Acid (commercial)	Lb.	33	@	36
Tartaric Acid, crystals	Lb.	30¼	@	—

INORGANIC CHEMICALS

Acetate of Lead (brown, broken)	Lb.	7¼	@	7½
Acetate of Lime (gray)	C.	1.50	@	1.55
Alum (lump)	C.	1.75	@	2.00
Aluminum Sulfate (high-grade)	C.	1.25	@	1.75
Ammonium Carbonate, domestic	Lb.	8	@	8½
Ammonium Chloride, gray	Lb.	5⅞	@	6⅛
Aqua Ammonia (drums) 16°	Lb.	2¼	@	2½
Arsenic, white	Lb.	3	@	3⅛
Barium Chloride	Lb.	1⅝	@	1¾
Barium Nitrate	Lb.	5	to	5¼
Barytes (prime white, foreign)	Ton	19.00	@	23.50
Bleaching Powder (35 per cent)	C.	1.20	@	1.25
Blue Vitriol	C.	4.50	@	4.70
Borax, crystals (bags)	Lb.	3¾	@	4½
Boric Acid, crystals (powd.)	Lb.	7⅝	@	8
Brimstone (crude, domestic)	Ton	22.00	@	22.50
Bromine, bulk	Lb.	30	@	35
Calcium Chloride, fused	C.	60	@	65
Chalk (light precipitated)	Lb.	4	@	4½
China Clay (imported)	Ton	14.00	@	16.00
Feldspar	Ton	8.00	@	12.00
Fuller's Earth, powdered, Foreign	Ton	16.00	@	17.00
Green Vitriol (bulk)	C.	55	@	60
Hydrochloric Acid (18°)	C.	1.15	@	1.65
Iodine (resublimed)	Lb.	3.55	@	3.60
Lead Nitrate	Lb.	8⅛	@	8½
Litharge (American)	Lb.	5½	@	5¾
Lithium Carbonate	Lb.	65	@	70
Magnesium Carbonate	Lb.	21	@	35
Magnesite "Calcined"	Ton	28.50	@	29.50
Nitric Acid, 36°	Lb.	3⅞	@	4¼
Phosphoric Acid (sp. gr. 1.75)	Lb.	20	@	24
Phosphorus	Lb.	45	@	1.00
Plaster of Paris	Bbl.	1.50	@	1.70
Potassium Bichromate, 50°	Lb.	6¾	@	7
Potassium Bromide	Lb.	39	@	40
Potassium Carbonate (calcined), 80 @ 85%	C.	3	@	3⅛
Potassium Chlorate, crystals	Lb.	7¼	@	7¾
Potassium Cyanide (bulk), 98-99%	Lb.	19	@	22
Potassium Hydroxide	C.	4.35	@	5.00
Potassium Iodide (bulk)	Lb.	2.95	@	3.00
Potassium Nitrate (crude)	Lb.	4¾	@	5¼
Potassium Permanganate (bulk)	Lb.	9¾	@	10
Quicksilver, Flask (75 lbs.)		35.50	@	36.00
Red Lead (American)	Lb.	6	@	6¼
Salt Cake (glass-makers')	C.	55	@	65
Silver Nitrate	Oz.	34¾	@	36¾
Soapstone in bags	Ton	10.00	@	12.00
Soda Ash (48 per cent)	C.	67½	@	72½
Sodium Acetate	Lb.	3¾	@	4¼
Sodium Bicarbonate (domestic)	C.	1.00	@	1.10
Sodium Bicarbonate (English)	Lb.	2¾	@	3
Sodium Bichromate	Lb.	4¾	@	5
Sodium Carbonate (dry)	C.	60	@	80
Sodium Chlorate	Lb.	7¼	@	7½
Sodium Hydroxide, 60 per cent	C.	1.55	@	1.57½
Sodium Hyposulfite	C.	1.30	@	1.60
Sodium Nitrate, 95 per cent, spot	C.	2.07½	@	2.10
Sodium Silicate (liquid)	C.	65	@	1.50
Strontium Nitrate	Lb.	6¾	@	7
Sulfur, Flowers (sublimed)	C.	2.20	@	2.60
Sulfur, Roll	C.	1.85	@	2.15
Sulfuric 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.	11¼	@	12½
Tin Oxide	Lb.	35	@	37
White Lead (American, dry)	Lb.	5¼	@	5½
Zinc Carbonate	Lb.	8½	@	9
Zinc Chloride (granulated)	Lb.	4½	@	5
Zinc Oxide (American process)	Lb.	5⅜	@	6⅜
Zinc Sulfate	C.	2.35	@	2.70

OILS, WAXES, ETC.

Beeswax (pure white)	Lb.	47½	@	50
Black Mineral Oil, 29 gravity	Gal.	13½	@	14
Castor Oil (No. 3)	Lb.	8	@	8⅛
Ceresin (yellow)	Lb.	12	@	22
Corn Oil	C.	6.35	@	6.40
Cottonseed Oil (crude), f. o. b. mill	Gal.	47	@	—
Cottonseed Oil (p. s. y.)	Lb.	7.⅛	@	—
Cylinder Oil (light, filtered)	Gal.	21½	@	32
Japan Wax	Lb.	11	@	11¼
Lard Oil (prime winter)	Gal.	92	@	95
Linseed Oil (raw)	Gal.	53	@	54
Menhaden Oil (crude)	Gal.	32½	@	35
Neatsfoot Oil (20°)	Gal.	96	@	98
Paraffine (crude, 120 & 122 m. p.)	Lb.	3⅛	@	3¼
Paraffine Oil (high viscosity)	Gal.	27	@	28
Rosin ("F" grade) (280 lbs.)	Bbl.	4.30	@	—
Rosin Oil (first run)	Gal.	—	@	27
Shellac, T. N.	Lb.	14½	@	15
Spermaceti (cake)	Lb.	30	@	31
Sperm Oil (bleached winter), 38°	Gal.	70	@	71
Spindle Oil, No. 200	Gal.	18	@	19
Stearic Acid (double-pressed)	Lb.	8¾	@	9
Tallow (acidless)	Gal.	64	@	66
Tar Oil (distilled)	Gal.	30	@	31
Turpentine (spirits of)	Gal.	48½	@	50

METALS

Aluminum (No. 1 ingots)	Lb.	17½	@	18
Antimony (Hallet's)	Lb.	6¾	@	7¼
Bismuth (New York)	Lb.	2.05	@	2.10
Bronze powder	Lb.	50	@	3.00
Copper (electrolytic)	C.	13.52½		
Copper (lake)	C.	13.67½		
Lead, N. Y.	C.	3.90	@	—
Nickel	Lb.	50	@	55
Platinum (refined)	Oz.	43.50	@	44.50
Silver	Oz.	54⅜	@	—
Tin	C.	32.10	@	33.00
Zinc	C.	5.00	@	5.10

FERTILIZER MATERIALS

Ammonium Sulfate	C.	2.55	@	2.57½
Blood, dried	Unit	3.25	@	—
Bone, 4½ and 50, ground, raw	Ton	30.00	@	—
Calcium Cyanamid	Unit of Ammonia	2.17½	@	2.20
Calcium Nitrate (Norwegian)	C.	2.05	@	2.15
Castor meal	Unit	3.25	@	—
Fish Scrap, domestic, dried	Unit	2.90	&	10
Phosphate, acid, 16 per cent bulk	Ton	7.00	@	—
Phosphate rock; f. o. b. mine:				
Florida land pebble, 68 per cent	Ton	2.25	@	2.50
Tennessee, 70-80 per cent	Ton	5.00	@	5.50
Potassium, "muriate," basis 80 per cent	Ton	39.07	@	—
Pyrites, furnace size, imported	Unit	0.13¼		
Tankage, high-grade	Unit	3.10	@	3.20 & 10