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EDITORIALS

RESEARCH

WHAT—WHO—WHERE—WHY

Industrial development, of the sort that comes with new and better processes, materials, and machinery together with improved methods of manipulation and production, independent of the influences of domestic and foreign trade relations, tariff or financial systems or legislation, must, as it always has, depend directly on the systematic searchings of the engineers, chemists and physicists familiar with present shortcomings and with the possibilities of their elimination. The urgent need of such development work has been repeatedly demonstrated by both chemists and engineers for many years, but, it must be confessed, with but little effect on those responsible for the appropriations without which it remains as impossible as if the need were not recognized nor the necessary talent available. The need is real and the talent is to be had, therefore, any lack of progress can be directly traced to lack of ability to convince financial managements that the employment of the talent is necessary or that it will be profitable.

Anything that will serve to help out this situation by demonstration or argument is worth while and worthy of encouragement on the broadest grounds. Such, for example, is the presidential address of Mr. A. D. Little, directed particularly toward the chemical industries and more especially toward the development of chemical products and processes rather than the engineering necessarily involved to make these industrial realities.

The extent of the influence of this address needs no better demonstration than the editorial notice given to it by the most excellent and conservative English journal, *Engineering* (quoted in full below).

Unfortunately some of the force of Mr. Little's arguments and the fundamental importance of the *thing* have been lost in subsequent quibbles over the meaning of the word "research," used by him as a name for the general and systematic finding of remedies for existing faults in the materials, processes, machinery or mechanical equipment of industrial plants. The trouble arises from the fact that the term has been for so long used in a narrow academic sense, entirely divorced from commercial utility, by men calling themselves scientific and regarding any search for knowledge as proper research only when the result has no money value. Is it any wonder, then, that a tempest in a teapot has arisen, first, on the part of the schoolmasters and their kind, who object to the desecration of their sacred "research" for the vulgar procedure of trade and money-making, and then on the part of financiers of the industries who fear that Mr. Little is urging them to spend money for that sort of research which its oldest advocates insist must not yield returns if true and proper.

REAL VS. ACADEMIC RESEARCH

"In a recent presidential address to the American Chemical Society, Mr. A. D. Little emphasized the importance of research work in industrial operations, and if the term can be rightly interpreted few will care to dispute his contention. The term 'research' is, however, a much abused one, and by chemists, at any rate, is generally made to cover not only investigations of fundamental importance, such as those of Willard Gibbs into chemical and physical equilibrium, but also mere measurements by some third-year students of, say, the refractive indices of a series of compounds, work, which though possibly quite valuable, could be equally efficiently effected by a grocer's apprentice. In fact, measurements as fully entitled as these to be classed as research are made as a part of the daily routine at every glow-lamp factory, where candle-powers are measured and checked by girls knowing as much of optics as a cow does of the calculus.

TRUE RESEARCH WORK NOT LIMITED TO LABORATORIES

"In common parlance, the term 'research' is accorded to any investigations made in a specially equipped laboratory, and by a special staff, while it is refused to, perhaps, more fundamentally original and intrinsically more valuable work carried out in the drawing office or in the works with improvised apparatus. Mr. Little was less eclectic than this in his own use of the term, and included among research workers those ingenious mechanics who have developed agricultural machinery, or such useful devices as the Westinghouse brake and the methods and instruments associated with the electric telegraph. With this view, though it is not the commonly accepted one, we fully agree. A draughtsman who schemes a new layout for a machine shop or a mechanic who 'practicalizes' a machine tool is, in fact, more truly engaged in research work than a chemist who shows, say, that in a certain organic compound one halogen may replace another.

GERMANY LEADS IN LABORATORY, NOT IN TRUE INDUSTRIAL RESEARCH

"If, however, the term 'research' be interpreted on this comprehensive basis, we think few will be prepared to concede to Germany the pre-eminence in research which Mr. Little claims for her. Such a claim is defensible only when the term is limited, we might almost say degraded, to cover a laboratory work solely, often partaking largely of a routine character. Undoubtedly much very valuable work has issued from German laboratories, but it can hardly be claimed that any undue proportion of the many great advances made in various departments of applied science during the past few years have thus originated. The Diesel engine, for instance, is balanced by the telephone, and incandescent gas lighting by the electric glow lamp.

THE BORN INVESTIGATOR VS. THE PAID FACTORY RESEARCH DEPARTMENT

"It seems to us that research work of value can generally be divided into two classes. In the first place, pioneering researches, in which the man is everything, and the equipment relatively unimportant. Behind these pioneers come, however, a whole army of other investigators, who, by patient and intelligent industry, develop the regions opened by the men of superior genius. Research work of this second kind leads often to very valuable results. It is, however, largely a matter of expenditure and organization, and can almost be bought in the open market, as if it were a material commodity. The labor is very great, so that the credit for the result achieved appertains as much to those bold enough to finance the work as to those who make the actual observations and measurements. Mr. Carnegie was, we believe, the first steel maker in America to employ a works chemist, and he has stated that the venture proved highly profitable, since it was found that by purchasing ore by analysis, rather than by reputation, very large economies were realized. No one, however, could contend that great insight into chemical theories and physical facts is needed for the analysis of an iron ore. Care, industry and average intelligence are the main essentials, and such qualities are not specially uncommon, while genius is seldom on sale.

"Though in one part of his address Mr. Little seems to take, as stated, a comprehensive view as to what constitutes research, in much of it he would appear to have most sympathy with the kind that can be organized in a works laboratory, and he makes a special plea for more work of this character. Much undoubtedly can be effected in this way, but how far the system should be extended depends very largely on the nature of the industry involved."

A distinction, frequently made here in America, and found more often in engineering than chemical lines, is indicated by the names Research, Development and Experimental Departments. The Research Department, proper, undertakes the more difficult problems of a broad or general nature without special reference to immediate commercial demand, the solution of which is most obscure and which requires, at least for the direction, men of the rarer sort with natural tendencies toward investigation, born research men. Development Departments, while doing research work also, are primarily concerned with perfection of a process or machine, the general nature of which is known at the start, and which is properly a product of the Research Department, and generally in the form of a patentable invention; the aim is now to find the best form and materials for commercial production and use. The third or Experimental Department merely performs routine tests, the end and aim of which are data for checking specifications of quality or performance, or for detecting those defects of routine factory source which an ordinary factory force can correct: the work of such an experimental department is purely routine, can be learned quickly by anyone and never should be called research at all—though it often is.

Frequently it happens that one establishment cannot afford three such departments so that the work is all thrown into one, variously named. Or, consultants are used to supply the sort of direction required of the first and second or to entirely replace them when the consultant has at command suitable apparatus, equipment and organization, in which case such an independent investigation or research establishment may serve to advantage many individuals in many different industries. It is this sort of thing that is now growing up as a proper bond between the staffs and laboratories of our better mechanical, electrical and chemical engineering schools and the industries with which they are concerned. Much of the best work now being done in this coöperative way by our independent research men or investigators and the industrial establishments is carried on either in the works themselves or in the field outside of the producers' works but without any laboratory proper. The important point here is that the place of doing the work is of no consequence in comparison with the finding of capable men to direct it and keeping them busy to avoid waste of good talent.

INDUSTRIAL LABORATORY VALUES AND LIMITATIONS

"We gather that chemists find that in the chemical trades new ideas can be completely and satisfactorily tested in a works laboratory. One of our leading cotton manufacturing firms has also found an organization of this character to be highly profitable, having established many years ago lavishly equipped experimental works in which new ideas are thoroughly investigated. Nothing, however, is published as to the results attained. If a proposed innovation passes satisfactory tests, it is adopted quietly and with as little publicity as possible. As a consequence, when the daily Press expatiates on some remarkable improvement in in textile methods as having been recently introduced abroad, it is the case, more often than not, that the identical device has been in commercial operation for years past in the factories of the firm in question. Other British firms pursue a similar policy, carrying out a very large amount of research work of this kind, while saying as little as possible about it. Sheep-dip makers, for instance, investigate, both in their laboratories and on the spot, the life-history and course of development of insect pests from every part of the world, but none of them advertise the fact.

"The organized research laboratory is not, however, so well adapted to the art of engineering as to some other industries, though even here it may unquestionably prove at times quite valuable. Its drawbacks have a twofold origin. In the first place engineering is an art rather than a science. Its exponents are to be classed with other creative minds, and only the routine portion of their work can safely be delegated to others. One of our most progressive engineers has refused for this reason to establish in his works a research laboratory for the solution of such difficulties as may arise. The man who has encountered the difficulties generally knows more about it than he can put in writing, or transfer to another in any other way. He is, therefore, in this engineer's view, the proper man to find the solution, and he is accordingly encouraged to experiment himself. The system in question has proved highly successful, but no doubt there are also cases where certain investigations can properly and conveniently be carried out on the lines advocated by Mr. Little. A striking example of highly valuable work conducted in a factory research laboratory is, in fact, afforded by the history of the tungsten filament lamp. The number of cases in which satisfactory solutions of engineering problems can be found in this way is, however, limited by the circumstances that engineering is concerned quite as much with dynamics as with statics. Laboratory tests may quite easily show the capabilities of a new metallic filament lamp or the value of a new dye-stuff, but in more truly mechanical matters the test of service is often the only really reliable one. The original Lee-Metford rifle, for instance, passed triumphantly through the most searching tests that those responsible for its design could conceive of, but a very few months' service showed that Mr. Thomas Atkins devised without difficulty much more trying ordeals for the weapon, and Mark I. was in consequence very rapidly superseded.

"Most of our large firms take very great precautions to secure the thorough reliability of a new product before definitely placing it on the market. In very many cases, however, it is absolutely necessary that the novelty shall be tested in actual service, and it is not always either convenient or possible to effect this at the maker's works. The machine is, therefore, tested by special arrangement with a customer and is neither listed in a catalog nor otherwise advertised till this, the final test, is completed.

"Considerations of this kind greatly restrict the applicability of organized research work in the field of mechanical engineering, and as one consequence, the openings offered to students from technical colleges are less promising than they are in many other departments of industry. Many such students do indeed find work on the test-beds of manufacturing firms, only to discover after a year or two that such duties offer no prospect of advancement, and add very little to their knowledge of engineering. In one case, after spending some years at the test-bed of a firm of steam turbine builders, an ex-student had not even learned the essential differences between a reaction and an impulse turbine. Such matters were not included in the curriculum of his college at the date of his graduation, and he added little or nothing to this ignorance by his years of testing."

With some of this we cannot agree, for no matter how poorly the laboratory may serve the purpose of profitable improvement, as is undoubtedly the case in many instances, and no matter how little may be the value of testing work to engineering graduates or to their employers, it does not follow that such considerations greatly restrict the applicability of organized research work in the field of mechanical engineering or in any other branch. The distinction here rests again on names; laboratories as generally understood are not essential to some very useful research nor is the existence of a testing department proof of the doing of research work. Forces of men may spend their lives making consumption tests of turbines, strength tests of metals or determining calorific powers of fuels in well equipped laboratories and improve related industries not one bit, and yet one man with no laboratory whatever may stroll leisurely through a few establishments or sit at his desk and evolve an improvement that may materially advance several industries at once when developed, though before getting it in shape for commercial use experimental development work is almost universally required. Depending on the case, this work may be most profitably done in laboratories, in shop or in the field, but it must be done. The International Harvester Company has added more to improvement of agricultural conditions by its machine and implement developments than any organization in the world, but it has no research laboratory, though maintaining testing and development departments. This does not mean that it does no research, for such results could not be produced without research, only it would be obviously absurd to try to develop standard plows, and tractors to pull them, suitable for every soil in the world by any laboratory tests; the machines must be planned, built and then tried and studied everywhere, then returned to the shops, changed to correct faults and tried again. The real research men here are those who plan and study operation in the plowing field, the only place where it can be studied, and who then analyze faults and plan again; these men spend most of their time in railroad trains rather than in laboratories; in the true sense their laboratory is the plowing field, as it should be.

Americans cannot agree with the idea that the foreman or superintendent or engineer, whose primary function is the production, at lowest cost, of goods of proper standard quality, is the best man to carry on research or development work; quite to the contrary, in fact he is the very worst. This is because, first, scheming always occupies the mind to the exclusion of executive routine, which is his main business, and second, but vastly more important, the type of mind and training that best fits for one is destructive, or exclusive, of the other. No man well adapted to pushing routine economic production can possibly discover faults and remedies with efficiency, and certainly the creative mind that can, becomes impatient with production routine and so neglects it.

RESEARCH AND THE PROFESSOR

"Experience in research work is often made a *sine qua non* for the holding of a professional chair at certain of our universities, and if the word 'research' be interpreted in a sufficiently liberal and comprehensive manner, the condition is, we think, a wise one. In many cases, however, the conduct of a few experiments on lubrication or on elastic moduli will be counted as research, though the experimenter may have displayed no deep knowledge of engineering and physical principles, and be quite incapable of giving material aid to the advancement of the art. He would, however, on the above basis, be preferred to a competitor who had never made a laboratory experiment in his life, but had been in responsible charge of, say, the bridge department of a large firm.

"On the other hand, there are men of exceptional ability in really original research who have not the gift of commending themselves to students and who fail accordingly to teach anything to any but a few exceptional men. At the same time they may do such good work in the study as to more than outweigh their class room deficiencies so far as the world at large is concerned, unfortunate as matters may be for the average student. It is important that work of this character should be done, but the difficulty is to reconcile the claims of abstract technics with the not unnatural demands of the average British parent. A University should certainly promote the former, but as teaching is also one of its functions, undergraduates have a right to demand that their interests shall not be wholly sacrificed to the claims of research."

It is true that a great many directors of engineering schools have insisted on a research record for newly appointed men without knowing just what they meant by the requirement, and while some still do it, times do change and so do standards. Few enlightened schools now fail to recognize that both teachers and investigators are absolutely necessary on the staff, and while it most commonly happens that ability in one line is inversely proportional to strength in the other, yet we know of quite a number of men who possess this dual power.

C. E. LUCKE

ORIGINAL PAPERS

THE BIOCHEMICAL OXYGEN DEMAND OF SEWAGES

By ARTHUR LEDERER[1]

Received September 26, 1914

This paper represents the result of a study of a test to determine the biochemical oxygen demand made by a subcommittee of the laboratory section of the American Public Health Association.

Interest in this subject has recently been revived through the adoption of standards of permissible stream pollution by the English Royal Commission on Sewage Disposal, embodied in an appendix of the 8th report of

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[1] Chemist and Bacteriologist, the Sanitary District of Chicago.

the commission. The test recommended by the commission will be hereafter referred to as the "English Incubation Test."

Before I go into the details of this test, it seems well to discuss briefly its meaning and importance.

As the title of the paper indicates, the oxygen referred to here is that utilized by microörganisms which take part in the decomposition of sewage. To what extent the reaction taking place is of a purely biological or chemical or physical nature is unknown. The process is most probably a combination of all three forces. In designating properly a test, which gives expression to the demand for oxygen such as is present in streams, one can hardly be criticized for using the expression "Biochemical Oxygen Demand." The danger of introducing the term "Oxygen Demand" alone is that it would be somewhat confusing with the time-honored expression "Oxygen Consumed." We know that "oxygen consumed" indicates the permanganate oxygen required for the oxidation of a small portion of the organic carbonaceous matter. This oxidation is a purely chemical reaction and bears no relation whatsoever to the "biochemical" oxygen demand. The biochemical oxygen demand of a sewage as a rule is much higher than the permanganate oxygen consumption and the figures bear absolutely no relation to each other. In certain cases the biochemical oxygen demand may be low and the permanganate oxygen consumption high. This may occur with trade wastes containing organic carbonaceous preservatives. The principal value of a test for the determination of the biochemical oxygen demand in a sewage lies in the fact that it is the best indicator of what may be called the "strength" of a sewage. Anyone who has ever employed one or the other of such tests is quickly convinced that none of the routine chemical determinations heretofore in use can furnish the same information. From the standpoint of stream pollution it means very little to the sanitary engineer and chemist to know how much organic nitrogen or "oxygen consumed" or chlorine a certain sewage will add to the stream. They are interested in the amount of oxygen that will be absorbed in the stream, particularly during the first stretch after discharge. Of the chemical constituents the suspended matter is of interest because of its relation to the aesthetic features of sewage disposal by dilution, and on account of its relation to the formation of mudbanks. Some instances of comparing the "strength" of certain sewages from the standpoint of the routine chemical analysis and the biochemical oxygen demand are indeed surprising. The writer has in mind one instance in particular, in which a certain sewage when compared to another from the standpoint of the routine chemical tests was twice as strong and when judged by the biochemical oxygen demand about forty times as strong. Personally, I do not advise chemists to disregard chemical determinations in sewages altogether; we surely want to know whether a sewage is alkaline or acid for instance. My principal plea is to subordinate the routine determinations of the chemical constituents to the determination of the oxygen-consuming capacity of a sewage.

The laboratory section of the American Public Health Association has recognized the importance of standardizing such a test and for some months past a subcommittee has devoted its attention to this question. The members of the subcommittee are: F. Bachmann, Chicago; R. H. Brown, New York City; J. W. M. Bunker, Cambridge, Mass.; Frederic Bonnet, Jr. Worcester, Mass.; W. M. Cobleigh, Bozeman, Mont., John R. Downes, Plainfield, N. J.; F. E. Hale, Brooklyn, N. Y.; C. B. Hoover, Columbus, O.; A. Lederer, Chicago; T. W. Melia, Brooklyn, N. Y.; F. W. Mohlman, Urbana, Ill.; John F. Norton, Boston, Mass.; E. B. Phelps, Washington, D. C.; and S. T. Powell, Baltimore, Md. A. Lederer is chairman of the subcommittee. The following sanitary engineers have been kind enough to give the subcommittee on various occasions the benefit of their valuable opinion: H. C. McRae, Baltimore, Md.; Langdon Pearse, Chicago, Ill.; and W. L. Stevenson, Philadelphia, Pa.

The standardization of a biochemical test differs from the standardization of a purely chemical test in various respects. One chemist might be put to work out a chemical method and his results would be of equal value anywhere. This is not the case with a biochemical test. Two sewages may be alike with reference to their chemical constituents and yet they may differ vastly in their biology. Rarely will two sewages be exactly alike in this respect. No biologic procedure can be expected to furnish ready formulae which would work out with mathematical precision everywhere at all times. Even if we had such a procedure at our disposal we would still have such factors to account for as obstructions in a stream, differences in velocity and temperature, influence of sunlight, absorption of oxygen by mud banks and other factors which of necessity are not represented in a laboratory procedure. It seemed evident, therefore, that in proposing and adopting a standard procedure we would have to confine ourselves for the present to methods furnishing fairly accurate, consistent results, comparable with each other. It could not be expected in the present state of our knowledge of self-purification of rivers with reference to oxygenation and de-oxygenation, that we should be able to work out a procedure which could tell us with certainty how much sewage is to be permitted in a stream to maintain a certain degree of purity further downstream. This could be done only if rivers in all parts of the country were alike with reference to temperatures, velocities, obstructions, etc. Any deeper study of de-oxygenation and oxygenation in a particular stream will apply only to another stream very similar hydrographically. With these conceptions in mind it seemed most advisable to standardize a procedure which would permit the expression of "total biochemical oxygen consumption" and to leave the practical application of this test for the purpose of controlling stream pollution to individual local study.

In order to compare the applicability of a standard procedure in various localities it is important to experiment with as many sewages as possible. Such tests were made with the sewages of Chicago, Ill., Plainfield, N. J., Champaign, Ill., Lawrence, Kan., New York City, Washington, D. C. and Worcester, Mass. Since the number of results obtained with Worcester and New York City sewage are too small, these sewages are not considered in connection with this study.

A method of determining the actual strength of putrescible material is given in the last edition of the "Standard Methods of Water Analysis." The method consists in making various dilutions of the putrescible material with aerated tapwater, adding methylene blue as an indicator, and calculating the oxygen demand from the "relative stability" figures obtained. The method is undoubtedly very useful and simple. It will be retained in the next progress report of the committee in a form elaborated upon by Prof. Phelps. The possible objections to this method are that the relative stability figures obtained are based upon empirical findings and that intermediate points of de-oxygenation, if such are desired, cannot be obtained.

The method proposed by the Royal Commission of Sewage Disposal contained much which seemed worthy of a study by American chemists. Briefly, the English procedure is as follows:

A definite volume of sewage or effluent is completely aerated by shaking. It is then mixed with a larger definite volume of tap water and the mixture again aerated. The dilutions recommended for raw sewages and settled sewages are about 99 to 1 and 49 to 1, respectively. The intention is to adjust the ratio of the aerated water to the sewage under test so that during the test only about 50 or 60 per cent of the oxygen in the diluting water will be used up. It is stated that if less than 30 per cent of the initial oxygen is absorbed the error of the experiment becomes large, but if more than 60 per cent is absorbed the error is even greater. A large dilution reduces the food supply of the bacteria and thus retards deoxygenation. The prepared dilutions are carefully put into 4 clean glass-stoppered bottles holding 11 to 12 ounces. The bottles are left unstoppered for 5 minutes to give the entrapped air at the shoulder a chance to escape. Stress is laid on the importance of having all the liquids in the mixture and even the bottles at incubation temperature before beginning the incubation. The incubation temperature recommended is 65° F. (18.3° C.), this representing the maximum summer temperature of even the most sluggish English streams. The 5-day incubation temperature has been found to give a smaller experimental error than longer incubation periods. Two of the bottles are tested for oxygen at once; the other 2 bottles are tested for oxygen at the end of incubation. The determination of the free oxygen was made by the Winkler method as modified by Rideal and Stewart. The principle of the modification consists in the oxidation of the organic matter and the nitrites by the addition of permanganate in acid solution followed by the addition of 1 cc. of potassium oxalate previous to the addition of the standard reagents employed in the Winkler method. The English standard for sewage effluents is one that absorbs less than 20 p. p. m. of oxygen in 5 days at 65° F.

It is not the purpose of this subcommittee to concern itself with the adoption of standards for sewage effluents but solely to fix a laboratory procedure which will give uniform results. It is thought that such a procedure will be a valuable aid to the sanitary engineer in establishing standards of permissible stream pollution.

There were a number of features in the original English test for the determination of the biochemical oxygen demand which did not appeal to the collaborators, and after considerable correspondence it was finally decided to do some comparative work with the method, employing, however, an incubation temperature of 20° C., and to extend the incubation period to 10 days in order to study the oxygen consumption from day to day. The assumption was that the oxygen consumption at the end of 10 days would be practically 100 per cent. It was also decided to work with three different concentrations simultaneously, so that the influence of concentration upon oxygen consumption could be studied. An ideal experimental series was to show oxygen absorptions of less than 30 per cent, between 30 and 60 per cent, and over 60 per cent, respectively. The preparation of the mixtures previous to incubation differed from the English procedure in that we employed aerated distilled water instead of tap water and 8-ounce bottles were used instead of 11-ounce bottles. The sewage was not aerated before mixing it with the distilled water, but the mixture was brought to the incubation temperature previous to incubation. The sewage was settled in the laboratory before the mixtures were prepared, for the reason that unevenly divided suspended matter might have introduced serious discrepancies in the final results. The original Winkler method was employed for the determination of the free oxygen. Later on, during the tests, it was recommended to employ Hale and Melia's modification of the Winkler method. Professor Phelps employed Rideal and Stewart's modification in the latter part of his series. A number of blue-printed record sheets were mailed to the co-workers in order to facilitate the compilation of the results obtained. It was suggested at the start that each collaborator should obtain at least 10 ideal series, but the time and labor involved was so great that it was impossible to live up to it. Unless one has worked with the same sewage for a considerable period it is almost impossible to prepare dilutions which will allow reductions of oxygen simultaneously to 30 per cent, to between 30 and 60 per cent and over 60 per cent. A great deal of time in such work is always lost with preliminary tests. In order to obtain an ideal series one has to incubate at least 30 bottles and preferably more in order to check doubtful results.

In his series, Mr. Mohlman recorded in addition to the oxygen consumption figures, Phelps' velocity coefficient "K" for each day. A subsequent calculation of K on all of the results obtained by the various collaborators gave some interesting information. The

TABLE I—PERCENTAGE OF TOTAL OXYGEN ABSORBED AND PHELPS' VELOCITY COEFFICIENT, K, AFTER 24 HOURS AND 5 DAYS INCUBATION AT 20° C.
Total Oxygen Consumption Compared with Initial Available Oxygen after 10 Days Incubation

Date of sampling 1914	LESS THAN 30 PER CENT					30 TO 60 PER CENT					MORE THAN 60 PER CENT				
	24 hours		5 days		K Average of 10 days incubation	24 hours		5 days		K Average of 10 days incubation	24 hours		5 days		K Average of 10 days incubation
	% O abs'd	K	% O abs'd	K		% O abs'd	K	% O abs'd	K		% O asb'd	K	% O abs'd	K	
SERIES: Phelps. SOURCE: Screened Washington Sewage															
April 21....											34	0.00052	78	0.00030	0.00032
22....											23	0.00031	76	0.00027	0.00025
24....	23	0.00031	75	0.00020	0.00020	23	0.00026	67	0.00015	0.00017					
28....	28	0.00026	61	0.00016	0.00018	26	0.00026	80	0.00019	0.00019					
29....						29	0.00037	77	0.00021	0.00022					
30....	38	0.00031	84	0.00015	0.00017										
	22	0.00018	88	0.00016	0.00016										
	20	0.00018	80	0.00016	0.00017										
May 1....						33	0.00034	85	0.00020	0.00018					
8....	17	0.00018	65	0.00016	0.00016	32	0.00037	77	0.00019	0.00019					
						25	0.00030	75	0.00021	0.00021					
12....	18	0.00018	52	0.00013	0.00014	30	0.00043	86	0.00030	0.00029					
13....	17	0.00013	60	0.00012	0.00011	37	0.00042	75	0.00019	0.00019					
						15	0.00015	81	0.00020	0.00017					
14....	47	0.00039	63	0.00010	0.00016	28	0.00042	88	0.00021	0.00023					
						41	0.00045	90	0.00024	0.00025					
15....	30	0.00031	86	0.00010	0.00018						34	0.00064	76	0.00037	0.00040
16....						27	0.00043	79	0.00028	0.00028					
						23	0.00035	89	0.00030	0.00027					
23....						26	0.00034	77	0.00024	0.00023					
						23	0.00034	83	0.00028	0.00024					
25....						20	0.00024	71	0.00020	0.00021					
						21	0.00028	79	0.00025	0.00021					
26....											34	0.00054	84	0.00037	0.00036
28....											36	0.00056	85	0.00035	0.00036
											36	0.00057	80	0.00033	0.00036
											46	0.00071	92	0.00038	0.00039
SERIES: Young and Bruckmiller. SOURCE: Settled Sewage—Lawrence, Kansas															
May 23....	25	0.0024	69	0.0015	0.0015	51	0.0060	51	0.0012	0.0020	63	0.0070	23	0.0027	0.0031
26....	27	0.0024	74	0.0016	0.0016	50	0.0013	67	0.00079	0.00079	53	0.0062	68	0.0018	0.0025
27....	14	0.0015	29	0.00049	0.00094	51	0.0058	65	0.0016	0.0022	59	0.0065	80	0.0021	0.0026
June 9....						45	0.012	77	0.0046	0.0054	38	0.0031	87	0.0019	0.0020
						33	0.0052	76	0.0027	0.0031					
10....	28	0.0015	77	0.0020	0.0018	38	0.0060	52	0.0017	0.0026	30	0.0024	89	0.0020	0.0018
11....	29	0.0034	41	0.00096	0.0016	58	0.0068	90	0.0023	0.0025	61	0.0060	77	0.0016	0.0020
SERIES: Downes. SOURCE: Screened Sewage—Plainfield, N. J.															
May 2....	18	0.0011	66	0.00075	0.00087	23	0.00086	67	0.00057	0.00060					
						44	0.0014	84	0.00062	0.00064					
15....	26	0.0011	84	0.00082	0.00080	35	0.0010	71	0.00045	0.00052					
						35	0.00094	78	0.00051	0.00054					
26....	37	0.0014	84	0.00066	0.00057						44	0.0016	81	0.00072	0.00068
											57	0.0018	89	0.0011	0.0010
June 1....	37	0.0012	86	0.00060	0.00059						44	0.0015	79	0.00070	0.00077
6....											28	0.0013	73	0.00099	0.0011
12....						45	0.0012	84	0.00050	0.00058	41	0.0014	70	0.00062	0.00075
SERIES: Mohlman. SOURCE: Crude and Septic Sewage—Champaign, Ill.															
Septic											34	0.0020	81	0.0013	0.0013
April 21....											27	0.0021	75	0.0014	0.0015
											25	0.0014	80	0.0013	0.0014
21....											18	0.0013	76	0.0015	0.0014
											14	0.0010	64	0.0011	0.0011
25....						15	0.0016	56	0.0014	0.0014	25	0.0017	72	0.0012	0.0012
30....						17	0.0013	58	0.0010	0.0011	18	0.0010	86	0.0015	0.0011
Crude						38	0.0045	76	0.0017	0.0020					
May 5....						28	0.0036	66	0.0021	0.0021					
						17	0.0017	65	0.0015	0.0016	25	0.0014	82	0.0014	0.0015
5....						26	0.0060	61	0.0031	0.0036	22	0.0035	61	0.0026	0.0028
9....											25	0.0072	73	0.0052	0.0053
11....						34	0.0058	60	0.0020	0.0025	14	0.0049	58	0.0025	0.0031
14....						28	0.0079	55	0.0032	0.0040					
SERIES: Lederer and Bachmann. SOURCE: Crude Sewage (Settled)—Chicago, Ill.															
April 20....	26	0.0012	78	0.00084	0.00088	16	0.00046	80	0.00051	0.00047					
	18	0.00059	76	0.00052	0.00049										
21....	28	0.0011	72	0.00057	0.00069	37	0.00074	74	0.00032	0.00036					
	26	0.00070	78	0.00045	0.00046										
22....	10	0.00036	78	0.00068	0.00055	11	0.00036	66	0.00043	0.00040					
						22	0.00043	81	0.00040	0.00043					
23....	24	0.0011	66	0.00063	0.00062	30	0.00086	70	0.00045	0.00046					
						33	0.00075	76	0.00039	0.00042					
28....	41	0.0011	91	0.00047	0.00049	25	0.00051	75	0.00037	0.00038					
	35	0.00069	91	0.00041	0.00039										
29....	22	0.00071	71	0.00044	0.00050										
	24	0.00056	68	0.00032	0.00036	31	0.00069	92	0.00048	0.00041					
30....	44	0.0016	83	0.00066	0.00077	42	0.00075	79	0.00032	0.00040					
						24	0.00062	82	0.00048	0.00049					
May 1....	33	0.0010	84	0.00059	0.00058	26	0.00060	82	0.00048	0.00049	33	0.00089	93	0.00067	0.00061
						29	0.00082	90	0.00058	0.00058					
4....	29	0.0016	79	0.00089	0.00084	26	0.00057	76	0.00039	0.00040					
6....	41	0.0016	94	0.00080	0.00088	31	0.00062	94	0.00049	0.00051					
						24	0.00032	79	0.00025	0.00023					
27....	30	0.00071	60	0.00031	0.00040										
	30	0.00039	78	0.00022	0.00021	33	0.00075	90	0.00051	0.00047	33	0.00096	81	0.00075	0.00065
28....	35	0.0012	65	0.00047	0.00055	24	0.00059	88	0.00059	0.00050	19	0.00047	83	0.00070	0.00066
June 4....	41	0.0011	91	0.00050	0.00053										

factor K is part of a formula developed by Prof. Phelps and Col. Black during an investigation of the pollution of New York harbor in 1911. The method employed by Phelps and Black consisted in the incubation of suitable mixtures of the sewage with aerated water for a specified time, say 24 hours. The oxygen is determined at the start and at the end of incubation. Considering the reaction between the organic matter of the sewage and the oxygen dissolved in the water, the following relation is said to hold:

log $\frac{O'}{O}$ = KC*t*. O′ represents the initial, O the final amount of oxygen present. C expresses the concentration of the sewage, *t* the duration of the incubation in hours, and K the velocity constant of the reaction to be determined. Knowing the form of the reaction curve, one computes first K and then by extrapolation to an extended period the total oxygen demand of the organic matter in the sewage. Originally it was claimed that K is independent of the extent of dilution. This, however, was found later to be not quite correct. It was my experience that K decreased as the concentration increased, and the results obtained in Tables I and II bear this out uniformly. To meet this objection, Phelps recommended that C in his formula be effected by a concentration exponent *n*, which would have to be determined for each particular sewage by a study of a series of dilutions.

TABLE II—PER CENT RELATION OF "MG. OXYGEN ADDED TO 1 LITER OF SEWAGE" TO "MG. OXYGEN ABSORBED PER LITER OF SEWAGE" AFTER 24 HOURS, 5 DAYS AND 10 DAYS INCUBATION AT 20° C.

DATE	COLLABORATOR	Per cent dilution	Mg. O added to 1 l. sewage	PER CENT O ABSORBED IN 24 hours	Av.	5 days	Av.	10 days	Av.
May 14	Mohlman	0.25	3488	10	10	20	20	36	36
23	Young and Bruckmiller	0.36	2111	5		14		21	
26			2111	2.5		18		24	
26			2111	5		14.5		20	
27			2111	2.5		5		18	
June 10			2111	2.5		18		24	
11			2111	7	4	9	13	22	21.5
5	Mohlman	0.50	1680	9.5		26		34	
9			1512	15		35		57	
11			1580	18		51		70	
14			1688	16	15	26	34	45	51
2	Downes		2132	3		10		16	
15			2080	3.5	3	11	10	13	15
May 21	Young and Bruckmiller	0.72	1055	20		20		46	
26			1055	20		26		40	
27			1055	21		28		42	
June 9			1055	19		42		55	
10			1055	21		32		55	
11			1055	24	21	37	31	41	46.5
May 26	Downes	1.00	938	7		16.5		20	
June 1			959	7	7	16	16	18	19
April 30	Molhman		856	8		31		55	
30			854	7		24		41	
May 5			884	22		38		57	
5			836	9		34		51	
9			728	18		50		82	
14			826	24	15	50	38	86	62
April 20	Lederer and Bachmann		870	7		21		26	
21			890	6		15		20	
22			870	2		17		22	
23			890	6		16		24	
28			870	6		13		14	
29			860	3.5		12		16	
30			880	8		17		20	
May 1			880	6		..		17	
4			870	8		22		28	
6			860	8		20		20	
27			840	4		..		12	
28			870	7		13		20	
June 4			840	6	6	13	16	14	19
April 20	Lederer and Bachmann	1.5	573	5		20		25	
21			586	6	5.5	17	18	21	23
May 23	Young and Bruckmiller	1.8	422	50		73		79	
26			422	46		59		87	
27			422	47		64		80	
June 9			422	26		61		70	
10			422	21		63		71	
11			422	45	39	57	63	73	77
2	Downes	2.0	530	9		27		40	
15			512	12	10.5	22	24	30	35
April 21	Mohlman		429	20		55		73	
21			409	14		58		75	
25			372	11		46		70	
30			430	17	15	48	52	67	71
22	Lederer and Bachmann		425	3.5		21		32	
23			435	9	6	22	21	31	31
30	Phelps		422	2		8		..	
May 5			437	1	1.5	..	8	11	11
April 28	Lederer and Bachmann	2.5	340	9		25		27	
29			336	7		20		30	
30			344	9		28		30	
May 1			344	8		..		34	
4			340	11	9	33	26	36	31
April 20	Lederer and Bachmann	3.0	280	7		35		43	
21			287	11		23		31	
May 6			280	10	9	28	29	36	37
April 21	Mohlman		282	28		66		80	
21			276	21		68		87	
30			276	15		70		82	
May 5			275	21	21	69	68	84	83
2	Downes		352	21	21	40	40	47	47
15		4.0	252	19		43		54	
26			225	30		55		69	
June 1			226	28		54		63	
6			230	26		66		90	
12			225	23	26	43		51	65
April 22	Lederer and Bachmann		210	9.5		36		44	
23			215	15		35		45	
May 27			202	9		22		28	
28			210	15.5		43		48	
June 4			202	12	12	46	36	52	43
April 24	Phelps		224	6		20		27	
28			222	6		16		25	
30			224	7		16		..	
May 8			217	4		16		25	
12			210	4		13		25	
13			221	4		12		..	
14			219	8		11		17.5	
15			221	7		19		22	
16			228	9		27		34	
16			219	7	6	28	18	32	26
April 28	Lederer and Bachmann	5.0	166	13		40		53	
30			168	19		36		45	
May 1			168	15		..		58	
4			166	22	17	60	45	65	55
26	Downes	6.0	150	54		85		96	
June 12			146	37	45	64	79	92	94
May 6	Lederer and Bachmann		135	18.5	18.5	55	55	59	59
April 24	Phelps		147	8		22		33	
28			146	9		26		..	
29			147	11		30		39	
30			148	6		24		..	
May 1			146	11		28		33	
5			139	5		..		26	
8			146	11		27		35	
13			141	13		27		35	
14			143	13		30		48	
15			144	14		..		49	
23			144	11		32		42	
23			141	10	10	37	28	44	38
27	Lederer and Bachmann	7.0	111	11		38		49	
28			116	31		77		94	
June 4			111	17	19	74	63	90	78
May 8	Phelps	8.0	107	13		38		50	
12			101	17		49		57	
13			102	6.5		36		44	
14			109	18		41		45	
15			103	25		58		73	
25			108	10		36		51	
25			104	11	14	42	43	53	53
April 21	Phelps	10.0	87	25		56		72	
22			82.5	16		52		69	
May 26			82	26		64		76	
28			83	26		62		72	
28			80	27		60		75	
28			80	32	25	65	60	70	72

In making a study of K, obtained in the experiments of the collaborators, the following facts present themselves very strikingly. K is almost invariably lowest at the highest concentration of the sewage. After 24 hours, K is much higher than after 2 days and it decreases (this does not show in the tables given) continuously up to the last day of incubation. However, after the fourth or fifth day the differences are by no means as marked as they are during the first few days. In many cases, K is fairly constant after 5 days. K after 5 days of incubation coincides quite well with the average of the 10 days period.

These results are given without comment or recommendation, for the reason that the formula is now undergoing a very comprehensive study in connection with the work of the U. S. Public Health Service on the self-purification of the Ohio and Potomac rivers. Possibly, the results obtained in connection with the investigation of the English incubation test will be of some service to the students of the formula.

Before discussing the results obtained by the collaborators and giving their comments, the results are compiled in Table I.

In some cases, as can be noted, the number of determinations was rather small, and in such cases one is hardly justified in drawing an average. The heading "Per Cent of Total Oxygen Absorbed" serves to indicate the per cent ratio of absorption, assuming that it is 100 per cent after 10 days. For instance, the column "Per Cent Oxygen Absorbed in 24 Hours" indicates the per cent ratio between the oxygen absorbed in 24 hours and 10 days.

Table II shows the per cent of oxygen absorbed after 1, 5 and 10 days incubation.

Table I shows very strikingly that the rate of absorption in certain dilutions with certain sewages is fairly uniform but that there is no uniformity whatsoever in this respect when comparing different sewages with each other. In other words, one might incubate a certain dilution of a certain sewage for 24 hours and assume with fair certainty the approximate oxygen consumption in 5 days and 10 days, provided he has once established the relation in preliminary tests. This, of course, implies a good deal of work which the busy works-chemist is not always in a position to do.

In all of the experiments, the number of mg. of oxygen absorbed per liter of sewage was lower the higher the concentration. The percentage of oxygen absorbed by the sewage increased with the concentration.

Some experiments were omitted in the tabulation, for the reason that there was a discrepancy in the results which apparently seemed illogical. Such discrepancies were noted in nearly all of the series. There is no doubt that some of these discrepancies are not merely analytical errors but due to reasons which still lack satisfactory explanation. It often happened that the oxygen consumption would suddenly increase on one day, to drop down to a logical figure on the next day. The greater part of the consumption has been reached as a rule by the fifth day. The consumption between the fifth and tenth day amounted to about 20 to 25 per cent of the total. On the whole the concentration did not matter greatly when comparing the per cent oxygen absorbed in 24 hours and 5 days (Table I). When the incubation was such that less than 30 per cent and between 30 and 60 per cent of the initial oxygen was consumed, the "per cent oxygen absorbed in 24 hours" was about 30 per cent (variation 17 to 46), and the "per cent oxygen absorbed in 5 days" about 75 per cent of the total (variation 58 to 81). When more than 60 per cent of the initial oxygen was absorbed, the ratio of absorption was somewhat higher. For the 1-day period the ratio was on the average 35 per cent (variation 22 to 51) and for the 5-day period, about 80 per cent of the total per cent consumption (variation 73 to 86). That this method furnishes only approximate figures at the best is apparent.

Some of the collaborators have given a more detailed opinion on the result of their tests, excerpts of which are given herewith.

Mr. Mohlman, who employed Jackson's bulb pipettes as seals for the bottles during incubation, states that "A number of runs were spoiled by variations in incubation temperature." Instead of preparing the required dilutions for each individual bottle, Mr. Mohlman prepared a larger quantity of the desired mixture and siphoned the solution into the 8-ounce bottles. (The procedure has been employed by the writer on previous dilution tests and seems much simpler and quicker than preparing individual mixtures. If carefully done, there need be no additional aeration and this procedure has the advantage of furnishing an absolutely uniform liquid.) "The most striking conclusion is the variability in the amount of oxygen used by the undiluted sewage, as it varies in every case directly with the amount added and is always higher in the higher dilutions."

Dr. Hale writes: "The parts per million of oxygen absorbed obtained with different dilutions by the English method do not agree. As such a result is not reasonable, instead of carrying out more series, we began to investigate immediately as to the cause of these discrepancies. We have found that aerated distilled water, even though not saturated when put into bottles and incubated at either 20 or 37° C., loses a certain amount of oxygen which varies with the temperature, with the initial oxygen, and with the type of the stopper. We have tested the rubber bulbs, rubber stoppers, glass stoppers, open bottles, and open tubes (Phelps) and found varying losses. We believe that oxygen collects under the stopper and upon the introduction of solutions for testing is forced out of the bottle and lost. This occurs whenever the oxygen in the bottle has not been exhausted. Such a correction would then apply to all determinations made by the English method, but as the correction is very uncertain, it makes the English method very unreliable and my conclusions at present are that the dilution method is the only reliable standard, that the English method cannot be recommended unless extensive experiments find a way of eliminating this uncertainty"...... "There is also another reason why the English method is unreliable and that is that different amounts of sewage require different lengths of time to reach the endpoint, consequently if such a method is adopted we shall have to choose a certain dilution, say one per cent, and determine the length of time it takes that dilution to reach completion, besides eliminating previous error of loss of oxygen that I have mentioned. It may be that by filling bottles and allowing them to stand in the incubator for three days before the addition of sewage, the error may be eliminated, since the loss appeared to be constant in two to three days. This means, however, a troublesome procedure."

Mr. Downes feels that efforts should be abandoned to secure absolute oxygen capacity figures. "On the other hand, I feel that we should work towards the shortest incubation period which will give compatible results indicative of the effect of the sewage in question on the stream which it is to enter. In plant and stream control the value of the results increase in proportion to the speed with which they can be obtained. I suggest a 24-hour period for routine work as best adapted to our American needs. From past experience I had been led to hope that I could show that such a period was more independent of the dilution than longer periods. This I have not been able to do to my satisfaction. On the other hand, results for 24-hour tests are just as compatible and just as reliable as results from longer periods. In cases when a comparatively stable condition of the sample has been reached between the fifth and tenth day without exhaustion of the available oxygen, the 24-hour results are about 40 per cent of the whole."......"It seems that we can hardly do better than to adopt a dilution that will leave a 30 per cent to 60 per cent residual oxygen in 5 days as the English do, for it is certain that too high a concentration would interfere with the life of the oxidizing organisms."

Mr. Hoover would prefer the term "dissolved oxygen consumed" to "biochemical oxygen demand."

Prof. Phelps finds the work not very satisfactory and it is his intention to develop some method which will take us entirely away from oxygen determinations.

Notwithstanding the shortcomings of the method, it is of some advantage to be able to know even approximately the 24-hour and total oxygen consumption of the sewage. As long as we lack proven methods which will give us this information accurately, the introduction of the "Modified English Incubation Test" as a provisional method at the next annual meeting of the American Public Health Association ought to serve some useful purpose. A method developed by me for the determination of the oxygen demand consists in the addition of saltpeter, the oxygen of which is utilized during incubation just as the oxygen in diluting water is used. The method has been published in the May number of the *Journal of Infectious Diseases*. The method has since been simplified by me and has given satisfaction in determining the strength of sewages in polluted waters. Various chemists are employing the method at present and their criticism and results will help to decide whether the method is of sufficient value to supplant the one discussed at length in this paper, or whether it is to serve as a matter of choice. It is also to be hoped that Prof. Phelps will be successful in his endeavor to originate a reliable method for the determination of the oxygen demand and the ratio of oxygen absorption.

It is the intention to present the provisional procedure as the "Modified English Incubation Test" for the determination of the biochemical oxygen demand in the following form:

"A definite volume of sewage or effluent is mixed with aerated distilled water or tap water, free from nitrites and nitrates, in such proportion that between 30 and 60 per cent of the available oxygen is consumed at the end of 10 days incubation at 20° C. Care should be taken to store the diluting water for some time (one or two days) at the constant temperature of 20° C., previous to the preparation of the mixture. The sewage and even the bottles which are to be incubated should be of the same temperature to obtain satisfactory results. The sewage may be added directly into the bottles or else a larger quantity of the mixture may be prepared and the mixture siphoned into the bottles, care being taken to avoid aeration. A bottle of 250 cc. capacity with a seal such as is often used for the methylene blue putrescibility test is employed. It is necessary to establish the ratio of absorption in a definite concentration for each particular dry weather flow sewage before resorting to short time incubation. Having established the per cent ratio of absorption for 1, 5 and 10 days at the proper concentration at various times, it may then suffice to incubate the mixture for 24 hours at 20° C. The results after incubation of 24 hours can be converted into approximate results obtainable after 5 and 10 days incubation by multiplying by the proper factors. It is assumed that a 10-day period of incubation coincides with the complete oxidation of the sewage mixture, which is correct for all practical purposes. Results should be expressed in "milligrams of oxygen absorbed per liter of crude sewage or effluent." For purposes of comparison with other sewages, it is desirable to state the oxygen consumption in milligrams for 24 hours and 10 days. The 10-day consumption figure may either be actually determined or obtained by calculation with the factor established in the initial experiments."

The writer wishes to thank heartily all those who have coöperated in this work by actual experiment and by suggestions. On the whole, the results of the experimental work have not been very satisfying to the collaborators, including myself. Even though we did not decide on a method which promises to be of a permanent character, I feel that we shall be able at least to obtain more uniform results by establishing a standard concentration, incubation temperature and period. If all those who are interested sufficiently in this test will establish the approximate ratio of oxygen exhaustion in their sewage during a 10-day period, the results obtained in various places ought to be fairly comparable with each other.

The Sanitary District of Chicago
39th St. and Lake Front

NOTES ON THE COMPOSITION OF MIDCONTINENTAL PETROLEUM[1]

By F. W. Bushong

Received August 14, 1914

The crude oil from which the products described herein were derived came from the wells of the Alluwe Oil Company in Oklahoma. It is a typical Oklahoma oil of specific gravity[2] 0.8513 at 15°/15°.

Although the writer is firmly convinced that a thorough series of fractional distillations begun on a factory scale and carried out to the highest limit of efficiency would richly reward the immense labor involved by opening up a new world of possibilities in the way of chemical products to be manufactured from petroleum he keenly feels his helplessness in the face of the enormity of such an undertaking. The time at his disposal permitted only a series of four distillations.

Two 8-liter portions of the crude oil were subjected to distillation from a copper retort until the temperature of the vapors reached 315° C. The distillates were collected in 10 fractions of 5 per cent each by volume. The redistillations were carried out in Jena

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[1] This work was done under the J. R. Greenlees Temporary Industrial Fellowship, established under the direction of the late Dr. Robert Kennedy Duncan, in the University of Kansas, 1908.

[2] There was a loss of gasoline during shipment. The oil at the well is lighter.

glass flasks. In the case of the gasoline fractions a LeBel-Henninger dephlegmator was employed. Twelve-degree fractions were collected in the second distillation, four-degree fractions in the third, and two-degree fractions in the fourth. Natural gas was used as the source of heat in the first three distillations, but in the final distillation electricity was employed in the following manner: The distilling flask was mounted upon an electric flask heater which was so regulated as to heat the oil nearly to its boiling point. A coil consisting of about five meters No. 24 German silver wire was held in place in the form of a ring within the distilling flask by means of two stout copper wire terminals which passed up through the cork stopper in the neck of the flask. The quantity of current passed through this coil in order to effect the distillation of the preheated oil was small, and was controlled by outside resistance. This arrangement permitted easy control and constancy of distillation, and did not require a great difference between the temperature of the heating coil and that of the oil.

Tables I and II show the fractions thus collected, their relative quantities, densities and indices of refraction.

TABLE I—GASOLINE FRACTIONS

Fraction	Bar. pr. mm.	Percentage by vol.	Sp. gr. 15°/15°	Ref. index 15° C.
Below 40°	739	0.5	0.6296	1.3616
40 to 50°	739	0.12	0.6448	1.3675
50 to 60°	739	0.35	0.6608	1.3750
60 to 62°	739	0.08	....	1.3806
62 ot 64°	744	0.08	....	1.3828
64 to 66°	744	0.10	....	1.3847
66 to 68°	744	0.34	0.6867	1.3873
68 to 70°	744	0.29	0.6926	1.3898
70 to 72°	744	0.27	0.6976	1.3921
72 to 74°	744	0.22	....	1.3946
74 to 76°	740	0.18	....	1.3965
76 to 78°	740	0.07	....	1.3987
78 to 80°	740	0.19	0.7171	1.4006
80 to 82°	740	0.13	0.7211	1.4023
82 to 84°	740	0.11	0.7221	1.4029
84 to 86°	740	0.11	0.7261	1.4042
86 to 88°	740	0.36	0.7260	1.4051
88 to 90°	740	0.31	0.7273	1.4056
90 to 92°	740	0.26	0.7286	1.4063
92 to 94°	740	0.44	0.7291	1.4068
94 to 96°	740	0.39	0.7306	1.4080
96 to 98°	740	0.93	0.7331	1.4093
98 to 100°	740	0.31	0.7364	1.4113
100 to 102°	731	0.41	0.7391	1.4120
102 to 104°	731	0.29	0.7407	1.4133
104 to 106°	731	0.28	0.7430	1.4143
106 to 108°	731	0.13	0.7432	1.4144
108 to 110°	731	0.15	0.7436	1.4147
110 to 112°	731	0.31	0.7440	1.4153
112 to 114°	731	0.29	0.7438	1.4150
114 to 116°	731	0.36	0.7433	1.4151
116 to 118°	731	0.36	0.7435	1.4152
118 to 120°	744	0.37	0.7443	1.4159
120 to 122°	744	0.43	0.7450	1.4162
122 to 124°	744	0.46	0.7467	1.4185
124 to 126°	744	0.34	0.7485	1.4195
126 to 128°	744	0.40	0.7526	1.4217
128 to 130°	744	0.25	0.7557	1.4238
130 to 132°	748	0.32	0.7600	1.4258
132 to 134°	748	0.24	0.7617	1.4267
134 to 136°	748	0.35	0.7652	1.4283
136 to 138°	750	0.31	0.7666	1.4297
138 to 140°	750	0.27	0.7679	1.4300
140 to 142°	750	0.22	0.7684	1.4307
142 to 144°	750	0.33	0.7679	1.4300
144 to 146°	750	0.40	0.7682	1.4299
146 to 148°	750	0.14	0.7686	1.4299
148 to 150°	750	0.22	0.7687	1.4300
TOTAL GASOLINE		13.77		

Results of analysis of some of the untreated higher kerosene fractions are here shown:

Fraction	Per cent C	Per cent H	Per cent O (dif.)
290 to 292°	86.07	13.31	0.62
292 to 294°	85.96	13.03	1.01
294 to 296°	86.24	13.18	0.58
296 to 298°	85.80	13.06	1.14
AVERAGE..........	86.02	13.14	0.84

Fractions dried by means of metallic sodium, and filtered, were found to have the following composition:

Fraction	Per cent C	Per cent H
252 to 254°	86.58	13.41
272 to 274°	86.39	13.43
292 to 294°	86.65	13.46
296 to 298°	86.29	13.26

Several fractions were treated with ozone, in the cold. After separating the resinified ozonides, by settling, the residual oils had the following composition:

Fraction	Per cent C	Per cent H	Per cent O (dif.)
302 to 304°	84.19	13.13	2.68
300 to 302°	83.88	12.88	3.24
298 to 300°	83.73	13.31	2.96
296 to 298°	84.54	13.35	2.11
Same after drying with Na	84.84	13.67	1.49

The residual oil from the 302 to 304° fraction, after refining with successive portions of concentrated sulfuric acid, washing in the usual manner and drying over calcium chloride, gave the following analysis:

TABLE II—KEROSENE FRACTIONS

Fraction	Bar. pr. mm.	Percentage by vol.	Sp. gr. 15°/15°	Ref. index 15° C.
150 to 152°	738	0.20	0.7715	1.4320
152 to 154°	738	0.50	0.7730	1.4330
154 to 156°	739	0.36	0.7744	1.4338
156 to 158°	739	0.49	0.7762	1.4350
158 to 160°	739	0.31	0.7784	1.4359
160 to 162°	739	0.55	0.7800	1.4372
162 to 164°	737	0.60	0.7818	1.4384
164 to 166° 166 to 168° } (a)		0.37	0.7844	1.4393
168 to 170°	744	0.36	0.7849	1.4391
170 to 172°	738	0.40	0.7868	1.4405
172 to 174°	733	0.56	0.7884	1.4418
174 to 176°	733	0.52	0.7897	1.4425
176 to 178°	733	0.35	0.7910	1.4430
178 to 180°	736	0.44	0.7920	1.4435
180 to 182°	736	0.41	0.7930	1.4440
182 to 184°	736	0.24	0.7944	1.4447
184 to 186°	735	0.44	0.7957	1.4450
186 to 188°	734	0.20	0.7969	1.4458
188 to 190°	734	0.48	0.7980	1.4466
190 to 192°	734	0.40	0.7997	1.4470
192 to 194°	734	0.51	0.8006	1.4478
194 to 196°	734	0.32	0.8026	1.4485
196 to 198°	734	0.30	0.8030	1.4492
198 to 200°	734	0.50	0.8050	1.4498
200 to 202°	731	0.33	0.8064	1.4505
202 to 204°	738	0.43	0.8075	1.4508
204 to 206°	738	0.51	0.8094	1.4518
206 to 208°	738	0.37	0.8105	1.4523
208 to 210°	738	0.47	0.8118	1.4530
210 to 212°	736	0.43	0.8129	1.4538
212 to 214°	736	0.51	0.8138	1.4544
214 to 216°	733	0.47	0.8154	1.4550
216 to 218°	733	0.51	0.8160	1.4552
218 to 220°	733	0.28	0.8175	1.4559
220 to 222°	732	0.40	0.8184	1.4563
222 to 224°	730	0.50	0.8190	1.4570
224 to 226°	730	0.38	0.8207	1.4579
226 to 228°	730	0.45	0.8219	1.4583
228 to 230°	730	0.41	0.8230	1.4592
230 to 232°	730	0.33	0.8244	1.4601
232 to 234°	730	0.41	0.8252	1.4607
234 to 236°	742	0.37	0.8264	1.4611
236 to 238°	742	0.40	0.8270	1.4617
238 to 240°	742	0.40	0.8290	1.4627
240 to 242°	742	0.42	0.8306	1.4632
242 to 244°	742	0.42	0.8322	1.4644
244 to 246°	741	0.34	0.8329	1.4651
246 to 248°	741	0.30	0.8339	1.4658
248 to 250°	741	0.31	0.8355	1.4662
250 to 252°	741	0.39	0.8360	1.4670
252 to 254°	741	0.51	0.8381	1.4675
254 to 256°	740	0.24	0.8388	1.4684
256 to 258°	740	0.39	0.8398	1.4690
258 to 260°	740	0.40	0.8410	1.4698
260 to 262°	738	0.34	0.8418	1.4700
262 to 264°	738	0.37	0.8434	1.4708
264 to 266°	738	0.46	0.8440	1.4721
266 to 268°	737	0.43	0.8449	1.4725
268 to 270°	737	0.45	0.8455	1.4729
270 to 272°	735	0.27	0.8462	1.4732
272 to 274°	735	0.44	0.8469	1.4738
274 to 276°	733	0.23	0.8480	1.4741
276 to 278°	733	0.41	0.8483	1.4745
278 to 280°	736	0.38	0.8483	1.4745
280 to 282°	736	0.43	0.8595	1.4747
282 to 284°	741	0.23	0.8500	1.4750
284 to 286°	741	0.33	0.8498	1.4750
286 to 288°	741	0.40	0.8508	1.4754
288 to 290°	740	0.28	0.8508	1.4754
290 to 292°	740	0.29	0.8510	1.4756
292 to 294°	739	0.37	0.8513	1.4755
294 to 296°	739	0.22	0.8518	1.4760
296 to 298°	739	0.28	0.8525	1.4760
298 to 300°	739	0.28	0.8530	1.4760
TOTAL KEROSENE		28.80		
300 to 302°	739	...	0.8533	1.4761
302 to 304°	739	...	0.8540	1.4765

(a) Mercury column of thermometer became shattered.

85.84 per cent C and 13.99 per cent H

The residual oil of the 300 to 302° fraction (after separation of the ozonide) was refined by means of liquid sulfur dioxide, according to the method of Edeleanu.[1] The oil thus refined, washed and dried, had the refractive index 1.4712 at 14°, and was found to contain

85.42 per cent C 14.12 per cent H
Calculated for C_nH_{2n} 85.62 per cent C 14.38 per cent H

The oil extracted therefrom by the liquid sulfur dioxide, after washing, etc., had the refractive index 1.5222 at 16° and contained

82.42 per cent C 10.31 per cent H 7.27 per cent O (dif.)

The 296 to 298° fraction, weighing 58.34 g. after treatment with sodium, and filtration, was treated in the cold with ozonized air for five successive days. The ozonide was washed with about 25 cc. of light gasoline, to which it gave only a slight color. After evaporation of the residual gasoline in a current of natural gas there remained 5.8 g. of ozonide—10 per cent of the weight of oil. Some of this ozonide was treated with anhydrous ether, yielding a red colored solution, which was poured off from a brick-red insoluble powder. After the evaporation of the ether there remained a transparent red syrup which hardened slowly like a varnish. A portion for analysis was spread in a film over the inner surface of a porcelain boat and dried in a desiccator. Its weight became constant at 0.4122 g. On combustion this gave 0.9623 g. CO_2 and 0.2336 g. H_2O.

Found 63.67 per cent C 6.34 per cent H
Calculated for $C_{17}H_{20}O_6$ 63.72 per cent C 6.30 per cent H 29.98 per cent O

This is in accordance with the results obtained by Molinari and Fenaroli[2] with distillates from Roumanian and Russian petroleums.

The 252 to 254° fraction—the largest of the upper kerosene—after drying over sodium, was refined with liquid sulfur dioxide.

A—The refined oil had a specific gravity of 0.8240 at 15° and the refractive index 1.4660 at 15°. Its composition was found to be

85.29 per cent C 13.98 per cent H

B—The sulfur dioxide extract, after washing, etc., had the refractive index 1.5412 at 12° and the composition

88.94 per cent C 10.19 per cent H 0.87 per cent O (dif.)
Calculated for $C_{15}H_{20}$ 89.93 per cent C 10.07 per cent H

This extract, B, was then treated with ozonized oxygen, in the cold. It yielded an ozonide which when freshly precipitated was flaky and almost white, but slowly resinified. It was taken up in absolute ether and shaken with successive portions of a dilute aqueous solution of potassium hydroxide until freed from acids. It was then washed, and dried over calcium chloride. After evaporation of the ether a thick resinous syrup remained. 0.4681 g. of the dry substance gave 1.2712 g. CO_2 and 0.2884 g. H_2O.

Found 74.06 per cent C 6.89 per cent H
Calc. for $C_{15}H_{16}O_3$ 73.73 per cent C 6.61 per cent H 19.66 per cent O

Molinari and Fenaroli isolated from the petroleum of Velleja, Italy, a flaky white ozonide having the composition $C_{15}H_{16}O_6$, which they believe to have been formed from the hydrocarbon $C_{15}H_{16}$ by the addition of two O_3 groups to two double bonds. Possibly our original product also may have been the same double ozonide, which on treatment with alkali lost half of its oxygen.

In the excellent work "Wissenschaftliche Grundlagen der Erdölbereitung," by Dr. L. Gurwitsch, Berlin, 1913, pp. 34–35, the significance of the suggestion of Molinari and Fenaroli regarding the preëxistence of hydrocarbons of the series C_nH_{2n-14} in kerosene is critically discussed, and it is pointed out that oxidation may precede the ozonide formation. The analysis of the sulfur dioxide extract of the unoxidized 252 to 254° fraction shows approximately the same hydrogen content as the hydrocarbon $C_{15}H_{20}$. Since, however, the extraction method cannot effect complete separation of the two classes of hydrocarbons it is very probable that this extract may consist essentially of the hydrocarbon $C_{15}H_{16}$, contaminated by small residual quantities of ordinary naphthenes.

The ozone reaction has given us a valuable working tool for detecting new constituents of petroleum.

The extraction method of Edeleanu enables us to remove these constituents from the main body of the petroleum, in concentrated form and apparently unaltered condition.

In the opinion of the writer, however, the proof of the chemical composition of these reactive constituents awaits the development of an independent method of attacking the problem.

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[1] U. S. Pat. 911,553, Feb. 2, 1909; *Chem. Abs.*, **3**, 1082.

[2] *Berichte*, **41** (1908), 3407.

EFFECT OF PRESSURE ON YIELDS OF PRODUCTS IN THE DESTRUCTIVE DISTILLATION OF HARDWOOD

By R. C. PALMER

Received August 5, 1914

INTRODUCTION

A study of the effect of pressure on yields was conducted at the Forest Products Laboratory as a part of a series of experiments to devise methods of increasing the amounts of valuable products obtained in the destructive distillation of hardwoods.

It is generally known that certain primary reactions occur in the action of dry heat on wood substance in the absence of air, resulting in the primary products: acetic acid, methyl alcohol, a very complex tar, charcoal, and such gases as carbon dioxide, carbon monoxide and methane. From a theoretical standpoint, it is possible to produce secondary reactions between these primary products such as $2CH_3COOH = CH_3COCH_3 + CO_2 + H_2O$, resulting in a decrease in acetic acid, or $CH_3OH + CH_3COOH = CH_3COOCH_3 + H_2O$, giving a decrease in both alcohol and acetic acid.

The decomposition reactions of wood which result in the formation of tar are at present too little understood even for speculation but undoubtedly a relation exists between the tar and charcoal, both products containing a high carbon content,[1] and a relation between acid or alcohol and tar is certainly not impossible

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[1] Ultimate analysis of birch tar has been given as $C_{36}H_{43}O_{16}$. Klason, *Arch. f. Kemie Min. and Geol.*, Vol. **5**, No. 7.

METHOD OF MAKING EXPERIMENTS

APPARATUS—A diagrammatic sketch of the apparatus used is shown in Fig. 1. This apparatus is a cast iron autoclave with walls 1 inch thick to withstand high pressure. The autoclave has a jacket filled with a heating medium. The heat is supplied by means of a giant Bunsen burner. A mixture of sodium and potassium nitrates was found to be a convenient bath material. A stirring device was provided for keeping the charge well mixed. It was found necessary to stir continuously during the exothermic reaction in order to secure check runs under any given conditions of pressure and size of chip.

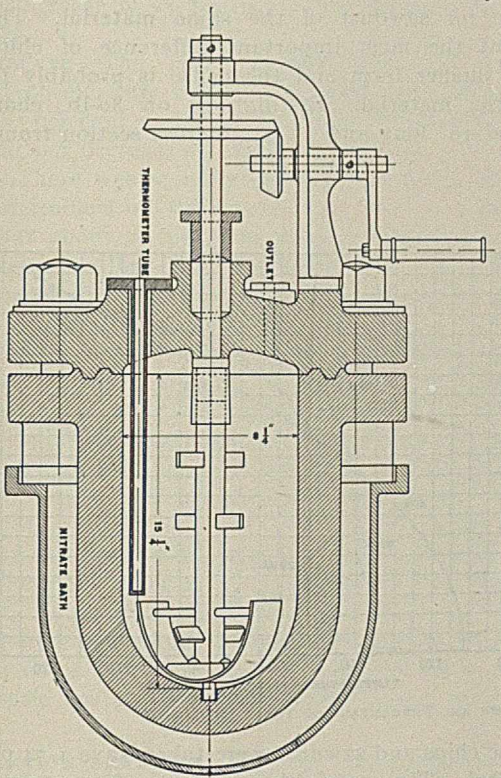


FIG. I—EXPERIMENTAL AUTOCLAVE

The temperature of the distillation was measured at a point as near the center of the charcoal residue as the stirrer would permit. In order that the reaction should be uniformly complete in all cases, the distillation was considered finished when the constant maximum temperature was maintained for 10 minutes with constant stirring. A final temperature of as near to 335° C. as possible was attained in each distillation.

In heating up the retort with air alone it was found that the temperature in the retort was constantly about 100° lower than the bath temperature, probably due to large conduction of heat through the heavy wall. Therefore, in making distillations, the bath was raised to about 450° C. and maintained at that temperature throughout the experiment.

OPERATION OF RETORT—Distillations were made using: (1) sawdust of two species, maple and birch; (2) chips averaging 1 by $^1/_8$ by $^1/_8$ inch of birch. For distillations in the autoclave the small material was selected because differences due to different qualities of material could be obviated. The objections to the use of small material because of difficulties in heating were avoided by stirring the charge. Also while probably not commercial in the ordinary types of distilling apparatus, sawdust or chips served the purpose of obtaining simply comparative results.

The different kinds of material were first distilled at atmospheric pressure under conditions as far as possible comparable with the ordinary methods of commercially distilling wood. Distillations were then made under different pressures up to 150 lbs. per sq. in. In the pressure distillations as soon as the first water distillate was coming in sufficient quantity to insure that all air had been displaced the outlet was closed until the desired pressure was obtained as indicated on a pressure gauge, the outlet then being opened just enough to maintain the pressure.

In most cases very little manipulation of the outlet valve was necessary to secure constant pressure conditions throughout the run except at the very last, when the quantity of distillate was very small. A typical data sheet is shown in Table I, which indicates the manner of making the distillations.

TABLE I—BIRCH CHIPS

Run No. 43. February 7, 1914.
Weight charge, 2903 g.
Oven dry weight, 2621 g.

Time	Temperature °C. Autoclave	Temperature °C. Bath	Pressure Lbs.	Total distillate Cc.	REMARKS
8.30 A.M.	...	...	..	....	Gas on
9.39	116	363	..	....	Distillation began
9.51	155	400	60	....	60 lbs. reached
9.57	179	415	60	100	
10.02	194	425	60	200	Tar started
10.06	209	429	60	300	Stirred continuously
10.09	225	435	60	400	
10.11	242	440	60	500	
10.13	250	442	60	600	
10.15	272	442	60	700	
10.16	286	443	60	800	
10.17	298	444	..	900	
10.18	311	447	60	1000	
10.23	325	450	60	1100	
10.27	331	452	60	1130	Gas off
10.30	335	452	60	1155	Kept on stirring
10.33	338	445	60	1162	
10.37	338	...	60	1166	
10.40	337	...	60	1168	
12.20 P.M.	220	...	0	1197	
				Total, 1229	

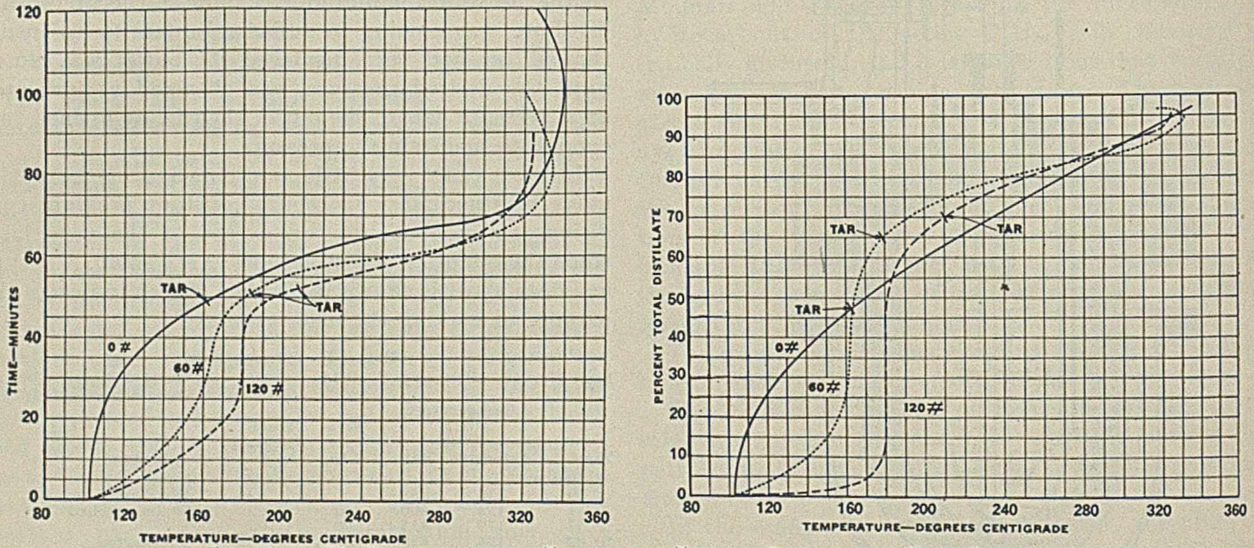
RESULTS

RELATION BETWEEN TIME, TEMPERATURE, AND PER CENT OF DISTILLATE—Figs. 2 and 3 show the relation between time, temperature, and per cent of total distillate for typical distillations made at 0, 60, and 120 lbs. pressure. Distillations were usually complete within two hours after the distillate began coming over. It is evident from the temperature distillate curve that the temperature was not the true average temperature of the autoclave but only served as an indication of the rate of rise of the temperature.

Free tar began coming over in the distillate after about the same lapse of time in each case, but at 160° for 0 lbs., 180° for 60 lbs. and about 210° C. for 120 lbs. pressure. From numerous other experiments by the author and from the reports of other investigators the destructive distillation point accompanied by the formation of free tar occurs at about 275° C. at atmospheric pressure. The thermometer reading is, therefore, evidently too low during the distillation stage. However, since with air alone the thermometer could not be rasied within 100° of the bath, and since the final temperature was in nearly all cases about 100° lower than the bath, the final indicated temperature was probably more nearly correct. No allowance is made for the heat developed by the exothermic reaction of distillation but with only about 3000 g. of wood this would not be very great.

In spite of the uncertainty of having measured the actual temperature the following effects of pressure or the manner of distillation are indicated:

I—The decided difference in the temperature-time and temperature-per cent distillate curves with increasing pressures is probably due entirely to the increase in boiling point of water under pressure. At 60 lbs. pressure, water boils at 155° C.; at 120 lbs. pressure, at 176° C. The flattening out of the curves for these pressures occurs very close to these points.



FIGS. II AND III—RELATION BETWEEN TEMPERATURE-TIME AND PERCENTAGE OF TOTAL DISTILLATE

II—The destructive distillation point as indicated by the formation of tar takes place at a higher temperature with increasing pressure.

III—The higher the pressure the more distillate is obtained before tar is formed during destructive distillation. The moisture content of the charge in the typical cases drawn would not account for this difference as the 0 and 120 lb. runs were 18.9 per cent and 19.1 per cent moisture, respectively, while the 60 lb. run was 25.4 per cent moisture.

TABLE II—EFFECT OF PRESSURE ON DESTRUCTIVE DISTILLATION (Results in percentages of oven dry weight of material)

MATERIAL	Pressure Lbs.	Acid	Alcohol	Charcoal	TAR Dissolved	TAR Total	Concentration of dissolved tar in distillate	Per cent. pyro acid minus moisture	Gas	Gas, tar and charcoal	Tar and charcoal
Maple sawdust..........	0	5.59	1.09	38.93	3.74	8.04	9.05	35.0	25.2	72.17	46.97
	60	4.81	1.18	41.49	1.33	3.23	3.49	28.8	30.3	75.02	44.72
	150	4.10	1.08	42.46	0.97	2.67	2.72	27.66	29.36	74.49	45.13
Birch sawdust...........	0	6.76	1.15	37.2	5.28	11.98	8.53	36.37	19.70	68.98	49.18
	60	5.34	1.23	40.38	1.40	4.25	2.93	29.95	25.10	69.73	44.63
	120	5.20	1.25	42.07	1.12	3.86	2.71	29.84	25.55	71.48	45.93
Birch chips.............	0	6.32	1.42	36.61	12.55	16.96	24.4	42.64	16.03	69.60	53.57
	60	5.61	1.50	39.5	6.29	11.70	12.1	34.23	20.13	71.33	51.20
	120	5.44	1.53	40.48	5.64	9.08	8.75	32.90	21.21	70.77	49.56

EFFECT OF PRESSURE ON PRODUCTS—The distillate from each run was allowed to stand until all free tar had settled out and the clear pyroligneous acid had separated. Both acid liquor and settled tar were then weighed and measured. The crude pyroligneous acid was analyzed for acid, alcohol, and dissolved tar. The results obtained from different forms of wood and different species are given in Table II. The results in each case are the average of at least three consistent distillations.

The alcohol yields from chips are decidedly higher than for sawdust of the same material. This was about the most important difference of chips over the smaller form and the cause is probably the size of the material. Distillations on 80-lb. charges of wood 18″ long and 3″ × 3″ cross section from which these chips and sawdust were taken gave 1.54 per cent alcohol. The same thing held true for maple. Sawdust gave lower yields of alcohol compared to large forms of wood.

The effects of pressure on the products of destructive distillation were independent of the form and species used and were in general as follows:

ACETIC ACID—Increased pressure tended to decidedly decrease the yield of acetic acid, the average effect of distilling at 120 lbs. over 0 lb. being a decrease of about 25 per cent. In the case of maple sawdust at 150 lbs. the yield of acid was 28 per cent less than at 0 lb.

ALCOHOL—Up to 120 lbs. the effect of pressure was to increase slightly the yield of alcohol, about 8 per cent more alcohol being obtained at this pressure over 0 lb.

Three-quarters as much increase, or 6 per cent, was obtained with 60 lbs. pressure. In the case of maple sawdust at 150 lbs. the yield was practically the same as at 0 lb., indicating that above 120 lbs. the effect of pressure is to decrease rather than increase the yield of alcohol. This was also substantiated by a number of preliminary distillations.

CHARCOAL—At 60 lbs. pressure, 8 per cent more charcoal was obtained than at 0 lb., and at 120 lbs. there was an increase of 11 per cent over atmospheric distillations.

DISTILLATE—The clear pyroligneous acid, independent of moisture content of wood, was decreased about 20 per cent under 60 lbs. pressure but had only small further decrease at 120 lbs. or 150 lbs.

GAS—There was a similar but reverse effect on the gas (determined by difference). At 60 lbs. pressure there was about 25 per cent more gas than at 0 lb., but 120 or 150 lbs. only gave very little more gas or even less than 60 lbs. (maple sawdust at 150 lbs. gave 2 per cent less than at 60 lbs.).

TAR—The most decided effect of distilling under pressures greater than 0 lb. was on the tar. At 60 lbs. the yield of total tar (tar which settled out of the distillate plus tar dissolved in the crude pyroligneous acid) was 60 to 65 per cent less than at 0 lb. and at 120 lbs. and 150 lbs. pressure about 68 per cent less. This same effect was even more apparent on the dissolved tar alone. A decrease of as much as 75 per cent at 150 lbs. over 0 lb. being obtained for maple sawdust. The high yield of tar from birch chips as compared to sawdust was probably due to the fact that the chips were very dry. Other work on a much larger scale has given the same effect using very dry wood.

RELATION BETWEEN GAS, TAR, AND CHARCOAL

It seemed probable that some relation might be established between gas, tar, and charcoal, and this has been indicated in Table II. Any such relation is not very marked, however, although the sum of the three products is fairly constant.

It is of interest to compare these results with some recent work of Klason[1] who has studied the effects of distilling birch under pressures lower than atmospheric, a pressure of 0.01 mm. being maintained even during the gas stage by immersing the receiver in liquid air. In brief, the same tendencies were obtained, *viz.*, the higher the pressure (in this case atmospheric compared to pressures of 0.01 mm.) the more alcohol and charcoal were obtained and less tar, but Klason reported practically no effect on the acetic acid.

SUMMARY

I—Destructive distillations of birch and maple were made on a small scale to study the effect of pressures greater than atmospheric on the yields of products.

II—In general, the effect of destructively distilling wood under increasing pressure is to increase the alcohol slightly when moderate pressures are used and to increase the charcoal and gas. Further effects were to decrease the acetic acid, the pyroligneous liquor, and tar.

III—The effects of 60 lbs. pressure over 0 lb. are much more decided on all products than the effects of increasing the pressure beyond 60 lbs.

IV—The most decided effect of pressure was on the tar. At 60 lbs. pressure this product was decreased 60 to 65 per cent.

V—From a practical standpoint, the most interesting effect of pressure is in connection with the yield of soluble tar.

Distillations were made at pressures as high as 450 lbs., but the exothermic reaction was so violent that it was not advisable to continue the experiments. At this pressure, the concentration of the dissolved tar in the pyroligneous acid was so low that redistillation was not necessary in order to titrate the distillate—or in practical operation the first distillation of the primary liquor would not be necessary in order to make gray acetate of lime. It is possible that pyroligneous acid free from soluble tar might be obtained by subjecting the distillate to a high pressure during the vapor stage but the application of this result is not yet apparent.

FOREST PRODUCTS LABORATORY
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[1] "Experiments on the Dry Distillation of Wood," Peter Klason, *Arch. f. Kemie Min. and Geol.*, Vol. **5**, No. 7.

OILS OF THE CONIFERAE: III. THE LEAF AND TWIG AND THE CONE OILS OF WESTERN YELLOW PINE AND SUGAR PINE

By A. W. SCHORGER

Received October 1, 1914

The leaf oil of western yellow pine (*Pinus ponderosa*, Laws.) has apparently never been examined chemically. Brown[1] in 1901 briefly described a plant in Oregon operating on the needles of *Pinus ponderosa*, the products obtained being oil and fiber. A ton of the needles produced ten pounds of oil, equivalent to a yield of 0.50 per cent of oil, which is considerably larger than the yield obtained from the California trees.

LEAF AND TWIG OILS OF WESTERN YELLOW PINE

The oils varied in color from bright yellow to green. When exposed to the light for two or three days the yellow oils also acquired a green color. Some oils showed a green fluorescence.

FRACTIONAL DISTILLATION OF THE LEAF OIL OF WESTERN YELLOW PINE

Boiling point, ° C.	Per cent
161–165	10
165–170	64
170–185	9
185–250	12.5
155–185 (35 mm.)	3

PHYSICAL AND CHEMICAL CONSTANTS OF THE OILS OF WESTERN YELLOW PINE

Nos. 2173–2443 distilled from needles only; 2497–2560, from needles and twigs

Sample No.	Sp. gr. 15° C.	Ref. index 15° C.	$\alpha_{D20°}$	Acid No.	Ester No.	Ester No. after acetylation	Percentage		
							Acetate	Free alcohol	Yield of oil
2173	0.8762	1.4815	—15.73	2.36	4.02	27.58	1.41	6.60	0.040
2174	0.8718	1.4812	—17.30	1.87	5.70	24.11	2.00	5.13	0.040
2384	0.8729	1.4794	—18.72	1.15	5.15	34.18	1.80	8.16	0.057
2385	0.8750	1.4793	—18.62	1.58	6.71	34.15	2.35	7.75	0.072
2386	0.8739	1.4789	—17.47	1.73	7.11	32.52	2.49	7.12	0.066
2387	0.8747	1.4797	—18.62	1.58	3.88	26.19	1.36	6.24	0.097
2403	0.8784	1.4807	—18.72	2.11	5.94	35.10	2.08	8.20	0.058
2404	0.8849	1.4832	—16.81	1.28	5.15	28.81	1.80	6.62	0.115
2442	0.8722	1.4802	—17.82	0.88	7.65	28.79	2.68	5.91	0.095
2443	0.8765	1.4808	—19.59	0.85	7.83	31.97	2.74	6.76	0.074
2497	0.8793	1.4805	—17.26	0.87	6.32	35.68	2.21	8.08	0.126
2498	0.8838	1.4837	—17.02	0.84	8.10	30.59	2.84	6.29	0.122
2499	0.8844	1.4838	—16.77	0.67	5.89	31.58	2.06	7.20	0.124
2560	0.8755	1.4812	—15.94	0.73	6.73	25.14	2.35	5.14	0.084

α-PINENE—The oil contains but a small amount

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[1] *Scientific American*, **84** (1901), 344.

of α-pinene, since after repeated fractionation only 7.25 g. (1.5 per cent) were obtained between 157 and 160°. The oil had a specific gravity of 0.8660 at 15° and the optical rotation $\alpha_{\mathrm{D}23^\circ}$ —27°.0. A small yield of pinene nitrosochloride melting at 102.5° was obtained.

Camphene was not detected in the portion b. p. 160–163°.

β-PINENE—The oil consists largely of β-pinene, 375 g. (75 per cent) boiling between 160–170°, mainly between 164–167°. The fraction boiling at 166° had the specific rotation α_{D} —19.87°. After oxidizing 150 g. of the oil with alkaline potassium permanganate, 76 g. of oil were recovered by steam distillation, while the oxidation liquor yielded 27.5 g. of sodium nopinate, equal to a yield of 37.2 per cent based on 74 grams of oxidized oil. The free nopinic acid melted at 126°. By further oxidation the ketone nopinone was obtained, the semicarbazone of which melted at 188°.

DIPENTENE—The oil boiling between 170–180° amounted to 33 g. (6.6 per cent). The fraction b. p. 170–175°, $\alpha_{\mathrm{D}20^\circ}$ —11.90°, yielded a dihydrochloride melting at 50°. The fraction b. p. 175–180°, $\alpha_{\mathrm{D}22^\circ}$, —11.83°, gave a tetrabromide melting at 124°.

BORNEOL—The oil boiling between 205–250° was saponified and the portion b. p. 205–217°, $\alpha_{\mathrm{D}25^\circ}$ —17.68°, heated with phthalic anhydride. The phthalic ester was purified in the usual way. On saponification and steam distillation a small amount of oil was recovered. On oxidizing the oil with Beckmann's reagent solid camphor was obtained. The amount of camphor was too small for recrystallization. After sublimation it melted at about 160°. The material had the appearance and odor of camphor and showed the property of the latter substance of rotating when dropped on water.

"GREEN OIL."—On distillation at 35 mm. pressure 15.5 g. (3.1 per cent) of oil distilled between 155–185°. The oil was greenish yellow in color and had: d_{15° 0.9270; $\alpha_{\mathrm{D}26^\circ}$ —8.39° for a 56 per cent solution in ether. No solid derivations were obtained. It gave the usual color reactions for "green oil."

ACIDS—The oil previous to distillation was extracted with sodium carbonate. Acetic and formic acids were found to be present in the extract by means of their silver salts. These acids were also obtained by hydrolysis of the esters.

CONE OIL OF WESTERN YELLOW PINE

The oil had the following properties: Color, light green; d_{15° 0.8757, $n_{\mathrm{D}15^\circ}$ 1.4789, $\alpha_{\mathrm{D}20^\circ}$ —11.48°, acid No. 1.27, ester No. 7.20, ester No. after acetylation 22.41, yield of oil 0.063 per cent.

Fractional Distillation of Cone Oil of Western Yellow Pine

Boiling point, ° C.	Per cent
164–170	57
170–195	29
195–250	3.5
250–290	3.5

FURFURAL—The aqueous extract from the first fraction gave a strong color reaction for furfural when treated with aniline and hydrochloric acid.

α-PINENE—The α-pinene fraction b. p. 159–164°, $\alpha_{\mathrm{D}25^\circ}$ —25.33°, amounted to 7.8 g. (6.3 per cent). Pinene was identified by means of the nitrosochloride melting at 103°.

β-PINENE—On oxidation of the fraction b. p. 164–170°, d_{15° 0.8659, $\alpha_{\mathrm{D}22^\circ}$ —18.62°, with alkaline $KMnO_4$ sodium nopinate was obtained. The free nopinic acid melted at 126–127°. The total β-pinene fractions amounted to 74.2 g. (60 per cent).

DIPENTENE—Two fractions, amounting to 15.8 g. (12.8 per cent), were collected between 170–176°. The fraction b. p. 170–173°, $\alpha_{\mathrm{D}20^\circ}$ —6.40, was examined for phellandrene with negative results. Dissolved in dry ether and saturated with dry HCl gas, the oil gave a good yield of dihydrochloride melting at 50°.

BORNEOL—The ester fraction was too small for examination. The free alcohol and ester content have been calculated as borneol and bornyl acetate.

"GREEN OIL"—The oil boiling between 250–290° was dark green in color and weighed 4.08 g. (3.3 per cent). A crystalline hydrochloride was not obtained.

LEAF AND TWIG OILS OF SUGAR PINE

The color of the oils of the sugar pine (*Pinus lambertiana*, Dougl.) ranged from pale lemon-yellow to dark reddish yellow and light green to greenish yellow.

Fractional Distillation of Oil of Sugar Pine

Boiling point, ° C.	Per cent
158–165	40
165–170	29
170–186	18
186–210	1
210–250	9

FURFURAL—This aldehyde was qualitatively detected in the first fractions.

α-PINENE—The fraction examined for α-pinene had: b. p. 156–158°, d_{15° 0.8645, $\alpha_{\mathrm{D}24^\circ}$ —10.16°. A good yield of pinene nitrosochloride, m. p. 103°, was obtained. The nitrolpiperidine melted at 119°. The total α-pinene fractions, b. p. 156–160°, weighed 89.5 g. (20.7 per cent).

β-PINENE—The β-pinene fractions amounted to 51 per cent and distilled largely between 164 and 167°. Oxidation of 100 g. of oil having a b. p. of 164–167°, d_{15° 0.8680, $\alpha_{\mathrm{D}25^\circ}$ —15.73, with alkaline $KMnO_4$ gave 12 g. of sodium nopinate, 64 g. of oil being recovered by steam distillation. The free nopinic acid melted at 126° and the nopinone semicarbazone at 188.5°.

Physical and Chemical Constants of the Oils of Sugar Pine

Sample No.	Sp. gr. 15° C.	Ref. index 15° C.	$\alpha_{\mathrm{D}20^\circ}$	Acid No.	Ester No.	Ester No. after acetylation	Percentage Acetate	Percentage Free alcohol	Percentage Yield of oil
2175	0.8738	1.4794	—11.07	2.38	4.04	28.46	1.41	6.84	...
2405	0.8703	1.4777	—16.50	1.34	2.22	29.68	0.78	7.71	0.045
2406	0.8710	1.4779	—16.18	1.44	3.55	32.04	1.24	8.01	0.052
2409	0.8676	1.4794	—15.52	0.68	4.51	24.35	1.58	5.54	0.098
2413	0.8686	1.4795	—15.49	0.97	5.91	23.25	2.07	4.84	0.097
2469	0.8705	1.4790	—11.83	1.06	5.42	29.27	1.90	6.68	0.110
2470	0.8695	1.4785	—12.70	1.02	4.19	28.49	1.47	6.81	0.120

DIPENTENE—Bromination of a fraction b. p. 174–178°, d_{15° 0.8581, $\alpha_{\mathrm{D}29^\circ}$ —22.17°, gave a tetrabromide melting at 124°. The dihydrochloride of the fraction b. p. 170–174° melted at 50°, indicating the absence of sylvestrene. The total dipentene fractions amounted to 52.4 g. (12 per cent).

BORNEOL—The fraction b. p. 205–235° was saponified, distilled with steam, and heated with phthalic anhydride. On saponification of the phthalic ester and distillation with steam an oil first passed over followed by a very small amount of solid borneol. On oxidizing, the oil camphor melting at 167–170° was obtained. An alcoholic solution of the camphor was *l*-rotatory.

COMBINED ACIDS—The acids obtained by saponification of the esters were precipitated in three fractions containing 35.27 per cent, 40.80 per cent and 64.86 per cent silver. The silver content of the fractions shows that acetic acid is present along with a higher fatty acid or acids.

"GREEN OIL"—About 1 per cent of "green oil" was obtained from the residue after removal of the esters, and appeared to be identical with the high-boiling fraction occurring in other needle oils.

CONE OIL OF SUGAR PINE

The oil and the following properties: Color, light green; d_{15° 0.8692, n_{D15° 1.4771, α_{D20° —23.18°, acid No. 0.63, ester No. 3.75, ester No. after acetylation 17.04, yield of oil 0.318 per cent.

FRACTIONAL DISTILLATION OF CONE OIL OF SUGAR PINE

Boiling point, ° C.	Per cent
159.5–165	64
165 –170	19
170 –194	11
194 –230	2.5
230 –255	1
255 –290	1

FURFURAL—Furfural was qualitatively detected in the first fraction.

α-PINENE—The fraction b. p. 155–159°, d_{15° 0.8646, α_{D17° —30.62°, gave a nitrosochloride melting at 98–99°. The pinene nitrolpiperidine melted at 116° after three crystallizations from alcohol and a fourth crystallization did not raise the melting point. The total α-pinene fractions amounted to 57.5 g.

CAMPHENE—The camphene fractions distilled as follows: (1) b. p. 160–161°, weight 21.5 g., (2) b. p. 161–163°, weight 33.9 g., d_{15° 0.8683, α_{D17° —26.42°. Fifty grams of the oil were treated with glacial acetic acid-sulfuric acid mixture. From the reaction product 6.5 g. of crystalline isoborneol were recovered. After repeated crystallization the isoborneol melted at 211–212° in a sealed tube.

β-PINENE—The β-pinene fractions amounted to 104.5 g. (39.43 per cent). It boiled between 163–170° and had: d_{15° 0.8688, α_{D17° —22.65°. On oxidation a yield of 35 per cent of sodium nopinate was obtained. The free nopinic acid melted at 126°. Five grams of sodium nopinate on further oxidation yielded 1.6 g. of nopinone whose semicarbazone melted at 188–188.5°.

DIPENTENE—The fraction b. p. 170–180°, α_{D17° —15.10°, amounting to 4 4 per cent gave a dihydrochloride melting at 49–50°.

ESTER FRACTION—The portion b. p. 194–230°, after saponification, was too small for further examination. The free alcohol and ester content have been calculated as borneol and bornyl acetate.

Between 255–290°, 1 per cent of a yellow oil was obtained that appeared to be a sesquiterpene. On dissolving the oil in ether and saturating with HCl gas the solution turned purple. A crystalline hydrochloride was not obtained.

SUMMARY

The percentage composition of the leaf and twig and cone oils is approximately as follows:

	WESTERN YELLOW PINE		SUGAR PINE	
	Leaf and twig oil	Cone oil	Leaf and twig oil	Cone oil
Furfural	..	Trace	Trace	Trace
1-α-Pinene	2	6	21	22
1-Camphene	..	..	..	21
1-β-Pinene	75	60	51	39–40
Dipentene	6	12–13	12	4–5
Ester as bornyl acetate	2	2.5	1.5	1.5
Free alcohol (1-borneol)	7	4	8	3.5
"Green oil"	3	3–4	1	..
Sesquiterpene(?)	..	..	..	1
Losses	5	10	7	7

FOREST PRODUCTS LABORATORY
FOREST SERVICE, DEPARTMENT OF AGRICULTURE
(In Coöperation with the University of Wisconsin)
MADISON

THE EFFECT OF RESENE ON THE LATHERING OF SOAP SOLUTIONS[1]

By CHAS. H. HERTY AND C. W. WILLIARD

The total annual production of rosin on a conservative estimate is not less than 2,500,000 barrels of 500 lbs. each. Not less than half of this rosin is used in the manufacture of soap. The reason for its use in this industry lies in the fact that the acids of the rosin readily form alkali salts which are very soluble in water, hydrolyze readily and form solutions which lather freely when agitated.

But rosin contains on an average, approximately 7 per cent of "resene" or unsaponifiable matter. As this resene possesses none of the properties which make rosin valuable for soap-making it must be considered as a filler. According to the above figures therefore, from 40,000,000 to 45,000,000 lbs. of this filler, resene, go into soap annually.

Is it true that resene is to be regarded simply as a filler in soaps? May it not have some positive action, either prejudicial or beneficial? A search of the literature failed to show any recorded experiments on this subject and conversations with chemists of soap works failed to elicit any very definite convictions on the subject. In view of the large amount of this material annually used it seemed desirable, therefore, to carry out some experiments to determine this point. The line selected was the effect of resene on the lathering of soap solutions.

PREPARATION OF RESENE

The resene used in these experiments was prepared as follows: 1200 g. of the oleoresin of *Pinus heterophylla* (Cuban or slash pine) were dissolved in 9 liters of *N*/2 alcoholic potash and the solution allowed to stand 18 hrs. After filtering, water was added almost to precipitation and the solution extracted three times by shaking out thoroughly with petroleum ether, boiling below 70° C. Eight liters of the petroleum ether were used in each extraction. The three extracts were combined and shaken out with 10 liters of 50 per cent alcohol, in order to remove dissolved po-

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[1] Presented at the 48th Meeting of the American Chemical Society, Rochester, September 8–12, 1913.

tassium salts of resin acids. The extract was then concentrated by distillation until the temperature of the escaping vapors of petroleum ether reached 65° C. The concentrated residue was again shaken out with 50 per cent alcohol and subjected to steam distillation in order to remove the spirits of turpentine and residual petroleum ether. The resene, mixed with water from condensed steam, was dissolved in petroleum ether (boiling up to 50° C.), separated from the water layer by a separatory funnel, again washed with 50 per cent alcohol as a final precaution against dissolved potassium salts, and the petroleum ether evaporated, at first spontaneously, then for a short time on a steam bath with constant stirring: 65 g. of resene, an amber colored, very viscous mass, resembling well strained honey, were obtained.

ANALYSES OF SOAPS USED

Three different types of soap were used throughout the experiments; toilet, castile and cheap laundry. These soaps analyzed[1] as follows:

ABLE I—RESULTS IN PERCENTAGES

Soap	Starch	Moisture	Inert mineral matter	Total alkali	Fatty acids
Toilet	None	19	None	8.57	70
Castile	None	19	15	5.60	60
Laundry	None	23	30	5.00	40

EXPERIMENTAL

With each of the three soaps mentioned above two solutions were prepared, one by dissolving 5 g. of the soap in distilled water to a volume of 250 cc.; the other by dissolving 5 g. of the soap and 0.14 g. of resene in 250 cc. of alcohol, in order to secure uniform mixing of the soap and resene, evaporating the alcohol on a steam bath, and dissolving the residue in water to a volume of 250 cc. In all of the experiments described below 5 cc. portions of these solutions were diluted with the necessary amount of distilled water, the solutions placed in salt-mouth bottles provided with well ground glass stoppers and the bottles, two at a time, the one containing simply the soap solution, the other the soap plus resene solution, were placed on a double shaking apparatus, such as is commonly employed in making milk-shakes. These were given a violent shaking for 30 seconds and allowed to stand. After five minutes the observations were made as to the amount of lather on the surface of each solution. Preliminary experiments showed that concordant results could not be obtained when the bottles were shaken in the two hands at the same time. Dilutions at each 100 cc. were tested both at 20° and 45° C.

Comparison of the depth of the layer of lather on the soap solutions with that on the soap solutions to which resene had been added showed a marked diminution due to the presence of resene at the following dilutions:

TABLE II

Soap	Dilution showing decreased lather due resene 20°	45°
Laundry	400 cc.	600 cc.
Castile	800 cc.	1000 cc.
Toilet	1000 cc.	1200 cc.

From the figures in Table I it is seen that these differences in dilution correspond roughly to the percentages of alkali salts of fatty acids in the respective soaps.

Another set of tests were made at 20° C., doubling the weight of resene added to the soap solution with the following results:

TABLE III

Soap	Dilution showing decreased lather due to resene
Laundry	400 cc.
Castile	600 cc.
Toilet	800 cc.

The identity of results in the case of the laundry soap is doubtless due to the crudity of the method of measuring the thickness of the lather layer. The decreased dilutions in the case of the castile and toilet soaps show again the injurious effect of resene on the lathering power of soap solutions.

A more marked evidence of the effect of added resene on the lather is shown by the time required for complete subsidence of the lather. These experiments were made at 20° C. Again, in each case, 5 cc. of the solutions used in Table II were diluted, shaken 30 seconds and allowed to stand until all lather had disappeared.

TABLE IV

DILUTION Cc.	Laundry S	Laundry S + R	Castile S	Castile S + R	Toilet S	Toilet S + R
100	24	6	72	36	168	120
200	6	1	50	30	168	36
300	4	0.66	48	24	72	24

The hours required for such subsidence are given in Table IV, in which S represents the standard soap solutions and S + R the solution of soap containing added resene.

UNIVERSITY OF NORTH CAROLINA
CHAPEL HILL

PRELIMINARY NOTE ON DYES AND OTHER PRODUCTS FROM THE WASTE LIQUOR OF THE SODA CELLULOSE PROCESS

By MARSHALL P. CRAM

Received August 20, 1914

If the crude black liquor obtained from the digesters in the soda process is treated with hydrochloric acid, a precipitate is formed which is wholly organic. The maximum yield of this precipitate is obtained when 100 cc. of the crude liquor of specific gravity 1.25 are treated with 30 cc. concentrated hydrochloric acid (sp. gr. 1.18), the yield from the 100 cc. crude liquor being 14 g. If the acidified solution is heated to boiling, the precipitate gathers in lumps which can be removed easily, the substance being plastic when hot and brittle when cold. It is soluble in alkalies and dilute alcohol. It is believed that the crude precipitate might be used for the following purposes.

I—SIZE FOR PAPER—The precipitate is soluble in dilute sodium hydroxide, 10 g. requiring about 470 cc. $N/10$ NaOH. For 10 g. dry pulp in 222 cc. water 0.22 g. of the precipitate dissolved in dilute NaOH, with an equal weight of aluminum sulfate added later, gave a paper which would be called hard-sized. This paper had a tint on the reddish brown, which could be increased by using more of the sizing substance. The color could not be removed by any method tried, but while this would prevent the use of the material for a size for white paper, it would not be objectionable for colored paper, and the color of the material

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[1] The analyses were made according to the method given in Lamborn's "Modern Soaps, Candles and Glycerine," p. 650.

itself would be desirable for certain purposes. For 10 g. dry pulp, 0.054 g. of the material, followed by an equal weight of aluminum sulfate, gave a well sized paper, and 0.0135 g. a very light size. The crude liquor, which contains this precipitate already dissolved in NaOH together with inorganic salts, can also be used as a size for colored papers.

II—STAIN AND VARNISH FOR WOOD—The precipitate dissolved in dilute alkalies or alcohol can be applied to wood for a brown stain. It cannot be used as a varnish, for the residue contracts on drying. If, however, the total crude precipitate is treated with chloroform, about half the precipitate by weight dissolves; this solution on drying leaves a surface which does not contract, and which resembles varnish. It can be applied in chloroform, methyl or ethyl alcohol, or other volatile solvent. The part insoluble in chloroform can be used for a stain. There is some prospect that by precipitating the original precipitate fractionally, a fraction which can be used for a varnish might be obtained without using chloroform, but this has not been accomplished with entire success as yet.

III—SULFUR DYE—If the dry precipitate is mixed with powdered potassium sulfide (sodium sulfide has not been tried) and sulfur, and heated to 185° to 230° C., an odorous gas is given off, and the residue when extracted with water gives a solution which dyes wool, silk, and cotton a dark brown or black. The dye is taken by cotton without a mordant, and is quite fast to sunlight. Heating the mass to 310° destroys the dye which is first formed.

IV—If the precipitate is treated with nitric acid a solution is obtained which dyes wool brown if the acid is weak, or yellow if stronger acid is used. These dyes appear to be fast. They may also be obtained by nitrating the crude liquor.

If the filtrate from the precipitate thrown down with HCl is distilled, the distillate obtained contains acetic acid and some other compound, probably a phenol. Ten cc. of the distillate obtained from 150 cc. crude liquor with 45 cc. conc. HCl, when titrated with NaOH with phenolphthalein as indicator, required 40.3 cc. $N/10$ NaOH. The distillate with silver nitrate gave no precipitate of silver chloride, but on standing a red crystalline precipitate appeared. With a cold water solution of potassium nitrite the distillate gave a crystalline precipitate, the filtrate from which dyed wool and silk brown, but did not dye cotton. Crystalline precipitates were also obtained with nitric acid (this precipitate was dissolved if stronger nitric acid was added), ferric chloride, bromine water, and potassium permanganate. When treated with chlorine gas or a solution of bleaching powder the distillate gave a red solution which dyed wool and silk brown. The coloring matter could be removed from the water solution by extracting with chloroform.

The residue from the distillation could not be evaporated to dryness on the steam bath, which shows that some organic substance is present. The principal compound present, however, is sodium chloride, from which the organic matter may be burned off. This residue left on evaporation if heated somewhat under certain conditions is partly changed to a substance soluble in dilute alcohol but not in water. The alcoholic solution on being evaporated leaves a varnish-like coating.

If the filtrate from the hydrochloric acid precipitate of the crude liquor, before being distilled, is extracted with chloroform and the chloroform evaporated, a red colored residue is left. This is somewhat soluble in hot water to a colloidal solution which dyes silk pink, but does not dye cotton or wool. The color on silk, however, fades very rapidly.

If this water solution is treated with bromine or chlorine, a solution is obtained which dyes wool brown and silk gray; these colors are much faster than the pink. Ammonium persulfate gives browns on silk and wool, but not on cotton. Potassium nitrite gives a brown for silk.

The reason for publishing this investigation in the above fragmentary form, is the hope that attention may be called by it to the possibilities of a present waste product and that investigation may be directed thereto, at this particularly opportune time.

BOWDOIN COLLEGE, BRUNSWICK, MAINE

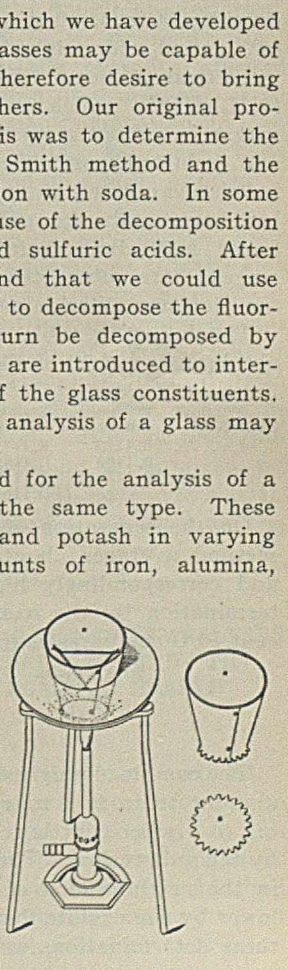
SOME RAPID METHODS FOR GLASS ANALYSIS[1]

By E. C. SULLIVAN AND W. C. TAYLOR

Received August 15, 1914

Some convenient methods which we have developed for the routine analyses of glasses may be capable of further application and we therefore desire to bring them to the attention of others. Our original procedure for a complete analysis was to determine the alkalies by the J. Lawrence Smith method and the other bases and silica by fusion with soda. In some cases we were able to make use of the decomposition of glass by hydrofluoric and sulfuric acids. After some experimenting we found that we could use oxalic acid in place of sulfuric to decompose the fluorides. The oxalates can in turn be decomposed by heat so that no bases or acids are introduced to interfere with the determination of the glass constituents. By this method the complete analysis of a glass may be finished in one day.

This method was developed for the analysis of a large number of glasses of the same type. These contained silica, lead, soda and potash in varying proportions with small amounts of iron, alumina,



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[1] The radiator used was made up from a description by W. F. Hillebrand in *Bulletin* No. **422**, U. S. Geol. Survey, p. 31, and is described here as it has considerable influence on the success of the method. R is of sheet iron, aluminum or nickel, 6 to 7 cm. high, 8 cm. wide at top and 5 cm. at bottom. The base B may be of iron, nickel or platinum but not of aluminum, which will not stand the temperature of the direct flame. B is attached to R by turning the cogs of B up and over those of R. A platinum triangle should be inserted about 4 cm. from the base. An aluminum ring with an opening slightly larger than the underlying crucible should be placed over the radiator to hasten evaporation.

manganese, lime and magnesia as impurities. For these glasses the following method was used: One gram of finely powdered glass is placed in a platinum crucible of about 40 cc. capacity, moistened with water, 2 g. of $H_2C_2O_4$ crystals added and enough 48 per cent HF to fill the crucible half full. This is evaporated to dryness on a radiator,[1] the temperature of which is just high enough to expel the excess of oxalic acid. When all the acid has been expelled the crucible is cooled and the evaporation repeated twice more with oxalic acid and water. The amount of oxalic acid used is about 5 g. in all. It was necessary to know the amount used as a blank showed 0.0012 g. of alkali chlorides from this source. After the third evaporation, when all the excess of oxalic acid is expelled, the remaining oxalates are taken up with hot water, allowed to cool and filtered. The residue which, in the case of the glasses mentioned, consists of PbC_2O_4 only, with trace of CaC_2O_4, may be titrated directly with $KMnO_4$ or dissolved in dilute HNO_3 and determined as sulfate. The filtrate from the PbC_2O_4 is evaporated to dryness in a platinum dish and then heated over a free flame until oxalates are decomposed. The carbonates are then taken up with water and HCl and the mixture is evaporated to dryness to remove the small amount of SiO_2. The salts are taken up with a few drops of HCl and hot water, a few drops of bromine water added, then a little ammonia, and the solution is boiled. The precipitate of hydroxides of iron, aluminum and manganese is filtered off, ignited and weighed. The filtrate is divided into two equal portions. To one are added NH_4OH and $(NH_4)_2HPO_4$, which precipitate a small amount of magnesia—about 1 mg. This is calculated to chloride and deducted from weight of NaCl, KCl. The other half is evaporated to dryness, ammonia salts expelled by heat and the chlorides weighed. The $MgCl_2$ found and alkali from blank determination on all reagents are subtracted and the K_2O determined by the platinum chloride method and Na_2O by difference.

The following table will show some of the results obtained on weight of alkali chlorides from 1 g. sample:

Glass No.	J. L. Smith method Gram	Oxalate Gram	Glass No.	J. L. Smith method Gram	Oxalate Gram
1.......	0.1170	0.1175	2.......	0.1177	0.1199
	0.1168	0.1162	3.......	0.1196	0.1198
	0.1176	0.1169	4.......	0.1290	0.1294
		0.1163	5.......	0.1168	0.1169

On the separation of soda and potash the oxalate method averages about 0.15 per cent lower in K_2O and correspondingly higher in Na_2O. The lead determination by the oxalate method expressed in per cent PbO compares as follows:

Soda Fusion	Oxalate
21.00	21.22
21.13	21.15
	21.30
	21.18

The combined weights of iron, alumina and manganese amount to from 1 to 1.5 per cent and average from 0.2 to 0.3 per cent lower by the oxalate method than by the soda fusion. The amounts of CaO and MgO are in the neighborhood of 0.1 per cent and are slightly lower by the oxalate method where determined though these determinations were usually omitted. We have used this method since on a large number of similar samples and have found it satisfactory for glasses of this type.

In applying this method to other glasses the procedure following the three evaporations must of course be varied. The first step is to separate the soluble and insoluble oxalates. From there on the procedure may vary according to what elements are present. The oxalates we have worked with group themselves as follows:

Insoluble			Soluble	
Lead	Copper 2	Magnesium 2	Sodium	Manganese 3
Calcium	Cobalt 2		Potassium	Iron 4
Zinc	Nickel 2		Aluminum	Arsenic
Cadmium 1	Barium 2		Chromium	Antimony 5

1—Almost quantitative; in presence of zinc traces present with soluble oxalates.

2—Though mostly insoluble, these elements must be looked for with the soluble oxalates unless particular precautions are taken to have conditions right to render the oxalates insoluble. Presence of other elements also affects the solubility of these oxalates.

3—Manganese up to 2 per cent gave no test for the element with the insoluble oxalates but a glass containing 6 per cent MnO showed nearly half this amount as an insoluble oxalate.

4—Does not occur with insoluble oxalates except in zinc glasses when a small amount is found with the zinc.

5—Normally soluble but has been found with insoluble oxalates when these were heated too strongly.

Arsenic or antimony, if present, should be removed from the soluble oxalates with H_2S before the oxalates are decomposed. This necessitates acidifying with HCl, which must be expelled before decomposing the remaining oxalates; otherwise alkali chlorides are volatilized. The insoluble oxalates are in general dissolved in dilute HCl and separations made as in any mixture of chlorides. Borates do not interfere with the analysis. A number of analyses of glasses and silicates of other types are given to show results obtained by this method. The figures given are the difference between the oxalate method from the soda fusion and J. Lawrence Smith method. They are expressed as + when oxalate method is higher and — when lower.

	A	B	C	D	E	F
Na_2O........	—0.08	+0.26	—0.16	—0.11	+0.18	+0.14
K_2O.........	—0.06	±0.00	+0.10	±0.00	—0.08	—0.04
CaO.........	—0.22	—0.05	..	—0.05	..	..
$Al_2O_3.Fe_2O_3$...	+0.04	—0.08	..	±0.00	+0.03	—0.04
ZnO.........	..	+0.13	+0.07	—0.30	+0.04	..

A—An ordinary soda lime glass
B—A soda lime, zinc borosilicate
C—A soda potash zinc glass
D—A soda zinc borosilicate
E—A soda potash zinc glass
F—A soda alumina borosilicate

The presence of more than 3 per cent alumina causes difficulty, owing to its interfering with the expulsion of fluorine by oxalic acid. Except the lead glass all those containing Al_2O_3 gave a test for fluorine in the soluble oxalates, and the amount of such fluorine was greater for high Al_2O_3 content than for low.

Feldspar gave very low results for alkali. A sample yielding 0.1246 g. of alkali chlorides by the J. Lawrence Smith method gave 0.0909 g. by the oxalate method. This was increased to 0.1102 g. by reprecipitation of the alumina and to 0.1230 g. by a second reprecipitation. With several alumina glasses low results were obtained on both Al_2O_3 and alkali, while with other glasses either Al_2O_3 was low and alkali high or alkali was low and alumina high. From the data at hand it seems as if both alkali and Al_2O_3 were apt to be lost at some stages of the analysis but so far our results are not consistent, probably due to the variation in temperature in different analyses. In some we get conditions favorable for a loss of alkali, in some for a loss of Al_2O_3 and sometimes for both. We have, with great care in heating, obtained only slightly low results where both Al_2O_3 and Na_2O were very high as in cryolite. The loss therefore probably can be prevented.

Boric oxide tends to alleviate the difficulty caused by alumina and it does not in any way interfere with later determinations. Borosilicates with up to 5 per cent Al_2O_3 give fairly good results. One showed 4.82 per cent Al_2O_3 and 0.1010 g. alkali chlorides by regular methods and 4.93 per cent Al_2O_3 and 0.1027 g. alkali chlorides by the oxalate method. The results on glass G mentioned in the table are not very good, however. With glasses not containing B_2O_3 the addition of boric acid before evaporation with HF and $H_2C_2O_4$ decreased the fluorine content of the soluble oxalates and also gave higher results for Al_2O_3 and alkali without showing any B_2O_3 present with the alkali.

From the results so far we do not feel confidence in the method for such glasses as show undecomposed silico-fluorides, for while accurate determinations may be obtained with special precautions the method has no advantages under such conditions. For glasses which do not contain much Al_2O_3 the method seems well adapted, especially for the analysis of a series of glasses of very nearly the same composition. We have also found it convenient for the rapid determination of As_2O_3 or Sb_2O_3 in glass.

DETERMINATION OF BORIC ACID

In the analysis of borosilicate glasses we have found that for the determination of boric oxide the method described by Wherry[1] is very useful:

> "Fuse the sample with about 3 g. of Na_2CO_3 for 15 minutes. Take up with 20 to 30 cc. of dilute HCl adding a few drops of HNO_3 to oxidize ferrous iron. Place in a 250 cc. round-bottomed flask, heat nearly to boiling, and add dry precipitated $CaCO_3$ in moderate excess. Connect with a return condenser and boil vigorously for about 10 minutes. Filter out the precipitate through a small Büchner funnel, washing several times with hot water, but keeping the total volume of liquid below 100 cc. Return the filtrate to the flask, add a pinch of $CaCO_3$ and again heat to boiling; then connect with a filter pump, through a splash trap, and continue suction until the boiling has nearly ceased. Cool to the ordinary temperature, filter if the precipitate has a red color from iron, add four or five drops of phenolphthalein and run in slowly *N*/10 NaOH solution until the liquid is strongly pink in color. Introduce about 1 g. of mannite and shake, whereupon the pink color will disappear. Add NaOH to end reaction, then another gram of mannite and if necessary more alkali until a permanent pink color is obtained."

The method was first tried by fusing 0.5 g. sand and 0.2 g. boric acid with 3 g. soda. The melted mass was taken up with water and 7 cc. conc. HCl added after transfer to a 250 cc. flask. The method was then followed as described above except titration was made with $Ba(OH)_2$. The B_2O_3 content came from 2 to 10 per cent low, due to retention of B_2O_3 by the precipitate from $CaCO_3$. By using suction in filtering and washing this precipitate practically 100 per cent of the B_2O_3 introduced was recovered. For 0.25 g. B_2O_3 = 12.40 $Ba(OH)_2$ we used 12.35 and 12.40 cc. As iron and alumina are rarely present in large amounts in glass and as the time of the soda fusion with glass can be cut to a few minutes the method seemed quite readily adaptable.

The first glass tried was a soda alumina borosilicate which, from analysis, showed a possible B_2O_3 content of 10.40 per cent by difference. Three determinations by Wherry's method showed 10.72, 10.57, 10.67 per cent B_2O_3 or an average of 10.64 per cent. A soda borosilicate containing a small amount of BaO and Sb_2O_3 showed 25.57 per cent B_2O_3 by Wherry's method and 25.75 per cent by difference. Other glasses of same type showed:

Per cent B_2O_3 by titration	Per cent B_2O_3 by difference
25.10	25.12
12.71	12.15
17.57	17.51
14.90	15.01

With a zinc borosilicate very unsatisfactory results were obtained, the B_2O_3 content by titration running from 4 to 9 per cent when only 2 per cent was present. Several mixtures of ZnO and sand with a known amount of B_2O_3 were run through by Wherry's method and results for B_2O_3 were always high even after very long boiling. Solutions of $ZnCl_2$ and borax were boiled with $CaCO_3$ for varying lengths of time and using slight excess and large excess of $CaCO_3$ and zinc was always found in the filtrate from the $CaCO_3$ precipitate. CaO was substituted for $CaCO_3$ but with no better success. Na_2CO_3 completely removed the zinc from solution and by a double precipitation, using first Na_2CO_3 and then $CaCO_3$, we obtained 0.0360, 0.0361 and 0.0365 g. B_2O_3 when the theoretical amount was 0.0365 g. PbO was found to cause the same trouble as ZnO and the same modification of the method gave satisfactory results. We have been able to use the modified method on a large number of glasses with satisfactory results.

The modified method then is as follows: Fuse 0.5 g. of glass with 3 g. Na_2CO_3 for one or two minutes after mass is liquid. Take up with 20 to 30 cc. of hot water and when the melt is entirely decomposed filter out any insoluble oxides. After washing, transfer filtrate and washings to a 250 cc. round-bottomed flask, add about 7 cc. concentrated HCl, heat nearly to boiling and add dry precipitated $CaCO_3$ in moderate excess. From here on the method is as given by Wherry except that we used $Ba(OH)_2$ instead of NaOH. It is also advisable to use suction for filtering the $CaCO_3$ precipitate.

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THE COMPOSITION OF MILK AS SHOWN BY ANALYSES OF SAMPLES OF KNOWN PURITY MADE BY THE MASSACHUSETTS STATE BOARD OF HEALTH

By Hermann C. Lythgoe

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Milk, without doubt, is the most extensively adulterated of any article of human food and, by reason of its variable composition, the detection of this adulteration is difficult and in some cases impossible. For these reasons most legislative bodies, in addition to prohibiting the sale of adulterated milk, prohibit the sale of milk, the composition of which falls below

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[1] *J. Am. Chem. Soc.*, **30** (1908), 1687.

specified standards and in some places, as in the State of Massachusetts, the penalty for the sale of milk which is adulterated is more severe than that for the sale of milk below the legal standard. The milk analyst in such localities must familiarize himself with the composition of natural milk in order to detect and distinguish between milk which is adulterated and that which is simply below the legal standard. The usual methods of adulterating milk are the addition of water, the removal of cream or performance of both acts, the ease of which as well as the resulting profit has considerable to do with the extent of milk adulteration. As water is a natural component of milk, the detection of added water, as well as the removal of cream, can be accomplished only by showing abnormal chemical or physical constants which are consistent with the nature of the adulteration. Either or both of these forms of adulteration may be practised to a limited extent and be impossible of detection.

During the past six years, from 600 to 700 samples of known purity milk have been examined in the laboratory of food and drug inspection of the Massachusetts State Board of Health of which nearly 500 samples have been subject to a fairly complete analysis, 434 of which came from individual cows and the balance from herds. These samples were obtained from Jerseys, Guernsey, Ayrshire, Dutch Belt, and Holstein cows, as well as from cross-bred or so-called grade cows. The methods of analysis used were as follows:

TOTAL SOLIDS, as used by the Massachusetts State Board of Health for thirty years: Evaporate 5 g. of milk in a flat-bottomed platinum dish over a boiling water bath for 2 hrs. and weigh the residue.

ASH: Burn in a muffle the residue obtained as above, and weigh the ash.

FAT: By the Babcock method.

PROTEINS: From the percentage of nitrogen by the Gunning method using the factor 6.38.

LACTOSE: By the polariscopic method of the A. O. A. C., mercuric nitrate being used as a clarifier. If lead is used as a clarifier, the results are low, owing to the precipitation of lactose.

MILK SERUM—(1) COPPER METHOD:[1] Add four volumes of milk to one volume of copper sulfate solution (72.5 g. per liter adjusted to read 36.0 at 20° C. on the scale of the Zeiss Immersion Refractometer or to a specific gravity of 1.0443 at 20/4° C.), shake well and filter.

(2) ACETIC ACID METHOD:[2] To 100 cc. of milk add 2 cc. of 25 per cent acetic acid, heat for 20 minutes in a water bath at 70°, cool 10 minutes in ice water and filter.

(3) MODIFICATION OF PFYL AND TURNAU[3] called tetra serum I, giving the same serum which has been substituted in some instances for the acetic acid method. Shake 50 cc. of milk with 5 cc. of carbon tetrachloride in a shaking machine for 5 minutes, add 1 cc. of 20 per cent acetic acid, shake again for 5 minutes, centrifuge and pour off the clear serum.

(4) SOUR SERUM:[1] Allow the milk to sour spontaneously and filter.

(5) ASH OF SOUR SERUM:[2] Measure 25 cc. of the sour milk serum into a platinum dish, evaporate to dryness and burn in a muffle at a temperature not above 550° C. Weigh the residual ash.

The summary of the analyses of the samples arranged according to breeds in the order of the average total solids is given in Table I. Determinations of solids, fat, proteins, ash, and sugar were made upon all the samples, and the serum was prepared from nearly all the samples by one or more methods.

The variation in the composition of milk is due primarily to the breed of the cow but is more or less influenced by the period of lactation and the season of the year. It is very generally known that cows of the Jersey and Guernsey type give better milk than those of the Holstein variety, that cows far along in lactation give richer milk than just after calving and that milk obtained in the summer is inferior in quality to that obtained in the winter although popular opinion is opposed to this latter statement. The solids naturally show the highest numerical variation, from 17.17 to 10.20 per cent in the milk from individual cows and from 14.57 to 11.56 per cent in herd milk. The constituents having the most influence upon this variation are first the fat and to a less extent the proteins, the former varying from 7.7 to 2.45 per cent in milk from individual cows and from 5.40 to 3.35 per cent in herd milk and the latter from 5.01 to 2 per cent in milk from individual cows and from 4.02 to 2.66 per cent in herd milk. The numerical variation of the ash is very slight and that of the sugar is the least of the major constituents, the latter being from 5.80 to 3.91 per cent in milk from individual cows and from 5.25 to 4.35 per cent in herd milk.

The percentage variation is more marked than the numerical variation, being the greatest in the fat and least in the sugar. Owing to the presence of a few samples of abnormally high concentration, the percentage variations above the average are greater than those below the average.

Solids vary from 32 per cent above to 21 per cent below the average
Fat varies from 83 per cent above to 42 per cent below the average
Proteins vary from 53 per cent above to 39 per cent below the average
Sugar varies from 32 per cent above to 18 per cent below the average

Minimum solids were 40 per cent below the maximum solids
Minimum fat was 68 per cent below the maximum fat
Minimum proteins were 50 per cent below the maximum proteins
Minimum sugar was 32 per cent below the maximum sugar

Excluding some of the abnormally high figures these variations would be reduced. It is unusual to find the solids above 17 or below 10.5 per cent, the fat above 7 or below 2.5 per cent, the proteins above 4.5 or below 2.4 per cent, the solids-not-fat above 10 or below 7.8 per cent, and the sugar above 5.5 or below 4.3 per cent. Using these limits, which eliminates 26 samples, the variations from the average are much less than those calculated from all the samples.

Solids would vary from 31 per cent above to 19 per cent below the average
Fat would vary from 66 per cent above to 41 per cent below the average
Proteins would vary from 38 per cent above to 27 per cent below the average
Sugar would vary from 15 per cent above to 10 per cent below the average

Minimum solids would be 38 per cent below the maximum solids
Minimum fat would be 64 per cent below the maximum fat
Minimum proteins would be 47 per cent below the maximum proteins
Minimum sugar would be 22 per cent below the maximum sugar

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[1] Lythgoe, *Mass. State Board of Health Report*, **1908**, p. 594

[2] Leach and Lythgoe, *J. Am. Chem. Soc.*, **1904**, p. 1195.

[3] *Arb. Kais. Ges.*, **40**, 247.

[1] Matthes and Muller, *Z. öffentl. Chem.*, **9** (1903), 173.

[2] Burr and Berberich, *Chem. Ztg.*, **32**, 617.

TABLE I—SUMMARY OF ANALYSES OF SAMPLES OF MILK OF KNOWN PURITY

BREED	Jersey	Guernsey	Grade Jersey	Grade Guernsey	Grade Durham	Grade Ayrshire	Ayrshire	Grade Holstein	Dutch belt	Holstein	All samples	Herd milk
NUMBER OF SAMPLES	36	28	27	20	16	52	27	131	41	56	434	47
TOTAL SOLIDS—No. of samples between												
16 and 17.17 per cent	5	2	...	...	...	...	...	...	...	...	7	...
15 and 16 per cent	11	11	2	1	...	1	...	4	...	...	30	...
14 and 15 per cent	11	6	8	4	1	7	2	14	2	...	55	8
13 and 14 per cent	7	5	12	5	9	21	7	36	4	7	113	8
12 and 13 per cent	2	4	4	8	3	19	11	40	14	11	116	27
11 and 12 per cent	...	...	1	2	3	3	7	26	20	25	87	4
10.2 and 11 per cent	...	...	...	...	...	1	...	11	1	13	26	...
Highest, per cent	17.17	17.00	15.28	15.45	14.89	15.32	14.68	15.68	14.09	13.96	17.17	14.57
Lowest, per cent	12.43	12.15	11.40	11.46	11.73	10.77	11.44	10.58	10.93	10.20	10.20	11.56
Average, per cent	14.75	14.60	13.74	13.20	13.10	12.98	12.64	12.62	12.15	11.69	12.98	12.79
FAT—No. of samples between												
7 and 7.7 per cent	2	...	...	...	...	...	...	...	...	...	2	...
6 and 7 per cent	14	5	...	...	...	2	...	1	...	...	22	...
5 and 6 per cent	10	14	6	3	1	5	2	13	...	...	54	6
4 and 5 per cent	10	8	19	12	10	27	10	44	4	6	150	16
3 and 4 per cent	...	1	2	5	5	18	15	67	37	39	189	25
2.45 and 3 per cent	...	...	...	...	...	...	...	6	...	11	17	...
Highest, per cent	7.70	6.40	5.80	5.70	5.10	6.05	5.40	6.30	4.75	4.60	7.70	5.40
Lowest, per cent	4.20	3.80	3.00	3.50	3.25	3.00	3.30	2.45	3.00	2.45	2.45	3.35
Average, per cent	5.65	5.23	4.65	4.35	4.29	4.22	4.01	3.95	3.56	3.41	4.21	4.03
PROTEINS—No. of samples between												
4 and 5.01 per cent	3	8	2	...	3	...	...	6	...	1	23	1
3 and 4 per cent	28	16	23	13	10	41	12	86	19	21	269	36
2 and 3 per cent	5	4	2	7	3	11	15	39	22	34	142	10
Highest, per cent	4.42	5.01	4.20	3.94	4.37	3.92	3.91	4.47	3.61	4.03	5.01	4.02
Lowest, per cent	2.79	2.26	2.78	2.43	2.65	2.11	2.22	2.33	2.34	2.00	2.00	2.66
Average, per cent	3.46	3.73	3.45	3.27	3.39	3.22	2.99	3.25	2.96	2.93	3.27	3.31
ASH												
Highest, per cent	0.84	0.84	0.86	0.78	0.80	0.85	0.87	0.87	0.77	0.84	0.87	0.79
Lowest, per cent	0.64	0.69	0.69	0.66	0.63	0.66	0.58	0.56	0.63	0.64	0.56	0.65
Average, per cent	0.72	0.75	0.75	0.72	0.73	0.75	0.76	0.73	0.70	0.72	0.76	0.74
SOLIDS-NOT-FAT—No. of samples between												
10 and 10.65 per cent	...	3	...	...	...	...	...	3	...	...	6	...
9 and 10 per cent	16	15	16	9	9	16	6	42	9	5	143	17
8 and 9 per cent	20	10	11	10	7	34	20	68	29	39	248	29
7.50 and 8 per cent	...	...	...	1	...	2	1	18	3	12	37	1
Highest, per cent	9.80	10.65	9.76	9.75	9.74	9.80	9.46	10.24	9.43	9.61	10.65	9.48
Lowest, per cent	8.13	8.00	8.40	7.96	8.47	7.77	7.89	7.50	7.63	7.55	7.50	7.63
Average, per cent	9.10	9.37	9.09	8.85	8.81	8.76	8.63	8.67	8.59	8.28	8.77	8.76
MILK SUGAR—No. of samples between												
5 and 5.80 per cent	20	7	9	10	4	17	16	40	14	9	146	11
4 and 5 per cent	16	21	18	10	12	35	11	90	27	47	287	36
3.91 and 4 per cent	...	...	...	...	...	...	...	1	...	...	1	...
Highest, per cent	5.80	5.22	5.46	5.34	5.29	5.75	5.30	5.58	5.35	5.20	5.80	5.25
Lowest, per cent	4.10	4.46	4.35	4.50	4.36	4.20	4.05	3.91	4.20	4.08	3.91	4.35
Average, per cent	4.94	4.84	4.87	4.94	4.86	4.85	4.88	4.65	4.93	4.70	4.78	4.83
PROTEIN—FAT RATIO												
Highest	0.80	0.82	0.86	0.90	0.91	0.98	0.92	0.99	0.97	0.99	0.99	0.95
Lowest	0.46	0.55	0.58	0.60	0.62	0.56	0.59	0.55	0.71	0.62	0.46	0.66
Average	0.61	0.71	0.74	0.75	0.79	0.76	0.75	0.82	0.83	0.86	0.78	0.82
FAT IN TOTAL SOLIDS												
Highest, per cent	47.4	38.6	38.8	35.9	35.4	40.4	36.3	40.0	31.8	33.5	47.4	37.1
Lowest, per cent	33.1	31.0	30.1	30.6	27.7	27.9	27.2	25.0	26.3	25.0	25.0	28.2
Average, per cent	38.3	35.9	33.9	33.0	32.7	32.8	31.8	31.3	30.9	29.2	32.5	31.6
REFRACTION OF COPPER SERUM AT 20° C.												
No. of samples between												
40 and 40.4	...	...	...	...	...	...	...	2	...	...	2	...
39 and 40	6	1	3	1	...	7	...	4	2	2	26	...
38 and 39	22	17	8	8	6	17	7	39	11	10	145	16
37 and 38	3	9	11	7	4	20	5	32	2	22	115	20
36 and 37	...	...	...	...	1	5	3	23	...	21	53	2
TOTAL NO. OF SAMPLES	31	27	22	16	11	49	15	100	15	55	341	38
Highest, scale reading	39.5	39.0	39.3	39.0	38.8	39.7	38.8	40.4	39.0	39.3	40.4	38.8
Lowest, scale reading	37.1	37.0	37.2	36.6	36.6	36.0	36.0	36.0	37.3	36.0	36.0	36.7
Average, scale reading	38.1	38.2	38.0	38.0	38.0	37.9	37.7	37.6	38.3	37.2	37.9	37.8
REFRACTION OF ACETIC SERUM AT 20° C.												
No. of samples between												
45 and 47.5	3	4	...	2	...	...	...	2	3	...	14	...
44 and 45	7	11	2	4	...	4	3	4	5	3	43	3
43 and 44	5	8	10	10	7	6	5	12	12	4	79	6
42 and 43	1	3	7	1	3	5	10	12	14	8	64	12
41 and 42	...	2	1	1	1	6	2	12	6	5	36	3
40 and 41	...	...	...	...	1	2	...	4	...	14	21	...
TOTAL NO. OF SAMPLES	16	28	20	18	12	23	20	46	40	34	257	24
Highest, scale reading	45.2	47.5	44.1	45.5	43.6	44.4	44.5	46.6	44.4	44.6	47.5	44.6
Lowest, scale reading	42.4	41.3	41.3	41.8	40.7	40.2	41.5	40.0	41.0	40.0	40.0	41.8
Average, scale reading	44.2	43.9	42.9	43.7	42.7	42.5	42.8	42.5	42.8	41.6	43.3	42.7
REFRACTION OF SOUR MILK SERUM AT 20° C.												
No. of samples between												
44 and 50.9	1	...	...	...	...	1	...	12	...	...	14	...
43 and 44	5	...	2	...	2	7	...	13	...	1	30	3
42 and 43	6	...	3	1	1	5	1	11	...	4	32	7
41 and 42	2	...	...	...	1	5	3	13	...	8	32	5
40 and 41	1	...	2	1	1	4	...	3	...	3	15	...
39 and 40	...	...	...	...	...	2	2	10	...	3	17	...
38.3 and 39	...	...	...	...	...	...	1	3	...	3	7	...
TOTAL NO. OF SAMPLES	15	...	7	2	5	24	7	65	...	22	147	15
Highest, scale reading	44.2	...	43.7	42.6	43.5	44.4	42.7	50.9	...	43.0	50.9	43.5
Lowest, scale reading	40.7	...	40.4	40.8	40.5	39.4	38.7	38.3	...	38.4	38.3	41.3
Average, scale reading	42.7	...	42.2	41.7	42.1	41.9	40.5	42.1	...	40.6	41.9	42.3
ASH OF SOUR MILK SERUM												
No. of samples between												
0.9 and 0.932 g. per 100 cc.	...	...	...	...	...	...	1	2	...	...	3	...
0.8 and 0.9 g. per 100 cc.	7	...	4	...	2	8	2	17	...	3	43	5
0.730 and 0.8 g. per 100 cc.	8	...	2	2	1	10	1	35	...	9	68	8
TOTAL NO. OF SAMPLES	15	...	6	2	3	18	4	54	...	12	114	13
Highest, g. per 100 cc.	0.828	...	0.824	0.774	0.836	0.868	0.916	0.932	...	0.860	0.932	0.852
Lowest, g. per 100 cc.	0.740	...	0.776	0.732	0.790	0.736	0.777	0.732	...	0.730	0.730	0.764
Average, g. per 100 cc.	0.786	...	0.804	0.753	0.811	0.790	0.856	0.793	...	0.795	0.794	0.792

The variations calculated from the analyses of the herd milk are, of course, much less than those obtained from the milk of individual cows. Experience has shown it to be improbable that cows giving abnormal milk will be present even in small herds of six or eight in sufficient numbers to render the herd milk abnormal. Of the herd milk,

Solids varied from 14 per cent above to 10 per cent below the average
Fat varied from 34 per cent above to 17 per cent below the average
Proteins varied from 21 per cent above to 20 per cent below the average
Sugar varied from 9 per cent above to 10 per cent below the average
Minimum solids were 21 per cent below the maximum
Minimum fat was 38 per cent below the maximum
Minimum proteins were 34 per cent below the maximum
Minimum sugar was 18 per cent below the maximum

The solids-not-fat (consisting of the proteins, lactose and ash) are much less variable than the solids or the fat and formerly was the only figure used in detecting added water, yet the variation here is considerable. A less variable figure, the soluble solids (consisting of the albumin, ash, and sugar varying between 5.95 and 6.45 per cent in herd milk and between 5.80 and 6.60 per cent in milk from individual cows), has been suggested by Cornalba[1] as a means of detecting added water, and this is substantially what is obtained when preparing the milk serum.

It has been known that the composition of milk is influenced by the season and by the time since calving. In order to show if these variations existed in the samples examined, the Grade Holstein, Grade Durham, Ayrshire and Grade Ayrshire milk were selected, thus excluding the exceptionally high Jersey and Guernsey and the exceptionally low Holstein and Dutch Belt figures. These 224 analyses were first arranged by months and because of the small number of samples obtained in some months, the averages were not representative and the arrangement was therefore made by seasons. Of these samples, the period of lactation was known in 194 cases and seasonal averages were made of these, together with averages of the same analyses arranged according to the period of lactation. These figures, together with the variation according to season of the herd milk, are shown in Table II.

TABLE II—KNOWN PURITY MILK SAMPLES ARRANGED ACCORDING TO SEASONS AND PERIOD OF LACTATION

HERDS	No. of samples	Total solids	Fat	Proteins	Ash	Solids not fat	Lactose	Refraction of serum			Ash of sour serum	Protein-fat ratio	Per cent fat in solids	Average period of lactation
								Copper	Acetic	Sour				
Winter (Dec.-Feb.)	9	13.23	4.20	3.41	0.76	9.03	4.88	37.9	44.3	42.2	0.779	0.81	31.7	..
Spring (Mar.-May)	15	12.87	4.14	3.13	0.73	8.74	4.92	38.3	43.3	42.5	0.789	0.76	32.2	..
Summer (June-Aug.)	8	12.39	3.73	3.15	0.75	8.66	4.71	37.5	42.3	42.2	0.853	0.84	30.1	..
Fall (Sept.-Nov.)	13	12.85	3.94	3.37	0.74	8.91	4.80	37.7	42.8	41.7	0.775	0.86	30.7	..
Average	45	12.79	4.03	3.31	0.74	8.76	4.83	37.8	42.7	42.3	0.792	0.82	31.6	..
INDIVIDUAL COWS														
Winter (Dec.)	40	13.16	4.24	3.39	0.75	8.92	4.80	38.2	43.7	43.1	0.778	0.80	32.2	..
Spring	88	12.72	4.00	3.16	0.75	8.72	4.78	37.7	42.5	42.0	0.811	0.79	31.4	..
Summer	36	12.46	3.97	3.18	0.77	8.59	4.55	37.3	41.9	39.8	0.803	0.80	31.8	..
Fall	60	12.79	3.97	3.28	0.73	8.82	4.84	37.9	42.4	40.4	0.801	0.83	31.1	..
Average	224	12.76	4.03	3.23	0.74	8.73	4.77	37.7	42.5	41.3	0.809	0.80	31.6	..
TIME SINCE CALVING														
1 month	25	12.70	3.98	2.93	0.73	8.72	4.90	38.1	42.1	42.6	0.785	0.74	31.3	3 weeks
2 to 5 months	82	12.76	3.97	3.19	0.74	8.79	4.86	37.7	42.6	41.8	0.779	0.78	31.1	3.4 months
6 to 9 months	58	13.03	4.14	3.43	0.75	8.89	4.71	37.7	42.3	42.0	0.817	0.83	31.7	7.5 months
10 to 15 months	29	13.15	4.22	3.43	0.76	8.93	4.75	37.7	43.4	42.2	0.788	0.81	32.1	10.6 months
Average	194	12.89	4.06	3.29	0.75	8.83	4.81	37.7	42.6	42.1	0.793	0.81	31.6	5.4 months
ABOVE SAMPLES ACCORDING TO SEASONS														
Winter	39	13.16	4.24	3.39	0.75	8.92	4.80	38.2	43.7	43.1	0.778	0.80	32.2	5.1 months
Spring	70	12.65	3.92	3.19	0.75	8.73	4.78	37.7	42.5	42.0	0.811	0.82	31.0	5.6 months
Summer	31	12.44	3.99	3.18	0.75	8.45	4.55	37.3	41.9	39.8	0.803	0.80	32.0	5.6 months
Fall	54	12.84	4.00	3.27	0.76	8.84	4.87	37.9	42.4	40.4	0.801	0.82	31.2	4.7 months

A perusal of this table concerning the seasonal variation shows that milk obtained in the winter is the best, that obtained in the summer is the worst, while milk obtained in the spring and fall is a mean of the summer and winter samples. These differences, however, are by no means as marked as those observed between the different breeds. The period of lactation appears to have no influence upon the variation by season for in the series of 194 samples arranged by seasons, the average period of lactation was practically the same in each season. All the results are affected by the seasonal variation and all but the sugar and serum figures are affected by the period of lactation. The protein-fat ratio and the percentage of fat in the solids of these samples were not materially affected either by the season or by the period of lactation.

RELATION BETWEEN THE MILK SOLIDS AND ITS CONSTITUENTS

RELATION BETWEEN THE SOLIDS AND THE FAT—The percentage of fat in the solids decreases with the solids; in the Jersey milk, it averages 38 and in the Holstein milk 27 per cent. The highest figure was 47.4 obtained from a sample of Jersey milk and the lowest 25.0 per cent, from a sample of Holstein milk.

RELATION BETWEEN THE SOLIDS AND PROTEINS—The amount of proteins in the solids is fairly constant at about 25 per cent. Olson[1] has given for the approximate calculation of the protein from the solids the formula $P = T\,S - \frac{T\,S}{1.34}$ where P equals proteins and T S equals total solids.

RELATION BETWEEN THE SOLIDS AND THE ASH—As the ash is nearly constant, the percentage of ash in the solids increases as the solids diminish, being 4.9 in Jersey milk and 6.7 per cent in Holstein milk.

RELATION BETWEEN THE TOTAL SOLIDS AND SUGAR—Like the ash the sugar is nearly constant and the percentage of sugar in the solids increases as the solids decrease. In Jersey milk the average figure is 30 and in Holstein milk 40 per cent.

RELATION BETWEEN THE DIFFERENT MILK CONSTITUENTS

PROTEIN-FAT RATIO—This has been extremely studied by Van Slyke[2] and his average ratios being based upon several thousand analyses are of more value than those shown in Table I. The figures for the protein-fat ratio for the different breeds are as follows:

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[1] *Ann. Fals.*, **2**, 529.

[1] THIS JOURNAL, **1**, 256.

[2] *J. Am. Chem. Soc.*, **30**, 1166.

Breed	Protein-fat ratio Van Slyke	From Table I	Breed	Protein-fat ratio Van Slyke	From Table I
Holstein-Friesan	1 : 0.87	1 : 0.86	Shorthorn	1 : 0.80	.....
Dutch Belt	.....	1 : 0.83	Devon	1 : 0.80	.....
Ayrshire	1 : 0.82	1 : 0.75	Guernsey	1 : 0.66	1 : 0.71
American Holderness	1 : 0.83	.....	Jersey	1 : 0.64	1 : 0.61

There seem to be three groups of cows according to the protein-fat ratio, those of the Jersey type with the protein-fat ratio below 0.7, those of the Holstein type with the protein-fat ratio above 0.85, and the balance of the breeds with a protein-fat ratio about 0.8. Van Slyke has given for the approximate calculation of the proteins from the fat, the formula $P = 0.4(F - 3) + 2.8$ where P equals proteins and F equals the fat.

TABLE III—CALCULATED SUGAR

FAT %	TOTAL SOLIDS																															
	10.5 %	10.6 %	10.7 %	10.8 %	10.9 %	11.0 %	11.1 %	11.2 %	11.3 %	11.4 %	11.5 %	11.6 %	11.7 %	11.8 %	11.9 %	12.0 %	12.1 %	12.2 %	12.3 %	12.4 %	12.5 %	12.6 %	12.7 %	12.8 %	12.9 %	13.0 %	13.1 %	13.2 %	13.3 %	13.4 %	13.5 %	13.6 %
2.5	4.63 4.70	4.70 4.80	4.78 4.90	4.86 5.00	4.93 5.10	5.01 5.20	5.08 5.30	5.16 5.40	5.23 5.50	5.31 5.60	5.38 5.70	5.46 5.80	5.53 5.90	5.61 6.00	5.68 6.10	5.76 6.20	5.83 6.30	5.90 6.40	5.98 6.50	6.05 6.60	6.13 6.70	6.20 6.80	6.28 6.90	6.35 7.00	6.43 7.10	6.50 7.20	6.58 7.30	6.66 7.40	6.73 7.50	6.80 7.60	6.88 7.70	6.96 7.80
2.6	4.53 4.56	4.60 4.66	4.68 4.76	4.76 4.86	4.83 4.96	4.91 5.06	4.98 5.16	5.06 5.26	5.13 5.36	5.21 5.46	5.28 5.56	5.36 5.66	5.43 5.76	5.51 5.86	5.58 5.96	5.66 6.06	5.73 6.16	5.80 6.26	5.88 6.36	5.95 6.46	6.03 6.56	6.10 6.66	6.18 6.76	6.25 6.86	6.33 6.96	6.40 7.06	6.48 7.16	6.56 7.26	6.63 7.36	6.70 7.46	6.78 7.56	6.86 7.66
2.7	4.43 4.42	4.50 4.52	4.58 4.62	4.66 4.72	4.73 4.82	4.81 4.92	4.88 5.02	4.96 5.12	5.03 5.22	5.11 5.32	5.18 5.42	5.26 5.52	5.33 5.62	5.41 5.72	5.48 5.82	5.56 5.92	5.63 6.02	5.70 6.12	5.78 6.22	5.85 6.32	5.93 6.42	6.00 6.52	6.08 6.62	6.15 6.72	6.23 6.82	6.30 6.92	6.38 7.02	6.46 7.12	6.53 7.22	6.60 7.32	6.68 7.42	6.76 7.52
2.8	4.33 4.28	4.40 4.38	4.48 4.48	4.56 4.58	4.63 4.68	4.71 4.78	4.78 4.88	4.86 4.98	4.93 5.08	5.01 5.18	5.08 5.28	5.16 5.38	5.23 5.48	5.31 5.58	5.38 5.68	5.46 5.78	5.53 5.88	5.60 5.98	5.68 6.08	5.75 6.18	5.83 6.28	5.90 6.38	5.98 6.48	6.05 6.58	6.13 6.68	6.20 6.78	6.28 6.88	6.36 6.98	6.43 7.08	6.50 7.18	6.58 7.28	6.66 7.38
2.9	4.23 4.14	4.30 4.24	4.38 4.34	4.46 4.44	4.53 4.54	4.61 4.64	4.68 4.74	4.76 4.84	4.83 4.94	4.91 5.04	4.98 5.14	5.06 5.24	5.13 5.34	5.21 5.44	5.28 5.54	5.36 5.64	5.43 5.74	5.50 5.84	5.58 5.94	5.65 6.04	5.73 6.14	5.80 6.24	5.88 6.34	5.95 6.44	6.03 6.54	6.10 6.64	6.18 6.74	6.26 6.84	6.33 6.94	6.40 7.04	6.48 7.14	6.56 7.24
3.0	4.13 4.00	4.20 4.14	4.28 4.24	4.36 4.34	4.43 4.44	4.51 4.54	4.58 4.64	4.66 4.74	4.73 4.84	4.81 4.94	4.88 5.00	4.96 5.10	5.03 5.20	5.11 5.30	5.18 5.40	5.26 5.50	5.33 5.60	5.40 5.70	5.48 5.80	5.55 5.90	5.63 6.00	5.70 6.10	5.78 6.20	5.85 6.30	5.93 6.40	6.00 6.50	6.08 6.60	6.16 6.70	6.23 6.80	6.30 6.90	6.38 7.00	6.46 7.10
3.1	4.03 3.86	4.10 3.96	4.18 4.06	4.26 4.16	4.33 4.26	4.41 4.36	4.48 4.46	4.56 4.56	4.63 4.66	4.71 4.76	4.78 4.86	4.86 4.96	4.93 5.06	5.01 5.16	5.08 5.26	5.16 5.36	5.23 5.46	5.30 5.56	5.38 5.66	5.45 5.76	5.53 5.86	5.60 5.96	5.68 6.06	5.75 6.16	5.83 6.26	5.90 6.36	5.98 6.46	6.06 6.56	6.13 6.66	6.20 6.76	6.28 6.86	6.36 6.96
3.2	3.93 3.72	4.00 3.82	4.08 3.92	4.16 4.02	4.23 4.12	4.31 4.22	4.38 4.32	4.46 4.42	4.53 4.52	4.61 4.62	4.68 4.72	4.76 4.82	4.83 4.92	4.91 5.02	4.98 5.12	5.06 5.22	5.13 5.32	5.20 5.42	5.28 5.52	5.35 5.62	5.43 5.72	5.50 5.82	5.58 5.92	5.65 6.02	5.73 6.12	5.80 6.22	5.88 6.32	5.96 6.42	6.03 6.52	6.10 6.62	6.18 6.72	6.26 6.82
3.3	3.83 3.58	3.90 3.68	3.98 3.78	4.06 3.88	4.13 3.98	4.21 4.08	4.28 4.18	4.36 4.28	4.43 4.38	4.51 4.48	4.58 4.58	4.66 4.68	4.73 4.78	4.81 4.88	4.88 4.98	4.96 5.08	5.03 5.18	5.10 5.28	5.18 5.38	5.25 5.48	5.33 5.58	5.40 5.68	5.48 5.78	5.55 5.88	5.63 5.98	5.70 6.08	5.78 6.18	5.86 6.28	5.93 6.38	6.00 6.48	6.08 6.58	6.16 6.68
3.4	3.73 3.44	3.80 3.54	3.88 3.64	3.96 3.74	4.03 3.84	4.11 3.94	4.18 4.04	4.26 4.14	4.33 4.24	4.41 4.34	4.48 4.44	4.56 4.54	4.63 4.64	4.71 4.74	4.78 4.84	4.86 4.94	4.93 5.04	5.00 5.14	5.08 5.24	5.15 5.34	5.23 5.44	5.30 5.54	5.38 5.64	5.45 5.74	5.53 5.84	5.60 5.94	5.68 6.04	5.76 6.14	5.83 6.24	5.90 6.34	5.98 6.44	6.06 6.54
3.5	3.63 3.30	3.70 3.40	3.78 3.50	3.86 3.60	3.93 3.70	4.01 3.80	4.08 3.90	4.16 4.00	4.23 4.10	4.31 4.20	4.38 4.30	4.46 4.40	4.53 4.50	4.61 4.60	4.68 4.70	4.76 4.80	4.83 4.90	4.90 5.00	4.98 5.10	5.05 5.20	5.13 5.30	5.20 5.40	5.28 5.50	5.35 5.60	5.43 5.70	5.50 5.80	5.58 5.90	5.66 6.00	5.73 6.10	5.80 6.20	5.88 6.30	5.96 6.40
3.6	3.53 3.16	3.60 3.26	3.68 3.36	3.76 3.46	3.83 3.56	3.91 3.66	3.98 3.76	4.06 3.86	4.13 3.96	4.21 4.06	4.28 4.16	4.36 4.26	4.43 4.36	4.51 4.46	4.58 4.56	4.66 4.66	4.73 4.76	4.80 4.86	4.88 4.96	4.95 5.06	5.03 5.16	5.10 5.26	5.18 5.36	5.25 5.46	5.33 5.56	5.40 5.66	5.48 5.76	5.56 5.86	5.63 5.96	5.70 6.06	5.78 6.16	5.86 6.26
3.7	3.43 3.02	3.50 3.12	3.58 3.22	3.66 3.32	3.73 3.42	3.81 3.52	3.88 3.62	3.96 3.72	4.03 3.82	4.11 3.92	4.18 4.02	4.26 4.12	4.33 4.22	4.41 4.32	4.48 4.42	4.56 4.52	4.63 4.62	4.70 4.72	4.78 4.82	4.85 4.92	4.93 5.02	5.00 5.12	5.08 5.22	5.15 5.32	5.23 5.42	5.30 5.52	5.38 5.62	5.46 5.72	5.53 5.82	5.60 5.92	5.68 6.02	5.76 6.12
3.8	3.33 2.88	3.40 2.98	3.48 3.08	3.56 3.18	3.63 3.28	3.71 3.38	3.78 3.48	3.86 3.58	3.93 3.68	4.01 3.78	4.08 3.88	4.16 3.98	4.23 4.08	4.31 4.18	4.38 4.28	4.46 4.38	4.53 4.48	4.60 4.58	4.68 4.68	4.75 4.78	4.83 4.88	4.90 4.98	4.98 5.08	5.05 5.18	5.13 5.28	5.20 5.38	5.28 5.48	5.36 5.58	5.43 5.68	5.50 5.78	5.58 5.88	5.66 5.98
3.9	3.23 2.74	3.30 2.84	3.38 2.94	3.46 3.04	3.53 3.14	3.61 3.24	3.68 3.34	3.76 3.34	3.83 3.44	3.91 3.64	3.98 3.64	4.06 3.84	4.13 3.94	4.21 4.04	4.28 4.14	4.36 4.24	4.43 4.34	4.50 4.44	4.58 4.54	4.65 4.64	4.73 4.74	4.80 4.84	4.88 4.94	4.95 5.04	5.03 5.14	5.10 5.24	5.18 5.34	5.26 5.44	5.33 5.54	5.40 5.64	5.48 5.74	5.56 5.84
4.0	3.13 2.60	3.20 2.70	3.28 2.80	3.36 2.90	3.43 3.00	3.51 3.10	3.58 3.20	3.66 3.30	3.73 3.40	3.81 3.50	3.88 3.60	3.96 3.70	4.03 3.80	4.11 3.90	4.18 4.00	4.26 4.10	4.33 4.20	4.40 4.30	4.48 4.40	4.55 4.50	4.63 4.60	4.70 4.70	4.78 4.80	4.85 4.90	4.93 5.00	5.00 5.10	5.08 5.20	5.16 5.30	5.23 5.40	5.30 5.50	5.38 5.60	5.46 5.70
4.1	3.03 2.46	3.10 2.56	3.18 2.66	3.26 2.76	3.33 2.86	3.41 2.96	3.48 3.06	3.56 3.16	3.63 3.26	3.71 3.36	3.78 3.46	3.86 3.56	3.93 3.66	4.01 3.76	4.08 3.86	4.16 3.96	4.23 4.06	4.30 4.16	4.38 4.26	4.45 4.36	4.53 4.46	4.60 4.56	4.68 4.66	4.75 4.76	4.83 4.86	4.90 4.96	4.98 5.06	5.06 5.16	5.13 5.26	5.20 5.36	5.28 5.46	5.36 5.56
4.2	2.93 2.32	3.00 2.42	3.08 2.52	3.16 2.62	3.23 2.72	3.31 2.82	3.38 2.92	3.46 3.02	3.53 3.12	3.61 3.22	3.68 3.32	3.76 3.42	3.83 3.52	3.91 3.62	3.98 3.72	4.06 3.82	4.13 3.92	4.20 4.02	4.28 4.12	4.35 4.22	4.43 4.32	4.50 4.42	4.58 4.52	4.65 4.62	4.73 4.72	4.80 4.82	4.88 4.92	4.96 5.02	5.03 5.12	5.10 5.22	5.18 5.32	5.26 5.42
4.3	2.83 2.18	2.90 2.28	2.98 2.38	3.06 2.48	3.13 2.58	3.21 2.68	3.28 2.78	3.36 2.88	3.43 2.98	3.51 3.08	3.58 3.18	3.66 3.28	3.73 3.38	3.81 3.48	3.88 3.58	3.96 3.68	4.03 3.78	4.10 3.88	4.18 3.98	4.25 4.08	4.33 4.18	4.40 4.28	4.48 4.38	4.55 4.48	4.63 4.58	4.70 4.68	4.78 4.78	4.86 4.88	4.93 4.98	5.00 5.08	5.08 5.18	5.16 5.28
4.4	2.73 2.04	2.80 2.14	2.88 2.24	2.96 2.34	3.03 2.44	3.11 2.54	3.18 2.64	3.26 2.74	3.33 2.84	3.41 2.94	3.48 3.04	3.56 3.14	3.63 3.24	3.71 3.34	3.78 3.44	3.86 3.54	3.93 3.64	4.00 3.74	4.08 3.84	4.15 3.94	4.23 4.04	4.30 4.14	4.38 4.24	4.45 4.34	4.53 4.44	4.60 4.54	4.68 4.64	4.76 4.74	4.83 4.84	4.90 4.94	4.98 5.04	5.06 5.14
4.5	2.63 1.90	2.70 2.00	2.78 2.10	2.86 2.20	2.93 2.30	3.01 2.40	3.08 2.50	3.16 2.60	3.23 2.70	3.31 2.80	3.38 2.90	3.46 3.00	3.53 3.10	3.61 3.20	3.68 3.30	3.76 3.40	3.83 3.50	3.90 3.60	3.98 3.70	4.05 3.80	4.13 3.90	4.20 4.00	4.28 4.10	4.35 4.20	4.43 4.30	4.50 4.40	4.58 4.50	4.66 4.60	4.73 4.70	4.80 4.80	4.88 4.90	4.96 5.00
4.6	2.53 1.76	2.60 1.86	2.68 1.96	2.76 2.06	2.83 2.16	2.91 2.26	2.98 2.36	3.06 2.46	3.13 2.56	3.21 2.66	3.28 2.76	3.36 2.86	3.43 2.96	3.51 3.06	3.58 3.16	3.66 3.26	3.73 3.36	3.80 3.46	3.88 3.56	3.95 3.66	4.03 3.76	4.10 3.86	4.18 3.96	4.25 4.06	4.33 4.16	4.40 4.26	4.48 4.36	4.56 4.46	4.63 4.56	4.70 4.66	4.78 4.76	4.86 4.86
4.7	2.43 1.62	2.50 1.72	2.58 1.82	2.66 1.92	2.73 2.02	2.81 2.12	2.88 2.22	2.96 2.32	3.03 2.42	3.11 2.52	3.18 2.62	3.26 2.72	3.33 2.82	3.41 2.92	3.48 3.02	3.56 3.12	3.63 3.22	3.70 3.32	3.78 3.42	3.85 3.52	3.93 3.62	4.00 3.72	4.08 3.82	4.15 3.92	4.23 4.02	4.30 4.12	4.38 4.22	4.46 4.32	4.53 4.42	4.60 4.52	4.68 4.62	4.76 4.72
4.8	2.33 1.48	2.40 1.58	2.48 1.68	2.56 1.78	2.63 1.88	2.71 1.98	2.78 2.08	2.86 2.18	2.93 2.28	3.01 2.38	3.08 2.48	3.16 2.58	3.23 2.68	3.31 2.78	3.38 2.88	3.46 2.98	3.53 3.08	3.60 3.18	3.68 3.28	3.75 3.38	3.83 3.48	3.90 3.58	3.98 3.68	4.05 3.78	4.13 3.88	4.20 3.98	4.28 4.08	4.36 4.18	4.43 4.28	4.50 4.38	4.58 4.48	4.66 4.58
4.9	2.23 1.34	2.30 1.44	2.38 1.54	2.46 1.64	2.53 1.74	2.61 1.84	2.68 1.94	2.76 2.04	2.83 2.14	2.91 2.24	2.98 2.34	3.06 2.44	3.13 2.54	3.21 2.64	3.28 2.74	3.36 2.84	3.43 2.94	3.50 3.04	3.58 3.14	3.65 3.24	3.73 3.34	3.80 3.44	3.88 3.54	3.95 3.64	4.03 3.74	4.10 3.84	4.18 3.94	4.26 4.04	4.33 4.14	4.40 4.24	4.48 4.34	4.56 4.44
5.0	2.13 1.20	2.20 1.30	2.28 1.40	2.36 1.50	2.43 1.60	2.51 1.70	2.58 1.80	2.66 1.90	2.73 2.00	2.81 2.10	2.88 2.20	2.96 2.30	3.03 2.40	3.11 2.50	3.18 2.60	3.26 2.70	3.33 2.80	3.40 2.90	3.48 3.00	3.55 3.10	3.63 3.20	3.70 3.30	3.78 3.40	3.85 3.50	3.93 3.60	4.00 3.70	4.08 3.80	4.16 3.90	4.23 4.00	4.30 4.10	4.38 4.20	4.46 4.30

Shortly after the Olson formula was published, it occurred to the writer that since Olson's formula and that of Van Slyke were correct only when applied to pure milk, a combination of both formulas might be used in distinguishing between pure and adulterated milk. The sugar was chosen as the possible index and calculations were made upon many samples of milk, using the following formulas:

I. $S = TS - [F + 0.7 + (TS - \frac{TS}{1.34})]$

II. $S = TS - [F + 0.7 + (0.4(F - 3)) + 2.8]$

where S equals the milk sugar, T S the total solids, F the fat, and 0.7 the ash.

It was found that the values of S obtained by both formulas were nearly the same when the milk was pure and varied from 4.5 to 5 per cent. In skimmed or watered samples, the values disagreed and were above 5 in the former and below 4 per cent in the latter. A table was then prepared, using the above formulas for milk with solids from 10.5 to 12.5 per cent and fat from 2.5 to 4 per cent. This table has been in constant use for 5 years for the purpose of distinguishing between skimmed milk, whole milk and watered milk. From an extension of this table a list of the maximum and minimum fat corresponding to the total solids from 10.5 to 4 per cent was prepared and published in the 1909 report of the Massachusetts State Board of Health. Subsequent experience, however, has shown that for practical purposes, the maximum and minimum values could be placed farther apart. In Table III of calculated sugar, the upper values for the sugar were obtained by Formula I, the lower values by Formula II. The positions of the heavy lines were determined by allowing the variations of not more than one-tenth in the calculated sugar values. The samples falling above the other heavy lines may be suspected of being skimmed, those falling below the lower line may be watered, and those falling between these lines are probably normal milk. If a sample is both skimmed and watered, it may be classed in this table as normal milk, but usually, when both such acts are performed, either one or the other preponderates to such an extent that the sample will appear adulterated.

Table IV

Relation between the Total Solids and Fat of 2168 Samples of Milk Which Were Not Declared Adulterated

FAT PER CENT	TOTAL SOLIDS PER CENT																											NO. OF SAMPLES
	11.0	11.1	11.2	11.3	11.4	11.5	11.6	11.7	11.8	11.9	12.0	12.1	12.2	12.3	12.4	12.5	12.6	12.7	12.8	12.9	13.0	13.1	13.2	13.3	13.4	13.5	13.6	
													NUMBER OF SAMPLES															
2.5	1																											1
2.6									1																			1
2.7					1	1																						2
2.8	1		1	1	1	1	2																					7
2.9		1	1	1	2	2		2	3	2		1																15
3.0	2		3	3	5	3	1	3	3		2	1																26
3.1			2	2	4	3	3	2	4	4	4	6	4	4														42
3.2	1	1		3	1	7	6	8	7	5	7	11	15	3	2	2	2	4		1								86
3.3			2		2	5	5	16	14	14	12	6	8	7	6	6	5	4					1					113
3.4				2	4	1	3	4	5	7	9	14	18	14	13	12	8	6	6	4	1							131
3.5					2	4	1	1	6	7	13	13	20	23	21	12	18	6	2	4	3	2		1				159
3.6				1	2	3		2	3	2	8	15	15	23	40	28	21	13	9	8	5	5	2	3		1		209
3.7					2			4	1	6	5	8	11	14	30	22	32	35	32	26	10	4	2	2		3	1	250
3.8						1		1	1	1	1	3	4	13	19	20	37	29	42	32	32	12	4	5	1			258
3.9											2	2	8	7	13	14	19	25	27	23	27	18	16	10	1	3	2	217
4.0											2		5	4	1	20	25	27	23	19	21	22	20	10	8	5	3	215
4.1											1				3	4	3	10	8	17	16	26	12	21	10	8	3	142
4.2															2	2	3	2	7	3	9	8	16	13	17	12	10	104
4.3															1	1		2	1	1	3	8	7	7	7	14	8	60
4.4															1					2	6	1	8	3	15	13	8	57
4.5															1						1	1	2	6	5	8	6	30
4.6																					3	3	2	4	6		5	23
4.7																							3	1		5	1	10
4.8																					1					5	1	7
4.9																						1		1			1	3
NO. OF SAMPLES	5	2	9	13	26	31	21	43	48	48	66	80	108	112	153	143	173	163	157	140	138	111	95	87	70	77	49	2168

Five hundred and seventy-four samples of milk of known purity and 2168 commercial samples which could not be declared adulterated with a variation in solids from 11 to 13.6 per cent have been tabulated with reference to the relation between the solids and the fat and the results of this tabulation are shown in Tables IV and V. In both of these tables the zone of pure milk is indicated as in Table III. It appears from these tables that the methods in use for the detection of added water are efficient but that those for the detection of skimming are not so reliable. A larger percentage of known milk purity fell below the lower heavy line than of the commercial samples not declared adulterated. The samples above the upper heavy line which may be suspected of being skimmed, constituted 17 per cent of the known purity samples and 47 per cent of the commercial samples. Of the samples containing less than 3.3 per cent of fat, 5 per cent of the known purity samples and 68 per cent of the commercial samples were above the upper heavy line. Table III is intended solely for the purpose of selecting the particular samples which are to be subjected to other tests for adulteration and to give a positive indication of the character and possible extension of the adulteration. From Table V it would seem that if a sample was 0.4 above or 0.4 below the maximum or minimum fat figure corresponding to the solids the sample is either watered or skimmed as the case may be. Considerable more work must be done, however, involving the tabulation of several thousand analyses of samples of known purity milk from individual cows in order to establish the accuracy of the above statement.

MILK SERUM—Milk serum has been extensively used for the detection of added water in milk[1] and its value for this purpose is due to the fact that in the preparation of serum the most variable components of the milk, the fat and casein, have been removed. Of the various methods for the preparation of the serum, the writer prefers the copper method on account of the simplicity and rapidity of its preparation, because it can be prepared without heat and requires but a small quantity of milk. With the small beakers now in use with the Zeiss immersion refractometer, it is possible to obtain sufficient filtrate from a 10 cc. sample and if one is in a hurry 17.6 cc. of milk will give sufficient filtrate in a few minutes. This method has been criticized by the author[2] and subsequently by Ackermann[3] on account of the dilution necessary in the preparation of the serum, but this is offset by less variation in the serum from different samples. It has another disadvantage, that it is not possible to use the values of the ash of the copper serum in detecting added water because the amount of copper in the serum is higher in watered milk than in unwatered milk and consequently the ash in the serum of watered samples is but little less than in the serum of the original milk before watering. This objection is also applicable to the calcium chloride serum of Ackerman, owing to the precipitation of the calcium phosphate in the preparation of the serum.[4]

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[1] For an extensive and complete review of the literature on this subject, see *Arb. Kais. Gesundheits.*, **40**, Heft. 3.

[2] Eighth Intern. Congr. of Appl. Chem., **1**, p. 308.

[3] *Z. Nahr. Genussm.*, **24** (1912), 612.

[4] *Arb. Kais. Gesundheits.*, **40**, pp. 248, 255 and 256.

The acetic method as modified by Pfyl and Turnau is fairly rapid when only a few samples are examined. It can be prepared at the room temperature, the dilution is but 2 per cent and the ash figures increased by 2.21 per cent are comparable with those obtained from the sour serum. The greatest value of the sour serum is in the preparation of the ash. Using 25 cc. of sour milk serum there is less than 2 g. of organic matter to be burned and the influence of the combustion of this upon the 190 milligrams of ash is slight. It is advisable to apply this test in addition to the refraction or specific gravity of the serum to all samples suspected of containing added water, for both figures depend upon different milk constituents and, furthermore, if milk is declared adulterated by both methods, it eliminates the possibility of the samples being naturally abnormal milk obtained from a sick cow. It will be noticed in Table I that the refraction of the sour serum is midway between that of the copper serum and the acetic serum. This should be borne in mind when making examinations of milk which have partially soured. Under such circumstances, the copper serum so prepared will give a higher reading and the acetic serum a lower reading than would be given by the same sample before souring. When a sample exhibits signs of becoming sour, the only serum that should be prepared is the spontaneously obtained sour serum.

TABLE V

RELATION BETWEEN THE TOTAL SOLIDS AND FAT OF 574 SAMPLES OF MILK OF KNOWN PURITY

FAT PER CENT	TOTAL SOLIDS PER CENT																											NO. OF SAMPLES
	11.0	11.1	11.2	11.3	11.4	11.5	11.6	11.7	11.8	11.9	120	12.1	12.2	12.3	12.4	12.5	12.6	12.7	12.8	129	130	13.1	13.2	133	13.4	135	136	
													NUMBER OF SAMPLES															
2.5																												
2.6																												
2.7																												
2.8	1	1		1																								3
2.9	1		1	2			1																					5
3.0	2	1	2	2	3	1		1	1																			13
3.1	2		1	2	2	1		2	2		1																	13
3.2	2	1	6	2	2	1	2	4	4		3		1															28
3.3	1	2	2	5	4	3	6	3	5	2	4	2	2	2														43
3.4			2	2	4	4	3	6	3	4	5	4	2	1			1											41
3.5				2	1	2	3	2	4	3	6	7	7	1	5	3	2	1										49
3.6			1	1			2	2	3	2	7	5	6	5	4	4		1										43
3.7			1			1		3	3	1	4	4	3	6	4	6	5	3	2	1								47
3.8									2		2	3	6	4	3	5	3	2	2	2								34
3.9												2	3	2	1	3	7	2	8	4	5	1	2					40
4.0											1	1	1	3	1	3	4	2	9	7	3	3	2	2	2			44
4.1													1			2	2	2	3	3	7	5	3	1	1			30
4.2															1	1	2	2	5		2	5	5	6	4			33
4.3															2	3		1	2	1	1	3	2	6	4	6	2	33
4.4																	1	2	1	2	2	1	4	3	4	2	2	24
4.5																	1	2		2	1	3	1	2	3	3	4	22
4.6																					1	1	4	2		1	3	12
4.7																						1	1	2	2	2	3	11
4.8																							1	1	2	1		5
4.9																										1		1
NO. OF SAMPLES	9	5	16	19	16	13	17	23	27	12	33	28	32	24	21	30	28	20	32	22	22	23	25	25	22	16	14	574

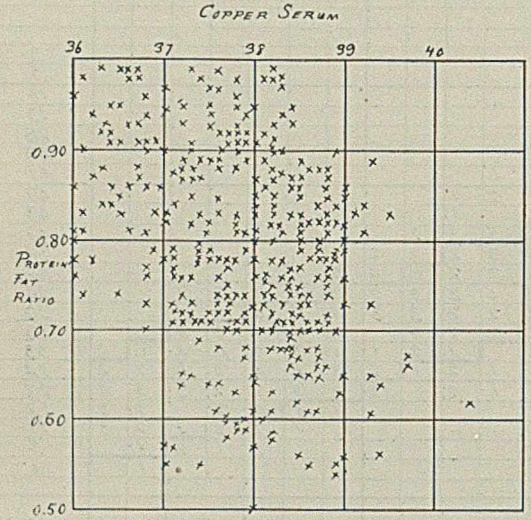
RELATION BETWEEN THE CONSTITUENTS OF MILK SERUM—Milk serum consists of water, sugar, lactic acid, more or less protein, and mineral matter, depending upon the mode of preparation. The acetic serum contains sugar, coagulable albumen, protein precipitated by tannic acid and all the mineral matter. The sour serum contains the same substances in addition to lactic acid formed from the sugar. The copper serum contains the sugar, coagulable albumen, protein precipitated by tannic acid, and some of the mineral matter. The calcium chloride serum contains the sugar, proteins precipitated by tannic acid, and a portion of the mineral matter, but no coagulable albumin.

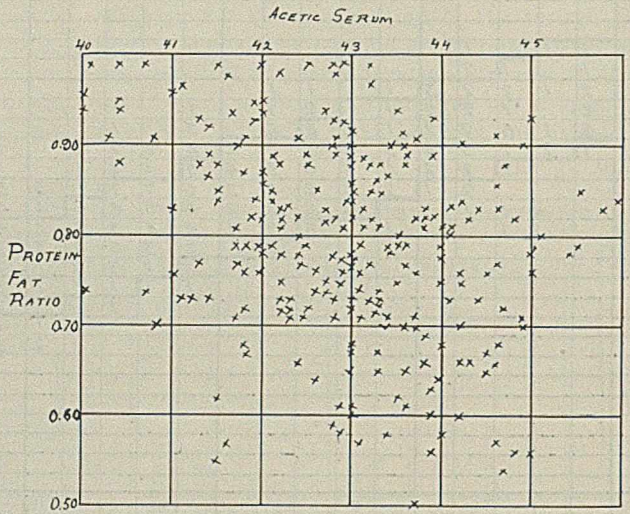
The refractive index of milk serum is an additive property consisting of the sum of the refractive indices of its constituents, and except in the case of the calcium chloride serum, bears no absolute relation to the composition of the milk from which it was made. In the calcium chloride serum, the refractive indices follow very closely the percentage of sugar in the milk. There is no specific relation between the ash of the

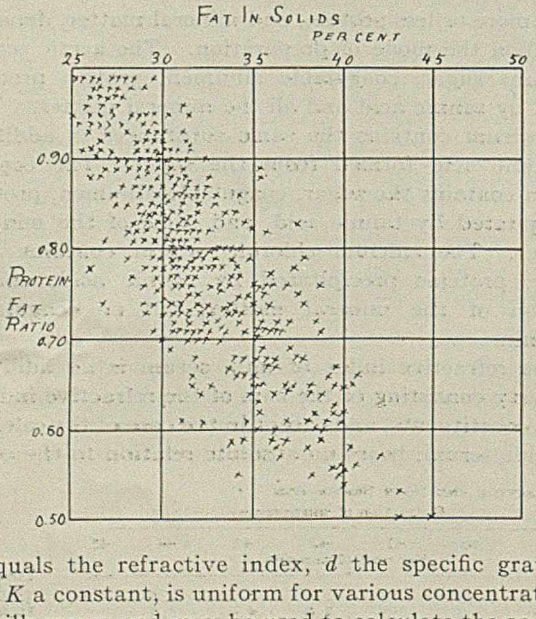
TABLE VI—RELATION BETWEEN SERUM REFRACTION AND SOUR SERUM ASH

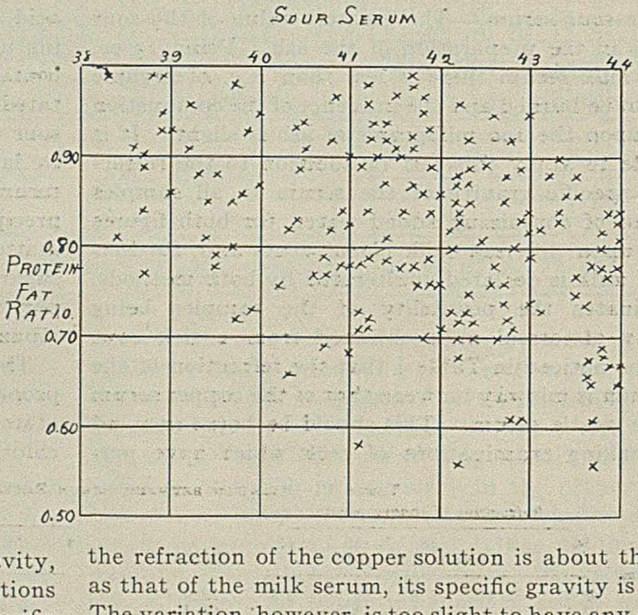
	Refraction of copper serum						Refraction of sour serum								
	36	37	38	39	40		38	39	40	41	42	43	44	45	
Ash of sour serum	Per cent of samples					Totals	Per cent of samples								Totals
0.730	0.7	1.4	7.8	2.1	0.7	12.7	...	...	2.3	0.8	3.1	3.1	2.3	2.3	13.9
0.750	2.1	6.4	6.3	3.5	...	18.3	...	0.8	2.3	2.3	4.6	4.6	2.3	...	16.9
0.770	1.4	6.4	9.9	5.0	...	22.7	0.8	1.5	3.1	3.8	6.2	6.1	0.8	0.8	23.1
0.790	2.8	5.6	9.2	3.5	...	21.1	0.7	2.3	2.3	3.8	3.9	7.7	0.8	...	21.5
0.810	1.4	2.1	5.6	2.1	...	11.2	...	...	..	1.5	4.6	2.3	1.5	0.8	10.7
0.830	1.4	2.1	0.7	0.7	0.7	5.6	...	...	..	..	..	..	..	...	...
0.850	0.7	0.7	2.8	..	...	4.2	0.8	...	0.7	0.8	1.5	..	0.8	...	4.6
0.870	0.7	0.7	0.7	..	...	2.1	...	...	0.8	..	1.5	..	1.5	0.8	4.6
0.890	0.7	..	1.4	..	...	2.1	...	...	0.8	0.7	0.8	0.8	..	...	3.1
0.910	..	..	..	..	...	...	...	0.8	..	..	0.8	..	..	...	1.6
TOTALS....	11.9	25.4	44.4	16.9	1.4	100.0	2.3	5.4	12.3	13.7	27.0	24.6	10.0	4.7	100.0

sour serum and the other properties of the serum of pure milk, as shown in Table VI, computed from the refractions of copper serums of 142 samples, the refraction of the sour serum of 130 samples, and the ash of the sour serums of the same samples.


Copper Serum


Acetic Serum


Fat In Solids Per cent


Sour Serum

It is possible, however, if one knows the refractive indices of the milk serum to calculate with accuracy the specific gravity or the solids of the same serum. The Lorenz and Lorentz formula $\frac{n^2 - 1}{n^2 + 2} \cdot \frac{1}{d} = K$ where n equals the refractive index, d the specific gravity, and K a constant, is uniform for various concentrations of milk serum and may be used to calculate the specific gravity from the refractive index. The formula evolved by Walter and Robertson[1] $\frac{n - n^1}{c} = A$ where n equals the refractive index of the solution, n^1 the refractive index of the solvent, c the concentration of the solution, and A a constant, is applicable for the calculation of solids of the milk serum. The values of these constants are given below. In the Lorenz and Lorentz formula, the difference in temperature makes no difference in the value of K, provided that the refractive index and specific gravity are determined at the same temperature and the latter referred to water at 4° C. Where the values of n and d are obtained at different temperatures, the value of K varies with the temperature. In the formula $\frac{n - n^1}{c} = A$, n and n^1 must be determined at the same temperature. The value of K in the copper serum is slightly less in watered milk than in whole milk, due to the fact that while the refraction of the copper solution is about the same as that of the milk serum, its specific gravity is higher. The variation, however, is too slight to have any marked effect upon the calculation of the specific gravity from the refractions. Table VIII gives the value of the specific gravity and solids calculated from the refraction figures of the acetic and copper serums and of the specific gravity calculated from the sour serum.

RELATION OF THE PROTEIN-FAT RATIO TO SERUM REFRACTION—It will be seen from Table I that in the samples obtained from Jersey and Guernsey cows, no figures for copper refraction were obtained below 37.0 and the figures for the protein-fat ratio were all less

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[1] *Wied Ann.*, **38** (1889), 107; *J. Phys. Chem.*, **13** (1909), 469.

TABLE VII—RELATION BETWEEN SERUM CONSTANTS

Serum	$\frac{n^2-1}{n^2+2}\cdot\frac{d}{1}=K$		$\frac{n-n^1}{c}=A$
Calcium chloride	n at 17.6° C. d at 15/15° C.	K = 0.2056 (a)	
	n at X° C. d at X°/4° C.	K = 0.2058 (a)	
Acetic	n at 20° C. d at 15°/15° C.	K = 0.20554 (b)	A = 0.00158 (b)
	n at X° C. d at X°/4° C.	K = 0.20592 (b)	
Copper	n at 20° C. d at 15°/15° C.	K = 0.20484	A = 0.00158 (b)
	n at X° C. d at X°/4° C.	K = 0.20526 (b)	
Sour	n at 20° C. d at 15°/15° C.	K = 0.20581	
	n at X° C. d at X° /4° C.	K = 0.20607 (b)	

(a) Weigner and Yakuwa, *Milchwertsch. Zentr.*, **5** (1909), 473.
(b) Lythgoe, *Proc. Eighth Intern. Congr. Appl. Chem.*, **1**, 309.

than 0.82 and from the average figures it appears that as the protein-fat ratio increases, the concentration of the serum diminishes. All the refraction figures corresponding to protein-fat ratio above 0.50 have been plotted and the results are shown in the chart on page 906. From this chart, it is apparent that normal milk with a protein-fat ratio less than 0.70, should give sera with refractive indices above 37 by the copper serum, 40 by the sour method, and 41 by the acetic method. The relation between the protein-fat ratio and the percentage of fat in the solids is shown in the plot. The protein-fat ratio increases as the percentage of fat in the solids decreases; therefore, if the per cent of fat in the solids is high (above 35), the sample should give a serum with a high refraction. The consideration of these relations should be studied in connection with the other figures obtained from the same sample, particularly with the sour serum ash, before the sample is called watered.

TABLE VIII—COMPARISON BETWEEN REFRACTIVE INDICES AND OTHER CONSTANTS OF MILK SERUM (CALCULATED FROM FORMULAS GIVEN IN TABLE VII)

Scale reading 20° C.	n_D 20° C.	Acetic Serum: Solids Per cent	Acetic Serum: Sp. gr. 15°/15°	Acetic Serum: Sp. gr. 20°/4°	Copper Serum: Solids Per cent	Copper Serum: Sp. gr. 15°/15°	Copper Serum: Sp. gr. 20°/4°	Sour Serum: Sp. gr. 15°/15°	Sour Serum: Sp. gr. 20°/4°
28.0	1.33820	3.30	1.0149	1.0131	3.30	1.0184	1.0163	1.0136	1.0121
29.0	1.33861	3.55	1.0160	1.0141	3.55	1.0194	1.0173	1.0146	1.0134
30.0	1.33896	3.78	1.0170	1.0151	3.78	1.0205	1.0184	1.0157	1.0144
31.0	1.33934	4.02	1.0180	1.0161	4.02	1.0215	1.0194	1.0167	1.0154
32.0	1.33972	4.26	1.0190	1.0172	4.26	1.0225	1.0204	1.0177	1.0164
33.0	1.34010	4.51	1.0200	1.0181	4.51	1.0235	1.0214	1.0187	1.0173
34.0	1.34048	4.74	1.0211	1.0193	4.74	1.0246	1.0225	1.0198	1.0185
35.0	1.34086	4.98	1.0221	1.0203	4.98	1.0256	1.0235	1.0208	1.0195
36.0	1.34124	5.22	1.0231	1.0213	5.22	1.0267	1.0246	1.0218	1.0205
37.0	1.34162	5.46	1.0242	1.0223	5.46	1.0277	1.0256	1.0229	1.0215
38.0	1.34199	5.70	1.0252	1.0233	5.70	1.0288	1.0266	1.0239	1.0225
39.0	1.34237	5.94	1.0262	1.0243	5.94	1.0298	1.0276	1.0249	1.0236
40.0	1.34275	6.18	1.0273	1.0254	6.18	1.0308	1.0287	1.0259	1.0246
41.0	1.34313	6.42	1.0283	1.0264	....	......	......	1.0269	1.0256
42.0	1.34350	6.66	1.0293	1.0274	....	......	......	1.0279	1.0266
43.0	1.34388	6.90	1.0303	1.0284	....	......	......	1.0290	1.0277
44.0	1.34426	7.14	1.0313	1.0295	....	......	......	1.0300	1.0287
45.0	1.34463	7.38	1.0323	1.0305	....	......	......	1.0310	1.0297

TABLE IX—ANALYSES OF HERD MILK OF KNOWN PURITY

No.	Total solids Per cent	Fat Per cent	Protein Per cent	Ash Per cent	Solids-not-fat Per cent	Lactose Per cent	Protein fat ratio	Fat in total solids Per cent	Refraction of serum: Copper 20° C.	Refraction of serum: Sour 20° C.	Sour serum ash G. per 100 cc.
1	14.18	4.70	3.46	0.73	9.48	5.03	0.74	33.2	38.5	42.8	0.790
2	13.96	4.70	3.25	0.78	9.26	5.16	0.69	33.6	38.6	42.2	0.802
3	13.34	4.30	3.20	0.70	9.04	5.05	0.74	32.2	38.3	42.2	0.762
4	13.10	4.20	3.22	0.75	8.90	5.12	0.77	32.1	38.8	42.7	0.812
5	12.97	4.40	3.07	0.76	8.57	4.80	0.70	33.9	38.0	42.1	0.772
6	12.85	4.10	3.17	0.66	8.75	5.04	0.77	31.9	38.6	42.0	0.772
7	12.80	3.85	3.35	0.74	8.95	4.85	0.87	30.1	38.2	42.2	0.788
8	12.76	4.10	2.98	0.76	8.66	4.60	0.73	32.1	37.7	40.8	0.768
9	12.58	3.60	3.38	0.74	8.98	4.64	0.94	28.6	38.0	42.0	0.812
10	12.44	3.70	2.98	0.66	8.74	4.93	0.81	29.8	38.0	42.0	0.762
11	12.30	3.80	3.01	0.72	8.50	4.96	0.79	30.8	37.6	41.0	0.764
12	12.26	3.70	3.03	0.74	8.46	4.56	0.82	30.3	37.5	40.7	0.820
13	12.19	3.65	2.94	0.70	8.54	4.63	0.81	29.9	37.7	41.3	0.762
14	12.14	3.40	3.15	0.75	8.74	4.70	0.93	28.0	37.8	41.7	0.796
15	11.74	3.30	2.96	0.78	8.44	4.59	0.90	28.1	37.4	40.3	0.786
16	11.28	3.20	2.83	0.74	8.08	4.35	0.89	28.5	37.1	39.5	0.752

During the months of March, April and May of this year, the milk of a large number of herds has been examined in connection with another investigation. From these, sixteen have been chosen, including the samples from which the highest and lowest figures have been obtained; the analyses are recorded in Table IX. The character of the herds, the number of cows and the amount of milk obtained at the milking, is given in Table X. None of these analyses were used in the preparation of Table I.

Sample No. 12 was obtained from a celebrated herd of thoroughbred Holstein Fresian cows, the majority of which were in the last stages of lactation. Sample No. 15 was obtained from the same herd two months later, many of the cows having freshened since the previous sample was taken. The analyses of these two samples show that while the solids and the fat were both much lower in the second sample taken, there was practically no difference between the figures obtained from the milk serum.

TABLE X—CHARACTER OF HERDS PRODUCING THE MILK RECORDED IN TABLE IX

No.	Jersey	Guernsey	Grade Jersey and Guernsey	Grade Ayrshire and Durham	Ayrshire	Grade Holstein	Holstein	Total no. cows	Wt. of milk: Lbs.	Wt. of milk: Av. per cow
	Number of cows									
1	20	..	..	..	..	..	..	20	...	....
2	..	35	..	2	..	2	..	39	450	11.6
3	4	4	..	...	..	5	..	13	...	....
4	2	4	..	..	8	8	..	22	250	11.7
5	2	5	8	..	..	12	..	27	329	12.2
6	4	..	..	4	8	14	..	30	400	13.3
7	1	1	..	4	..	..	13	29	240	12.6
8	1	..	4	10	3	4	3	25	260	10.4
9	4	..	..	4	..	20	..	28	273	9.7
10	..	..	2	..	..	13	..	15	180	12.0
11	..	..	..	..	..	..	39	39	500	12.9
12	..	..	..	..	..	..	25	25	217	8.7
13	..	..	9	1	..	..	36	46	580	12.6
14	..	..	..	..	..	..	10	10	...	....
15	..	..	..	..	..	..	24	24	325	13.5
16	..	..	..	..	..	..	12	12	167	14.3

All the other samples were taken from different herds. The milks from herds Nos. 14, 15 and 16 are not sold at retail until after being mixed with milk of good quality, in order to bring it up to the requirements of the Massachusetts law.

SUMMARY

Variations in the composition of milk are due primarily to the breed, and to a less extent to the season of the year and to the time since calving.

The least variable milk constituents are the lactose and ash, both of which are of value in detecting added water.

It is possible, within reasonable limits, to indicate from the percentage of solids and fat, whether or not a sample has been watered, skimmed, or is normal milk.

No relation exists between the refraction of the serum and the sour serum ash; therefore, if both figures are below the minimum for pure milk it is positive indication of the presence of added water.

The protein fat ratios in all cases have been less than 1. If this figure exceeds 1, skimming is indicated, the amount being greatest in samples possessing the highest ratio.

If the protein-fat ratio is less than 0.7 or the percentage of fat in the solids is above 35.0, samples may be declared watered by a low refraction of the serum, not necessarily below the minimum for all samples of known purity. This is particularly so when dealing with herd milk.

In the absence of a refractometer, the specific gravity or the per cent of solids of the serum is just as valuable as the refractive index in detecting added water.

The writer wishes to acknowledge his thanks to his assistants, Messrs. Charles H. Hickey, Louis I. Nurenberg, and Clarence E. Marsh, to whom he is greatly indebted for their valuable coöperation in making the analyses of the samples.

Laboratory of Food and Drug Inspection
Massachusetts State Board of Health
Boston

SOME CHARACTERISTICS OF CHLORINE-BLEACHED FLOUR

By C. A. A. Utt

Received July 3, 1914

Since the Government ruled against flour treated with the oxides of nitrogen (F. I. D. 100; N. T. 722, U. S. Dept. of Agr.), chlorine-bleached flour has made its appearance. United States Patent 1,071,977, September 29, 1913, deals with a process in which "flour is treated with anhydrous chlorine (diluted with an inactive gas) in order to mature and whiten it." This process and a few others in which chlorine is the active agent are used. By this means, it is claimed, the flour is whitened and aged.

That chlorine will bleach flour has been known for many years, but its activity and difficulty of control have caused its use to be viewed with suspicion. In connection with the pure food work of Kansas it was found necessary to collect some information on chlorine-treated flour. The results of this investigation are presented in this paper.

Samples were obtained directly from the mills by the Kansas food inspectors, of the same flour before and after bleaching. These were placed in screw-top glass jars, sealed and shipped to the laboratory. The following determinations were made: (1) Chlorine qualitatively and quantitatively; (2) moisture; (3) acidity. A number of gluten and baking tests were also made.

Chlorine was determined by Jacobs' method as used in the Plant Chemistry Laboratory of the U. S. Department of Agriculture. It is as follows: "To 25 grams of flour in a platinum dish, add 25 cc. of a solution containing 25 grams of KOH and 25 grams KNO_3 per liter. Evaporate to dryness on a steam bath, and ignite in a muffle at a dull red heat until thoroughly charred. Extract the charred mass with 25 cc. 5 per cent HNO_3; filter. Return residue to the platinum dish, char further and extract again with 25 cc. 5 per cent HNO_3; filter, wash with hot water, and ignite to an ash. Dissolve the ash in 5 per cent HNO_3, filter and wash. Combine the filtrates and determine the chlorine with silver nitrate."

Qualitative determinations of chlorine were made by the copper wire method as given by Alway (*Bull.* **102**, Nebraska Experiment Station, page 53) as follows: "One ounce (30 grams) of flour is extracted with benzene (ether was used) and the latter evaporated. A small amount of oil remains. A piece of copper wire is heated in a colorless gas flame until it is black and no longer colors the flame green. The hot end of the wire is dipped into the oil and again brought into the flame. If chlorine or bromine has been used as a bleaching agent a green or blue coloration is produced."

Moisture determinations were made by drying the samples for five hours in a steam oven at the temperature of boiling water.

The determinations of acidity were made in accordance with Method 5 in *Bull.* **152,** of the Bureau of Chemistry, U. S. Department of Agriculture, which is as follows: To 20 grams of flour in a 500 cc. Erlenmeyer flask add 200 cc. freshly boiled water. Digest at 40° C. for two hours, shaking at 10-minute intervals. Decant the clear liquid through a folded filter and titrate 50 cc. *N*/20 NaOH.

Table I indicates the results obtained on inspection samples. It will be noted that the moisture does not vary any more between the bleached and unbleached flour than might be expected in duplicate determinations. An increase in acidity in the bleached flour as compared with the corresponding unbleached sample is noted in nearly every instance. The chlorine content varies from 442 parts per million to 576 parts per million in the unbleached flour; when bleached the variation is 648 to 972 parts per million. All bleached samples reacted positively with the copper wire reaction for chlorine.

Table I—Some Characteristics of Chlorine-bleached Flour

NO.	Description	Moisture	Acidity as lactic acid	Cl p. p. m.	Copper wire reaction	Vol. of loaf	Gluten		Grade of loaf	
							Moist	Dry	Color	Texture
46–47	Unbleached patent	13.36	0.126	484	—	1870	43.1	12.99	94	95
	Bleached patent	13.68	0.144	764	+	1860	42.8	13.07	93	94
48–45	Unbleached, clear	14.22	0.198	532	—	1780	47.5	16.10	..	83
	Bleached, clear	14.18	0.288	916	+	1800	48.6	16.07	..	85
52–54	Patent unbleached	10.70	0.162	442	—	1940	38.87	12.67	93	92
	Patent bleached	11.12	0.18	881	+	1950	39.16	12.87	93	89
65–66	Unbleached patent	12.66	0.126	556	—	2020	39.34	12.40	94	92
	Bleached patent	12.88	0.126	648	+	1980	39.98	12.92	93	89
95–96	Unbleached	12.20	0.144	494	—	1920	41.83	14.05	94	94
	Bleached	12.24	0.189	716	+	1970	41.78	13.67	93	94
91–92	Patent unbleached	13.10	0.126	540	—					
	Patent bleached	13.12	0.135	844	+					
51–55	Unbleached, clear	12.44	0.216	504	—					
	Bleached, clear	12.32	0.252	928	+					
97–98	Unbleached	11.46	0.189	544	—					
	Bleached	11.40	0.198	868	+					
70299	Bleached	10.99	0.198	736	+					
70300	Bleached	11.22	0.207	900	+					
65–63	Unbleached	12.88	0.306	576	—					
	Bleached	12.69	0.324	667	+					
70–72	Unbleached	12.56	0.18	501	—					
	Bleached	12.68	0.234	972	+					
73–71	Unbleached	12.42	0.216	496	—					
	Bleached	12.42	0.270	855	+					

The differences in loaf volume are not much greater than one would expect to find in individual loaves from the same flour. Loaf volume favors the unbleached flour in some cases, in others the bleached flour. All loaves were graded against a standard loaf made from hard wheat flour under the same conditions, as is the custom. It will be noted that in nearly every case the bread made from the unbleached flour grades better. The bleached flour gives a loaf having an objectionable color and texture.

The gluten tests run practically uniform for the bleached and unbleached flour, there being no more difference than on duplicates. However, physically the gluten of the chlorine-treated flour is somewhat softer in some cases, showing that the chlorine may have affected the gluten to some extent.

Several samples of unbleached flour gave the following amounts of chlorine, expressed in parts per million: (1) 445; (2) 503.8; (3) 492; (4) 448; (5) 348; (6) 373; (7) 452; (8) 484; (9) 496; (10) 544. A number of samples of chlorine-treated flour on the Kansas market yielded the following amounts of chlorine expressed in parts per million: (1) 742; (2) 260; (3) 591; (4) 608; (5) 732; (6) 712; (7) 1056; (9) 904. All of these gave a positive test with the copper wire reaction.

A number of samples of bleached and unbleached flour were shipped to the laboratory in cloth sacks, packed together. The unbleached flour yielded the following amounts of chlorine, parts per million: (1) 528; (2) 552; (3) 612; (4) 598; (5) 592. In each case a slight color developed in the copper wire reaction, showing that some chlorine was probably taken up by the unbleached flour. A sample of soft wheat gave 452 parts chlorine per million; a sample of hard wheat gave 496 parts, and two samples of bran gave 464 and 431 parts chlorine per million.

SUMMARY

The chlorine content of untreated flour may run as high as 576 parts per million. Chlorine-treated flour will contain over 600 parts per million of chlorine.

The chlorine can be detected with certainty by means of the copper wire reaction. Samples of unbleached flour in contact with chlorine-treated flour may give the reaction.

Chlorine-treatment increases the acidity of the flour and does not improve its breadmaking qualities.

In conclusion credit should be given to Miss Leila Dunton of the Department of Milling Industry of the Kansas State Agricultural College for making the baking and gluten tests, and to Dr. J. T. Willard, of the Department of Chemistry, for suggestions in carrying out the work.

Kansas State Agricultural College
Manhattan

DETERMINATION OF PRUSSIAN BLUE IN TEA[1]

By G. W. Knight

Received August 31, 1914

This method of determining the artificial coloring matter, Prussian blue, on tea is the conclusion of a series of experiments to ascertain an analytical method that would be rapid, accurate and quantitative. By means of it, 1 part in 200,000, and sometimes even 1 part in 300,000, can be detected. A man inexperienced in the manipulation can run four determinations in a day easily, and doubtless with experience could run many more. Two operators working independently on the same sample obtained 0.0019 and 0.0016 per cent of Prussian blue.

METHOD—100 g. of tea are ground to a fine powder in a coffee grinder, placed in a round-bottomed distilling flask of sufficient capacity and moistened with enough 85 per cent phosphoric acid to thoroughly moisten all of the tea. (Usually from 30 cc. to 60 cc. are sufficient.) The flask is then fitted with a delivery tube, which passes through a two-hole stopper into a mixture of 4 cc. of 10 per cent NaOH solution and 30 to 40 cc. of water contained in a 100 cc. Erlenmeyer flask. The Erlenmeyer flask is supported in a beaker of cold water.

An outlet tube bent at right angles passes through the other hole of the two-hole stopper for the escape of unabsorbed gases. The apparatus is placed in a well ventilated hood and a Bunsen burner flame is placed in front of the outlet tube to burn the unabsorbed gases.

The flask is then heated, slowly at first, with a small flame and finally more strongly until the phosphoric acid begins to distil over. Usually 10 or 15 minutes are sufficient for the distillation.

After the distillation is completed, the distillate is filtered and the filtrate placed in a casserole; if acid, it is neutralized with 10 per cent NaOH solution, then 3 cc. of 10 per cent NaOH solution in excess are added. A crystal of $FeSO_4$ about the size of a pea and a few drops of 10 per cent $FeCl_3$ solution are added and the solution boiled for 1 minute. HCl (sp. gr. 1.2) is then added, drop by drop, to the hot solution till it is distinctly acid. The solution is filtered and the precipitate washed with 95 per cent alcohol, until the washings run colorless. Cold 10 per cent NaOH solution is dropped on the filter, using as little as possible but washing the whole area of the filter, and then the filter is washed with as small an amount of water as possible. It is best to drop the wash water, drop by drop, from a pipette. About 4 cc. of NaOH and 8 cc. of water are sufficient for this operation.

The filtrate is acidified with acetic acid and a few drops of HCl (sp. gr. 1.2), a few drops of 10 per cent $FeCl_3$ solution are added and then HCl (sp. gr. 1.2) is added until any brown color that may have developed has disappeared.

The solution is then placed in a casserole and evaporated to half its bulk on the water bath; more water is added to dissolve any salts that may have crystallized out, and the Prussian blue is filtered on a Gooch crucible, washed with very dilute HCl, water, alcohol and ether, and dried at 100° C. to constant weight.

The weight in grams gives directly the per cent of Prussian blue in the sample.

Several samples of uncolored China and Japan teas were run by this method, and no Prussian blue detected. Then varying amounts of Prussian blue, from 1 part in 75,000 to 1 part in 400,000, were mixed with these uncolored teas. Prussian blue was obtained in all cases up to 1 part in 200,000 and in some cases up to 1 part in 300,000. The amount appeared proportionate to that put in, but the amount was too small to weigh except in the case of 1 part in 75,000; and in this case where 1.5 mg. was put in 1 mg. was recovered. As the purity of the Prussian blue put in was questionable, this was a fairly quantitative recovery.

Three samples which gave 1 spot, 2 spots and 3

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[1] Contributed with the permission of the Secretary of the Treasury and the U. S. Appraiser, Port of New York.

spots, respectively, by the Read test,[1] gave 0.0005, 0.0022 and 0.0022 per cent, or 1 part in 200,000, 1 part in 45,000, and 1 part in 45,000.

Three other samples of colored tea that gave an average of 50 spots, 48 spots and 32 spots, respectively, by the Read test, and showed color distinctly in 1 and 2 and barely perceptibly in 3 by a qualitative infusion method devised by W. G. Berry (unpublished) gave 0.0072, 0.0044 and 0.0016 per cent, or 1 part in 14,000, 1 part in 23,000, and 1 part in 63,000. Sample number 3 repeated by a different operator gave 0.0019, checking fairly well with 0.0016 by the first operator.

The writer contemplates making a more exhaustive study of the method as to its suitability in the analysis of various classes of tea.

U. S. Customs Laboratory
Port of New York

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[1] "Eighth International Congress of Applied Chemistry," Vol. XVIII, p. 301.

AN INVESTIGATION OF THE DIASTASE OF ALFALFA AND THE EFFECT OF RAPID CURING UPON THE FOOD VALUE OF ALFALFA[2]

By Ralph C. Shuey

Received May 22, 1914

INTRODUCTION

In a search for a commercial source of diastase among the green plants, alfalfa was found to have an exceptionally high diastatic content, and further work indicated a close relation between diastatic content and the proportion of water-soluble constituents of the dried plant. It was found possible, by careful and rapid curing, to increase the diastatic value very materially; and this paper will deal principally with these relations and their possible economic importance. Before taking up the experimental work, however, it might be well to review briefly the occurrence of diastase, its role in the economy of the green plant and the chemical changes related thereto.

Diastase, or amylase, may be defined as that enzyme or organic catalyst which is elaborated by the living organism for the purpose of assisting in or bringing about the conversion of starch into sugar. But little is known of the chemical nature of diastase. As ordinarily prepared, the substance contains nitrogen and might be classed with the proteins, but some work of Frankel and Hambourg[3] and others indicates that the protein may not be necessarily an integral part of the substance, but that the protein and diastase are almost inseparable on account of their colloidal nature and other physical properties. The action of diastase is easily affected by slight variations in conditions. Aside from the temperature and concentrations of hydrolyte, hydrolyst and hydrolytic products, the presence of very slight amounts of hydrogen—or hydroxyl-ions or of salts may produce very great changes in the activity or even completely inhibit action. In the moist state or in solution, diastase is easily destroyed by heat, continued heating at 80° C., being sufficient but if perfectly dry a temperature of 100° C. for a considerable time has no noticeable effect.

As we are not concerned with the diastases of animal origin, they will not be discussed. The vegetable sources of diastase may be roughly divided into three groups:

I—In the green plants diastase is present for the conversion of the deposited storage material, starch, into the soluble and transportable sugars which may, after transportation, be again deposited as one of the less soluble carbohydrates, starch or cellulose, or may be used up in the metabolic processes of the plant. The diastase from green plants possesses the property of dissolving unboiled or granular starch to a much greater degree than does that from the other two sources.

II—The germinating seeds elaborate a very active diastase for the purpose of making available to the growing embryo the stored up material of the endosperm. Although this diastase attacks unboiled starch, it does so only very slowly. Malted or sprouted grain is the most generally known source of diastase. Aside from its use in the fermentation industries as malt, the soluble portions, concentrated to a syrup or powder, are used in the baking industry and in medicine.

III—Many of the fungi and bacteria secrete diastase for the purpose of making available the food material of a starchy medium in which they are growing. This has found application in the moyashi or yeast used in making the Japanese alcoholic drink, *sake*, from rice. The diastatic extract from this fungus, *Aspergillus oryzae*, is used in medicine under the name Takadiastase.

HISTORY: THE PRESENCE OF DIASTASE IN GREEN PLANTS

The first investigation of diastatic activity in green plants noted was that of Kosmann[1] in 1877. He made aqueous infusions of lichens, moss, algae and fungi, precipitated with alcohol, and obtained a substance which showed diastatic action in every case when starch paste was used as hydrolyte, and even in some cases when unaltered starch was used.

The following year a monograph was published by Baranetsky,[2] describing similar work on the seeds, bulbs, stems and leaves of plants. His conclusions were that the quantity of enzyme present at any one time was very small, it being elaborated as needed and used up as fast as formed.

J. Boehm[3] agreed with the former investigators and added this piece of information, that freezing and thawing the leaves stops the depletion of starch, as does also immersion in an atmosphere of hydrogen. None of these investigators used any antiseptic precautions and their tests were more qualitative than quantitative.

In 1884, Brasse[4] followed Kosman and Baranetsky but used chloroform as an antiseptic and measured the diastatic activity by means of the quantitative reduction of copper solutions in place of using the iodine

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[2] This investigation was made in connection with Industrial Fellowship No. 2, in the University of Kansas, during the years 1907–10, and has been withheld from publication in fulfilment of the conditions of the Fellowship Agreement.

[3] *Woch. für Brauw*, **23** (1906), 473.

[1] *Bull. Soc. Chim.*, **27** (1877), 251.

[2] "Die Stärkeumbildenden Fermente in den Pflanzen," Leipsic, **1878**.

[3] *Zeit. für d. g. Brauw*, **6** (1883), 76.

[4] *Comptes Rendus*, **99** (1884), 878.

test for starch. He found diastase in the precipitate formed by adding strong alcohol to solutions of potato, dahlia, Jerusalem artichoke, corn, beet, tobacco and ricinus leaves.

Schimper[1] found feeble diastatic action in all leaves he investigated and noted that *Allium cepa* did not form starch within its chlorophyll granules. He thought that perhaps this might be due to a high diastatic activity in the leaf preventing the formation of solid starch. However, comparisons of Allium with Euphorbia and Tropaeolium, which form starch abundantly, showed the latter to possess much higher diastatic activity, leading to the conclusion that the diastase bears a direct relation to the starch present.

Then Wortman[2] raised a dissenting voice. Using the clear filtrate obtained by shredding and pounding leaves with water, he found no diastatic action in 27 out of the 32 species examined and only very feeble action in the other 5. Both 0.5 per cent starch solution and unaltered wheat starch were used as hydrolyte. Leaves kept in an atmosphere of CO_2 in the dark did not lose starch, while those kept in oxygen lost starch readily. From these results he concluded that the role of diastase in the plant was either very unimportant or that it had no function whatever and that the solution of the starch was brought about by the direct action of the living protoplasm. He admitted one exception, that of germinating seeds.

S. H. Vines[3] almost immediately published a criticism of Wortmann's work, objecting to the iodin starch determination in the presence of leaf extract, for Wortmann himself had shown that coloring matter and foreign substances interfered with the color reaction. In his own work he found the turbid extract much more active than the clear filtrate. In some cases the added starch solution hindered the hydrolysis of the starch naturally occurring in the plant. He concluded that the carbohydrate formed was not maltose. Vines' work agreed with that of Baranetsky and Boehm and he concluded that, although the amount of diastase that could be extracted was small, yet the secretion was doubtless a continuous process, so that the amount produced during a given time might suffice to effect the observed conversion of starch into sugar.

A. Prunet[4] observed that the end sprouts of a sprouting potato developed much faster than those near the middle and examination showed much more diastase in the ends of the potato, thus showing a relation between the production of diastase and the dissolution of starch. He also found a relation between the appearance of diastase and the commencement of growth in the tubers.

A. Meyer[5] studied and tabulated the starch-forming ability of the leaves of different plants and found that many of the monocotoledons do not store starch. He concluded, however, that this was not due to the rapid removal of carbohydrates. He arranged the plants into five orders of decreasing starch storage, placing the Solanaceae and Papillonaceae first. He also found that leaves could convert sugars into starch when the plucked leaves were immersed in sugar solution.

Brown and Morris[1] in 1893 published an extensive research into the diastase of leaves. After determining the diastase in the leaves of many different species, they concluded that it was always present in quantities sufficient to hydrolyze more starch than the leaf could contain at any one time, sometimes enough to hydrolyze many times the dry weight of the leaf itself. Tannin very often prevented the making of an extract of any power, although by precipitating the tannin with rawhide raspings the diastase could be demonstrated. They concluded that neither the leaf nor the powdered tissue gave a full measure of the diastase present, for drying and powdering the leaf and using a suspension of the powder in water gave an activity about seven times greater than the filtered extract of the crushed green leaf. The Papillonaceae and Solanaceae proved to be exceptionally high in diastase. Expressing the diastatic activity by the number of grams of maltose produced in 48 hours' hydrolysis at 30° by ten grams of dry leaf, they found in *Pisum sativum* an activity of 240.3°, about one-third the activity of pale barley malt.

The diastase was found to be from 35 per cent to 70 per cent more active in leaves plucked after being kept in the dark some hours than after a full day's insolation. In one case keeping in the dark for four days increased the activity 153 per cent, but this was with a very feebly diastatic sample. Although floating leaves on water in the dark increased the diastase just as keeping the growing plant in the dark had done, yet floating on a dilute solution of dextrose in the dark decreased the diastatic activity. From this and the results of similar experiments[2] on sprouting grains they concluded the secretion of diastase to be a starvation phenomenon.

Leaf diastase was found capable of acting on solid starch, especially that of buckwheat. In the presence of 0.006 per cent formic acid a suspension of *Pisum sativum* caused complete disintegration of many of the soaked buckwheat starch grains placed in it for 10 hours at 30° C. When acting on boiled starch the resulting carbohydrates were found to be maltose and dextrin, but no dextrose.

After studying the relation of leaf starch to the total products of assimilation, they concluded that "There is no evidence whatsoever of starch being a necessary link between the sugars of assimilation and the sugars of translocation; it is far more probable that the starch is only elaborated within the cell when the supply of nutrient is in excess of the cell requirements and that most of the assimilated products never pass through the stage of starch at all." They found sucrose to be the prevailing sugar in the juice of the plants examined.

Browne and Blouin[3] found in the sugar cane leaves

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[1] *Bot. Zeit.*, **43, 1885**, p. 738.

[2] *Ibid.*, **1890**, p. 582.

[3] *Ann. of Bot.*, **5** (1891), 409.

[4] *Comptes Rendus*, **115** (1892), 751.

[5] *Bot. Zeit.*, **1885**, pp. 27-32.

[1] *Jour. Chem. Soc. Trans.*, **63** (1893), 604.

[2] Brown and Morris, *Jour. Chem. Soc. Trans.*, **57** (1890), 458.

[3] La. Agr. Exp. Sta., *Bull.* **91**.

a much higher percentage of sucrose in the evening than in the morning. The carbohydrates were transported as reducing sugars which were reconverted to sucrose and stored up in the pith cells. A portion of the invert sugar was used up in the vital processes of the cane (formation of new tissue, etc.) for which purpose levulose appeared to be used in greater amount.

Butkewitsch[1] found a very active diastase in the bark of a number of plants and stated that in the barks of some of the Papillonaceae it is only slightly inferior to malt in its activity.

The presence of diastase in the leaves, stalks, bark and ripening fruit[2] makes it appear that diastase is present in all parts of plants, at least at some period during their growth.

The success of these investigations, demonstrating the presence of such appreciable quantities of diastase, indicated the probability of the diastatic content of fodders bearing an important relation to the availability of the food constituents. Experiments were conducted along similar lines, using alfalfa as an example of a highly diastatic plant, and endeavoring to learn the optimum conditions for the production and retention of diastase in a cured hay.

METHODS AND PROCEDURE

PREPARATION OF SAMPLES—All samples of alfalfa, except when otherwise noted, were cut when from $^1/_{10}$ to $^3/_{10}$ in bloom, the stems from the different plants thoroughly mixed and afterwards divided into 1000 or 2000 gram portions for curing. The control samples were placed in ovens immediately and dried at 45–50° C. for 48 hours. The "air cured" samples were allowed to lie on the floor of the laboratory for three days and afterwards dried at 45–50° C. for 48 hours to bring them to the same moisture content as the controls. All samples, after the treatment noted, received this final drying.

In the sampling of the stacks several samples were taken from different parts of the stack by raising a portion of the hay on poles and removing an armful from the undisturbed portion, being careful not to shake off any leaves. These samples were mixed, coarsely ground and resampled for final grinding.

If leaves and stems were determined separately, after drying, the leaves were stripped from the stems by hand, weighed and ground separately. This method of separation, although extremely crude, gave a maximum error of about 2 per cent.

DIASTASE DETERMINATION—Starch paste—2000 grams of distilled water were roughly weighed into a tared beaker and boiled. Forty grams of neutral soluble starch prepared according to Lintner[3] were accurately weighed out and stirred with about 100 cc. of water and added to the bulk of the water with stirring and the whole boiled and stirred for five minutes, then cooled and made up to exactly 2000 grams.

Two and one-half grams of the dry pulverized plant were accurately weighed into a 100 cc. wide-mouthed bottle and exactly 50 cc. of water added from a pipette. Two drops of toluene were added and the whole allowed to digest for eight hours at room temperature with occasional shaking. This was filtered through an empty porcelain Gooch crucible until clear, the pulverized plant acting as filtering medium. This gave about 45 cc. of liquid which was assumed to contain $^{45}/_{50}$ths of the water-soluble substance of the plant. Experiment showed this assumption to be within experimental error.

For digestion 100 cc. portions of the starch solution were measured into 120 cc. tubes, placed in a water bath at 40°, and allowed to come to that temperature: 5 cc. of plant solution were added to a tube of starch solution which was then stoppered and well shaken and 25 cc. immediately withdrawn and placed in a 200 cc. Erlenmeyer flask containing 5 drops of alkaline Fehling solution. This sample was used for the purpose of determining the amount of sugar present before digestion and the alkaline solution was used merely to stop further action and so allow the solution to stand until cupric reduction could be determined. The time required for filling the tubes was noted and at the end of exactly one hour 25 cc. portions were withdrawn into flasks as before, so gauging the time that both the first and last tubes had exactly one hour for digestion.

Ten cc. each of Allihn's modification of Fehling's solution[1] and 25 cc. of water were measured into an Erlenmeyer flask and heated to boiling. This solution was added to one of the digestion samples, the whole heated to boiling and allowed to boil for exactly four minutes. The mixture was filtered immediately through a Gooch filter containing a good thick mat of asbestos. After thoroughly washing, the filter, tube and stopper were transferred to a 250 cc. flask and 4 cc. of concentrated nitric acid were added to the precipitate: 1 cc. of acid was also added to the precipitating flask to dissolve any adhering copper oxide and all thoroughly washed into the flask.

The resulting copper solution was evaporated to dryness on a hot plate and the last traces of oxides of nitrogen removed by a blast of air. After cooling, 10 cc. of 50 per cent acetic acid were added and boiled until solution was completed, then cooled and made up to 25 cc.

Five cc. of a solution containing 50 grams of potassium iodide per 100 cc. were then added and the solution titrated immediately against standard sodium thiosulfate, 1 cc. of 2 per cent soluble starch being added as indicator after the color had begun to fade. The thiosulfate solution contained about 9.5 grams per liter, equivalent to about 0.0025 gram of copper and was standardized against pure copper.

The amount of maltose equivalent to the copper found was read from a curve prepared in this laboratory from determinations on pure maltose. The maltose per unit of copper oxide obtained by this method is about 96.9 per cent of that obtained by the Munson and Walker method.[2]

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[1] *Biochem. Zeit.*, **10** (1908), 314.

[2] Geerlings, *Intern. Sugar Jour.*, **10**, 372.

[3] *Jour. prakt. Chem.*, **34**, 378.

[1] U. S. Dept. Agr., Bur. of Chem., *Bull.* **107** (1909), 49.

[2] The difference in the maltose constant of these two methods is due largely to the difference in concentration of the alkali and the substitution of potash for soda. This method was used because it allowed of somewhat more rapid manipulation.

The weight of plant represented by the 25 cc. of starch solution withdrawn for analysis was:

$$2.5 \text{ g.} \times 5/50 \times 25/105 = 0.0595 \text{ g.}$$

for 5/50ths of the extract were added to the starch and 25/105ths of this digestion were used for analysis. The activity of the samples was expressed by the number of grams of maltose produced by one gram of sample during one hour's digestion at 40° C., that is, the difference in maltose content of control and digestion, divided by 0.0595.

DETERMINATION OF WATER-SOLUBLE EXTRACT—For this purpose a glass dialyzing apparatus was used, heavy filter cloth being substituted for the parchment: 25 grams of the dry sample were allowed to digest for eight hours at room temperature with 1000 cc. of water and a little toluene. The cloth and alfalfa were then squeezed as dry as possible and fresh water added. The total time of extraction was 48 hours and five changes of water were made, the sample finally being squeezed out and dried. The difference in weight before and after extraction represented the "water-soluble extract."

DISTRIBUTION OF DIASTASE IN THE PLANT

For the purpose of determining the distribution of diastase in the plant, the leaves and stems were examined separately and in every case there was much more diastase in the stems than in the leaves. The average of all separate determinations on laboratory-cured samples showed a ratio of 4.3 to 1, the ratio number varying from 3.3 to 5.2. A sample having 53.6 per cent leaves showed the following distribution:

Sample	Activity of leaves	Stems	Whole
106	0.34	1.75	0.99

Blossoms plucked a few days later showed an activity of 0.35, or about the same as that of leaves. A later separation of hay taken from the mow showed:

Sample	Part of plant	Activity
84	Coarsest stems	1.17
85	Finer stems	0.79
86	Petioles	0.55
87	Leaves	0.21

Whether the presence of tannin is the sole explanation of the low activity of the leaves is doubtful. As there is much more starch in the stems than in the leaves and the plants were actively growing and flowering when cut, it is conceivable that the diastase is present for the maintenance of the sugar-starch equilibrium which seems to exist in the plant juices.

FACTORS WHICH AFFECT THE AMOUNT OF DIASTASE DURING THE GROWTH OF THE PLANT

The variation of diastase with light and darkness can be shown by these samples:

Sample	Cut	Cured	Activity	Per cent increase
24	July 8, 8 P.M.	Air-dried	0.57	..
27	July 9, 5 A.M.	Air-dried	1.05	84
55	Oct. 6, 6 P.M.	At 50° C.	0.92	..
49	Oct. 6, 8 A.M.	At 50° C.	1.25	36

agreeing very closely with the daily changes observed by Brown and Morris with Tropaeoleum.

Samples were also cut and kept in the dark in water but the relative increase observed in this case was very much smaller; for example:

Sample	Cut	Treatment	Activity	Per cent increase
26	July 9, 5 A.M.	Dried immediately	0.84	..
36	July 9, 5 A.M.	Dried in dark for 50 hrs.	0.97	15
43	Oct. 3, 8 A.M.	Dried immediately	0.90	..
46	Oct. 3, 8 A.M.	In water in dark 72 hrs.	0.93	3
55	Oct. 6, 6 P.M.	Dried immediately	0.92	..
57	Oct. 6, 6 P.M.	In water in dark 22 hrs.	0.95	3

These differences average slightly less than those obtained by Brown and Morris with Tropaeoleum and are very much less than in their experiments with Hydrocharis in which an increase of 153 per cent was observed.

SEASONAL VARIATIONS—There seems to be a gradual increase in diastase with advancing summer, followed by a decline at the approach of cold weather. Determinations on the five crops were as follows:

Sample	Crop No.	Date cut	Activity
94	1	May 23, 8 A.M.	0.75
26	2	July 9, 5 A.M.	0.84
147	3	Aug. 2, 8 A.M.	1.51
49	4	Oct. 6, 8 A.M.	1.25
69	5	Nov. 9, 8 A.M.	1.03

The first four samples were cut at the proper time for hay-making; *i. e.*, $^1/_{10}$ to $^3/_{10}$ in bloom. The fifth, perhaps, ought not to be included, as it was only about a foot high when cut—just two days before the first frost. A sample but six inches high and cut at the same time showed an activity of 1.24, indicating that the younger plants are higher in diastase.

THE EFFECT OF DIFFERENT CURING CONDITIONS UPON DIASTATIC ACTIVITY

CHANGES DURING DRYING—Brown and Morris exposed a number of their samples to chloroform vapor before drying and assumed that the diastase found after chloroforming and drying was the amount present at the time of cutting and that the values obtained by drying without chloroforming were due to a change brought about by the plant activity.

Exposing alfalfa to chloroform vapors caused the plants to wilt as if frozen and the samples so treated, after drying, showed activities from 42 to 84 per cent lower than the controls. Whether the observed difference was due to the chloroform breaking down a certain resistance to the action of some substance which destroys diastase, or to some activity of the living plant producing diastase during drying, is not known. Chloroform itself has a very slight inhibiting action on enzymes. It was found impossible to get concordant results from the fresh plant, either by grinding with sand or grinding in liquid air with and without sand, but in every case the activity was very low. Thus it has been impossible to obtain values for the activity of the fresh plant.

Samples dried at 50° C. in an oven showed but from 79 to 99 per cent of the activity displayed by the samples allowed to dry at room temperature and afterwards placed in the oven at 50°. This was probably due to the warm, humid atmosphere of the ovens, for from some experiments which will be described later it was found that drying in a current of air at 50° increased the diastatic activity as much as 50 per cent. The effect of oven-drying can easily be seen from the following determinations. All samples were cut the morning of May 23rd:

		Activity					
Sample	Temp.	Whole	Per cent	Leaves	Per cent	Stems	Per cent
98	Room	0.88	100	0.29	100	1.43	100
94	50°	0.75	85	0.35	83	1.17	83
95	100°	0.19	22	0.08	28	0.31	22
97	150°	0.03	3	0.015	3	0.06	4

Drying at room temperature in the dark and in full sunlight compared as follows:

Sample		Activity	Decrease Per cent
98	Dried in dark	0.88	..
99	Dried in full sunlight	0.68	23

A ground sample exposed to direct sunlight for a year in a closed bottle showed the following loss in activity:

		Activity
Sample 53	Before exposure	1.03
	After exposure, interior portion	0.76
	After exposure, portion next to bottle	0.70

The portion next to the bottle had lost a good share of its color, while the interior portions had lost but little color in comparison. The bleached layer was less than a quarter of an inch in thickness.

The effects of weathering are apparent from the following parallel experiments:

Sample	Treatment	Activity	Loss Per cent
106	Cut and immediately cured at room temp.	0.99	..
109	Cut and allowed to lie in the field for a week during which several showers occurred	0.25	75
107	Cut and placed in sunlight, with occasional sprinkling, for two weeks	0.09	91

Even a single, short night rain has considerable effect:

Sample	Treatment	Activity	Loss Per cent
147	Cut morning of Aug. 2nd, after night's rain, dried at 50°	1.51	..
150	Cut evening of Aug. 1st, lay in windrow without wilting during rain, was dried following morning at 50°	0.99	34
148	Cut morning of Aug. 1st, thrown into cock in evening, dried following morning at 50°	0.48	69

In comparison, the hays harvested and stacked under the regular season's conditions were very much lower in diastatic activity:

Sample		Activity
82	First crop, some of it had been exposed to rain, stacked	0.14
73	Second crop, stacked	0.50
76	Third crop, stacked	0.57
89	Fourth crop, stored in mow	0.60

Three samples of alfalfa meal obtained in the market showed activities of 0.23, 0.40 and 0.41. These were supposed to be made from selected alfalfa, but were about six months old when analyzed.

DIGESTIBILITY—WATER-SOLUBLE EXTRACT

It is natural to ask whether the enzyme content of a hay is of any real value. That can be answered positively only by extensive feeding experiments and even then with difficulty, for the conditions that make for high diastase are also the conditions which are influential in the production of good hay. The buyer who selects choice hay of good color and odor is selecting hay of high diastatic content, for it was noticed throughout this research that diastase and color, odor and flavor went hand in hand.

However, there is good reason to expect a relation between enzyme content and digestibility. It was pointed out that there is much more diastase present in good hay than is needed to transform all the starch present. The alfalfa contains other enzymes as well which may or may not vary in the same manner. Some work of H. T. Brown[1] indicates that all the cellulose digested by both the horse and pig is digested by the cytase or cellulose-dissolving enzyme in the food, and not by the enzymes secreted by the digestive tract. It is true that much greater action was observed in the animal than *in vitro*, but foods which were deficient or lacking in cytase showed little or no cellulose digestion. It is a common observation that enzymes show greater activity under the conditions obtaining in the digestive tract than under laboratory conditions.

In thirteen series of digestion experiments made under the direction of the Department of Agriculture[2] ten of the trials showed a positive loss due to cooking grain before feeding: that is, "The amount of food required to produce a pound of gain was larger when the food was cooked than when it was fed raw. In some cases the difference was considerable." Soaking the food on the other hand, produced a larger gain in weight per pound of feed than when dry grain was fed. E. F. Ladd[3] found the loss in digestibility of clover hay by cooking to be about the same as that of grain.

As a rough measure of probable digestibility, samples were subjected to autodigestion and the proportion which was soluble in water determined. In nearly every case factors which made for high diastase were found to also make for greater solubility, although the diastase varied much more widely than the solubility. This is illustrated by the following determinations on the first and third cuttings:

FIRST CUTTING

Sample	Treatment	Activity	Per cent soluble
97	Dried at 150°	0.03	28.4
144	Stacked while damp, somewhat "burnt"	0.10	30.7
95	Dried at 100°	0.19	32.2
92	Dried at 100°	0.41	34.9
108	Dried at 100° (gas turned off after a few hours, finished following day)	0.53	35.8
99	Dried in full sunlight	0.68	38.0
94	Dried at 50°	0.75	36.6
98	Dried in dark	0.88	37.7
106	Dried at room temp.	0.99	40.5

THIRD CUTTING

Sample	Treatment	Activity	Per cent soluble
148	Exposed to rain in cock, dried at 50°	0.48	32.8
150	In windrow during rain, dried at 50°	0.99	35.4
147	Dried at 50°	1.51	36.8
149	Dried in blast of air, average temp. about 50°	2.27	37.0
151	Dried in blast of air, average temp. about 50°	2.28	37.2

The accompanying curves may illustrate the variations perhaps still better. The three circled points below the "1st cutting" curve represent two samples injured by rain and one sprinkled in the laboratory. In these the loss of diastase has been much greater than the loss of soluble matter. The variations in diastase and solubility of leaves and stems are also shown for the first cutting.

It appears that the percentage of water-soluble substance does not continue to increase beyond a certain point, even when the diastatic activity is much higher and it was thought probable that all the substances acted on by the enzymes might be dissolved out. The leaves and stems of sample 106, which was 40.5 per cent soluble, were digested separately with

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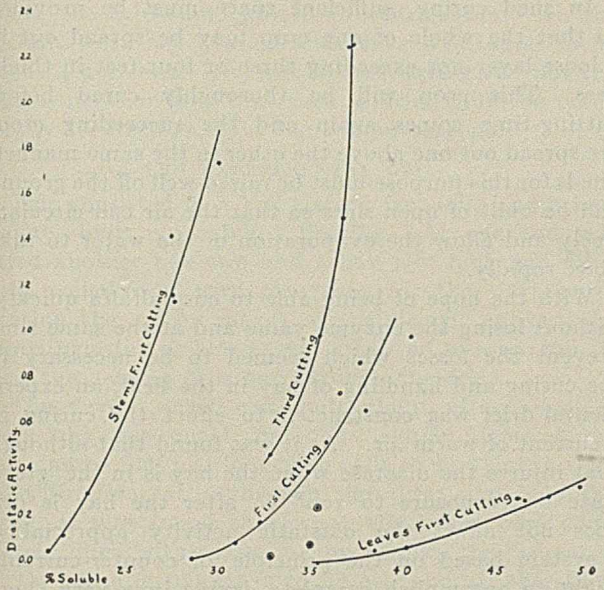
[1] *Jour. Chem. Soc. Trans.*, **1892**, p. 352.

[2] U. S. Dept. Agr., *Farmer's Bull.* **22**, 25.

[3] *4th Ann. Rep. N. Y. Agr. Exp. Sta.*, **1885**, p. 348.

cold water as usual and then parallel digestions made with this difference: that after the eight hours at room temperature the whole digestion apparatus was placed in an oven at 50° for five hours, then heated to boiling and afterwards washed as usual. The results were as follows:



LEAVES

Activity	
0.34	49.6 per cent soluble at room temperature 51.6 per cent soluble by heating
	2.0 per cent gain by heating

STEMS

Activity	
1.75	30.0 per cent soluble at room temperature 30.4 per cent soluble by heating
	0.4 per cent gain by heating

showing that in the weakly diastatic leaves there were still present substances which could be dissolved out by this treatment, while in the strongly diastatic stems the loss was but one-fifth as great. As this sample was 53.6 per cent leaves and 46.4 per cent stems, this would represent a total solubility of:

40.5 per cent at room temperature
41.8 per cent by heating

1.3 per cent gain by heating

In alfalfa analyzed at the Colorado Experiment Station[1] it was found that a total of 40.53 per cent was soluble by consecutive extractions with four changes of 80 per cent boiling alcohol, 24 hours' digestion with cold water and subsequent treatment with hot water and malt extract. From this it would be inferred that the substances soluble by water and diastase had been pretty thoroughly removed. These substances would include the sugars, dextrins and starch, about half the protein and a part of the coloring matter and mineral constituents.

A partial analysis of sample 89 (4th cutting, field-dried) showed the relative proportion of these constituents in choice hay:

	Leaves	Stems	Whole
Cane sugar	1.35	3.90	2.43
Maltose	0.20	0.17	0.19
Dextrose	1.38	0.50	1.00
Levulose	0.78	0.39	0.62
Starch	8.34	14.22	10.84
Crude protein	25.97	10.42	19.29

LOSSES THROUGH HANDLING AND CURING OF HAY

Mention has been made several times of separations of leaves and stems. These separations give some interesting figures as to the losses met with in field curing. The average percentage of leaves found in the laboratory-cured samples, where no losses occurred, was 52.6 per cent. Two samples were allowed to lie in the rain but were dried in the laboratory, so that no diminution in the number of leaves occurred, and both gave 47.4 per cent leaves, or a difference of 5.2 per cent. The average amount of leaves in samples cured in the field under favorable conditions was 46.2 per cent, or a loss of 5.6 per cent. One sample which was cured and stacked after having been exposed to rain in the windrow showed but 35 per cent leaves, or a loss of 17.6 per cent. Assuming that the stems were unaltered by the rain or curing and figuring that all samples originally contained the same proportion of leaves (52.6 per cent), then the rain must have caused a loss in weight of 10 per cent of the total weight of the hay, *this loss all being leaves.* The field curing caused a loss of 12 per cent and both rain and field curing showed a loss of 22.8 per cent in the one sample examined. These figures show loss in weight but not loss in food value, which was much greater, as shown by the following analyses:

Sample	Description	Protein	Sugar	Starch	Fiber
Average	Lab. cured (no loss)	17.83	4.18	10.71	27.50
Average	Field cured (12.0% loss)	13.77	2.25	12.40	30.51
80	Exposed to rain Field cured (22.8% loss)	11.33	0.75	14.12	36.49

Calculating the constituents on the original 100 per cent:

Description	Protein	Sugar	Starch	Fiber
Field cured	12.11	1.98	10.91	26.92
Exposed to rain, field cured	8.75	0.58	10.91	28.18

which amounts to, in pounds loss per 100 pounds of hay:

Description	Protein	Sugar	Starch	Fiber
Field cured	5.72	2.20	0.20 (gain)	0.58
Exposed to rain, field cured	9.08	3.60	0.20 (gain)	0.68 (gain)

showing losses of 32 per cent and 51 per cent, respectively in the protein, and 53 per cent and 86 per cent in the sugar content. There must also have been a loss of starch and fiber through the mechanical loss of leaves, but the experimental error in the determination of these substances is relatively large; so, considering other possible errors in sampling, etc., this discrepancy is not surprising.

Fleischmann[1] has shown that in the curing of hay the cellulose content does not change and the starch content drops somewhat when curing takes place slowly. The Kansas Experiment Station[2] has found in weathered hay a calculated total loss of 31.7 per cent, in which 60 per cent of the protein was lost.

W. P. Headden[3] estimated the loss due to weathering of alfalfa at $^4/_{10}$ of the total crop, exclusive of loss by shattering and estimated the loss of leaves and stems by shattering at from $^1/_5$ under favorable conditions to $^2/_3$ under extreme conditions and repeated handling.

C. Lipscomb[4] in some determinations on timothy

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[1] Colo. Agr. Exp. Sta., *Bull.* **124**, 12.

[1] *Landwirtschaftlichen Versuchsstationen,* **762** (1912), 237–447.

[2] Kans. Agr. Exp. Sta., *Bull.* **155** (1908), 288–90.

[3] Colo. Agr. Exp. Sta., *Bull.* **110**, 7.

[4] U. S. Dept. of Agr., *Farmers' Bull.* **362**, 26.

hay found from 20 per cent to 40 per cent of "no grade" hay on the outside of stacks which graded No. 1 in the interior, showing the weathering of the outside of the stack to be considerable. Alfalfa is perhaps even more sensitive to weathering than timothy.

Returning to our first figures and assuming the market value of choice alfalfa hay to be $20 per ton, the loss of from 12 to 23 per cent means a loss of from $2.75 to $6.00 worth of hay for every ton harvested; or, for $20.00 worth harvested the crop should have been worth $22.75 to $26.00. This is regardless of the fact that the remaining hay is of less value. Taking the reduced value into consideration, not $20.00 but perhaps only $13.00 to $18.00 would be realized per ton of hay; that is, land which could have produced $26.00 worth of choice hay may, on account of weathering, produce but $13.00 worth, giving a loss of 50 per cent. Or, land which could have produced $22.75 produces but $18.00, giving a loss of over 20 per cent.

METHODS OF CURING AND STORING HAY

Perhaps the most approved method[1] for field curing is to begin cutting as soon as the dew is off in the morning and, if the weather is favorable, to rake and put into small cocks the same afternoon. After allowing to cure in the cocks for several days, the cocks are opened for a short time and the hay taken up before the leaves become dry enough to shatter appreciably. Storing under cover is, of course, preferable, but if the hay is stacked in the open the stack should be well protected with canvas or "slough grass." Curing in the windrow requires less labor, but has the disadvantage that as the leaves dry much faster than the stems a larger proportion is lost by shattering.

Several methods have been suggested for reducing the losses due to weathering and shattering, such as storing in the green state as ensilage, or curing in ventilated stacks or sheds. Any process which requires the removal of the hay from the field while still in the green state necessitates the handling of from three to four times as great a weight of hay, owing to the contained water.

Alfalfa does not lend itself to the making of ensilage as readily as some other fodders, partially owing to the fact that it does not pack well in the silo. The ensilage spoils readily around the edges and the losses due to changes in curing amount to about 10 per cent of the dry weight of the feed. Feed stored in this form must be used within a reasonable time after removal from the silo and, therefore, cannot be easily shipped and marketed.

Curing in ventilated stacks and sheds has met with considerable success when properly conducted. For curing in the stack, poles are erected and the green hay piled in layers two to three feet in thickness, each layer being separated from the lower layer by cross pieces nailed to the poles, thus allowing the free circulation of air during drying. Some sort of a cover is also necessary to prevent excessive weathering of the loosely-piled hay.

In shed curing, sufficient space must be provided so that the whole of one crop may be spread out in a loose layer not exceeding three or four feet in thickness. This crop will be thoroughly cured before cutting-time comes again and the succeeding crops are spread out one above the other in the same manner. Sheds for this purpose must be raised well off the ground and be built of open slats so that the air can circulate freely and allow the evaporation of the water to take place rapidly.

With the hope of being able to cure alfalfa quickly, without losing the enzyme value and at the same time prevent the losses which seemed to be necessary in the curing and handling of hay in the field, an experimental drier was constructed to effect the curing in a current of warm air. As it was found that although heat injures the diastase when the hay is in the green state but exposure to 100° C. after the hay is dry does not affect the diastatic activity appreciably, a system based on the principle of counter-currents ought to accomplish complete drying in a very short time without the loss of any of the valuable properties.

The hay produced by the drier, which will be described later, appeared to be even better than was expected. It had a bright green color equal to that of the growing plant and had the odor and flavor of freshly-cut alfalfa. Shaken up with water, it appeared to have all the properties of the green hay. A sample kept for two years has largely retained these properties, although the color has become, perhaps, a little lighter. The appearance on the whole was far superior to that of any field-cured alfalfa ever examined. Its diastatic activity was 2.27 or an increase of 50 per cent over that of the same hay dried at 50° C. Its solubility in water was, however, but slightly greater.

[NOTE—After these experiments in artificial drying had been started, there was brought to our notice through State Secretary of Agriculture, F. D. Coburn, another method of drying alfalfa by steam heat. The process, briefly described, was this: After the hay is cut and finely chopped, it is passed into a drier which consists of a large cylinder containing pipes for the circulation of steam under pressure. The whole cylinder is revolved and a temperature of about 130° C. is maintained, which is claimed to completely dry the hay in 17 minutes. The process is continuous. A sample of this meal was examined and it was found to have an activity of only 0.40 and but 34.8 per cent was soluble in water. This would place it with the samples which were oven dried at 100° C. in the laboratory and would indicate that the digestibility had been lessened by the heat. It was not as sweet in taste as a good field-cured sample, on account of the inversion of a portion of the cane sugar. The hay had something of a peptone odor and the color was about the same as that of the best field-cured samples.

After the completion of this work H. B. McClure[1] published a brief outline of some experiments by

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[1] LITERATURE ON METHODS OF CURING—U. S. Dept. of Agr., *Farmers' Bull.* **339** and **499**; Wis. Agr. Exp. Sta., *Bull.* **121** and Special Bull. "Seeding, Growing and Curing of Alfalfa;" Kansas Agr. Exp. Sta., *Bulls.* **155** and **175**; Ohio Agr. Exp. Sta., *Circ.* **91**; Miss. Agr. Exp. Sta., *Bull.* **84**; "Alfalfa," F. D. Coburn, Orange Judd Co., 1911; "Alfalfa Farming in America," Jos. E. Wing, Sanders Pub. Co., 1909.

[1] U. S. Dept. Agr., Bur. of Plant Indus., *Circ.* **116**, 27–31.

T. P. Russell on steam drying of alfalfa and cowpea hay using a plant of the belt conveyor type. A single set of duplicate analyses only was given. This showed the artificially cured hay to be about 5 per cent above the field-cured hay in protein content. In the present work the average difference was found to be about 4 per cent. No cost figures were given but the final conclusion was that such a drier could be made to pay for itself in from one to four seasons.]

THE EXPERIMENTAL DRIER

This consisted of a box sixteen feet long and a foot square, built of matched flooring. At one end was fitted another box two and a half feet long and filled with coiled iron wire resistance for the purpose of heating the air by means of the electric current. A centrifugal fan or blower was arranged to force the air over the heating coils and through the drier.

The drying shaft was built about fifteen degrees from the horizontal and four closely-fitting boxes three and a half feet long with ends of wire screen were built to slide easily through the drier and hold the hay. It was found that when the boxes were completely filled with coarsely-chopped hay the resistance to the air was too great to be economical; therefore, a wire screen was placed diagonally through the boxes in such a manner as to allow the air to pass up through a four or five inch layer of hay placed upon the screen. With the boxes all filled in this manner, the air had a velocity of about 160 feet per minute at the open end of the drier. Air velocities were determined by means of a portable anemometer placed in different positions at the open end of the shaft and the average reading taken. Even by using averages, the velocities so obtained were valueless, owing to the eddy currents produced by the uneven distribution of the hay. Kent[1] cites some work to show that the anemometer can give errors as high as 40 per cent when used for measuring velocities in pipes less than two feet in diameter. On this account the anemometer readings were not used in the calculations. Temperatures and humidities were measured by means of wet and dry bulb thermometers placed at intervals along the drier, using the psychrometric table of the U. S. Weather Bureau[2] to convert the observed fall in temperature due to evaporation into percentage humidity. The evaporation of the water caused a drop in the temperature of the air passing through the drier so great that occasionally the temperature of the escaping air was even lower than that of the air at the intake before passing over the heating coils. At these times the escaping air was practically 100 per cent saturated.

When the drier was in operation, a box was removed from the lower or warm end of the shaft every thirty minutes, then all the boxes shifted down one place and a box of fresh hay added at the upper or cold end of the shaft. By this means each box of hay was exposed to a temperature of 25° to 35° C. for a period of half an hour, then moved down to a region of 35° to 45° for a like period, then to 45° to 55° and finally exposed to a temperature of 55° to 65°, the limit obtainable with the heating arrangement used.

When the drier was operating normally and the boxes all being advanced one position every half hour, a period of two hours was always sufficient to dry the hay so thoroughly that allowing it to stand in the open after removal from the drier caused it to take up moisture.

The results of two half-hour periods will be given as examples. The hay for these runs was cut after sundown on August the 2nd and allowed to lie in a pile covered with canvas until it was chopped preparatory to putting into the drier. The following morning the drier was started on two boxes, and an additional box added every half hour, advancing those already in and removing the dry boxes as fast as necessary to keep up the half-hour additions. After the irregularly-timed boxes had all been removed, the existing conditions were as follows:

Time of run	11:00–11:30		1:00–1:30	
Temp. of air at intake	28.5° C.–83.3° F.		29° C.–84.2° F.	
Temp. of wet bulb at intake	24	75.2	24	75.2
Equal to a humidity at intake		70%		66%
Temp. of air at warm end	65° C.–149° F.		64° C.–147° F.	
Temp. of wet bulb at warm end	30	86	30	86
Equal to a humidity at warm end	About 9%		About 9%	
Temp. of air at cold end	31.5° C.–88.7° F.		33.5° C.–92.7° F.	
Temp. of wet bulb at cold end	31	87.8	31.5	88.7
Equal to a humidity at cold end		96%		85%
Velocity of air through 10″ × 10″ area, ft. per minute		161		237
Volume of air per minute, cu. ft.		112		165

The weights of hay and losses during these runs were:

Box	Weight of green hay Pounds	Weight at 11:00 Pounds	Weight at 11:30 Pounds	Loss Lbs.	Per cent loss	Total per cent loss
1 warm	6.00	2.90	2.20	0.70	11.7	63.3
2	5.10	3.30	2.30	1.00	19.6	54.9
3	4.85	4.45	3.45	1.00	20.6	28.9
4 cold	5.40	5.40	4.80	0.60	11.1	11.1
Total	21.35	.....	....	3.30	15.5	....
			Weight at 1:00	Weight at 1:30		
1 warm	5.40	2.65	1.95	0.70	12.9	63.9
2	4.85	2.50	1.85	0.65	13.4	61.9
3	5.60	4.50	2.30	1.20	21.4	58.9
4 cold	4.90	4.90	4.10	0.80	16.3	16.3
Total	20.75	....	....	3.35	16.0	....

The total losses of moisture in pounds of 3.30 and 3.35 correspond to losses per minute of 0.110 and 0.112 pounds, respectively.

The calculations of results which follow were made by the use of Grosvenor's "Calculations for Dryer Design,"[1] and compared with results obtained by the use of the tables and formulae found in Kent's "Mechanical Engineers' Pocket Book"[2] and the "Psychrometric Tables" of the U. S. Weather Bureau.[3] Values obtained from these sources are marked with an asterisk. (*)

The air at the fan intake was 83.3° F. and the percentage humidity corresponding to the observed drop of 8.1° F. at that temperature is 70 per cent (*). One pound of air under these conditions has associated with it 0.0172 pounds (*) of aqueous vapor. When the temperature of the air is raised to 149° F. the saturation drops to 8.5 per cent (*); that is, this weight of vapor is but 8.5 per cent of the maximum quantity of aqueous vapor, which could be present at that temperature under atmospheric pressure. A humidity

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[1] "Mechanical Engineers' Pocket Book," Wiley & Sons, **1904**, p. 491.

[2] U. S. Dept. of Agr., *Weather Bureau Bull.* **235**.

[1] *Trans. Am. Inst. Chem. Eng.*, **1** (1908), 184.

[2] **1904**, p. 491.

[3] *Loc. cit.*

of about 9 per cent (*) was calculated from the difference between the temperatures of the wet and dry bulbs placed in the warm end of the drier. The humidity at the outlet of the drier was found to be 90 per cent (*). If the cooling effect while passing through the drier had been due solely to the evaporation of water, the exit temperature should have been 91.5° F. (*); but in a drier as small as this the loss must have been considerable and the observed temperature was only 88.7° F. At a temperature of 88.7° F. and 96 per cent saturation there is present 0.0278 (*) pound of water per pound of air, or a gain of 0.0106 pound. To effect the observed evaporation of 0.110 pound of water per minute would, therefore, require 10.37 pounds of air per minute.

One pound of dry air at 88.7° F. occupies 13.82 cu. ft. (*) and one pound of "saturated" air occupies 14.48 cu. ft. (*). Interpolation shows that one pound of 96 per cent saturated air would occupy 14.45 cu. ft. Therefore, 10.37 pounds would occupy 150 cu. ft. and 150 cu. ft. per minute would be necessary to effect the observed evaporation of 0.110 pound of water per minute.

Table I—Data Obtained (and Calculated) from Drying Experiments

	11:00–11:30 Run		1:00–1:30 Run		Calculated		
Rate of evaporation of water, pounds per minute..	0.110	0.110	0.112	0.112	100	100	100
Temperature at intake, ° F....................	83.3	83.3	84.2	84.2	84.0	84.0	84.0
Saturation at intake, per cent.................	70	70	66	66	70	70	70
Equivalent to pounds of water per pound of air....	0.0172	0.0172	0.0166	0.0166	0.0178	0.0178	0.0178
Maximum temperature, ° F....................	149	149	147	147	212	212	175
Resulting humidity, calculated, per cent........	8.5	8.5	8.7	8.7	.....	.....	.....
Resulting humidity, observed, per cent.........	about 9	about 9	about 9	about 9	.....	.....	.....
Humidity at outlet, per cent...................	96	96	85	85	90	85	90
Temperature at outlet, calculated, ° F..........	.....	91.5	....	93.5	103.5	105.5	98
Temperature at outlet, observed, ° F...........	88.7	.....	92.7	....	.....	.....	.....
Pounds of water per pound of air at outlet......	0.0278	0.0305	0.0285	0.0292	0.0430	0.0425	0.0356
Pounds of water per pound of air at inlet.......	0.0172	0.0172	0.0166	0.0166	0.0178	0.0178	0.0178
Gain in passing through drier..................	0.0106	0.0133	0.0199	0.0126	0.0252	0.0247	0.0178
Pounds of air per minute necessary to remove water at observed rate.........................	10.37	8.27	9.41	8.89	3970	4050	5620
Volume of 1 pound of dry air at outlet temperature, cu. ft..............................	13.82	13.90	13.92	13.95	14.20	14.25	14.06
Volume of 1 pound of saturated air at outlet temperature, cu. ft.........................	14.48	14.62	14.68	14.72	15.30	15.42	14.98
Difference in volume, cu. ft....................	0.66	0.72	0.76	0.77	1.10	1.17	0.92
Multiplied by per cent saturation equals, cu. ft....	0.63	0.69	0.65	0.65	0.99	1.00	0.83
Volume of 1 pound of moist air at outlet temperature and saturation, cu. ft..................	14.45	14.59	14.57	14.60	15.19	15.25	14.89
Volume of outgoing air, calculated, cu. ft........	150.00	120.5	137.1	129.8	60300	61800	83700
Volume of outgoing air, observed, cu. ft.........	112	112	165	165	.....	.....	.....
Specific heat of moist air at intake, B. T. U. per lb.	0.246	0.246	0.245	0.245	0.246	0.246	0.246
B. T. U. per pound necessary to effect observed rise in temperature..........................	16.16	16.16	15.43	15.43	31.5	31.5	22.4
B. T. U. per minute imparted to ingoing air.....	167.8	133.7	145.1	136.3	125000	127600	126000
B. T. U. per 100 pounds of water evaporated....	152500	121700	129500	121600	125000	127600	126000
Volume of air per 100 pounds of water evaporated, cu. ft....................................	94200	75200	85500	81700	60300	61800	83700
Pounds of coal per 100 pounds of water evaporated	28.2	22.5	24.0	22.5	23.2	23.6	23.3

The specific heat of dry air is 0.2373 (*) and of water vapor 0.475 (*) at constant pressure, and one pound of air and 0.0172 pound of water vapor require 0.264 B. T. U. (*) for each degree of rise in temperature. A change in temperature of from 83.3° F. to 149° F., or 65.7°, would, therefore, require an expenditure of 16.16 B. T. U. for each pound of air used and 10.37 pounds of air would require 167.8 B. T. U. per minute.

There are placed side by side in Table I the calculations using first the observed exit temperature, as representative of the experimental drier, and those using the calculated exit temperature, as representing more nearly a drier of commercial dimensions. The results of both runs recorded are given and it is to be noticed that the difference between calculated and observed exit temperatures was much less in the second run after the drier had been in operation for four hours than after the first run.

The last three columns of the table represent calculations using the average observed inlet temperature and humidity of 84° F. and 70 per cent saturation, outlet humidities of 90 and 85 per cent and the much higher maximum temperatures of 212° F. and 175° F. These calculations are given as a basis for comparison with driers sufficiently long to allow slow and uniform rise to these higher temperatures, thus shortening the time necessary for drying.

For large-scale drying the process would be made continuous either by the use of a horizontal rotating cylinder containing baffles arranged for the agitation of the coarsely-cut hay or, by means of a vertical shaft containing open-mesh shelves and some sort of a dumping mechanism. The dumping might be accomplished either by revolving rakes fastened to a central shaft or by a mechanism which would lower and raise the shelves on hinges.

COMMERCIAL POSSIBILITIES OF DRYING BY ARTIFICIAL HEAT

No data was at hand for determining the probable efficiency of a drier of commercial size heated by steam. However, the following approximations were made by calculating from assumed values based upon information from several manufacturers of drying machinery and from various other sources.

Assuming the heat equivalent of coal brought at $2.60 per ton to be 12,000 B. T. U. and that the boiler gave an efficiency of 75 per cent or evaporated 10.3 pounds of water at 100 pounds boiler pressure for every pound of coal and that there was a total radiation and indirect loss of 40 per cent in the heating system, then the total efficiency of the plant would be 0.75 × 60 per cent or 45 per cent and the B. T. U. imparted to the air from every pound of coal would be 45 per cent of 12,000 or 5400 B. T. U. Reducing all calculations to a basis of 100 pounds of water evaporated and dividing the B. T. U. so obtained by 5400, we arrived at values, in the seven different columns, of 28.2, 22.5, 24.0, 22.5, 23.2, 23.6, and 23.3 pounds of coal per 100 pounds of water evaporated.

The amount of moisture in green alfalfa varies considerably. A sample cut during a rain contained 81 per cent moisture while in other samples the moisture content was as low as 60 per cent. The average of those samples dried in the laboratory was nearly 75 per cent. This of course is much greater than would be found in hay cut under ordinary conditions. The samples used for these tests contained about 64 per cent water, while a sample taken at the same time, but dried immediately, contained 74 per cent water, showing a loss of 10 per cent from handling and lying in the pile over night. Mowing, raking and hauling on a bright day would probably show a greater loss.

Assuming the moisture content of a hay to be 75 per cent when it reaches the drier, it would require the evaporation of 6000 pounds of water per ton of dry hay; $6000 \times 23.2/100 = 1390$ pounds of coal per ton of dry hay. At $2.60 per ton, this would amount to $1.81 per ton of hay for heat. To this should be added something like 25 cents per ton for interest and depreciation of plant and about $1.00 per ton for chopping, power and labor, making a total cost of $3.06 for drying one ton, dry weight, of hay.

Assuming the moisture content to be 64 per cent, as was found in the trials here shown, the production of one ton of dry hay would require the evaporation of but 3600 pounds of water, using 835 pounds of coal at a cost of $1.09. Adding to this $1.25 for interest, power, labor, etc., a total cost of $2.34 per ton is shown. Although these cost figures are only approximations, they lead to some interesting conclusions.

As it was shown that the total loss in the value of hay due to field curing and handling amounts to from 20 per cent under favorable conditions to 50 per cent under adverse weather conditions, and as the calculated cost for artificial drying is from $2.35 to $3.00 per ton, producing only choice alfalfa of uniform grade, it is apparent that artificial drying may be conducted at a profit in districts where the drier can be situated near both field and source of fuel. The alfalfa meal industry has grown to considerable proportions in the last few years and the demand is for well-cured alfalfa of good color. Several alfalfa millers have expressed the opinion that a hay of such dryness could be ground at about half the cost of the average hay, taken from the stack.

Some millers subject their hay to a short, preliminary drying before grinding. A drier run in connection with an alfalfa-grinding plant would be an excellent combination.

This same principle of drying could doubtless be applied to other fodders and perhaps even to small fruits and other farm products which are occasionally damaged by unfavorable weather during the drying season. Among the other fodders to which drying might be applicable might be mentioned the pea vines from the canning factories and the common weed, sweet clover or yellow Mellilot. Pea vines are often made into ensilage but as such they have but a limited demand and the canner often has trouble disposing of the enormous quantity of vines which accumulate and become a nuisance. Pea-vine meal has been used to a certain extent as an addition to alfalfa meal. Young sweet-clover is used as forage to a small extent in Europe but sun curing does not produce a good hay. Drying in an oven at 50°, however, gave a hay of good appearance and flavor. Samples of these plants examined gave analyses as follows:

	Protein Per cent	Diastatic activity	Water solubility Per cent
Pea vines	17.73	0.54	44.2
Sweet clover	18.85	0.03	32.7

The moisture contents of the two plants in the green state were 84.7 per cent and 83.2 per cent and this would probably be the principal drawback in curing them for feed.

SUMMARY

I—The diastatic activity of alfalfa is greater in the morning or after a period of darkness than after a period of exposure to light. There is much more diastase present in the plant during the warm, active, growth-producing summer than during the spring or fall. Young plants contain more diastase than older ones.

II—Drying at elevated temperatures in a humid atmosphere decreases the diastatic activity, even though the temperature is only 50°. Drying in a current of air with gradually increasing temperature, on the other hand, increases the activity markedly. Light and weathering in the field tend to destroy the diastase. Rain during curing is very detrimental.

III—Highly diastatic alfalfas generally show a greater solubility in water by auto digestion than samples low in diastase. However, the degree of solubility in water cannot be increased above a certain limit.

IV—The loss in digestible constituents during handling and curing in the field may vary from 20 per cent under favorable conditions to as much as 50 per cent under adverse weather conditions.

V—Curing by artificial heat, using the principle of counter-currents, gives a hay of better color, odor and flavor than can be produced by other means. The hay appears to retain many of the valuable properties of the green plant, which are ordinarily lost in curing.

VI—The cost of artificial drying is estimated to be less than the losses generally sustained in field curing and, therefore, it ought to be possible to conduct drying at a profit when the drier can be located near both field and source of fuel.

The writer desires to acknowledge his indebtedness to the late Robert Kennedy Duncan for helpful direction and valuable advice in connection with this work.

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THE ORIGIN OF VANILLIN IN SOILS—VANILLIN IN WHEAT AND IN THE WATER IN WHICH WHEAT SEEDLINGS HAVE GROWN

By M. X. Sullivan

Received August 19, 1914

Vanillin, the chief odorous principle of the vanilla pod, the fruit of vanilla planifolia, has been reported as present in a number of plants and plant products. The presence of vanillin in plants and its possible passage into the medium of growth is of great interest since (1) vanillin has been found injurious to plant growth[1] and (2) it has been found in a number of soils.[2] As yet it has not been reported as formed by microörganisms.

Among the plants and plant material in which vanillin has been reported are asparagus sprouts, seeds of white lupine, ilex leaves, dahlia tubers, grain of oats, and roots of couch grass, potato, pine wood, peat, raw beet sugar, and in resins such as Asafoetida and Siam benzoin.[3] It has been found also in orchid flowers exposed to sudden frosts[4] and in the incrusting pigment of sugar cane on warming with dilute acids.[5]

Vanillin or a closely related mother substance, in large or small quantities, seems to be fairly wide-spread in the vegetable world. Accordingly, as a possible explanation of its occurrence in field soils, it became of interest to determine whether or not vanillin could be found in wheat as a type of field crop and in the water in which wheat had grown.

VANILLIN IN WHEAT—When wheat seedlings were extracted with hot alcohol (recently distilled) there was obtained on evaporating the alcohol extract a syrupy mass, part of which was soluble in ether. The ether extract was treated with a half saturated solution of sodium bisulfite in the usual way in testing for aldehydes. The bisulfite solution was freed from sulfite by means of dilute sulfuric acid and the excess of sulfur dioxide driven off by passing air through the liquid. After extraction with ether and evaporation of the ether solution a small amount of matter which smelled of vanillin was obtained. This gave the characteristic vanillin color reactions: blue with ferric chloride, green with ferrous sulfate and bromine water, violet with a mixture of hydrochloric and sulfuric acids and acetone water.

With the recognition that wheat contained vanillin, it became of interest to determine how much of the aldehyde was present. For the quantitative estimation recourse was had to the colorimetric method described by Folin and Denis.[6]

For the quantitative determination, 200 g. of wheat seeds were extracted with alcohol and the extract was then treated in the customary way for extracting aldehydes. The final ether extract from the solution freed from bisulfite was evaporated and taken up with warm water. This water solution was treated with equal parts of lead acetate and lead subacetate as long as a precipitate formed. The filtrate or an aliquot part of it was treated with 5 cc. of the phosphotungstic-phosphomolybdic reagent as described by Folin and Denis and after 5 minutes a saturated solution of sodium carbonate was added until the volume of the liquid was 50 or 100 cc. After standing 10 minutes, the solution was filtered and the blue color generated in the reactions compared in a Schreiner colorimeter with that produced by a similarly treated standard solution of vanillin. The standard was of such a strength that 10 cc. diluted with the reagents to 100 cc. contained 1 mg. of vanillin or 10 parts vanillin per million. The stock solution of vanillin was made, as recommended by Harder,[1] by dissolving 2 g. of vanillin in 200 cc. of 95 per cent alcohol and diluting to 1 liter and then using 10 cc. of this solution to make 200 cc. of the standard solution as needed. Ten cc. of this standard were treated with 5 cc. of the phosphotungstic-phosphomolybdic reagent and then with sodium carbonate as outlined above.

Vanillin was similarly determined (1) in the ether-soluble part of a solution obtained by heating wheat seeds 4 hours on a steam bath with 5 per cent sulfuric acid; (2) in the alcohol extract of wheat bran; (3) in the alcohol extracts of the roots, tops, and seeds of wheat seedlings 5 to 10 days old; (4) in the seed water or the water bathing the seedlings for the first 24 hours; (5) in the root water or the water which bathed the roots for 4 to 10 days with a change of water every two days. The water solutions were concentrated under reduced pressure and extracted with ether. The quantitative results are given in the following table:

TABLE I—VANILLIN IN WHEAT AND IN THE WATER IN WHICH WHEAT SEEDLINGS HAD GROWN

MATERIAL	QUANTITY	VANILLIN Parts per million	
Wheat seeds	200 and 500 g.	1–6	3
Wheat seeds digested with 5% H_2SO_4	200 g.	5–14	11
Wheat bran	200 g.	3(a)	3
Roots of wheat seedlings	1500 seedlings	7–18(a)	13
Tops of wheat seedlings	1500 seedlings	13–16(a)	15
Seeds of wheat seedlings	1500 seedlings	6–8(a)	7
Seed water	4000 cc.	Trace–3	
Root water	5000 cc.	Trace to 10(a)	

(a) Based on weight of original seeds.

The effect of germination on the amount of vanillin in wheat may be seen more clearly in the following experiment where the vanillin in 1717 ungerminated seeds and in the same number of seeds germinated is compared:

TABLE II—VANILLIN IN UNGERMINATED SEEDS AND IN SEEDS, TOPS, AND ROOTS OF SEEDLINGS 5 DAYS OLD

	P. p. m.	
Seed	3.6	
Plant seed	7.7	
Plant tops	15.2	(Based on weight of 1717 seeds or 58 g.)
Plant roots	13.0	
WHOLE PLANT	35.9	

The tables show that vanillin occurs free in ungerminated wheat to a slight degree, that it is increased in amount during the early growth of the plant and can pass from the plant to the medium of growth either directly or more probably as a result of cell sloughing and disintegration. Treatment of ground seeds with dilute sulfuric acid increases the amount of vanillin extractable. Accordingly, it would seem that a mother substance of vanillin occurs in wheat and yields vanillin on hydrolysis by acids or in the process of germination.

Coniferin is regarded by many as the mother substance of vanillin. Coniferin gives a blue color with phenol and hydrochloric acid especially in the presence of a little potassium chlorate, gives glyco-vanillin on treatment with potassium permanganate and chromium trioxide, yields vanillin on treatment with chromic

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[1] Schreiner and Reed, *Bull.* **47**, Bur. of Soils, U. S. Dept. Agric. (1907); Schreiner and Skinner, *Bull.* **77**, Bur. of Soils, U. S. Dept. Agric. (1911).

[2] E. C. Shorey, *J. Agr. Res.*, **1** (1914), 357.

[3] Abderhalden, *Biochemische Handlexikon*, **1** (1911), 837.

[4] V. Lippmann, *Ber. d. chem. Ges.*, **45** (1912), 3431.

[5] Langguth and Steuerwald, *Chem. Zentr.*, **1912**, I, 83.

[6] *J. Biol. Chem.*, **12** (1912), 239; THIS JOURNAL, **4** (1912), 670.

[1] THIS JOURNAL, **5** (1913), 619.

acid mixture, yields glucose and a resin by boiling with dilute sulfuric acid. From the roots of wheat seedlings there was obtained, by extraction with hot water and hot alcohol and precipitation from alcohol by means of ether, material which gave a greenish blue color with phenol and hydrochloric acid; a blue color with phenol, hydrochloric acid and a little potassium chlorate; a reducing substance on boiling with dilute sulfuric acid. The method of obtaining the material, its reaction with phenol, and the formation of reducing substances on boiling with acid would indicate the presence of coniferin in the wheat roots. Coniferin, it might be said in passing, has been found in the lignified tissue of a number of plants.

Vanillin we have found also in rotten oak wood, in pineapple pulp and parings and in the hot water extract of lawn grass, consisting of blue grass and a small amount of white clover. The amount of vanillin extractable from grass is considerably increased by heating with 5 per cent sulfuric acid for 4 hours on a steam bath. Undoubtedly it occurs to a greater or less degree in many plants either free or in a conjugated form, from which it may be liberated by oxidation and hydrolysis. Its presence in wood and various forms of vegetation would lead to the conclusion that the vanillin in soil has its origin in vegetable débris and to a minor degree also in direct excretion or cell sloughing by growing plants.

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AN EXACT AND EASY METHOD FOR PREPARING A NEUTRAL AMMONIUM CITRATE SOLUTION

By J. M. McCandless

Received August 8, 1914

Since the writer made his official report as Referee on Phosphoric Acid, in 1908 to the Association of Official Agricultural Chemists, there have appeared a number of interesting articles on the subject matter of that report showing how the ammonium citrate solution could be rendered neutral both by physical and chemical methods. All of this work has confirmed the accuracy of the work done, and the conclusions reached by the writer in his original report. As this report was never published in any chemical journal, being printed only in the Proceedings of the A. O. A. C.,[1] and has therefore never been seen by many who are interested in the subject, the writer may be pardoned for reproducing here a part of that report.

PARTIAL REPRODUCTION OF REPORT OF REFEREE ON PHOSPHORIC ACID FOR 1908

"As the referee was to decide whether the various solutions of ammonium citrate sent him were neutral or not, and as scarcely any two chemists can agree upon the exact point of neutrality, whether from lack of sensitiveness of the indicators, or color-blindness on the part of the operators, he decided to make an analysis of each sample according to the method outlined in his last report to the Association, and be guided by those results in deciding upon neutrality.

METHOD OF ANALYSIS—"Twenty-five cc. of each solution were pipetted into a 250 cc. flask, diluted to mark, shaken, and 25 cc. of this solution were pipetted into a distillation flask. To the solution in the flask, 40 cc. $N/4$ caustic soda solution were added, and the contents of the flask distilled into 20 cc. $N/2$ acid, continuing the distillation till the volume of the distillate measured from 65 to 70 cc. The ammonia in the distillate was then titrated by means of $N/10$ alkali and cochineal. The residue in the distillation flask was washed into an Erlenmeyer, excess of standard acid added, a few drops of phenolphthalein, and the excess acid estimated by $N/10$ alkali. From the result, the weight of citric acid originally combined with the ammonia was calculated. Calculating from the formula of the pure salt, $(NH_4)_3C_6H_5O_7$, that the ratio of ammonia to citric acid was as 1:3.765, a basis of comparison was established. Results obtained are given in table below:

Number of analyst	Milligrams of ammonia in 25 cc. of diluted solution = 2½ cc. original	Milligrams of citric acid in 25 cc. of diluted solution = 2½ cc. original	Ratio of ammonia to citric acid	Ratio in neutral salt $(NH_4)_3$-$C_6H_5O_7$	REACTION WITH CORALLIN
1	113.9	433.2	1:3.803	1:3.765	Neutral
2......	109.3	412.8	1:3.775	1:3.765	Alkaline
3......	104.9	424.96	1:4.051	1:3.765	Acid
4......	113.7	433.9	1:3.816	1:3.765	Neutral
5......	110.5	430.08	1:3.891	1:3.765	Slightly acid
6......	111.5	436.48	1:3.915	1:3.765	Acid
7......	108.7	421.1	1:3.874	1:3.765	Slightly acid
8......	104.7	398.7	1:3.808	1:3.765	Neutral
9......	102.8	430.7	1:4.189	1:3.765	Acid

"In the above table, all the solutions which showed materially more citric acid than 3.765 parts to 1 of ammonia, also showed a decidedly acid reaction to corallin.

"It appears that some chemists prepare their ammonium citrate solution by treating the citric acid with excess of ammonia, and then leave the hot solution to neutralize itself, or finally adjust by means of red and blue litmus paper, or corallin. No. 3 in the above table was prepared in this way. The heat of the mixture not only drove off sufficient ammonia to render it neutral, but *continued* and left it decidedly acid."

The writer has, only in the past few days, had his attention called to the article of Patten and Marti[1] where in referring to the solutions, analyses of which are given in the above table, they use the following language: "The three solutions *claimed* to be neutral by McCandless contained 44.3 g. NH_3, and 168.76 g. $C_6H_8O_7$ per liter, the ratio being 1:3.809. The results obtained by us conclusively prove that such a solution would be slightly acid, which fact is further substantiated by the ratio of ammonia to anhydrous citric acid being too wide."

Patten and Marti had evidently failed to note the headings of Columns 5 and 6 in the above table, or they would not have attributed to the writer the "CLAIM" that solutions Nos. 1, 4 and 8 were really neutral, since the heading of Column 6 expressly stated that the words "neutral," "acid" and "alkaline" in the column below referred to the reactions with corallin, and the heading of Column 5 showed that the only ratio of ammonia to citric acid which the referee recognized as being neutral was that of 1 : 3.765.

The method given by Patten and Marti is an interesting and excellent method of preparing a neutral solution. The writer proposes the following exact and easy method of making a neutral solution of ammonium citrate which involves no analyses or distillations, but only a couple of titrations with solutions always ready in every laboratory:

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[1] Bur. of Chem., U. S. Dept. of Agr., *Bull.* **132**, 11.

[1] This Journal, **5** (1913), 568.

PROPOSED METHOD

Carefully sample the lot of citric acid on hand, by grinding a sufficient quantity to get an average sample through a coffee or other suitable mill. Mix thoroughly, and weigh 7 g. into a liter flask. Dissolve in water, and dilute to mark. Pipette out 50 cc. or 0.35 g. of the citric acid, and titrate with $N/10$ caustic soda and phenolphthalein. If the acid is pure and uneffloresced, just 50 cc. of $N/10$ alkali will be required. Weigh 1850 g. of pure uneffloresced acid or its equivalent in acid value of effloresced or impure acid into a large bottle or carboy, and cover with 7 liters of cold water. Calculate the exact number of g. of anhydrous citric acid present. Run from a burette 25 cc. of concentrated ammonia into a 500 cc. flask containing cold distilled water. Dilute to mark and mix. Carefully measure 25 cc. of this solution and titrate with $N/2$ acid and methyl orange. Calculate the volume of concentrated ammonia necessary to neutralize the citric acid in the ratio of 1 of ammonia to 3.765 of anhydrous citric acid. (If a stock of approximately 10 per cent ammonia is on hand, it is perhaps preferable to use it instead of concentrated ammonia using, of course, a correspondingly suitable volume of water for the citric acid.) Add the carefully measured ammonia solution to the citric acid in the bottle or carboy, close immediately with a tightly fitting rubber stopper, and shake till the acid is dissolved; allow to stand tightly stoppered until cold, then shake again before removing the stopper. Bring to a gravity of 1.09 at 20° C. The volume of the solution should approximate 10 liters. The accuracy of the solution may be confirmed if desired, by analysis, using either the distillation method already described in this paper, or the method of Patten and Marti,[1] or that of Eastman and Hildebrand.[2]

It was suggested by one of my associates that we attempt to prepare the pure salt, tri-ammonium citrate, and determine the ratio of ammonia to citric acid in it. As anticipated it was found impossible to prepare, by evaporation and crystallization, but by adding to a solution of ammonium citrate made distinctly alkaline with ammonia, a large excess of strong alcohol, a salt was precipitated which on standing over night became beautifully crystalline. The supernatant liquid was filtered off, and the crystals washed thoroughly on the pump with a large excess of strong alcohol; the mass which was a felt of interlaced crystals, was dried quickly by pressure between blotting pads, and a portion dissolved in water; its reaction with corallin was distinctly alkaline, and an analysis of the solution showed the ratio of ammonia to citric acid to be 1 to 3.768. The remainder of the crystals left exposed over night to the summer temperature of the laboratory had entirely changed the nature of its crystalline structure, and a portion of it, when dissolved in water and tested with corallin, was decidedly acid to that reagent and upon analysis showed a ratio of 1 to 3.94. It is evident, therefore, that the normal salt is not entirely hypothetical, that it can be actually prepared and dissolved in water, and its solution then shows an alkaline reaction to corallin and has very nearly the ratio of 1 of ammonia to 3.765 of citric acid.

There seems little reason to doubt that the neutral ammonium citrate solution which the A. O. A. C. has been prescribing since the date of its organization many years ago, and which able and conscientious chemists have ever since been earnestly trying to make exactly neutral, succeeding sometimes perhaps by accident, but usually only approximating it, was really intended to be a solution of the normal salt. This opinion was expressed by the writer in his report as Referee in the following words: "While the referee has a strong conviction that the only proper method of making the solution is by analysis and calculation of the exact quantity of ammonia and citric acid to be added to it, still he hesitates to urge it officially, as no work has yet been done by any other referee along this line, and because the referee is himself no longer an official chemist." In this opinion he has since been supported by those who have given the most earnest thought and painstaking experiment to the subject, as Patten and Marti, Eastman and Hildebrand and others.

The laboratory with which the writer is identified still makes its solution as prescribed by the A. O. A. C., approximating neutrality as closely as possible by the use of corallin, since that is still one of the legal and official methods, but the writer knows of other chemists who have already adopted the neutralization by analysis, and it is little wonder that under these conditions analyses for available phosphoric acid on tankages and bone meals, and fertilizers containing those ingredients should vary quite widely. Let us hope that the A. O. A. C. at their next meeting will conclude that the subject has been investigated long enough, and take some definite action at that meeting, or else appoint a small committee in whom they have confidence, with power to act in prescribing a method which shall be legal and official after a definite date.

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THE INFLUENCE OF FINENESS UPON THE AVAILABILITY OF BONE MEAL

By S. S. Peck

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It has been thoroughly established that the availability of raw phosphate rock or of basic slag depends primarily on its fineness of subdivision. These two purveyors of phosphoric acid and bones or bone meal comprise the three forms in which insoluble phosphoric acid is supplied in fertilizers. In the case of basic slag, the phosphoric acid exists as a tetra-calcic or a four-lime phosphate. In phosphate rock and bones the phosphoric acid is combined with three parts of lime, and is known as tri-calcic phosphate, to which the general term of bone phosphate is applied.

As superphosphate, phosphoric acid is supplied in a form soluble in water. It is termed available not because after being applied to the soil it remains permanently soluble but because it is fixed in a finely divided

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[1] This Journal, 5 (1913), 567.

[2] *Ibid.*, 6 (1914), 577.

form and well distributed. From this it can be logically concluded that the finer the state of subdivision of rock phosphate, and the more thorough its distribution in the soil, the greater will be its availability to the crop. As a matter of fact, the latter condition is directly dependent on the former, since any given quantity of material can be more evenly distributed as its state of fineness increases. The influence of fineness in increasing yields has been demonstrated by the New York Agricultural Experiment Station,[1] and the University of Wisconsin Agricultural Experiment Station[2] has shown that thoroughness of mixing has a decidedly beneficial effect on plant growth.

Truog has published tests showing that the availability of raw phosphate rock is directly influenced by the simultaneous presence of fermenting organic material, this favoring the chemical and biological processes that give rise to carbon dioxide and other agencies which attack the fine rock and ultimately give the material a finer and more uniform distribution through the soil. For this reason the experimental data from phosphate rock experiments cannot be used in arriving at conclusions relative to bone meal action, since here the solvent action is influenced directly by the decomposition of the nitrogenous part of the bone particles, with the accompanying evolution of carbon dioxide and formation of nitric nitrogen. Experimental data, however, is not wanting on this point. The Berlin Agricultural Experiment Station has found that the finer bone meal is ground the better its utilization, coarse meal having but 66 per cent of the action of fine meal, when each contained the same phosphoric acid per cent. The importance of this condition has always been recognized. A hundred or more years ago when bones first began to be used in England, they were applied either unbroken, or later in coarse fragments, at the rate of ten or twelve hundred pounds to the acre. Afterwards, when bone meal came to be manufactured, 600 or 700 pounds of the meal per acre were deemed a sufficient dose, while later 100 or 200 pounds of superphosphate (in which a state of subdivision is reached that would be impossible by grinding) were found to produce the same effect on the same soils and crops.[3]

Storer[4] says: "The fineness of the meal to which bones are ground is a very important consideration. Not so many years ago it was the custom to use crushed bones,......but there is no longer any question that fine meal is greatly to be preferred to that which is coarse. The finer the meal, so much the more readily will it putrefy and dissolve in the earth, so much the more quickly can the plants be fed by it, and so much the sooner and the more surely will the value of the crop be increased."

Voorhees[5] also states in positive terms the necessity of fineness of division of bone meal. Many of the experiment stations in the United States attach different values to the phosphoric acid and nitrogen in fine, medium, and coarse bone meal respectively, but do not in all instances agree in their definitions of these terms. In general, by fine bone meal is signified such as will pass through a sieve with circular holes one-fiftieth of an inch in diameter, and coarse such as will not. The New Jersey Agricultural Experiment Station uses values on this basis as follows: Fine bone meal—nitrogen 19 cents, phosphoric acid 4 cents per pound; coarse—nitrogen 15 cents, phosphoric acid 3.5 cents per pound.[1] The Kentucky Agricultural Experiment Station[2] defines fine bone meal as that which passes through a 25 mesh sieve, and medium as that which passes through a 6 mesh sieve, valuing the phosphoric acid from the former at 4 cents and from the latter at 3 cents per pound. Other stations, particularly that of California, no longer indicate valuations depending on the degree of fineness, since such a gradation is purely arbitrary; nevertheless, they insist on the necessity of such a condition.

There is a limit to which bone meal should be ground on three accounts: (1) When ground too fine to an impalpable powder, known as "floated bone," it is apt to be carried away by the wind when being applied; (2) in this condition it is extremely liable to putrefy, especially in moist air; and (3) there is a question whether its availability is raised for ordinary cultural purposes in a measure commensurate with its extreme fineness. In experiments with various crops, and using bone meal ranging from that passing a 60-inch sieve to that passing through bolting cloth, the New York Agricultural Experiment Station[3] found that within the limits tested, fineness seemed to have little or no influence on availability.

Attempts have been made to measure the availability of raw phosphates by their solubility in various dilute solutions of acids, organic or inorganic, but it has not been found possible to duplicate or even approximately represent conditions in the field with laboratory tests. The solvent action of the soil is being exerted on the insoluble phosphates over a long duration of time, during which a part of the dissolved material is being gradually but constantly removed by the growing crop, and also probably suffering other alterations in character not possible to determine. It may be said that at the present time, there is no chemical method of determining this point in which absolute confidence can be placed.

It has already been stated that bacterial action with its consequent evolution of carbon dioxide and development of acids increases the solubility of rock phosphate, and that this condition exists in the decomposition of bone meal in the soils. In an endeavor to measure the availability of various grades of bone meal, this station has completed a series of tests in which attempts were made to answer the question of availability, and in which the decomposition of the organic matter of the bone was presumed to have a direct relation to the relative availability of the phosphate content.

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[1] *Bulletin* **358**, Feb., 1913.

[2] *Research Bulletin* **20**, January, 1912.

[3] B. H. Hite, *Bulletin* **80**, West Virginia Experiment Station, April, 1902.

[4] "Agriculture," Vol. I.

[5] "Fertilizers," 1900, p. 73.

[1] *Bulletin* **259**, September, 1913.

[2] *Bulletin* **168**, December, 1912.

[3] *Bulletin* **358**, February, 1913.

EXPERIMENTAL WORK

For the purpose of these tests, a commercial bone meal was sifted and divided into four sizes. The sizes and analyses of each lot were as follows:

Number	State of division	Nitrogen Per cent	Phosphoric acid Per cent
1	Less than 40 mesh sieve	3.98	17.84
2	From 20 to 40 mesh sieve	4.34	22.28
3	From 12 to 20 mesh sieve	4.20	23.00
4	Greater than 12 mesh sieve	4.09	23.34

TEST NO. 1

This test was intended to measure the relative rates of ammonification of the nitrogen of the different sizes of bone meal. To Station soil representing 200 g. of dry matter placed in beakers enough of each grade was added to supply 200 mg. of nitrogen; to one lot no bone was added. The bone was thoroughly mixed, and then enough water added to bring the soil to two-thirds saturation.

The beakers and contents were weighed, and every two days during the test were again weighed and water added to replace that lost by evaporation. At stated times one series of each was analyzed for ammonia nitrogen by distilling the whole sample, thoroughly mixed and diluted with water, with recently calcined magnesia into $N/10$ acid. As the results of the fourth distillation showed a considerable drop in ammonia nitrogen, on the fifth and last test the residue from distillation was transferred to a graduated vessel, cooled, made up to the mark and filtered. In an aliquot of the filtrate, nitrate nitrogen was determined. The results are given in Table I.

TABLE I

Bone meal	Mgs. Ammonia Nitrogen				Mgs. after 18 days as		
No.	2 days	5 days	9 days	11 days	Ammonia	Nitrate	Total
Blank	0.28	0.14	0.14	0.14	0.14	2.1	2.24
1	5.46	12.88	6.72	4.20	1.8	29.32	31.12
2	1.96	4.48	2.10	2.38	3.08	13.40	16.48
3	1.40	3.92	3.92	0.98	1.12	10.8	11.92
4	1.26	2.24	2.10	0.28	1.26	13.4	14.66

Up to the fifth day, the rate of ammonia formation was greatest with the finest bone meal and least with the coarsest. On the ninth day a considerable drop in ammonia content is noticed in the lot with the finest material, which progressed until the 18th day. From the figures obtained for nitric nitrogen, this can be explained by the fact that nitrification had started in and was progressing rapidly. On the ninth day the three coarser materials showed practically the same state of ammonification. The final figures for nitrogen, ammonia and nitrate of the 18th day show that decomposition of the bone meal had taken place in the fine material to double the extent it had in the coarser; and that in the coarser materials there were but small and irregular differences.

TEST NO. 2

This test was a repetition of the previous one with the exception that the soil was kept at a moisture content equivalent to half saturation, and that nitric nitrogen as well as the ammonia was determined in each instance; except that in the first determination, only the ammonia was determined, nitrification not having in two days sufficient opportunity to make much difference, and at the last determination only the nitrates were determined. The results appear in Tables II, III, and IV.

TABLE II—AMMONIFICATION OF BONE MEAL—MGS. AMMONIA NITROGEN

No.	2	4	7	10	14	17 days
Blank	1.40	2.31	0.70	0.84	0.70	1.26
1	8.47	9.80	12.32	7.42	1.26	2.38
2	7.42	9.94	8.68	5.18	0.70	1.96
3	6.09	10.08	12.74	4.76	1.12	0.98
4	5.18	8.12	10.22	2.24	0.70	1.26

TABLE III—NITRIFICATION OF BONE MEAL—MGS. NITRATE NITROGEN

No.	4	7	10	14	17	21 days
Blank	4.20	4.20	4.62	4.62	4.20	3.08
1	3.92	4.54	9.24	20.30	17.92	24.64
2	3.22	4.76	10.64	14.70	14.98	15.40
3	3.08	2.10	7.70	9.66	15.56	14.70
4	3.08	2.24	9.94	9.94	13.30	14.40

TABLE IV—MGS. TOTAL NITROGEN AMMONIA AND NITRATE

No.	4	7	10	14	17 days
Blank	6.51	4.90	5.46	5.32	5.46
1	13.72	16.86	16.66	21.56	20.30
2	13.16	13.44	15.82	15.40	16.94
3	13.16	14.84	12.46	10.78	16.54
4	11.20	12.48	12.18	10.64	14.56

In this test, the total water-soluble nitrogen at the end of the 17-day period showed a direct relation to the size of the bone meal; this may be said to hold true for most of the tests, the few irregularities occurring being only what may be usually expected in investigations of this character. It was thought, however, that these irregularities might be explained by the fact that the nitrate nitrogen as formed was accumulating to a much larger degree than usually obtained in nature (amounting to as high as 123 parts per million of dry soil), and perhaps the results would be more regular if the nitrate nitrogen formed were removed at intervals. With this in view, a new series of tests was carried out as follows:

TEST NO. 3—LYSIMETER TESTS

For this purpose, galvanized iron containers, with facilities for collecting the drainage, were filled with station soil. The lysimeters were 2 feet in height by eight inches in diameter, the bottoms being perforated and covered with coarse sacking, above which was one inch of animal charcoal, previously digested with acid and washed. Each lysimeter was given 40 pounds of soil. The analysis of this soil by the official acid digestion was:

	Per cent		Per cent
Loss on ignition	10.28	Potash	0.29
Insoluble residue	34.39	Soda	1.56
Iron oxide	24.96	Sulfuric oxide	0.16
Alumina	19.56	Phosphoric oxide	0.68
Manganese oxide	0.15	Chlorine	0.01
Lime	2.01	Nitrogen	0.21
Magnesia	5.35		

To each test where bone was added, sufficient was given to represent an application of 100 pounds of nitrogen per acre, amounting actually to 363.5 mg. per lysimeter. In addition to the bone tests, three were carried out with blood and fine ground phosphate rock (60 mesh), alone and together, to see if the effect of the decomposing action of the blood would render more of the phosphate rock soluble, and also to observe whether the presence of the phosphate rock would make any difference in the rate of decomposition of the blood. The blood supplied contained nitrogen at the rate of 100 pounds per acre, while the phosphate rock was equivalent in its phosphoric acid content to the fine bone meal. The plan of the tests was as follows:

LYSIMETER TESTS

0.3635 g. N per lysimeter (100 lb. N per acre)

		Grams per lysimeter		Pounds per acre	
No.	MATERIAL ADDED	Material	Phosphoric acid	Material	Phosphoric acid
1	(Blank)	...	...	....	...
2	Fine bone meal	9.133	1.629	2513	448
3	No. 2 bone meal	8.375	1.866	2304	513
4	No. 3 bone meal	8.655	1.991	2381	548
5	Coarse bone meal	8.888	2.068	2445	570
6	Blood	2.878	...	792	...
7	Blood and phosphate rock	7.218	1.629	1985	448
8	Phosphate rock	4.340	1.629	1193	448

The materials were added by removing from the top of each lysimeter the surface two inches of soil, incorporating thoroughly the respective materials with half of this, replacing in the lysimeters and covering with the remainder of the soil. The bone, etc., was thus one inch below the surface and thoroughly admixed in the second inch. To each lysimeter 500 cc. of water were added, and further additions of water made when the surface of the soil was showing signs of dryness. After three weeks, and every three weeks thereafter, the lysimeters were flushed with 3 liters of water and the percolates analyzed. In the interim between irrigations small applications of water were made when the surface soil showed need of it.

In the analyses, nitrate nitrogen and lime were determined in large aliquots of the percolates, the whole drainage being measured and the results figured to milligrams removed. Portions were concentrated and set aside for phosphoric acid determinations. In all, six percolations were completed, representing a total time of 18 weeks.

In the following tables will be found the amounts of nitrate nitrogen and lime removed at each irrigation.

TABLE V—NITRATE NITROGEN REMOVED (MILLIGRAMS)

Irrigation No.	Lysimeter number 1	2	3	4	5	6	7	8
1	49.0	56.2	52.7	52.0	62.3	69.4	67.2	91.2
2	23.3	41.2	37.1	33.2	33.7	97.6	81.9	40.5
3	18.1	27.8	24.9	21.1	18.8	90.4	95.7	19.7
4	13.0	20.5	20.3	18.6	16.6	31.4	45.8	9.8
5	17.9	29.0	22.1	22.1	23.0	22.1	27.3	19.4
6	13.6	25.5	20.2	22.5	22.0	17.1	17.3	14.9
Total	134.9	200.2	177.3	169.5	176.4	328.0	335.2	195.5

TABLE VI—CALCIUM OXIDE REMOVED (MILLIGRAMS)

Irrigation No.	Lysimeter number 1	2	3	4	5	6	7	8
1	47.2	53.5	19.0	44.1	45.3	48.6	53.4	63.6
2	54.7	70.2	37.8	66.1	58.1	85.5	86.3	80.6
3	64.8	79.1	38.8	71.8	67.3	111.6	116.6	95.8
4	61.4	70.0	39.8	73.8	69.3	77.1	94.2	70.4
5	58.4	62.2	46.8	61.3	46.9	66.8	22.2	121.4
6	50.1	36.4	40.0	61.0	58.3	41.1	94.8	82.1
Total	336.6	371.4	222.2	378.1	345.2	430.7	467.5	513.9

It will be noticed that in the first irrigation, the lysimeter to which phosphate rock only was added gave the highest returns for nitrate nitrogen, and of the bone meal tests, the coarsest ranked first in this respect. It is apparent that this discrepancy is due to an unequal condition of the soil at the time of being placed in the lysimeters, which was corrected after the first irrigation. In the following tables, the total amounts of the elements removed in the last five irrigations are reported in terms of pounds per acre:

TABLE VII—POUNDS OF ELEMENTS REMOVED PER ACRE (CALCULATED ON SURFACE AREA OF LYSIMETER)

Lysimeter No.	Nitrate nitrogen Removed	Excess over check	Lime Removed	Excess over check	Phosphoric acid Removed	Excess over check
1	23.6	....	79.6	....	4.39	...
2	39.6	16.0	87.4	7.8	6.4	2.1
3	34.3	10.7	55.9	....	5.2	0.9
4	32.3	8.7	91.9	12.3	5.4	1.1
5	31.4	7.8	82.5	2.9	6.0	1.7
6	71.1	47.5	105.1	25.5	5.2	0.9
7	73.7	50.1	113.9	34.3	8.1	3.8
8	28.7	5.1	123.8	44.2	5.0	0.7

From this table it again appears that the fineness of division of bone meal is a measure of its rate of decomposition in the soil, based on the formation of nitric nitrogen from the organic matter in the bone. It was thought that the amount of lime found in the percolates might give some indication of the rate at which the lime phosphate was dissolved within the soil, but the results are too irregular to allow any interpretation. This is partly caused by the fact that, as in lysimeter 6, where no lime was added, the rapid nitrification of the blood and the consequent nitrate nitrogen produced, made for an increase in the lime withdrawn from the soil itself. At the same time, it is interesting to note that the greatest amount of lime appeared in the test to which lime phosphate as phosphate rock was added, and in which the nitric nitrogen produced was less than in any other of the tests with the exception of the check. The phosphoric acid determination showed the greatest solubility in the case of the phosphate rock and blood test, and here the lime content is second in quantity to that of the rock alone. In the bone meal, the difference in results is within the limits of experimental error, but the fine bone shows a greater solubility than the coarser. The second size of bone showed a drop below the check in lime and was less in phosphoric acid than the two coarser bones; the lime drop is significant and points to some fault in the soil or its method of packing and nature of drainage, but the nitrogen transformation was apparently not affected.

While not germane to the question, it is nevertheless of interest to compare the results of the blood and rock tests with those from the bone. Where the phosphate rock alone was employed, an increased nitrification of the soil nitrogen to the extent of 5 per cent is noted. With one exception, all the drainages from this test showed a higher nitrate content than the check. Of the nitrogen added as blood, 47.5 and 50.1 per cents were recovered in the period of 18 weeks as nitric nitrogen, while the best yield from the bone was 16 per cent. Nitrification of the blood nitrogen was accelerated by the addition of phosphate rock just as was the soil nitrogen, but to a lesser extent. More phosphoric acid was found in the test with blood alone than in the check, which points to a solvent effect exerted by the fermenting action of the blood on the soil phosphates.

TEST NO. 4

A final test was made with an attempt to measure the amount of phosphoric acid rendered soluble by bacterial action. In this test, quartz sand previously digested with acid and washed with water till free of acid was mixed with the various materials. Fresh station soil was shaken thoroughly with water, allowed to settle for twenty-four hours, and the sand tests moistened with the supernatant liquid. Two series were started, being allowed to stand three and five weeks, respectively. Five grams of the various sizes of bone meal were placed in 200 grams of sand. In two further tests, blood and phosphate rock or phosphate rock alone, were added, in amounts equivalent to the phosphoric acid and nitrogen content of the fine bone meal. At analysis, the contents of the beaker were transferred with water to a filter, and washed through paper until the runnings amounted to 300 cc. The entire filtrate was analyzed for phosphoric acid. In the case of the phosphate rock tests, the filtrate was very turbid. The results, therefore, do not express what was in solution, but represent material in so finely divided a condition that it passed through the pores of filter paper, and went into solution immediately on the addition of acid. The results were as follows:

TABLE VIII—PHOSPHORIC ACID DISSOLVED IN SAND TESTS 896.5 MG. OF PHOSPHORIC ACID APPLIED

	3 weeks	5 weeks	Total
Fine bone meal	4.0	3.4	7.4
No. 2 bone meal	2.2	3.8	6.0
No. 3 bone meal	2.6	3.7	6.3
Coarse bone meal	1.3	3.1	4.4
Phosphate rock	5.1	7.8	12.9
Phosphate rock and blood	7.5	11.1	18.6

It would appear from these tests that the phosphoric acid in fine bone meal is more available than that passing a 20 mesh sieve by 23 per cent, and almost 70 per cent more available than that passing through a 6 mesh sieve. The two intermediate sizes are about equal, and both superior to the coarsest. The phosphate rock gave, as was expected from the appearance of the filtrate, a considerably greater phosphoric acid content of the filtrate, which was augmented to an important extent by the decomposing action of the blood.

SUMMARY

The results of these tests, based on those from the fine bone meal as 100, may be seen from the following comparative tables·

TABLE IX—AMMONIFICATION IN TWO-THIRDS SATURATION

Days	2	5	9	11	18	
Bone meal Size No.	Ammonia nitrogen				Soluble nitrogen	Average
1	100	100	100	100	100	100
2	32	34	30	55	49	40
3	22	30	57	21	34	33
4	19	17	30	3	43	22

TABLE X—NITRIFICATION IN HALF SATURATION

Days	2	4	7	10	14	17	21	
Bone meal Size No.	Ammonia nitrogen	Ammonia and nitrate nitrogen					Nitrate nitrogen	Average
1	100	100	100	100	100	100	100	100
2	85	92	71	92	62	77	57	77
3	66	92	83	62	34	75	54	67
4	53	65	64	60	33	62	52	56

Table XI—Nitrification in Lysimeters

Weeks Bone meal Size No.	6	9	12	15	18	Average
1	100	100	100	100	100	100
2	77	70	93	38	55	67
3	55	31	75	38	75	54
4	58	7	48	46	71	46

Table XII—Sand Tests—Water-soluble Phosphoric Acid

1	100	3	85
2	81	4	60

CONCLUSIONS

I—The fineness of bone meal determines the rate at which its nitrogenous part will decompose in the soil to ammonia and thence to nitric nitrogen.

II—The solubility of bone phosphate is directly influenced by bacterial action, and an increased ammonia or nitrate decomposition may be held to indicate a more efficient phosphoric acid solvent action.

III—Since there is a limit to which bone meal can be ground to permit of its convenient handling, fine bone meal should possibly be defined as that which passes through a 50 mesh sieve.

IV—Since, however, it is not commercially practicable to prepare so fine a product without also including a considerable proportion of the very fine dust, a standard of fine bone meal of 65 per cent to pass a 50 mesh sieve, and at least 90 per cent of the remainder to pass a 25 mesh sieve is presented as one to which no reasonable objection can be offered by the dealers, and from which satisfactory results will accrue to the crops.

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A RAPID METHOD FOR THE DETERMINATION OF CAMPHOR AND OF CERTAIN ESSENTIAL OILS WHEN IN SOLUTION IN ALCOHOL

By W. B. D. Penniman and W. W. Randall

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As the result of series of experiments carried out in this laboratory at intervals during several years, a method has been devised for the assay of spirits of camphor and of peppermint, and of the extracts of lemon, orange, peppermint, anise and nutmeg, which appears to be more rapid and much more accurate than any method with which we are familiar. The facts which form the basis of the method may be grouped under three heads, as follows:

1—Camphor and the several oils enumerated above are completely expelled from solution in alcohol, when these solutions are mixed with from four to ten volumes of a strong solution of calcium chloride.

2—The separated camphor or oil dissolves with the greatest ease in low-boiling gasoline, an operation with which alcohol, at least in the presence of such a calcium chloride solution, does not interfere.

3—Within certain fairly wide limits, the volume of the gasoline solution formed is exactly equal to the sum of the volumes of the gasoline itself and the solid camphor (or oil) which has been dissolved.

The method here described is by no means entirely new. Schmatolla[1] noted that when camphor dissolves in light petroleum oil, the volume-relation stated in "3" obtains. He employed a burette graduated in tenths cc. as a measuring apparatus, and weighed out the camphor spirit, which was later precipitated by means of saturated sodium chloride solution. We have secured better results by the use of calcium chloride solution, and prefer graduated milk bottles and the use of the centrifuge as means of accurate measurement of small quantities. Arnost[1] used a somewhat similar method to determine camphor in celluloid, correcting for alcohol dissolved. Chittick,[2] we have found since these experiments were made, used a method similar to ours for peppermint, precipitating the oil with water and, by means of a blank, correcting for alcohol dissolved. We have not found water a satisfactory precipitant, and believe that much time can be saved without decrease in accuracy by the use of pipettes and the avoidance of weighings.

The apparatus called for consists simply of several accurate full pipettes, a Babcock centrifuge, and one or more accurately graduated Babcock milk bottles. If the divisions on the neck of the bottle be from 0 to 10, then the graduated portion will contain just 2 cc. With a magnifying glass the volume of a column of supernatant solution in the neck of the bottle can be read with accuracy, probably to 0.008, perhaps to 0.004 cc.

As the volume of gasoline used should not be much less than, nor much more than twice as great as that of the camphor or oil to be dissolved (if the volume-relation mentioned under "3" is to hold good), it is well to work with such quantities that not much over 0.5 cc. of camphor or oil is to be determined. Thus we have found that 5 cc. of the alcohol solution serves well for strengths from 5 to 15 per cent; 10 cc. is probably better for 4 per cent solutions or anything weaker. The quantity of gasoline should in general be somewhat greater than that of the oil.

METHOD OF ANALYSIS

FOR STRENGTHS BETWEEN 7 AND 15 PER CENT—Pipette 5 cc. of the solution into the Babcock bottle; fill nearly to the neck with clear calcium chloride solution of sp. gr. 1.37; shake, add *exactly* 1 cc. of gasoline (b. p. 40° to 60° C.); shake, fill with the salt solution to near the top of the graduation; stopper tightly; shake violently, and whirl in the centrifuge at high speed for about five minutes. If now the salt solution is still cloudy, shake thoroughly, and whirl again. Read the menisci as in a milk-fat determination; *i. e.*, the lowest point of the lower meniscus and the extreme edge of the upper. For example, suppose the readings are 9.32 and 1.77; the column corresponds to 7.55 (= 1.51 cc.). Of this 5.00 (= 1 cc.) is gasoline, and 2.55 (= 0.51 cc.) is oil. Then 4 × 2.55 = 10.20 = percentage of oil in the extract.

FOR STRENGTHS LESS THAN 7 PER CENT—Use 10 cc. of the solution and a quantity of gasoline not more than twice that of the oil or camphor to be set free;

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[1] *Apoth. Zeit.*, **16**, 290; *Abstr. Chem. Centr.*, **1901**, 1 (20), 1117; *J. Soc. Chem. Ind.*, **20** (1901), 756; Allen's "Commercial Organic Analysis" (new ed.), Vol. IV, p. 200.

[1] *Z. Unter. Nahr. u. Genussm.*, **12** (1906), 532; *Abstr. J. Soc. Chem. Ind.*, **25**, 1169.

[2] *Proc. Assn. Am. Dairy, Food & Drug Off.*, **1913**, p. 160; *Abstr. Chem. Abstr.*, **8** (1914), 1847.

otherwise the operation is as before. Now, however, the volume of the oil (2.55 in the example given above) must be multiplied by 2 to yield the percentage.

For strengths of 3 per cent or less, the accuracy of the method naturally is not as great as in the case of those first mentioned. To collect without loss in the neck of the Babcock bottle 0.2 cc. of oil and 0.2 to 0.4 cc. of added gasoline (as must be done in the case of a 2 per cent extract), and to read the volume of the resulting solution with accuracy, is not easy; nevertheless we have met with considerable success.

RESULTS

CAMPHOR—Using a bottle which had been calibrated with the aid of mercury, the following typical results were obtained:

Standard 10 per cent spirit of camphor—5 cc. used with 1 cc. gasoline. Readings: 8.38 and 0.87. 8.38 — 0.87 = 7.51; 7.51 — 5.00 = 2.51; 2.51 × 4 = 10.04 per cent.

Standard 5 per cent spirit—10 cc. used with 1 cc. gasoline. Readings: 8.60 and 1.09. 8.60 — 1.09 = 7.51; 7.51 — 5.00 = 2.51; 2.51 × 2 = 5.02 per cent.

Sample No. 6826—Rotation indicated 9.93 per cent. 5 cc. used and 1 cc. gasoline. Readings: 10.40 and 2.90. 10.40 — 2.90 = 7.50; 7.50 — 5.00 = 2.50; 2.50 × 4 = 10.00 per cent.

Sample No. 6828—Rotation gave no satisfactory result on account of the marked cloudiness of spirit—between 9.00 and 9.40 per cent indicated. 5 cc. used with 1 cc. gasoline. Readings: 9.00 and 1.71. 9.00 — 1.71 = 7.29; 7.29 — 5.00 = 2.29; 2.29 × 4 = 9.16 per cent.

Sample No. 6831—Rotation indicated 7.32 per cent. 5 cc. used with 1 cc. gasoline. Readings: 9.08 and 2.27. 9.08 — 2.27 = 6.81; 6.81 — 5.00 = 1.81; 1.81 × 4 = 7.24 per cent.

The angles of rotation were determined in all cases in a 200 mm. tube at 20° C. Percentages were calculated on the assumption that under such conditions a 10 per cent camphor spirit shows a rotation of 8.22°.

In order to try out the method, 68 samples were assayed, using milk bottles of all sorts, just as they happened to come from the shelf; probably forty different bottles were thus brought into use. Many of these, on close examination, were clearly seen to be quite inaccurately graduated. Assuming that the percentage strength was actually that deduced from the rotation observed, this method in the 68 assays made, showed an average error of 0.25 per cent; in each of 22 assays the error was less than 0.10 per cent. Other assays with calibrated apparatus indicated that the errors referred to were in large measure to be charged to the inaccuracy of the graduation upon the bottles.

PEPPERMINT—Six extracts of peppermint were made from as many peppermint oils, and labeled A, B, C, D, E and F. From experiments made with these extracts, it was found that the laevo-rotations of the oils varied from 21.0° to 28.9°. Assays by this method gave:

SAMPLE	Stated strengths Per cent	Cc. used		Per cent peppermint found
		Extract	Gasoline	
A	9.0	5	1.0	9.04
		5	0.5	9.00
B	10.0	5	1.0	9.92
C	10.0	5	0.5	10.00
D	15.0	5	1.0	15.04
E	12.5	5	1.0	12.48
F	10.0	5	1.0	10.04

An attempt to make an assay of "C," in which 10 cc. of extract and 1 cc. of gasoline were employed, resulted in the figure 11.10 per cent. Apparently, alcohol, when present to such an extent as this with oil of peppermint, is also taken into solution. Hence it would seem best to restrict the amount of peppermint extract used (when of about 10 per cent strength) to 5 cc.

A 3 per cent extract gave the following results:

Extract Cc.	Gasoline Cc.	Per cent found
10	0.5	3.06
10	0.5	3.00
20	1.0	1.75
15	0.5	2.92
15.0	1.0	3.33
12.5	0.5	3.23
12.5	0.5	3.36

From a study of these results it would appear that the method will give good results with weak extracts of peppermint, only when the quantity used is not over 10 cc.

Other extracts analyzed are reported below:

SAMPLE	Strength Per cent	Cc. extract	Cc. gasoline	Per cent found
Oil of lemon, A	5	10	1.0	4.92
	5	10	1.0	5.04
Oil of lemon, B	5	10	1.0	4.82 (*a*)
	5	10	1.0	4.96
Oil of orange (sweet)	5	10	1.0	4.96
	5	10	1.0	5.02
Oil of anise	3	10	1.0	2.94
	3	10	1.0	2.98 (*b*)
	3	10	1.5	2.80 (*c*)
Oil of nutmeg	2	10	0.2	1.94
	2	10	0.4	1.88

(*a*) Here a notable amount of solid precipitated insoluble in gasoline.

(*b*) Clear solution in gasoline difficult to obtain.

(*c*) Probably, as the volume-relation, oil : gasoline = 1 : 5 in this case, the limit for accurate results had been passed.

It will be noted that, in the case of the oils listed above, extracts of the standard Pharmacopoeial strengths were made as well as several of greater strength. In addition, U. S. P. extracts were prepared from oil of wintergreen (3 per cent), oil of cassia (2 per cent), and oil of cloves (2 per cent). So far, successful results have not been secured with these extracts. Oil of cassia is too insoluble in gasoline, and oil of wintergreen and oil of cloves gave low results, possibly because of the presence of phenolic compounds, for the oils were colored dark red and deep violet, respectively, when shaken with the calcium chloride solution.

SAMPLE	Strength Per cent	Cc. extract	Cc. gasoline	Per cent found
Oil of wintergreen	3	10	1.0	2.46
		10	1.0	2.68
		10	0.5	2.38
Oil of cloves	2	10	0.2	1.40
		10	0.4	1.40

In many instances in the course of the experiments here described, there was thrown out of solution, by the calcium chloride solution, a notable amount of solid particles only slowly soluble, or entirely insoluble, in gasoline. This material collected as a layer between the two solutions; by thorough shaking and whirling in the centrifuge it could be washed by the gasoline and packed into a thin, flat layer. The question naturally arises in such cases where the lower reading of the gasoline column should be made. We have in general followed the rule that, where the solid material may be regarded as an impurity in the oil—*e. g.*, the green coloring material in extract of peppermint—the gasoline column extends upward from its upper surface; where, on the other hand, the solid material is probably a normal constituent of the oil, but is not entirely soluble in gasoline, we have read from the lower surface of the solid layer.

So far as our experiments have gone, no solvent other than petroleum oil has been found which possesses the peculiar volume properties mentioned above under headings "2" and "3." In the case of cassia oil, a mixture of equal volumes of gasoline and benzene readily dissolved the oil set free, but a marked contraction of volume appeared to take place on solution. Ordinary kerosene oil will serve in many cases, but in our experience, the low-boiling oils will dissolve essential oils more readily. We have so far noted no case where the volume relations described under "3" above, failed to hold, provided a petroleum oil was employed, and solution took place readily. Other strengths of calcium chloride solution may serve as well as that employed; we have used only the one.

This work is to be continued, and experiments made with other solvents than gasoline. Any results of interest that may be obtained will be published in due time.

ADDENDUM

After the foregoing paper had been written and submitted to the editor, a suggestion was made by the Publication Committee of This Journal that we endeavor to replace the solvent originally called for (gasoline of b. p. 40° to 50° C.) by some other more readily obtained and more safely handled. A series of experiments was accordingly undertaken, under our direction, by Mr. C. O. Miller, in the hope that a less volatile oil would be found to serve as well as the low-boiling gasoline which we had used. Commercial benzine was distilled and fractions collected:

50°–60°, 60°–70°, ..., 160° to 170°

Mr. Miller, who had not, up to this time, worked with the method described in this paper, was able to check most satisfactorily our results as long as he made use of the 40° to 50° gasoline which we had employed, or of the 50° to 60° benzine fraction, which he had distilled; but as soon as he attempted to employ a benzine boiling above 60°, variations began to make their appearance; the volume relation no longer held good in all cases. As a rule too high results were obtained, and the higher the boiling point of the benzine fraction used, the greater became the error. In addition, with repeated shaking and rewhirling the percentage of essential oil indicated continued to rise, instead of coming, as in earlier experiments, quickly to a final value. It may be that continued shaking and rewhirling caused the alcohol present to dissolve more and more in the higher boiling oils.

As a result of these experiments we are apparently justified in advising the use of a gasoline boiling at or below 60° C. as applicable in the assay by this method of spirits of camphor, and of extracts of lemon, orange, peppermint, anise, and nutmeg. We have therefore changed the boiling point given in the body of this article so as to read 40° to 60° C.

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STUDY OF THE METHODS FOR EXTRACTIONS BY MEANS OF IMMISCIBLE SOLVENTS FROM THE POINT OF VIEW OF THE DISTRIBUTION COEFFICIENTS. II

By J. W. Marden and Vanna Elliott

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The use of the distribution coefficient in indicating better conditions for the extraction of certain substances from aqueous solution by means of immiscible solvents has been shown in a previous communication.[1] The present paper is a continuation of that work, studying several more of the common methods for extractions and, if better conditions are indicated, suggestions are made which, it is believed, aid in obtaining better results. Also, a further use of the distribution coefficient is suggested in which, if its value is accurately known and conditions are strictly adhered to, it is unnecessary to make successive shakings and separations, but with one extraction and a calculation from the distribution coefficient, the percentage of substance can be determined.

The value of such a study will be seen from a consideration of the large number of alkaloidal extractions that it is necessary to make in some laboratories and, also, of the great variance in directions given by different authors for the determination of the same substances. Many analysts still extract alkaloids several times and then stop to test a small portion of the non-aqueous solvent to ascertain if the material is all extracted. This is unnecessary because these substances always distribute themselves in the same way. The same number of washings that will remove a large portion of an alkaloid will remove a small portion, provided, of course, that the limits of the solubilities are not exceeded in either of the two solvents.

It has been shown that by a determination of the distribution coefficient and a subsequent algebraic calculation the number of washings can be determined for given volumes of aqueous and non-aqueous solvents which are necessary to extract 99.9 per cent of the material in question. The distribution ratio (d) is indicated by the expression

$$\frac{\text{Concentration in 10 cc. water}}{\text{Concentration in 10 cc. non-aqueous solvent}} = \frac{C_1}{C_2} = (d)$$

The algebraic expression for the calculation of the number of washings necessary for an extraction is indicated by $\frac{x_n}{x_o} = \left(\frac{da}{e + da}\right)^n$, where

a = volume of aqueous solvent,
e = volume of non-aqueous solvent,
d = distribution ratio, as given above,
x_o = original amount of material to be extracted in the water layer, and
x_n = the amount of material in the water layer after n extractions.

The expression $\frac{x_n}{x_o}$ = the fraction of material in the water layer after n extractions.

For the calculations of (d), the solubilities of chloroform and water in each other, except in the case of

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[1] This Journal, 6 (1914), 315.

strychnine, were assumed to be negligible for our purposes and the volume of each, upon saturation with the other, was taken as that originally used. For ether and water, however, where there seems to be considerable diversity of opinion and, since in the case of ether and water we are seeking an indication of better conditions rather than absolute accuracy, the solubility of ether in 100 cc. of water was assumed to be 8 cc. and of water in 100 cc. of ether to be 2 cc. at 25° C.[1] From a consideration of the work of Herz[2] and others, the volumes of these two solvents, when 100 cc. of water and 50 cc. of ether were mixed and saturated with each other, were taken as 104 cc. and 43 cc., respectively. These are perhaps more nearly the true volumes than the values previously taken (100 cc. water and 42.2 cc. ether). However, the final results are affected but little.

The materials used for determinations were of Merck's best, carefully prepared for analysis and the alcohol, ether, chloroform or other non-aqueous solvents were of U. S. P. strengths. The shakings were made in 200 cc. glass-stoppered bottles in a thermostat regulating at 25° C. to within 0.1° C. variation. The thermostat was so arranged that six bottles could be placed in a rack and turned end over end at a rate of 30–40 revolutions per minute during a time interval of 35–40 minutes. The bottles were then allowed to hang for a short time in the thermostat till the two solvents were clear; a portion of the non-aqueous solution was pipetted off and the material determined. In addition to the data as tabulated in the previous paper the volumes assumed for both aqueous and non-aqueous solvents are inserted so that the data can be more readily recalculated.

It must be admitted at the beginning of this paper that the value of (*d*) is by no means always a constant over very wide variations in concentration but in most cases with the concentrations ordinarily used in the laboratory, the results were found to be very nearly so and certainly can be used to good advantage in this work. A slide rule was thought sufficiently accurate for the calculations of this paper. Where modifications of old methods are suggested it is simply intended to indicate better conditions under which the experiments can be done.

ACONITINE

The United States Pharmacopoeia suggests the extraction of aconitine with ether from aqueous solution made alkaline with ammonia. The distribution ratio was run using 100 cc. of water, 5 cc. of NH_4OH and 50 cc. of ether with the following result:

TABLE I

Wt. aconitine	Wt. found in 25 cc. ether	Wt. in ether layer (Vol. 43 cc.)	Wt. in water layer (Vol. 109 cc.)	(*d*) Conc. 10 cc. water. / Conc. 10 cc. ether
0.0693	0.0302	0.0508	0.0185	0.143
0.1000	0.0435	0.0748	0.0252	0.142
0.1780	0.0773	0.1330	0.0450	0.134
			Average,	0.140

From this, about $^1/_7$ of the aconitine remains in the aqueous layer on one extraction, where equal volumes of the two solvents are used. When 50 cc. of aqueous liquid are washed with 10 cc. portions of ether (14 cc. for the first and 10 cc. for the subsequent washings, assuming that 4 cc. of the first ether portion saturate the aqueous layer) the value of (*d*) would be $\frac{0.140 \times 50}{0.140 \times 50 + 10} = \frac{7.0}{17.0}$ or 0.417. It takes six such washings, $\left(\frac{1}{2.4}\right)^6 = \frac{1}{191}$, to extract more than 99 per cent and eight washings for more than 99.9 per cent of the aconitine present. This would appear to be a fairly good separation but there are other non-aqueous solvents which have a greater solubility for aconitine and are less soluble in water.

From a consideration of these solubilities it was found that chloroform and benzene were better solvents than ether and it was judged that the distribution ratios between these substances and water would be more favorable than in the case of ether. It is difficult, however, to obtain benzene sufficiently free from thiophenes and other impurities which are not volatile and for this reason, attempts with commercial benzene did not meet with much success.

It is difficult to obtain good results where (*d*) is so small but the best set of results, using 100 cc. of water, 5 cc. of NH_4OH and 30 cc. of chloroform, is given here.

TABLE II

Wt. aconitine	Wt. found in 20 cc. chlor.	Acon. in chlor. layer (30 cc.)	Acon. in water layer (105 cc.)	(*d*)
0.1030	0.0644	0.0966	0.0064	0.019
0.1463	0.0932	0.1398	0.0065	0.013
0.1784	0.1113	0.1670	0.0114	0.019
			Average,	0.017

A very few washings, using even comparatively small volumes of chloroform, would almost completely extract the aconitine. Two extractions from 50 cc. of aqueous solution, containing 5 cc. (1–1) NH_4OH with 10 cc. portions of chloroform, separate out more than 99 per cent and three extractions more than 99.9 per cent of the alkaloid. It is, moreover, more convenient to use chloroform than ether because the chloroform is heavier than the aqueous solution and, hence, in our ordinary Squibb separatory funnels, can be drawn off without the use of another funnel.

To prove these conclusions on aconitine, samples were weighed out into 50 cc. of aqueous solution which contained 5 cc. (1–1) NH_4OH and the solution washed with two 10 cc. portions of chloroform.

TABLE III

Wt. aconitine	Total wt. found	Residue in chlor.	Corrected wt. acon.	Percentage found
0.1032	0.1035	0.0010	0.1025	99.3
0.1025	0.1026	0.0010	0.1016	99.1
			Calculated,	99.2

Portions of aconitine were tried in the same way using two portions of ether, 14 cc. for the first, allowing 4 cc. for the saturation of the aqueous layer, and 10 cc. for the second. In every case the separatory funnel was shaken for two minutes and several minutes time allowed for the separation of the layers. This set of results appears to be low, however, due, no doubt, to the difficulty in getting anything like a complete separation with the ether.

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[1] In the previous paper these values were assumed to be 1.2 cc. for water in ether and 7.8 cc. for ether in water.

[2] *Ber.*, **31** (1898), 2670.

TABLE IV

Wt. aconitine	Total wt. found	Residue in ether	Corrected wt. acon.	Percentage found
0.2000	0.1570	0.0005	0.1565	78.5
0.2035	0.1592	0.0005	0.1587	78.2
			Calculated,	82.6

It is suggested from the above results, then, that aconitine be extracted from 50 cc. of aqueous solution, containing 5 cc. (1–1) NH_4OH, with three 10 cc. portions of chloroform. This will give over 99.9 per cent of the aconitine present.

ATROPINE

It was found that the distribution ratio of atropine between water and chloroform was very small and that three washings from 50 cc. of aqueous solution with 10 cc. portions of chloroform were quite sufficient for all practical purposes.

CITRAL IN LEMON OIL

A practical application of the distribution ratio has been made in the determination of (*d*) between lemon oil and 45 per cent alcohol. In the preparation of "Terpeneless" lemon extract, lemon oil is treated with 45 per cent alcohol, the alcohol being supposed to dissolve out all the citral which is considered the active constituent of this kind of lemon flavoring. Varying volumes of lemon oil and 45 per cent alcohol were shaken in 200 cc. bottles, the percentage of citral in the oil being determined before and after the experiment. The pure lemon oil showed, by analysis, 3.61 per cent of citral. The alcohol was carefully made up and checked at 15.6° C. to be 45 per cent.

TABLE V

Cc. alcohol	Cc. oil	G. citral in oil used	G. citral found in oil	G. citral in alcohol	(d) $\frac{\text{Wt. in 10 cc. alcohol}}{\text{Wt. in 10 cc. oil}}$
100	50	1.80	1.58	0.22	0.070
150	30	1.08	0.825	0.255	0.062
100	100	3.61	3.34	0.27	0.081
				Average,	0.07 or $^1/_{14}$

With equal volumes of the oil and 45 per cent alcohol [although (*d*) is not a constant] one part of citral goes into the alcohol and thirteen parts remain in the oil. From this it is apparent that it would be difficult for the manufacturers to get all of the citral. It is well known that it is better to wash precipitates on the filters repeatedly with small portions of wash water than once with a large portion and this principle is equally true of extractions of this kind. If one volume of lemon oil were shaken out with eighteen volumes of 45 per cent alcohol, about 60 per cent of the citral would be obtained, while, if six portions using three volumes for each washing were employed, about 75 per cent of the citral would be extracted.

The distribution ratio for lemon oil and 50 per cent alcohol was also run to see if the concentration of the alcohol greatly affected the results. In this case (*d*) was found to be about 0.2 or $^1/_5$. If one volume of oil is extracted with 18 volumes of 50 per cent alcohol, about 90 per cent of the citral will be extracted. It is better, then, and more economical, to use 50 per cent alcohol for the extraction and to dilute to the proper strength of alcohol later.

COCAINE

The distribution ratio of cocaine alkaloid between ether and water was found to be very small, in the neighborhood of 0.01. If 50 cc. of aqueous solution, made alkaline with NH_4OH, are shaken out with 10 cc. portions of ether, three washings extract more than 99.9 per cent of the cocaine alkaloid. It was found that the concentration of NH_4OH does not affect this ratio greatly.

CODEINE

The distribution ratio of codeine between 100 cc. of water, 5 cc. of NH_4OH and 50 cc. of ether was run with the following result:

TABLE VI

Wt. codeine	Cod. in 25 cc. ether layer	Cod. in ether layer (43 cc.)	Cod. in water layer (109 cc.)	(*d*)
0.0688	0.0118	0.0203	0.0485	0.943
0.1258	0.0215	0.0370	0.0888	0.947
0.2086	0.0362	0.0622	0.1464	0.928
			Average,	0.939 = $^1/_{1.06}$

This means that when using equal volumes of water and ether under the above conditions, about as much of the codeine remains in the aqueous layer as goes into the ether layer. Extractions from aqueous solution with ether are impracticable. From a study of the solubilities it would seem that ether should extract the codeine better than it does but with ether it is difficult to prophesy what the value of (*d*) should approximate. The aqueous layer containing several per cent of ether makes a much better solvent for codeine than pure water and nearly as good as ether saturated with water.

Between 100 cc. of water, 5 cc. of NH_4OH and 30 cc. of chloroform, the results with codeine were as given in Table VII.

TABLE VII

Wt. codeine	Cod. in 20 cc. chlor.	Cod. in chlor. layer (30 cc.)	Cod. in water layer (105 cc.)	(*d*)
0.0738	0.0480	0.0720	0.0018	0.0071
0.1060	0.0691	0.1037	0.0023	0.0063
0.1729	0.1126	0.1689	0.0040	0.0068
			Average,	0.0067

Three washings, using 10 cc. of chloroform for each extraction, would remove the codeine as completely as could be desired in the analytical laboratory.

These conclusions were tried by analysis. Fifty cc. of the aqueous solution were washed three times with 10 cc. portions of chloroform:

TABLE VIII

Wt. cod. used	Total residue	Residue of chlor.	Corrected wt. cod.	Percentage found
0.2007	0.2011	0.0010	0.2001	99.7
0.2001	0.2019	0.0010	0.2009	100.3
			Calculated,	99.9

Using ether instead of chloroform:

TABLE IX

Wt. codeine	Total residue	Residue of ether	Corrected wt. cod.	Percentage found
0.1997	0.1055	0.0010	0.1045	52.4
0.2000	0.1080	0.0010	0.1070	53.5
			Calculated,	45.0

The agreement in the case of ether is not so good but the results show how much better chloroform is for this work than the ether and from these experiments a satisfactory method for the extraction of codeine would be as follows: Dissolve the codeine substance in dilute acid, make up to about 45 cc., neutralize and add 5 cc. of strong NH_4OH. Extract with three 10 cc. portions of chloroform, shaking two minutes at each extraction and allowing the separatory funnels to stand after each shaking so that the two layers of liquid separate as completely as possible. This method gives 99.9 per cent of the codeine present.

CONIINE

Trials were made with coniine to find its distribution ratio. They did not meet with much success, however, due to the failure to obtain results which checked well. Coniine alkaloid is so volatile that when 0.14 g. of this substance was exposed to the laboratory air at the ordinary temperature where there was a slight draft, it lost 93 per cent of its weight in one hour. Even when the alkaloid was changed to the hydrochloride salt consistent results were not obtained. The value of (*d*) was about 0.05, so that three to five washings with 10 cc. portions of ether would be sufficient to remove from 99 to 99.9 per cent of the coniine from 50 cc. of aqueous solution, made alkaline with NH_4OH.

MORPHINE

Morphine and its salts present much difficulty when an attempt is made to extract them from aqueous solution because of their insolubility in most non-aqueous solvents. Chemical literature seems to give no solvents which are immiscible with water that serve very satisfactorily for this extraction. Perhaps the best extraction is with a chloroform and ethyl alcohol mixture from a saturated salt solution but with such a method not much over $^1/_{10}$ g. could be extracted, even after six or seven washings, using only a moderate amount of non-aqueous solvent for each extraction.

Schaeffer[1] has shown recently that morphine can be extracted from aqueous solution by means of a mixture of fusel oil and chloroform. The fusel oil must be especially distilled and dried before use. Schaeffer has also shown that commercial methyl alcohol (Columbian Spirits) dissolves morphine in the ratio 1 : 15, and a mixture of equal volumes of methyl alcohol and chloroform nearly as well. When a 1 : 1 methyl alcohol-chloroform mixture is shaken with water, however, practically all of the methyl alcohol dissolves in the water, so that this mixture could not be used to extract morphine directly from aqueous solution.

There have been many other ways suggested for the estimation of morphine, mostly for crystallizing the morphine in ether and subsequent weighing or titration. This method and its difficulties for the extraction of this alkaloid are well known. The very great number of modifications of this method and suggestions for new ones indicate that there is a feeling of need for a method which will extract large and small amounts of morphine with equal ease and accuracy and that any information which would help to solve the problem would be welcome to chemists who have morphine to determine.

It is well known that various inorganic salts precipitate the higher alcohols from aqueous solution. According to Linebarger[1] and Frankforter and Frary,[2] potassium carbonate is the only substance which is capable of salting out methyl alcohol, while many salts have been found by various investigators which will salt ethyl alcohol.

The distribution coefficient of morphine was determined between water, nearly saturated with K_2CO_3, and methyl alcohol, also with a 1 : 1 mixture of methyl alcohol and chloroform. It was found with methyl alcohol alone and water that considerable amounts of K_2CO_3 went through into the methyl alcohol and the ability of this liquid to dissolve morphine (as has been noted by Schaeffer) is very much diminished by even small amounts of water. An equal volume mixture of chloroform and methyl alcohol was next tried. Very little water and K_2CO_3 dissolved in the mixture. It was found, however, that morphine, under such conditions, did not go into the non-aqueous layer as pure morphine but as a definite mixture of K_2CO_3 and morphine, which gave by titration just twice the normal value of morphine. Chastaing[3] has prepared a compound of morphine corresponding to the formula $(M)_2K_2CO_3.2H_2O$. When the substance above was extracted and dried, a creamy, amorphous solid was obtained which, on standing exposed to the air, changed to a white crystalline condition. Under the microscope at least three distinct crystals were identified, two forms of morphine and one of K_2CO_3. This indicates that the substance is a physical mixture in the solid condition but in all probability a chemical compound in solution. Analysis showed that the composition corresponded very nearly to the formula $(M)_2K_2CO_3.2H_2O$. This substance could be titrated very readily but in extraction it would be exceedingly difficult to remove the non-aqueous layer without getting small amounts of the aqueous liquid, which, being a concentrated solution of K_2CO_3, would vitiate the results.

For this reason, in determining the value of (*d*), the non-aqueous liquid could not be evaporated and the morphine titrated directly. A portion of the non-aqueous liquid was pipetted off into a small beaker, the chloroform evaporated gently on the hot plate, 25 cc. of water and enough methyl alcohol added to keep the morphine in solution, 5 cc. of a 5 per cent solution of $BaCl_2$ added and the precipitated $BaCO_3$ allowed to stand and settle. The precipitate was then filtered off and washed four times with 2 cc. portions of the methyl alcohol-chloroform mixture. The filtrate was again evaporated gently on the hot plate until most of the methyl alcohol was removed. This step is necessary, for too large amounts of methyl alcohol interfere with the end point of the titrations. An excess of standard acid was then added and the titrations made in the usual way, using methyl red as an indicator. The volume of each layer was determined in order to make the subsequent calculations of the distribution coefficient. By observing in a narrow cylinder, accurate to 0.1 cc., it was found that when

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[1] *Am. Jour. Pharm.*, **85**, 439.

[1] Linebarger, *Am. Chem. Jour.*, **14** (1892), 380.

[2] Frankforter and Frary, "Studies in Chemistry," Vol. I, Univ. of Minnesota.

[3] Chastaing, *Jahr. die Forsch. der Chem.*, **1881**, p. 928.

20 g. of K_2CO_3 were dissolved in 25 cc. of water and this liquid mixed with 25 cc. of the methyl alcohol-chloroform mixture, there resulted 32.0 cc. of aqueous liquid and 23.0 cc. of non-aqueous liquid.

The following results were obtained by this method, using 50 cc. of water, 40 g. of K_2CO_3 and 50 cc. of the chloroform-methyl alcohol mixture.

TABLE X

Wt. morphine used	Wt. found in 25 cc. non-aq. layer	Mor. in non-aq. layer (46 cc.)	Mor. in water layer (64 cc.)	(*d*)
0.0660	0.0302	0.0556	0.0104	0.134
0.1205	0.0512	0.0942	0.0263	0.200
0.1943	0.0898	0.1652	0.0291	0.127
			Average,	0.154

Although these results are in the same order of magnitude, they are not very constant. The difficulty seemed to be that when the $BaCO_3$ was precipitated a little of the morphine was carried down and not easily washed out. Titrations were tried without the use of $BaCl_2$ to get a titration twice the value of the morphine but no more constant results were obtained in this way, although they had about the same average value of (*d*). If the average value reached above, 0.154 or $^1/_{6.5}$, is taken for (*d*) and 50 cc. of aqueous solution shaken out with 20 cc. portions of the 1 : 1 chloroform-methyl alcohol mixture, it would take four washings to remove 99 per cent of the morphine present.

This method, therefore, suggests a possibility that morphine can be determined in this way and that fairly large amounts could be extracted. The above results are recorded for the purpose of indicating a heretofore untried field, that is, the extraction of substances by means of the alcohols which can be nearly quantitatively salted out from aqueous solution. It is unfortunate that in the case of morphine, methyl alcohol can be salted out with only K_2CO_3, which salt must be completely removed before the morphine can be determined. If a suitable neutral salt could be found for this purpose, no doubt more satisfactory results could be reached.

Trials were made for the distribution ratio between 100 cc. of water, nearly saturated with 35 g. of NaCl, and 45 cc. of a 2 : 1 mixture of chloroform and ethyl alcohol. Table XI shows the results:

TABLE XI

Wt. morphine used	Wt. in 20 cc. non-aq. liquid	Wt. in non-aq. layer (40 cc.)	Wt. in water layer (100 cc.)	(*d*)
0.0358	0.0085	0.0160	0.0198	0.495
0.0552	0.0111	0.0222	0.0330	0.595
0.0736	0.0175	0.0350	0.0386	0.441
0.0972	0.0194	0.0388	0.0584	0.602
			Average,	0.528 or about $^1/_2$

Closely checking results were not obtained here either, the variance probably being due to slight differences in weight of the sodium chloride. If (*d*) is equal to $^1/_2$, it would take at least seven washings to extract 99 per cent of the total amount of morphine present, using 50 cc. of aqueous solution and 25 cc. portions of the ethyl alcohol-chloroform mixture after the aqueous solution is saturated. This would make a total volume of 175 cc. of non-aqueous solvent and it would, therefore, be a tedious task to extract morphine in this way.

Since the solubility of morphine is somewhat higher in ethyl alcohol than in chloroform, a 1 : 1 mixture of chloroform and ethyl alcohol was tried, using 33 g. of NaCl, 0.5 cc. of NH_4OH, 100 cc. of water and 50 cc. of the non-aqueous solvent. The results indicated that the mixture previously used (about 1 : 3) worked better, for, as the alcohol content was increased, the tendency of the NaCl to come through with the morphine increased and this in turn caused much trouble.

The value of (*d*) was also determined for morphine between water and a 3 : 1 mixture of chloroform and amyl alcohol. The solubility of morphine is more favorable in amyl alcohol but this alcohol boils at such a high temperature that it is hard to remove by evaporation. For this reason, although numerous trials were made, only this one is given here as being the most favorable. One hundred cc. of water, 0.5 cc. of NH_4OH, 30 cc. of chloroform-amyl alcohol mixture and morphine hydrochloride were used. Since there were no other substances used in the solutions, 20 cc. of the non-aqueous liquid were pipetted off, evaporated and the residue weighed as morphine.

TABLE XII

Wt. (M)HCl	Wt. morphine	Wt. in 20 cc. non-aq. layer	Wt. in non-aq. layer (30 cc.)	Wt. in water layer (100 cc.)	(*d*)
0.0600	0.0455	0.0140	0.0210	0.0245	0.350
0.0787	0.0598	0.0192	0.0288	0.0310	0.324
0.0993	0.0753	0.0225	0.0338	0.0415	0.367
0.1198	0.0910	0.0284	0.0426	0.0484	0.341
				Average,	0.345

If the average value of (*d*) is taken as 0.34, it would take three washings of 20 cc. each of the above mixture to remove 90 per cent of the morphine from 50 cc. of aqueous solution or six washings to remove 99 per cent. This would, of course, be extremely tedious and too long for the analytical chemist.

From a consideration of the formula $\frac{x_n}{x_o} = \left(\frac{da}{e+da}\right)^n$, it is to be seen that, if the value of (*d*) is accurately known, it is possible to take only the material from the first extraction for a determination. If (*d*) is known, and from that, the value of $\frac{x_1}{x_0}$ calculated,[1] using the desired volumes of the two solvents, and then the amount of material in the non-aqueous liquid in the first extraction estimated, this should equal $\left(1 - \frac{x_1}{x_0}\right)$ of the total material present. Consequently, if the amount found is represented by (W), the total weight of material will equal $\frac{W}{\left(1 - \frac{x_1}{x_0}\right)}$.

The distribution coefficient, therefore, opens the way to determine, with much less labor, substances which take continued extractions. It might be said, however, that when such determinations are made, the value of (*d*) should be determined with that set of reagents and somewhere near the same conditions. If results were desired within 1 per cent of the true value, about as accurate as most of our extraction

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[1] $\left(\frac{x_1}{x_0}\right)$ = the fraction of material in the aqueous liquid after one extraction.

determinations, this should be of considerable advantage in the commercial laboratory where many such extractions are made.

The conclusions drawn in the preceding paragraph were tested in the estimation of acetanilid and saccharin and later, morphine. The mixtures were made in 150 cc. glass-stoppered bottles and the bottles shaken by hand for ten minutes, the laboratory temperature being kept as nearly 25° C. as convenient. Portions were pipetted off and the materials determined. This checking was not done in a thermostat because the average analytical laboratory does not have a constant-temperature bath. The determinations of acetanilid and saccharin are based upon the values of (*d*) as found in the previous paper on this subject. When acetanilid was shaken with 30 cc. of chloroform and 50 cc. of water, containing 5 cc. (1–1) NH_4OH, 82.3 per cent of the material should go into the chloroform:

TABLE XIII

Wt. acetanilid	Wt. in 20 cc. chlor.	(3) Wt. chlor. layer (30 cc.)	$\frac{(3) \times 100}{82.3}$	Percentage found
0.2017	0.1122	0.1683	0.2044	100.5
0.2013	0.1119	0.1678	0.2019	100.4

When 30 cc. of amyl acetate were shaken up with 50 cc. of water containing saccharin and $2^1/_2$ cc. of concentrated HCl, 95 per cent of the saccharin should go into the non-aqueous layer:

TABLE XIV

Wt. saccharin	Wt. in 20 cc. am. acet.	(3) Wt. in am. acet. layer (30 cc.)	$\frac{(3) \times 100}{95.0}$	Percentage found
0.1990	0.1279	0.1920	0.2021	101.5
0.2000	0.1290	0.1935	0.2038	101.8

It might be observed that the results here vary with the amount of concentrated HCl used, so that they are good considering the many errors involved.

Weights of morphine hydrochloride were shaken out, using 50 cc. of water, 0.5 cc. of NH_4OH and 30 cc. of the chloroform-amyl alcohol mixture. Under these conditions we should get 63.8 per cent of the morphine in the non-aqueous layer. Although difficulty was experienced in removing the amyl alcohol by evaporation without loss of morphine, the results give an idea of how well the method could be worked.

TABLE XV

Wt. (M)HCl	Wt. morphine	Wt. in 20 cc. "mixture"	(4) Wt. in non-aq. layer	$\frac{(4) \times 100}{63.8}$	Percentage found
0.0775	0.0588	0.0250	0.0375	0.0588	100.0
0.0828	0.0628	0.0264	0.0396	0.0621	98.9

PICRIC ACID

The solubility of picric acid between water and several immiscible solvents, chloroform, toluene, amyl acetate, etc., is given by Seidel[1] but there are no data given, nor was there any obtained in this investigation, which shows, upon calculation, a value of (*d*) sufficiently small to make a possible quantitative extraction from aqueous solution. It is, moreover, of interest to know that the expression $\frac{C_1}{C_2} = d$ does not hold, nor can the expression $\frac{C_1}{\sqrt{C_2}} = d$ be applied more than approximately. It is only with the expression $\frac{{}_nC_1}{\sqrt{C_2}} = d$, where (*n*) equals 1.65 to 1.95, depending upon the organic liquid used as the immiscible solvent with water, that (*d*) is equal to a constant.

QUININE

Between water, made alkaline with NH_4OH, and chloroform, the distribution coefficient of quinine was found to be very small so that three washings from 50 cc. of aqueous solution with 10 cc. portions of chloroform would nearly completely remove the quinine.

STRYCHNINE

There is much variance of opinion as to the best method for the extraction of strychnine from aqueous solution. Some authors prefer to use chloroform while others use a mixture of ether and chloroform. The United States Pharmacopoeia gives the solubility of strychnine in chloroform as 1–6 and in ether as 1–5500. At first thought it would seem that the value of (*d*) would be very much smaller when a 3 : 1 mixture of ether and chloroform was used for the extraction instead of chloroform. But in the case of a mixture like ether and chloroform, the ether acts more as a medium and a diluent for the chloroform rather than as a hindrance to the strychnine when dissolving in the non-aqueous layer.

The distribution ratio, using 100 cc. of water, 2 cc. of NH_4OH and 30 cc. of chloroform, is given below. Dried strychnine sulfate was used for these trials.

TABLE XVI

Wt. dry strychnine sulfate	Wt. strych.	Wt. found in 20 cc. chlor.	Wt. in chlor. layer (29.5 cc.)	Wt. in water layer (100.5 cc.)	(*d*)
0.0570	0.0498	0.0336	0.0495	0.0003	0.002
0.0949	0.0828	0.0556	0.0820	0.0008	0.003
0.1621	0.1417	0.0956	0.1410	0.0017	0.003
				Average,	0.003

In this case, where (*d*) is so small, the solubility of chloroform in water and *vice versa* was taken into consideration. The solubility of chloroform in water is about 0.5 cc. per 100 cc. of water and, hence, the volume of chloroform at equilibrium was assumed to be 29.5 cc. and of water, 100.5 cc.

The results show that (*d*) is very low and that two washings with 10 cc. portions of chloroform would extract 99.9 per cent of the strychnine, provided, of course, that none of the material was lost around the stoppers of the separatory funnels, etc.

With 100 cc. of water, 2 cc. of NH_4OH and 30 cc. of the 1 : 3 chloroform-ether mixture, the value of (*d*) is somewhat larger.

TABLE XVII

Wt. dry strychnine sulfate	Wt. strych.	Wt. found in 10 cc. non-aq. liquid	Wt. in non-aq. layer (22 cc.)	Wt. in water layer (106 cc.)	(*d*)
0.0503	0.0440	0.0140	0.0308	0.0132	0.089
0.0587	0.0513	0.0163	0.0359	0.0154	0.089
0.1717	0.1023	0.0330	0.0726	0.0297	0.084
				Average,	0.087

One washing, using 10 cc. of the mixture and 50 cc. of aqueous liquid, would extract 66 per cent of the total amount and two washings 90 per cent. It takes four such washings to extract 99 per cent of the strychnine present.

Trials were made to prove these conclusions. Ex-

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[1] "The Solubility of Inorganic and Organic Substances," D. Van Nostrand Co.

tractions were made with two 10 cc. portions of chloroform from 50 cc. of aqueous solution, made alkaline with 0.5 cc. of NH_4OH:

TABLE XVIII

Wt. strychnine used	Total wt. found	Corr. for residue in chlor.	Corrected wt.	Percentage found
0.1594	0.1623	0.0015	0.1608	100.8
0.1594	0.1622	0.0015	0.1607	100.8
			Calculated,	100.0

Using 50 cc. of water, 0.5 cc. of NH_4OH, one 10 cc. portion of the 3 : 1 ether-chloroform mixture and 4 cc. of ether (allowed for saturating the water) for the first extraction and 10 cc. of the mixture for the second extraction, the following results were reached:

TABLE XIX

Wt. strychnine used	Total wt. found	Corr. for residue in ether-chlor.	Corrected wt.	Percentage found
0.0638	0.0582	0.0010	0.0572	89.7
0.0626	0.0570	0.0010	0.0560	89.5
			Calculated,	90.8

We must conclude, then, that chloroform alone is to be preferred in this extraction. It is possible that some authors may have other reasons for using the mixture.

CONCLUSIONS

I—The distribution coefficients of a number of substances have been studied with a view to finding the best set of conditions under which to make extractions.

II—It has been shown that chloroform serves to extract aconitine and codeine from aqueous solution better than ether. Chloroform extracts strychnine better than mixtures of chloroform and ether, as suggested by many authors, while ether serves very satisfactorily for the extraction of cocaine alkaloid.

III—The distribution of citral between lemon oil and 45 per cent and 50 per cent alcohol has been discussed from this point of view.

IV—A study of the extraction methods for morphine has been made and none has been found to be short and accurate for the analytical chemist.

V—Under morphine, a use of the distribution ratio has been suggested to avoid laborious and continued extractions.

SOUTH DAKOTA FOOD AND DRUG DEPARTMENT
VERMILION, SOUTH DAKOTA

LABORATORY AND PLANT

THE EXPLOSIBILITY OF GRAIN DUSTS[1]

By HAROLD H. BROWN

Received October 8, 1914

As a result of a number of explosions in grain mills and industrial plants in this country and in Europe, and more especially as a result of an explosion in a feed-grinding plant at Buffalo, New York, in June, 1913, by which thirty-three men lost their lives and upwards of seventy were injured, a coöperative movement between milling interests generally and the Bureau of Mines was arranged for the purpose of making a scientific study of the explosibility of grain dusts, and of methods pertaining to the prevention of such explosions. The milling interests were represented in the conduct of the work by Messrs. Lawrence E. Harmon, President of Buffalo Cereal Company; Frank F. Henry, Manager Washburn-Crosby Company; and George P. Urban, Secretary George Urban Milling Company, all of Buffalo, New York.

This work was started August 1, 1913, being placed under the direction of Prof. George A. Hulett, Chief Chemist of the Bureau of Mines. David J. Price was assigned to the field-engineering work, and on February 1, 1914, Dr. H. H. Brown began a laboratory study of the problem.

During the preliminary study thirteen explosions were investigated which have occurred since 1905. Three of these took place in Iowa, three in New York, two in Illinois, and one in Vermont, Indiana, Kansas, Ohio and Texas. These explosions were classified among the various lines of milling as follows: Cereal mills, 4; elevators, 3; feed mills, 2; starch factories, 2; glucose factory, 1; flour mill, 1. It is reported that, as a result of these explosions, at least 78 men were killed and 119 injured. The total damage to property exceeded $2,000,000.

Since 1911 four explosions have occurred in Europe, two in dextrine works, one in a provender mill, grinding peas, beans, and wheat, and one in a linseed mill. As a result 47 men were killed and 119 injured.

In order to make a laboratory study of the problem, samples of the following dusts were collected, and the conditions under which they were produced were studied:

1—Dusts produced during the process of elevating and handling grain, and known as elevator dusts
2—Wheat-flour dusts from rolls, bolters, purifiers, conveyors, packing machines, etc.
3—Wheat-flour dusts from beams, rafters, elevator heads, etc.
4—Dusts produced during the cleaning of oats
5—Dust from grinding white corn
6—Dust from grinding yellow corn
7—Dust from grinding oat hulls
8—Oatmeal dust from packing machines
9—Floor dusts from elevator sweeping
10—Oat-groat dusts after aspirator

These dusts were first analyzed in the United States Food and Drug Laboratory, Chicago. Determination of moisture, ether extract, proteins, crude fiber, ash, and nitrogen-free extract or carbohydrates, were made, to ascertain, not only the chemical nature of the materials, but also wherein they might differ from the grains from which they originated.

Experiments were then started in the Bureau of Mines, Pittsburgh, to determine the ignition-temperature of these dusts, using the method of Wheeler.[1] This consisted in forcing the dust in a cloud through a

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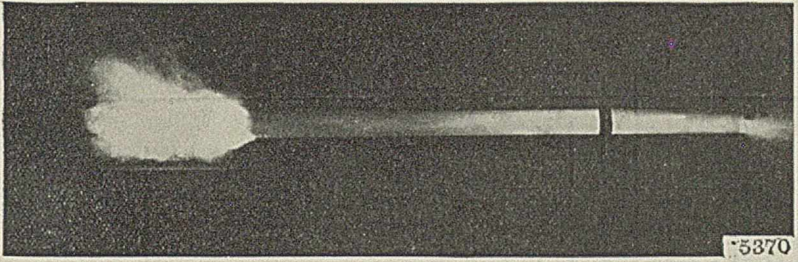
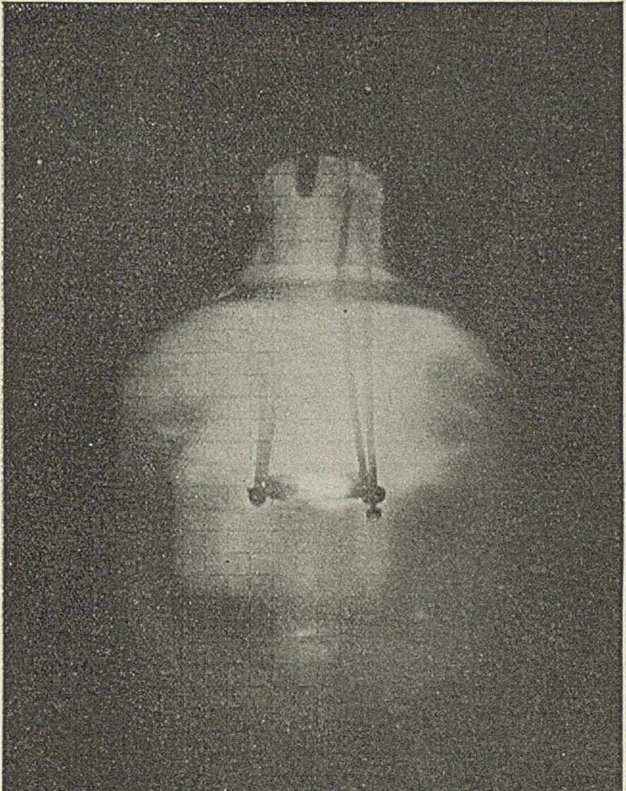
[1] Abstract of a Preliminary Report by David J. Price and Harold H. Brown, published by the Millers' Committee of Buffalo, N. Y.

[1] "Report on the Inflammability and Capacity for Transmitting Explosions of Carbonaceous Dust, Liable To Be Generated on Premises, under the Factory and Workshop Acts," 1913. R. V. Wheeler.

glass tube, 3 inches in diameter and 55 inches long, against a heated platinum coil, which was 15.75 inches from one end of the tube. The temperature of the coil was obtained by a Pt-PtRh thermocouple, having its hot junction within the quartz tube upon which the coil was wound. Using this method, Wheeler determined the ignition-temperature—temperature of propagation—of many dusts, obtaining results varying from 805° C. for sugar, 960–1035° for starch, 990° for oat husks, 995° for grain (flour-mill), to 1060° for flour and 1100° C. for castor-oil meal. The results obtained upon grain dusts by the author varied from 995° C. for oat and corn elevator dusts, 1015° for feed dust from dust collector, 1020° for ground oat hulls, 1025° for yellow-corn dust, to 1115° for wheat elevator dust and 1235°–1270° for flour dusts. Wheeler worked with samples which had been dried at 107° C.; the author used the samples as received from the mill.



Explosion in Wheeler's Apparatus—No. 61, Yellow Corn—1150° C. (2102° F.)
Dust from First Break in Dry Milling, as Received



Explosion in Bureau of Mines Inflammability Apparatus
No. 35, Wheat—Pressure, 11.6 Pounds
Dust from Sidewalls of Elevator, Dried

While this work gave the relative ignition-temperatures it did not give the lowest temperature of ignition or the relative inflammability. This latter was determined by means of an apparatus developed in the Bureau of Mines. It consists of an explosion flask of about 1400 cc. (85.36 cubic inches) capacity having two tubulures, a platinum coil, a device for driving a dust cloud against the coil, and a Crosby pressure-gauge for measuring the pressure developed. In each determination 50 mg. (0.00176 oz.) of the dust are forced in a cloud against the coil, which has been previously heated to a known temperature determined by a thermocouple. The temperature is that inside the coil and, therefore, higher than the actual temperature on the outside of the coil. The dust is ignited by the heated coil and a pressure developed within the flask, which is registered by the gauge. The relative inflammability at any temperature is measured by the difference in the pressures developed within the flask.

Determinations were made of pressures developed by the different dusts, as received and dried at 105° C., when they were forced against the coil heated to 1200°, 1100°, 1000° and 900° C. As no standard has been taken for carbonaceous dusts, other than coal dust, Pittsburgh standard coal dust, which is very constant in its properties, and which is used as a standard in the Bureau of Mines, was taken as a standard and all determinations run against it and checked against the average value obtained for it at each temperature.

Tables and curves are given which indicate that most, if not all, the grain dusts are more inflammable than Pittsburgh standard coal dust, higher pressures being developed in most cases, and especially so at the lower temperatures. The results also seem to indicate that the dusts from oats and yellow corn are more inflammable than those from wheat or other grain. However, the results are only very preliminary and it is possible that later work will change this supposition, and probably will change the curves, extending them to still lower temperatures.

It is interesting to note the difference in the inflammability of the dried and undried dusts. In nearly every case the pressure developed was appreciably increased after drying. Three are especially noticeable. These gave 0.5 pound pressure or less at 1200° when undried and over 8.0 pounds when dried, Pittsburgh standard coal dust giving 9.0 pounds at the same temperature. This is an indication of what may be expected when the humidity of the air is decreased.

Experiments carried out by the Bureau of Mines[1] have shown that an explosion could be produced when there was only 0.032 ounce of coal dust suspended in each cubic foot of air, or one pound in 500 cubic feet of air. In the experiments of M. J. Taffanel, at the Lievin Experiment Station in France, in one instance as low a weight as 0.023 ounce of coal dust per cubic foot of space was sufficient to produce an

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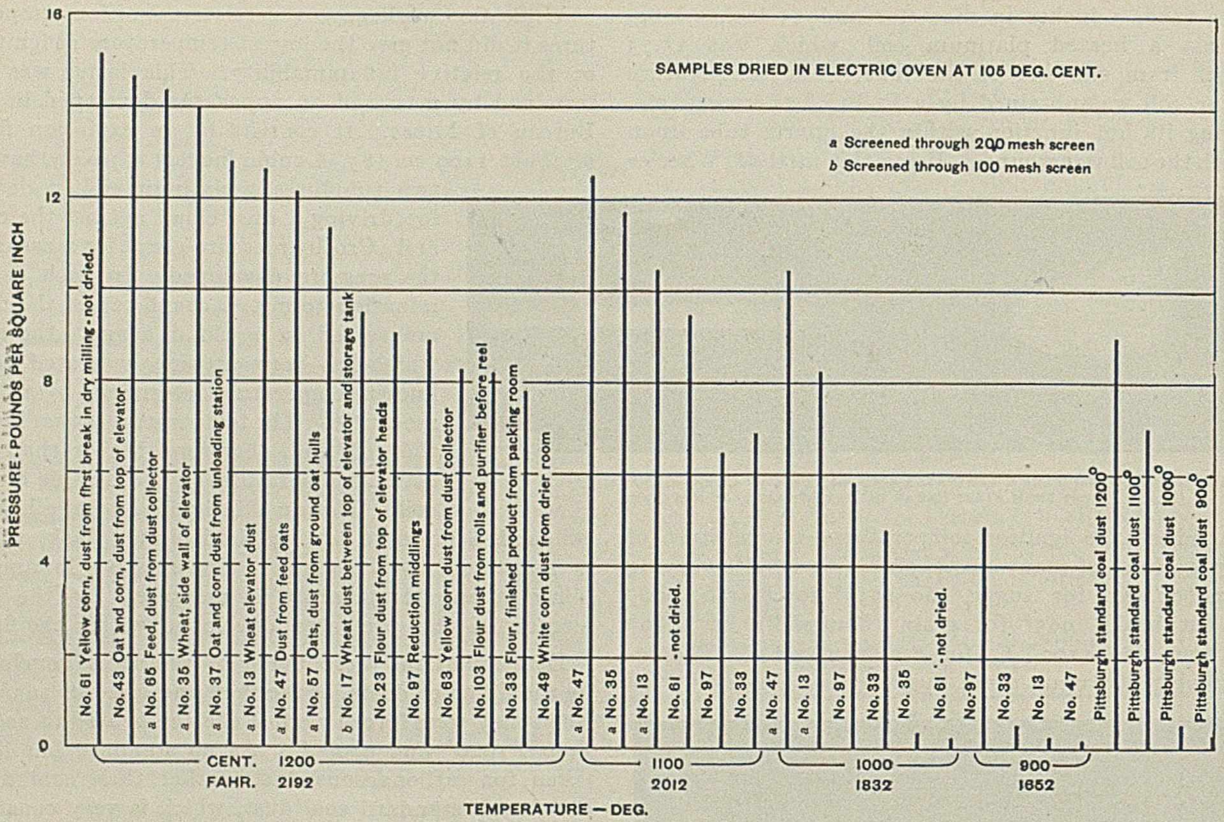
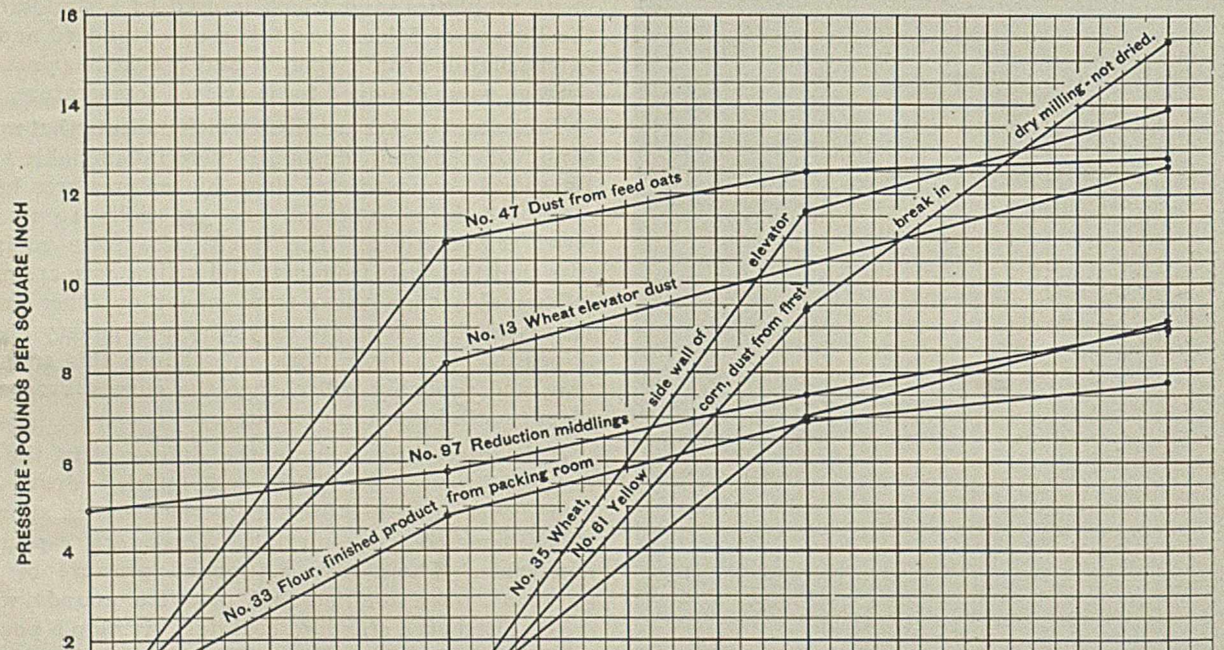
[1] "The Explosibility of Coal Dust," *Bull.* **20**, Bureau of Mines, p. 102.





ignition. Since preliminary experiments already conducted indicate that many of the grain dusts have relatively a lower ignition-temperature than many kinds of coal dust and are relatively more inflammable, it may be possible that an ignition of dust of this nature might be produced with a smaller proportion per cubic foot than is necessary for coal dust.

During the investigations it has developed that the following causes have been assigned to many of the explosions in milling plants in this country and abroad:

1—Use of open lights, or naked flames, such as lamps, torches, gas jets, lanterns, candles, matches, etc.

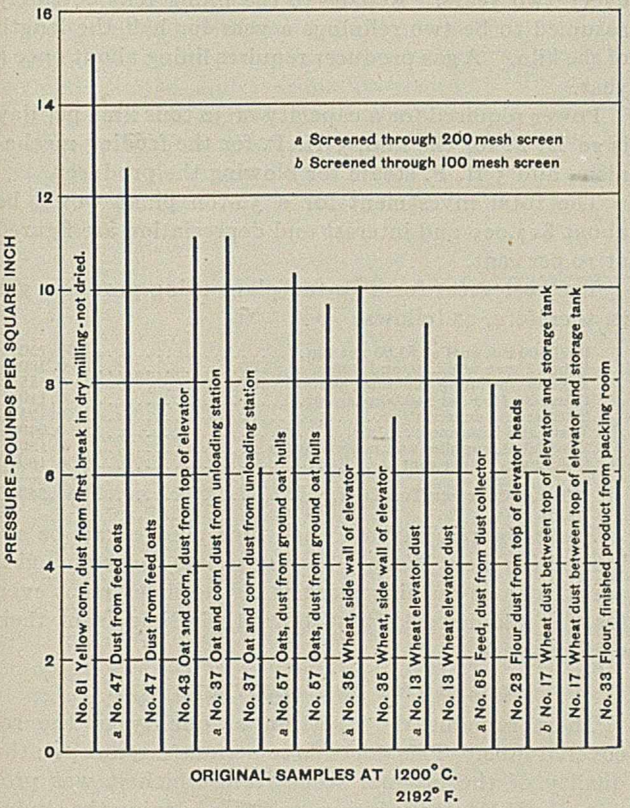
2—Property fires.

3—Introduction of foreign material in grinding machines.

4—Electric sparks from motors, fuses, switches, lighting systems.

5—Static electricity produced by friction of pulleys and belts, grinding machines, etc.

The investigation has indicated that a large number of the recent explosions and fires have been caused by the introduction of foreign material into grinding machines. It would appear that a possible means of prevention would be to devise some system by which the foreign material might be removed before it reached the mill. Other preventions suggested are: a complete electric-lighting system, the use of portable electric lamps instead of lanterns or naked lights, the inclosing of the electric-light bulbs in strong wire guards or protectors, and the possible use of vapor-proof globes, and the locating of all fuses, switches, starting boxes, motors, etc., at points where no dust is present. It is also advised to have the receiving bins from the grinding machines as small as practical with the operations, as increased size gives increased space for dust clouds and, therefore, opportunity for a more violent and destructive explosion.



THE RECOVERY OF THE SPENT LIME FROM CAUSTICIZING OPERATIONS

By James H. Payne

Received September 30, 1914

The disposal of the large quantities of lime sludge that are daily produced in the causticizing operation by those pulp mills using the soda or the "sulfate" process and by the alkali works has long been a serious problem for a number of the mills. In most cases it is not lawful to dump this material into the streams, hence the nearest available low ground is used as a dumping pond. These ponds have in many instances grown to alarming proportions, often using space that is needed for plant extensions.

Another and a more important phase of the problem is that this waste lime itself carries so much potential and actual value that it should not be thrown away after all. It is doubtful if in the average soda pulp mill practice the amount of alkali that goes to the dump will fall below $1^1/_2$ per cent calculated as sodium hydrate. This means a value of about 30 cents per ton. The average price paid for lime is probably $4.00 per ton delivered into the plant. The actual ultimate cost of disposing of lime mud varies at different plants with conditions, but will not fall below 25 cents per ton in any case, all factors being taken into consideration. This waste lime, therefore, represents a possible value of not less than $4.50 per ton to the average pulp mill or alkali works if burned back to quicklime. In other words, the mill can afford to spend $4.50 per ton upon a recovery process and still break even.

Some two years ago the writer made a study of the problem simultaneously for a large alkali works and a pulp mill. Burning tests of their sludge were made in a 20-foot test kiln, and all available data were submitted to them. After due consideration, both of these companies have installed recovery plants which are now in successful operation.

A brief summary of the facts in the case may be of interest to the readers of This Journal.

STATE OF THE ART

About 1900, one of the large pulp mills installed a rotary kiln 6 ft. in diameter and 60 ft. long preceded by a rotary driver 4 ft. in diameter and 40 ft. long which used the hot gases from the kiln. A 10-ft. producer was used to furnish gas. The results were so unsatisfactory as regards output and fuel economy that the simple 4-ft. driver was later replaced by a Ruggles-Coles drier, with a fan at the outlet of the system to produce sufficient draft. This introduced a dust trouble so serious that the plant has never been able to operate successfully.

About the same time the Western beet sugar plants began to use the rotary kiln for re-burning their spent lime. The results in their case were entirely satisfactory and today a number of kilns are in operation. The size, at first 6 ft. × 60 ft., has later been increased to 7 ft. × 60 ft. and even larger. Beet sludge differs from causticizing mud in that it contains less alkali and is of coarser grain, so that filter cakes with as low as 35 per cent water can be produced. These plants use oil as fuel exclusively.

About 1905 one of the alkali works installed a rotary kiln 6 ft. × 100 ft. for re-burning causticizing mud. The rotary was preceded by a tunnel system of drying the cakes which used waste heat from the kiln. After drying, the cakes were crushed to about 1 in. size and fed to the kiln. The tunnel system seriously interfered with the draft and the dry feed produced an excessive amount of dust. This installation is now, however, working satisfactorily, after being remodeled several times.

In Sweden and other European countries several pulp mills using very long kilns 100 to 125 ft. in length, are now reburning their sludge successfully, in spite of the high price they have to pay for fuel.

In the Portland cement industry it is now standard practice to furnace material very similar to lime sludge according to what is known as the "wet process" of cement manufacture. A mixture of limestone and clay is ground to 100 mesh, mixed with 35 per cent water and fed directly to kilns 7 to 9 ft. in diameter and 120 to 180 ft. long. In passing through, it is heated to a temperature of 2700° F. by a jet of powdered coal, oil or gas, which burns the limestone first to lime and then at the high temperature clinkers or fuses the lime with the clay. Experience has shown that a kiln 8 ft. × 125 ft. will handle 120 tons of mixture on a dry basis per 24 hours with a consumption of 434 lbs. powdered coal per ton, heating same to 2700° F.

It is also now standard practice to burn limestone to quicklime in rotary kilns. The limestone is crushed to about $^1/_2$ in. and fed dry through kilns 6 to 8 ft. in diameter and 100 to 150 ft. long, fired with producer gas. A kiln 6 ft. × 100 ft. will handle 75 tons limestone per 24 hours with a consumption of 210 lbs. coal fed to producer per ton of limestone, this coal also furnishing the power to drive the kiln. Figured to quicklime this is 45 tons of lime produced with 350 lbs. coal per ton.

The standard practice in burning cement mixture by the dry process is for a 6 ft. × 100 ft. kiln, under similar conditions as in limestone burning, 340 lbs. coal per ton of mixture, or 520 lbs. per ton of clinker produced. The fuel consumption for an 8 ft. × 125 ft. kiln is about the same, although the capacity is much greater.

FUEL REQUIREMENTS

A comparison of these figures shows that the fuel required to burn dry limestone to lime in the rotary kiln is only two-thirds of that required to burn dry cement mixture to cement. Further, we find that the fuel used in the wet process is 30 per cent higher than in the dry. Therefore, the fuel required to burn wet lime sludge may be safely figured to be 30 per cent higher than the figures for dry limestone, or 210 plus 30 per cent, which is 270 lbs. coal per ton dry sludge, or 470 lbs. per ton of quicklime.

It is to be regretted that neither of the installations that have recently been put into operation are provided with independent gas supplies so that the fuel can be measured with sufficient accuracy to verify the above figure. One plant uses natural gas from the service mains, and the other uses producer gas from a main used in common by other furnaces. There is every indication that the estimate is correct. For instance, the natural gas burner was designed amply large for fear the estimate might be low. On starting up, this burner proved to be two sizes too large and had to be replaced by a smaller one.

DISTRIBUTION OF COSTS

As only two men are required per shift, over and above those that would be required to place the sludge upon the dump or otherwise dispose of it, it is apparent that the principal item is fuel. As two men can handle a kiln capable of turning out 50 tons lime per day as easily as they can one turning out 25 tons it follows that the labor cost varies with capacity. Fuel charges should be about the same.

Repairs are very low to the moving parts of a rotary kiln, as there is so little to wear out. The life of a kiln is 20 years, with a replacement of the rolls and bearings every two years. Repairs to the lining may be safely assumed to be two relinings a year for half the length of the kiln. A gas producer requires lining about once a year.

Power required for a capacity of 30 tons lime per day is 20 H. P. for the kiln, 5 H. P. for the feeding mechanism, and 5 H. P. steam for blowing the producer.

The total investment for a 30-ton plant would be about $17,000 and interest and depreciation are figured at 10 per cent.

The cost sheet for a 30-ton plant using producer gas is, therefore, as follows:

Fuel 500 lbs. coal at $3.00 net ton	$0.750
Labor 2 men at $2.50, and 2 men at $2.00	0.300
Repairs (including one lining per year at $900)	0.155
Power 30 H. P. at $40.00 per year	0.110
Interest and depreciation	0.195
Taxes and insurance	0.040
Yard labor, supplies and miscellaneous	0.150
Unforeseen 10 per cent	0.160
TOTAL COST PER TON LIME	$1.860

These figures indicate that lime sludge can be reburned far more cheaply than new lime can be bought, and that a re-burning plant is a good investment even for the alkali works that burn their lime from their own quarries.

QUALITY OF THE RECOVERED LIME

There remains the question of quality of the recovered lime. This depends to a great extent upon the quality of the original stone from which it was produced. If the stone is pure and free burning the sludge produced from it is of coarse grain and is also free burning, retaining this property after repeated trips through the circuit. Certain sludges tested by the writer in a 20-foot test kiln have shown a tendency to roll into hard lumps which it was impossible to burn completely to the center of, although nothing unusual could be detected from their analyses or appearance except that they were of extremely fine grain.

It is, of course, impossible to re-burn the same lime indefinitely as it gradually becomes contaminated from constant use, mainly from the lining of the kiln. The customary practice is to introduce a certain quantity of new lime into the circuit periodically. This usually amounts to about 15 per cent of the lime used.

Comparative causticizing and settling tests made upon fresh lime and recovered lime show that recovered lime slakes more slowly and, therefore, causticizes more slowly, but eventually shows the same percentage of causticity. On the other hand it settles much more rapidly, due to its coarser grain and slower hydration. Therefore, it is safe to say that any time lost in causticizing the liquor is made up in settling time.

DUST AND HEAT LOSSES IN BURNING

Contrary to the usual supposition, there is practically no dust produced by a properly designed plant.

At one of the plants now in operation the temperature of the waste gases as they leave the kiln is maintained around 350° F., which is about the limit even for good boiler practice.

CONCLUSIONS

The development of the long rotary kiln in the cement industry together with improved methods of filtration and dewatering have made the recovery of the lime sludge from causticizing operations a perfectly simple and feasible proposition. To all soda fiber mills and to most alkali works there is such a wide margin of profit that an installation cannot but be a profitable investment, one likely to pay for itself in two or three years.

202 North Calvert St.
Baltimore, Md.

A LARGE INCUBATOR FOR LABORATORY USE

By F. Alex McDermott

Received June 29, 1914

In view of the large number of incubators for laboratory use which have been described or listed in the catalogues of dealers in chemical apparatus, it might seem that the design of further apparatus of this type was rather superfluous. However, the apparatus here described has proven so easily and cheaply constructed and set up and so satisfactory that it is believed others may profit from our experience with it.

The first incubator constructed on the plan here described was 5 ft. long, 3 ft. high and 2 ft. deep outside. The walls, including top, bottom and doors, were made of two thicknesses of one-half inch poplar, separated by a one-half inch space; this space was filled with powdered cork. (In constructing further apparatus of this type, the writer would make this space one inch.) Four doors were provided, the two upper ones opening upward until they were flush with the top of the incubator, where they were held by a slotted brass rod and pin, while the two lower doors dropped down and were held pendant from the bottom of the incubator. Median vertical and horizontal cross-pieces in the front of the box were provided, upon which were placed the door catches. These cross pieces were beveled at an angle of 45°, as were also the front edges of the box, and the doors. The doors thus formed a fairly tight joint when closed. An upright was placed against the back, inside, and shelf brackets were placed between this upright and the front vertical cross-piece and also at the ends of the box, inside. The shelves rested upon these brackets. The shelves were made of galvanized iron, perforated with $^1/_2$ inch holes, spaced on about 4-inch centers, and each shelf had two "V" shaped braces on the under side for the sake of rigidity.

The heating and temperature control were both entirely electrical and both were operated on a 110 volt lighting circuit. The heating (for 30° C.) was secured by means of four coils each containing 50 ft. of No. 26 Nichrome wire, two sets, each set of two coils in series, being connected in parallel, the total heating current being about one ampere. In these heating coils or elements, the wire was wound on a frame consisting of two strips $^1/_2$ inch square in cross section and the necessary length (in this case 8 inches) of heavy, hard asbestos board, spaced at the desired distance (14 inches) by means of $^3/_{16}$ inch bolts; extra nuts on the ends of these bolts served as binding posts for the terminals. Each element was supported by cylindrical, porcelain insulating knobs, such as are used in electrical work. Two elements were fastened to the ceiling and two to the floor of the incubator.

For the temperature control, a 200-ohm main line relay arranged for back contact, was connected in series with a 10 watt carbon lamp and an electrical contact thermometer (Eimer and Amend, No. 6838) constructed for the desired temperature. Of course, the S. M. Co. incubator thermostat may also be used. The total current in the temperature control circuit was about 0.08 ampere. A small 110 volt motor with a 6 inch fan was placed upon the upper shelf at one end of the incubator and connected in parallel with the sets of heating units, to secure more even distribution of temperature. The contact thermometer, which was constructed to close the circuit at 30° C., actually closed it at about 29.75° C. and the temperature in the incubator held, according to a large incubator thermometer placed centrally, at 29.5 to 30.5° C., depending upon the temperature of the room. The above regulation is sufficiently close for many purposes and the range of variation would be considerably reduced in a smaller apparatus. The outside of the box was painted white with two coats of bath-tub enamel over two coats of ordinary white paint.

A number of modifications of the design are possible. The contact thermometer may be obtained so constructed as to close the circuit at any one of a number of points, and a small incubator has been constructed on this principle to hold 45°, 50° or 55° C. A three-point battery switch was provided to cut in and out the different leads. In this case, an ordinary double-wall steam oven was used for the box and a single heating element was used. Instead of the 10 watt lamp, it is better to provide an adjustable resistance, as the sensitiveness and smoothness of operation of the relay may thereby be improved; for this purpose the student's rheostat (made by Jas. G. Biddle, of Philadelphia) has been found satisfactory. A similar resistance may be employed in series with the heating system in order to vary the temperature of the heating coils. The apparatus, as described, works well on direct current. On alternating current it is necessary to adjust very carefully the tension of the relay spring, the distance of the poles from the armature, length of travel of the armature, etc. Attempts to utilize the electrolytic valve rectifier in the temperature control circuit were unsatisfactory. The humming of the relay on alternating current is, of course, objectionable, but by proper adjustment may be largely eliminated. While no trouble was experienced in the breaking of a 110 volt circuit at the contact thermometer, using as low a current strength as here employed, it is advantageous to run the temperature control circuit on the secondary of a small toy or bell-ringing transformer giving 10 or 15 volts.

The total cost of material of the large wooden box incubator was about $50.00. The labor cost would vary with the circumstances of construction.

Mellon Institute of Industrial Research
University of Pittsburgh
Pittsburgh

A PROPOSED NEW STANDARD LOOP FOR USE IN BACTERIOLOGICAL TESTS OF DISINFECTANTS

By A. D. St. John

Received July 7, 1914

The work described herewith was undertaken with a view to obtaining a method of transferring small quantities of a liquid from one containing vessel to another, with rapidity and a fair degree of accuracy; with special reference to the use of such method in the inoculation of broth cultures, as practised in the principal tests of the antiseptic value of disinfectants.

As is pointed out by Duyser and Lewis,[1] the main objection to these tests lies in the unreliability of the "standard loop," which (1) transfers too small a quantity of liquid, *i. e.*, about 0.003 cc., and (2) transfers a quantity which varies as much as 80 per cent from the average.

Tests made in connection with this paper confirmed the second of these objections and indicated that the variation was due to two principal causes:

I—The position of the loop on leaving the surface of the liquid.

II—The rate of removal from the surface.

The variation between removing the loop slowly edgewise, and rather quickly flat to the surface, was from 0.002 to 0.008 g., respectively.

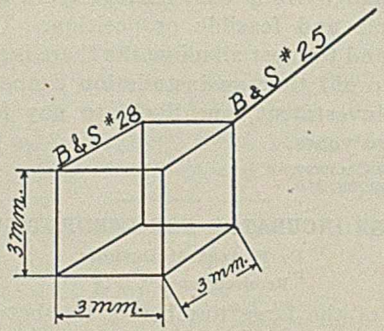
In order to obviate the variation due to position two loops placed with their planes at right angles to one another were tried; and this arrangement gave about equal results when lifted out at any angle perpendicular to the supporting wire, but varied from the result when lifted out with the wire support vertical to the surface of the solution.

Hence a third loop was added with its plane perpendicular to the wire support, giving three concentric loops, the plane of each at right angles to those of the other two. As a tendency of the drop to break away from the wire at a point farthest from the junction of the wires had been observed, this loop was further modified by changing the spherical shape of the loops to squares, joined at the corners. The loop, or rather cage, thus formed, has the appearance of the outline of a cube, supported by a wire from one corner, and measuring about 3 mm. on an edge. The corners should be welded rather than twisted. The wire of the cube is conveniently made of No. 28 B. and S. Pt wire, and that of the support of No. 25.

This last described loop gave drops varying in weight from about 0.019 to 0.021 g., according to the angle at which it was lifted from the solution; while the most unfavorable results obtained, varying the rate of lifting out from as slowly as possible, to a quick jerk, was from 0.017 to 0.023 g., respectively; while with ordinary care, several consecutive results of from 0.020 to 0.021 g. were obtained.

Up to this point the measurement of the drop was made by hanging the wire quickly on the balance and weighing by swings. Only slight error was caused by evaporation, as the drop was rather large.

The results with the cube-shaped loop appeared, however, to justify further trials, and tests were now made according to the method of Duyser and Lewis (above), *i. e.*, by dipping out drops of a strong iodine solution, placing in distilled water, and titrating, using dilute thiosulfate. Eight consecutive tests gave the following ratio:



	Thiosulfate cc.		Thiosulfate cc.
1	35	5	38
2	36	6	35
3	36	7	36
4	35	8	36

Putting the mean, 35.9 = 100.0, we get a maximum variation of 6 per cent.

It will also be noted that the volume of the drop carried by this loop is about 0.020 cc., or over six times the volume given by Duyser and Lewis as that of the present "standard loop," thus overcoming largely the first objection advanced by them in the article quoted.

It would therefore appear that a loop such as the one described above would eradicate some of the difficulties at present encountered in making determinations of the antiseptic value of disinfectants by the methods mentioned.

The valued aid of Mr. Walter Erlenkotter, of this laboratory, in connection with the preparation of this paper, is gratefully acknowledged by the author.

Standard Testing Laboratory
Board of Estimate and Apportionment
New York City

[1] This Journal, 6, 199.

NOTE ON SUBSTITUTE FOR THE BLAST LAMP

By Paul J. Fox[1]

Received July 15, 1914

To the many substitutes for the blast lamp, the writer begs to add one, which, though extremely simple, he has not seen in use in any laboratory that he has visited. It consists of an ordinary assayer's crucible of convenient dimensions, of which the bottom has been ground or sawed off, forming a jacket

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[1] Scientist in Soil Laboratory Investigations, Bureau of Soils, U. S. Dept. Agriculture, Washington, D. C.

of truncated conical shape, open at both ends. Thus prepared, the jacket is placed over the crucible or dish to be ignited, with the larger end down. The top is partly closed by a porcelain crucible cover which can be easily adjusted to secure the maximum amount of heat without unduly impeding the draft. Using a Tirrill burner of ordinary laboratory size, it is possible to convert even large amounts of calcium carbonate to the oxide. The crucibles in which the ignitions take place should be covered, but with the lid partly placed to one side to leave a small opening. Besides doing away with the necessity of compressed air, this method of ignition also avoids the strong air current of a blast lamp by which small amounts of light precipitates may be lost. A platinum crucible, also, appears to be less attacked than when a blast lamp is used.

A transparent crystal of calcite was found on analysis to have the following composition:

	Per cent
$CaCO_3$	99.46
$MgCO_3$	0.53
Silica	0.05
	100.04

This would correspond to a loss on ignition of 44.01 per cent. Two samples of the same material were then ignited, using the jacket as described. Sample No. 1 consisted of 1.0308 g. and after fifteen minutes ignition weighed 0.5779 g., or a loss of 43.95 per cent. Sample No. 2 weighed 1.3117 g. and after ignition for fifteen minutes yielded 0.7355 g. CaO, or a loss of 43.93 per cent. In neither case was there any additional loss on further heating.

A convenient size of assayer's crucible is the Denver Fire Clay No. 9, which measures 3 inches in diameter and $5^{1}/_{2}$ inches high. If a clay ring piece of the same diameter as the assayer's crucible is available, it may be advantageously used as a rest for the triangle that carries the platinum or porcelain crucible containing the sample. This has the effect of extending the jacket below the triangle. The results quoted above, however, were obtained without the use of such a ring piece.

Bureau of Soils, Washington

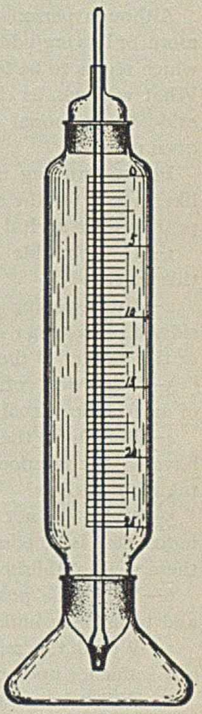
A CONVENIENT FORM OF WEIGHING BURETTE

By H. S. Bailey

Received August 19, 1914

In making a large number of determinations on various oils the writer at first attempted to use Ripper weighing burettes. He soon found, however, that their weight and especially the necessity for providing some sort of rack for them, when filled, made their use impracticable. As a result of numerous attempts to devise a suitable weighing burette, the one shown in the accompanying illustration, which can be placed directly upon the pan of an ordinary analytical balance, has been finally adopted. Its construction is clearly shown by the drawing in which the three ground joints are indicated by *stippled* areas. The bottom cap serves both as a base to support the burette and as a catch-cup for any leakage. As the sample does not ordinarily come in contact with the two large ground joints, these need not be especially tight when the burette is used for homogeneous non-volatile liquids. The small valve at the tip, which of course must be tight, can be readily made by merely drawing down the end of a glass rod and grinding it into place with a little carborundum and water.

When the burette is used for volatile substances or non-homogeneous mixtures which require frequent agitation, such as milk, a small rubber sleeve is slipped over the top of the stopper and rod, making the joint between them air-tight.



These burettes may, of course, be of any suitable size, the ones commonly used for weighing oil samples having a capacity of about 30 cc. A rough graduation greatly facilitates the weighing out of definite quantities of material for such determinations as the Reichert-Meissl number, in which it is necessary to use approximately the same weight of sample.

Food Investigation Laboratory, Bureau of Chemistry
Department of Agriculture, Washington, D. C.

SYMPOSIUM ON AMERICAN DYE INDUSTRY

The New York Section of the American Chemical Society devoted its first regular meeting of the 1914–1915 season, on October 9th, at the Chemists' Club, to a discussion of the need and practicability of enlarging the production of dyestuffs in this country. The program was as follows:

Introductory Remarks—Chairman Allen Rogers.

Dyestuffs and the Textile Industry—J. Merritt Matthews, Consulting Chemist to the Textile Industries.

Campaign for American Dyestuff Industry—Arthur Prill, Editor *Daily Trade Record*, Mill Man's Section.

Coal Tar Colors in America—I. F. Stone, President National Aniline and Chemical Co.

Needs of the Textile Industry—Alfred L. Lustig, Chairman of Dyestuff Committee, National Association of Finishers of Cotton Products.

All the papers presented are published in full below. After the reading of the papers, discussions were called for: those by David W. Jayne, of the Barrett Manufacturing Company, Bernhard C. Hesse and I. F. Stone are printed in full herewith.—[Editor.]

INTRODUCTORY

By Chairman Allen Rogers

At the last meeting of the New York Section of the American Chemical Society, which was held in June of this year, we little dreamed that before another meeting practically the whole of Europe would be involved in the greatest struggle the world has ever known. Many of those who attended that meeting are at present in the ranks of those great armies now engaged in deadly conflict. It is especially sad for us to think that perhaps some of our dearest friends, and members of this society, may be fighting face to face at this very moment. Just why such a conflict should have been brought about is extremely difficult for many of us to understand. Even as we get the meagre newspaper accounts from day to day we can hardly realize the magnitude of the struggle taking place.

The cause of the European war is a matter with which we are not able to cope, but the effect upon our chemical industries is a topic well worthy of our careful consideration. As chairman of this section, it, therefore, seemed advisable that a conference should be arranged, whereby all sides of the question might be discussed and a more definite understanding of the existing conditions determined.

Although personal feelings and selfish motives may make us more or less prejudiced, we must eventually be influenced by that which seems to be for the best interests of the nation as a whole. What we seek, as chemists, is the *truth*. Let us, therefore, put aside the personal factor and approach the problem with an open mind.

Before entering upon the program of the evening, I should like to ask, for the sake of argument, a few questions which appear to have a vital bearing upon the subject in hand.

1—Is it feasible to manufacture chemicals and dyestuffs in this country?

2—In answering this question should we not take into consideration whether or not we are to seek the American market or the market of the world?

3—Have we a sufficient supply of coal tar to meet the demands of an American coal tar chemical and color industry?

4—If we have the necessary amount of coal tar in this country have we the interlocking chemical industries to make the undertaking a success?

5—If we do not at present have the interlocking chemical industries, is it possible for us to develop the same in face of these well-established industries in European countries?

6—Will it be possible to start with American raw materials and from them build up all-American dyestuffs?

7—Would the manufacture of chemicals and dyestuffs have any influence upon our other export trade?

8—Will it be possible for the European nations to furnish the same quantities of dyestuffs when hostilities have terminated, as they have in the past?

9—Have we a sufficient number of technically trained men to carry on such an industry?

10—What will our universities and technical schools do to train young men for this great industry?

11—What will the Government do to make our patent laws protect American invention?

12—What will the Government do to protect American enterprise?

13—What guarantee will the textile, paper, dry color, leather and other industries give to an American Coal Tar, Chemical and Color Industry?

14—If it is not possible to produce at present all of the great variety of dyestuffs required by these industries, will they guarantee to use such dyestuffs and chemicals as can be made?

15—What support can be expected from the trade and daily papers?

16—Will such an industry meet with financial support?

17—Why is it that we have not in the past manufactured some of the more important chemicals, such as barium chloride, magnesium chloride, oxalic acid, zinc dust and many others?

18—Have we any commercial source of potash?

These are a few of the many questions which must be answered before we can hope to make any headway on the problem. Some of these points will no doubt be covered in the papers of the evening and it is also hoped that those taking part in the discussion will throw some light on the other important questions.

Pratt Institute, Brooklyn

DYESTUFFS AND TEXTILE INDUSTRY

By J. Merritt Matthews

That the manufacture of fabrics is an industry dependent to a very large degree on the element of color is a fact which is apparent to almost any one. Textile fabrics are employed in great variety for clothing, for art and utility, as essentials in many lines of industry—in fact, the number of uses for textile fabrics is almost legion. And yet in a great many of these uses color enters as an essential factor in the preparation of the fabric. As color in textile fabrics is obtained by the use of dyestuffs, the latter agents become a very important adjunct to the textile industry.

Although we have come to regard dyestuffs and their colors as highly important factors in the production of fabrics, nevertheless, if we approach the subject from the utilitarian point of view, we find that dyestuffs do not add any real quality to the fabric; the color of a cloth may add much to its artistic appearance and give it beauty and charm that appeal to our esthetic taste, but it cannot be said that the color increases the durability, the strength, or the wearing quality of the fabric. Outside of a certain influence on heat and light rays it is doubtful if color has any real influence on the material value of the fabric; its influence is a purely subjective one. In other words, the practical utility of the fabric is but slightly affected by its color. Our clothes would be of the same practical value to us if they were undyed as if they were dyed; our carpets would wear just as well—in fact better—if they had never been ornamented by the dyer's art.

IMPORTANCE OF COLOR

Wherein, then, is the value of dyestuffs to the textile industry? In the first place, color is employed in fabrics to satisfy the taste for beauty and the desire for ornamentation. Man from the earliest stages of his existence appears to have had a strong predilection for colors; we find the lowest orders of savage tribes decorating their simple costumes with the varied, though limited, colors at their command. Eve no doubt selected a fig leaf as her costume more from its pleasing shade of green than on account of its utilitarian value as a means of protection against the inclemencies of the weather. It is this innate desire to decorate oneself and the things which one possesses and uses that has led to the wide-spread and almost universal application of dyestuffs in the manufacture of textile fabrics. In the second place, and wholly aside from its artistic value, color is employed in fabrics in order to avoid, or rather to cover up, certain undesirable features. When we wear our clothes for any length of time they become soiled, and the dust and dirt they acquire soon proclaim our intimate associations with Mother Earth. If the fabrics we use were white or undyed, their soiled condition would quickly become apparent in a very disagreeable manner. Consequently, we dye them in suitable colors, and, though they still acquire the same objectionable impurities, these are not visible to the eye, and what we do not see we frequently ignore. I am quite sure that had my present suit of clothes been undyed I should have experienced some hesitancy in appearing before you this evening, but being dyed as they are, I stand here unabashed and thoughtless of their appearance. Our undergarments, our collars, our bed linen, our table linen, our towels, and many other articles of apparel in daily use are now generally left in the undyed condition and even whitened thoroughly by bleaching, in order that when they become soiled they may present a disagreeable appearance and force us to take proper steps towards cleansing them. Have you ever stopped to consider why the blankets in Pullman sleeping cars are dyed a dark grey, why Italians prefer red bandanna handkerchiefs, and why khaki colored shirts are so popular with camping parties? There is food for much thought in these reflections.

In the early days our forefathers naturally employed those coloring matters which were nearest to hand in the decoration of the fabrics they manufactured. Various colored earths and mineral compounds were used no doubt at first, and then when the tinctorial properties of various plant juices and decoctions became known, these were employed as dyestuffs; all this gradually led to a rather complicated art of the application of dyer's materials. It was found that certain plant juices, though highly colored in themselves, could not be properly fixed in a direct manner upon the textile fibers. But by first treating the fabric with a solution of a suitable metallic or mineral substance, such as alum or copperas or bluestone, pleasing and permanent colors could be produced. This led to a knowledge of the mordant dyes, and this art of dyeing textile fabrics gradually became a highly developed and organized art, and more or less of a chemical science. In fact, the preparation of these vegetable coloring matters and the numerous adjuncts and assisting materials which were employed in their proper application to the fiber, gave rise to important and extensive chemical industries. There were various limitations, however, in the use of these natural dyestuffs. In the first place, the range of color was somewhat narrow, the qualities of fastness were often deficient, there was much variation in the strength and shade of successive lots of dyestuff, the methods of application were often complicated and cumbersome, and it was hard to refine the art of dyeing into an exact science.

SYNTHETIC VS. NATURAL DYES

The discovery of America gave a great impetus to the dyeing of textiles by reason of the large number of new dyewoods which were discovered in this hemisphere, especially in the West Indies, and Central and South America. Among these were logwood, which, next to indigo, soon became the most important dyestuff in use; fustic, a yellow wood; cochineal, a very important red coloring matter consisting of the bodies of certain small insects which grow on the leaves of the cactus plant; Brazil wood, also a red dyewood of considerable importance, and many others of minor note.

The great step, however, in the dyeing of textile fabrics, came in the discovery of the synthetic coal tar dyes. This led to an intimate connection between dyeing and chemistry, and in consequence placed the art of dyeing on a more systematic and scientific basis. The discovery of the various coal tar dyes led to the introduction of a wide range of colors, many tones and shades of which were hitherto unknown and unobtainable in dyeing. It also resulted in the introduction of many fast colors, far exceeding the natural dyestuffs in this respect. It gave rise to the possibilities of many new effects and easier, cheaper and simpler processes of dyeing. In fact, the general methods of dyeing soon became standardized to a few definite processes, with the result that the art of dyeing became widely disseminated among the textile mills. It was no longer a secret and mysterious art jealously guarded by the members of its guild, but became an open profession.

It was not long before the coal tar dyes almost entirely replaced the cruder vegetable coloring matters. This was not only due to the fact that the synthetic dyes could be produced cheaper and could be applied more simply and conveniently, but was also because most of the vegetable dyes were of an inferior quality as compared with the coal tar products. In the first place, the vegetable dyes were far from pure coloring matters; they consisted principally of wood extracts, and contained, besides the actual coloring matters, many other extractive substances, such as tannins, sugars, resins, and pectinous bodies of a nondescript character. It was a very costly proceeding to isolate the pure coloring matter from these complex vegetable extracts; in fact, in most cases it was commercially impossible. On this account, the colors given by most vegetable dyes were more or less impure and not clear in tone; they were also liable to be quite variable in different lots of the extracts. In the second place, there are only a few of the vegetable dyes which may be classed as really fast colors in the modern sense of the term. Indigo was no doubt the fastest color, and still represents the standard for comparison. Logwood, which was once universally employed for the dyeing of black on all classes of fabrics, could be employed for the dyeing of colors fast to washing, but was not especially fast to light and exposure to weather. Before the introduction of the fast coal tar blacks, those of us who are old enough can well remember that our black coats had a tendency to turn to a rusty faded color; this was because logwood was the dyestuff employed. At the present time this defect is very seldom noticed even with the cheaper grades of material, as the alizarine blacks employed for this purpose are eminently fast. Fustic was another much used dyewood for yellow and browns, and this cannot be classed as a fast dye at all; in fact, hardly any of the many yellow and brown vegetable dyes have any remarkable degree of fastness. Among the red colors we had madder and cochineal as the principal representatives. Madder was very fast, being used for the production of the well-known turkey-red; but the coloring matter of madder is alizarine red and in the vegetable extract it is in a rather impure condition, being mixed with other extractive matters, so that when this coloring principle, alizarine red, was prepared synthetically in the pure condition from coal-tar, it very rapidly replaced the crude madder extract. Cochineal was used very largely for the dyeing of scarlets on woolen materials and would be classed as a fairly fast color. The coal tar acid scarlets, which were first introduced, were not as fast as cochineal, and though they were cheaper and easier to apply and displaced cochineal to a very large extent, nevertheless this latter dye held an important position for the dyeing of high class and fast scarlets for a long time. When the anthracene and chrome scarlets, however, were prepared from coal tar, and proved to be even faster than cochineal, this dyestuff gradually fell into disuse. There was also a long list of red dyewoods, but all of these were of inferior fastness as compared with the coal tar dyes and at present are no longer used. Archil and its dried extract, cudbear, were once very extensively employed as the basis of fast purplish red and reddish brown colors on wool and silk materials. It was also used as a bottom color on wool for the dyeing of heavy shades of indigo, giving a rich, deep, and bloomy color. Archil was prepared from the extract of a certain species of parasitical plant growth to be found principally along the sea-coasts of subtropical countries. Enormous quantities of it were once obtained from the western coast of lower California. The coloring matter did not exist ready formed in the plant extract but had to be developed by a series of chemical processes. A large number of fast brown coloring matters, however, have been prepared from coal tar and have almost entirely displaced archil preparations in this country, at least.

EASE OF DYEING COTTON WITH SYNTHETIC DYES

As every one knows, the fate of the other vegetable dyes soon overtook indigo, at least as far as its natural source was concerned, and this dyestuff is now almost exclusively made synthetically from coal tar. The introduction of other synthetic dyes of the indigo class and known as the "vat" dyes has greatly raised the quality of dyed cotton materials. The dyeing of cotton with the old vegetable dyes was always a rather difficult matter as compared with the dyeing of wool or silk. This was due to the relatively inert character of the cotton fiber towards the coloring matters, and also to the fact that cotton could not be mordanted with metallic salts with the same readiness as animal fiber; consequently, the processes of dyeing cotton and the colors obtainable were rather limited, which, of course, greatly restricted the use of cotton materials. The discovery of the direct cotton dyes derived from coal tar opened up a new field for cotton dyeing. Though these dyes yielded a very wide range of clear and beautiful shades, they did not possess any great degree of fastness, and consequently could not be employed on cotton fabrics that required much washing and laundering.

This still kept colored cotton goods in a rather restricted and cheap class. The discovery of the fast vat dyes, however, which are eminently adapted to the dyeing of cotton, opened up a new era for the use and manufacture of colored cotton fabrics. With these dyes cotton can be dyed in all manner of beautiful shades, and the colors are as permanent almost as the fiber itself. So remarkably fast are these colors that they withstand the bleaching action of hypochlorites and severe washing and laundering. It is on this account that we can now manufacture colored cotton fabrics for dress goods, shirtings, etc., that will resist the strong chemicals employed in modern laundry methods. It is also possible to adopt many new styles in the manufacture of these fabrics. For instance, cloth may be woven from partly dyed and partly undyed yarns, and then bleached in the piece, the colored yarns not being affected by the bleaching. These improvements in the dyeing of cotton have led to a great development in cotton manufacture, and cotton fabrics are being employed more and more extensively in apparel and other lines of domestic economy.

Dyes, however, are more extensively employed on woolen materials, and the great bulk of the dyestuffs manufactured go into this industry. This condition results from a very simple fact—woolen materials cannot be washed and laundered with the same readiness and impunity as cotton goods. If we washed our woolen clothes, for instance, in the manner we do our cotton ones, they would shrink up and otherwise be sadly injured. Therefore, as I have already pointed out, it is inconvenient to have undyed woolen clothes—they become soiled too easily. Therefore, practically all of our woolen clothing fabrics are dyed, and generally in rather dark colors, and this requires a large quantity of dyestuff. Furthermore, the carpet and rug industry requires an enormous quantity of woolen material, and all of this has to be dyed, for again it is not practical to use undyed carpets.

The woolen industry uses large quantities of the acid dyes and the anthracene and alizarine colors. Indigo is also very extensively used, together with a limited number of the other fast vat dyes. Most of these, however, are not as adaptable to wool as to cotton by reason of the fact that they are employed in strongly alkaline solution, which is not a good thing to use in connection with the wool fiber.

GREAT VARIETY OF DYES NEEDED

The textile industry, as you all know, is a very broad one and its products go into almost every other line of industry. Generally speaking, textiles are most often regarded as limited to materials woven for clothing and household and domestic economy. But the term is really much more extensive; for instance, textiles are used for the manufacture of automobile tires, ropes, and cordage, sail-cloth, awnings, window shades, insulating fabrics in electrical apparatus, cloth for bookbinding, and a thousand other uses. The extent to which dyestuffs are employed and the character of these requirements, will, of course, depend on the nature of the textile and the use to which it is to be put. Fabrics used for underwear, for instance, are generally not dyed; cotton hosiery is chiefly dyed black, to a lesser degree brown, and to a very small extent in colors, while silk hosiery is dyed in all manner of colors. It would be foolish to dye fabrics for automobile tires, whereas fabrics for window shades must nearly always be dyed, and with colors of exceptionable fastness to light, other qualities of fastness, such as washing, being disregarded as unessential. And so it goes, the wide diversity of fabrics leads to a wide diversity of color requirements both as to shade and fastness. On this account, there must be a wide diversity of dyestuffs to take care of the varied demands of the textile industry, and, in consequence, it has been found impossible to reduce the manufacture of dyestuffs to a few standardized and staple products. In any discussion relating to the establishment of a large American dyestuff industry this fact must be borne in mind. It must be prepared to take care of the manufacture of relatively small quantities of this, that, and the other dyestuff for some particular purpose and quality of color.

MANUFACTURE OF DYES BY THE TEXTILE INDUSTRY

There has been of late a good deal of talk as to the feasibility of the textile industry itself becoming interested directly in the manufacture of dyestuffs and, consequently, I have interviewed numerous textile men on this subject with the view of obtaining a broad opinion of the matter. The general feeling, however, is that the dyestuff industry is entirely separate and distinct from the general textile industry itself; the manufacture of dyes is in reality a highly developed chemical enterprise, and the average textile manufacturer has no more desire to go into the manufacture of dyestuffs than he has of going into the business of mining coal or making steel. The dyestuff manufacturer must be prepared to stand on his own feet and develop his industry through his own energy and capital; he must meet the conditions which confront him (as must every other manufacturer).

When the European war broke out and the regular shipments of dyestuffs were cut off from this country, the textile trade was thrown into a very excited condition. Most of the mills, however, had several months' supply of dyestuffs on hand and this, together with what they have been able to pick up in the market, has kept them going rather satisfactorily up to the present time. There have also been some fresh shipments from Rotterdam to give a further supply to a now practically depleted market. If these shipments can be maintained with more or less regularity during the period of war, there is no doubt but that our textile industries may be maintained without any serious setback. There will, no doubt, be special cases where the necessary suitable dyestuffs cannot be obtained, and this will necessitate a readjustment of styles to a certain extent. If, however, the shipments of dyestuffs from Germany cannot be brought through, or if the manufacture of these dyes is seriously interfered with so that we cannot obtain them at all, then the textile industries here will, of course, be under the necessity of putting undyed goods upon the market. This would be a considerable hardship, for there is no doubt but that the demand for such goods would fall far below the normal, and furthermore satisfactory prices could not be obtained.

MEETING PRESENT DEMAND FOR DYES

In this event there are two possibilities to consider: (1) To revive the use of the vegetable dyes to take the place of the German synthetic colors; (2) to manufacture the required dyestuffs in this country. The first alternative does not offer much hope except in a minor way. In the first place, it would require a considerable time to get together the necessary raw dyewoods from the countries in which they grow; then the coloring matters would have to be extracted and properly treated in order to develop a satisfactory strength and quality, and in addition to all this, there would have to be a considerable readjustment of conditions and usages in the dyehouse before the natural coloring matters could be properly utilized to give satisfactory shades. Even then, there would be a great many colors which could not be obtained with these natural dyestuffs, and a great many of our fast colors could not be obtained at all. There are some cases, it is true, where natural dyes would be readily available and could be used as substitutes for some of the coal-tar colors. The output of logwood could, no doubt, be considerably increased in a short time, and this could be utilized for blacks on wool and cotton goods, though fastness of color would, of course, have to be sacrificed. There are large quantities of archil which could also be brought into use on short notice, and this could be employed in many cases with much satisfaction in wool dyeing and carpet dyeing for the production of reds and browns. There is probably quite a supply of yellow dyewoods which could be made available in a short time. With indigo, however, it is not probable that the production could be much increased for several years, as this requires the careful planting, cultivation and harvesting of crops.

The other alternative open to us is the manufacture of dyestuffs in this country on a scale sufficient to take care of our needs, both with respect to amount and kind of dyestuff. There is already a fair production of dyestuffs in this country, and there is no doubt but what this industry could be satisfactorily developed under proper conditions. It will, however, require time, organized technical effort, and capital, and I am sure we have all three of these commodities in this country, together with the other necessary raw materials for the production of coal-tar colors. But I leave the discussion of this feature of the case to Mr. Stone, who, being a manufacturer of dyestuffs, can tell you all about the possibilities of this industry.

PROBLEM TO BE SOLVED BY CHEMISTS

In closing, I would say that the textile industries of this country are very dependent on a proper supply of dyestuffs, and I am sure the textile manufacturers would heartily welcome the firm and permanent establishment of a dyestuff industry in this country, so that we would be self-contained and not dependent on foreign countries. However, they feel that this dyestuff industry must be developed independent of themselves, and while they are willing to give it all legitimate support and opportunity, I doubt if they are at all inclined to grow it as a hothouse product. They believe that the dyestuff industry can be established here based on sound economic principles. The opportunity is here and our chemical manufacturers should lose no time in taking advantage of it. The appeal of the textile industry to the chemist at present is: "We need dyestuffs, so get busy and make them; don't hem and haw, and make excuses, but get right on the job."

50 East 41st St., New York City

CAMPAIGN FOR AMERICAN DYESTUFF INDUSTRY

By Arthur Prill

The technical and commercial aspects of the campaign for an American dyestuff industry are on this program already in better hands than mine, but you may be interested in the publicity features of the movement, for nowadays nothing of moment that effects the general public can be accomplished except by molding public opinion.

You will perhaps permit me to state a fundamental proposition upon which rests the reason for some of the publicity which has been given to the campaign for an American dyestuff industry. A newspaper has two functions, first, to gather, collate and distribute news; secondly, to make men think. The latter of these functions is by far the more difficult to accomplish, but can in a given instance be of the highest value.

The newspaper man has an advantage of position in receiving news at the earliest possible moment. Hence, he is in a position to foresee coming events before the general public or sometimes even before a special industry gets any inkling of such future trend.

Now, if under such circumstances he uses his knowledge to show future possibilities to the paper's readers, he will find unbelievers, well meaning but often short-sighted. Further, if he advocates a change he is certain to arouse the enmity of the old system—hence, the need of a campaign. We ask two far-reaching changes, patent revision and tariff aid. When foreigners obtain Uncle Sam's protection for their brain-work, they should be compelled to use such protective ideas, in part, at least, for the benefit of Uncle Sam's citizens. Again, if we seek American capital to lay out funds for the construction of dyestuff factories, this capital has a right to demand that foreign competition be kept out of the country until the whole industry has obtained a firm footing.

In the case of American dyestuffs such a campaign should not really be necessary. A three-fold genius who fully grasped the technical as well as the commercial aspects of the coal-tar situation and who also possessed rhetorical and literary ability to place the matter adequately before all interested, would logically convince them and move them to act.

As no decisive action for the establishment of an American dyestuff industry has as yet been taken, it is evident that this three-sided genius has not yet appeared, but the possibility of united action by such men as compose the *American Chemical Society*—you men here tonight could wage this campaign with certainty of success.

The question which arises in your mind is, Should you take it up and take it up not merely in academic manner, but should you put into this campaign that practical effort and vital force which is essential to victory? The most apparent incentive is the fact that certain branches of the textile trade are today slackening for want of suitable dyestuffs. Not only are mills hampered in production, but human beings are suffering for lack of their usual means of livelihood. Further, every housewife in the land, when she goes into a department store today, finds that her dollar will buy only eighty cents worth, in some cases only fifty cents worth of textiles, as gauged by prices which ruled three months ago. As a result, the household budget of every family in the land suffers more or less.

Another incentive, although little argument need be wasted upon it, is that every country should as far as possible be independent in its industrial activities. America, above all, with her wonderful natural wealth, offers unlimited raw material to the coal-tar dye maker.

But humanitarian and patriotic reasons might not budge you far if a certain other incentive be lacking. The dominating factor in all commercial questions is "Would it pay you to take action?" Here, in the dollars and cents equation, we have the real obstacle to the campaign for an American dyestuff manufacture. It is useless for anyone to cry "American dyes for American textiles," while the majority of persons directly connected with the dyestuff industry get their bread and butter from non-American dyestuff makers and while these persons retain control of the so-called campaign.

I have met many a technical man in the last three months who said: "Yes, we could in from one to two years establish local manufacture of dyestuffs within certain limits perhaps, but sufficient to supply pressing needs. We can do this if we get revision of our patent laws and tariff so as to protect American capital in such venture but—my salary or my retainers come from so and so who do their dyestuff making not far from the Rhine. I can take no action without ruining myself financially. I beg you not to publish a word of this conversation."

The *Daily Trade Record*, having served the textile business for some twenty-two years, also has some good friends among the mill men, to whom we can go in confidence. We recently called the attention of certain of these to an advertisement in a textile journal which ran as follows: "Do not worry about lack of dyestuffs; we herewith assure our customers that we can supply all their needs." The *Daily Trade Record* asked the mill men: "You know this is not true; you yourself have tried to buy dyestuffs from that firm without getting what you were after. Will you back us in our campaign by allowing us to prove the facts by your own business correspondence?" The mill men replied: "If we did, the chances are we would get no dyes at all; this firm would be black-listed by all the importers and practically have to give up business."

Under such conditions, it is evident that the only way to obtain the necessary patent and tariff legislation is to arouse widespread public sentiment among people whose bread and butter does not depend on the enemies of the movement. You, chemical engineers, if you act as a body, are independent; you could lend the weight of your professional reputation and technical knowledge to prove to the country that we can overcome the technical obstacles. Ten million people in the United States from mill to clothing merchant are dependent on the textile trades and to show these where their bread and butter lies is your problem. Win their votes and you win this campaign. The opponents of American dyestuff manufacturers never mention tariff or patent-revision—they know such proposals would meet with public approval. The foreign makers' agents simply reiterate: "You *can not* do it."

If you take hold of this subject as a society, show America that we can do it and explain to the other technical organizations in the country how profitable it would be to the United States to develop her coal-tar resources, and through your technical publications and publicity departments obtain the aid of the great American newspaper world, you will certainly succeed in so laying the facts before the American public that the solution we offer will be accepted and appreciated. Home manufacture of dyestuffs is the only solution.

Since a carpenter's union and an iron worker's organization have brains enough to work together for their common good, why could not chemists and civil engineers, even the botanist and the astrologer, possess acumen enough to take united action? Technical workers are the one great intelligent force of civilization, although they hardly seem to understand their strength. In such a campaign as this they could use their strength.

If we do arouse the all powerful public sentiment of the American people, compelling needed legislation at Washington, there will result increased chemical activity not only in dyestuffs, but in all other branches of those numberless industries which are based upon the work of chemists. Your profession will rise to higher and unattained heights in the estimation of the country; financial recompense will similarly multiply as the call for your service increases and future generations will, due to your efforts, worthily call this early twentieth century the "Dawn of American Chemistry."

COAL TAR COLORS OF AMERICA

By I. F. Stone

Mr. Chairman and Gentlemen:

It gives me great pleasure to be able to appear before you this evening, to clear up, if I can, the general skepticism which seems to exist in connection with the manufacture of coal tar dyes in the United States.

DYE INDUSTRY IN THE U. S. FOR 30 YEARS

That there is such an industry in the United States is a fact and has been for over thirty years. That we cannot compare with Germany in magnitude is of course true, and that we shall be able to increase our production in the near future to take over all of the colors now supplied by Germany is also manifestly impossible, but that it is possible to increase the American production very materially is a fact, depending on certain conditions of which I shall speak later. That there has been more or less prejudice against dyes made in America is also true, and these dyes are fully as good as any made in Europe, although it has been a struggle to prove that the latter statement is absolutely true. Even at this late day there are people who would always give the preference to European dyes at the same price and quality, if they had an opportunity to do so, and they are abetted in their belief very naturally by the European representatives.

Only a few days ago, among other letters we have received asking about the manufacture of dyes in this country, was one from a very substantial trade journal which circulates largely among the textile mills. Among other things it says: "No one believes that the American dyestuff manufacturer can compete with the German. The Germans are counted wizards in dyestuff chemistry and I doubt if you could interest a great number of manufacturers in a domestic product at the same price as quoted on exactly the same thing from Germany." After a couple of pages of such argument it finally suggests that we take up the matter of advertising with them to change the sentiment of the buyers, which is very naive to say the least.

But the point is, if a journal with the influence of this one should express such sentiments among its subscribers, how unfair it would be to the American manufacturers of dyes, and it is simply an instance of one of the small things against which we are struggling. On the other hand, in the past few weeks we are encouraged by numerous letters from actual consumers of dyes, among them some of the largest textile mills in the country, complimenting us upon the way we have been handling our products during the present abnormal conditions, and advising us that they would in the future give their preference to American colors whenever we are able to offer them in competititon with foreign colors; *i. e.*, when we can supply them with the quantity of colors consumed, which hitherto we have not been able to do by reason of not having a production sufficiently large to take care of all the trade. So life does have its compensations and the American dyestuff industry from now on starts out on an equal footing with the German industry, as far as the good-will of the consumers is concerned. It is therefore only a question of being able to produce a large enough quantity at competitive prices to insure a large proportion of the business of the United States for the American manufacturers.

Barely two months ago a comparatively small percentage of the population of the United States knew anything about aniline dyes or dyestuffs, those who did know something being mainly connected with industries which used these products. Even those who did use them had only a vague idea, as a rule, what they were and their source, except in a general way, that they were made from coal tar and that Europe was the principal source of supply. They were even regarded by a large percentage of the consumers as a mere detail of their business, and were put in among the sundries with such items as oil, soap, and I might almost say paper, string, and such miscellaneous supplies, notwithstanding that it requires the highest order of scientific training to produce these colors and a long experience and knowledge of them in order to sell them successfully. The average dyestuff salesman was received only with tolerance and usually referred to some minor employee for his interview. Suddenly something happened. A great war was declared, and the great source of supply was one of the principal nations involved. Some buyer, more intelligent than the ordinary one, discerned that the stock of dyestuffs would be more or less limited if not entirely cut off under these conditions, and immediately made attempts to secure a good supply for his future wants. The news soon spread among others until there was a general scramble for dyestuffs and men who ordinarily gave the matter very little attention are now looking after it personally, and interviewing and corresponding with the heads of such firms as they think can accommodate them. The newspapers took up the matter and published columns of more or less accurate information as to the situation. The general public was therefore given an idea of what was going on, and now know more of the source and supply of aniline products than they ever knew before.

The unfortunate conditions now prevailing have at least been of some good in demonstrating to our people that they should be as independent as possible of other nations in connection with their supply of such products as are needed in this country, and there is now a general demand that the production of aniline dyes as one item should be immediately developed to such an extent that we may be independent of all other nations.

The serious question now therefore is whether or not such an industry can be developed to such an extent, and this question can be answered only by some extended and more or less superficial explanation of conditions. It is not my intention to put before you a scientific or technical paper on the subject, as most of you are more or less familiar with the general conditions surrounding the manufacture of these products, or at least can easily read up the details. I do wish to give you, however, a practical statement of the facts so that you may see why the industry has not developed in this country as it has in Europe, more particularly in Germany, for other nations are no further advanced than are the United States.

RAW MATERIALS FOR DYES

Aniline is a product of coal tar, that is, coal tar is the primary raw material from which colors are produced, and it was obtained originally in the manufacture of coal gas; but recently the coke ovens used for making hard coke have furnished a large and constantly increasing quantity.

The first distillates are such products as benzole, toluole, xylole, phenol (carbolic acid), naphthalene, anthracene, etc., and these are produced largely in the United States as well as in Germany; benzole, for instance, which is probably the most important of the group, is not only the base for the manufacture of the intermediate products of aniline dyes, but is also used largely as a solvent in place of benzine and gasoline, and in fact, in Europe is largely used as a fuel for automobiles as a substitute for the same products. The prices at which it sells in this country are practically the same as in Europe, as are also the prices of the other distillates first mentioned. Up to now, the supply has kept pace with the demand, and there is no overproduction, but if the manufacture of dyes is to be considerably extended it will then be also necessary to extend the production of benzole which can be done in the course of time by substituting by-product coke ovens for those that do not at present recover their benzole. This, however, hinges on the ability to make a profit on this recovery, so that there is a chance that the price of benzole may increase to some extent.

Another base of importance is naphthalene, which is made largely because there is a great demand for it, the consumption in the United States being upwards of nine or ten million pounds, not alone for the manufacture of dyes but more as a moth preventive. Of the quantity consumed here about one-third is produced in the United States while the balance comes about equally from Germany and England.

It is evident, therefore, that the United States starts out on an even basis with Europe as far as the supply of the first raw materials is concerned, and that the natural resources of this country are available for an increase in the products which are manufactured from this source. So, in the beginning, we are as well placed for raw material here as they are in Germany; in other words, this is not a hot-house industry as some people have claimed, but is a part of the natural resources of the United States.

From these distillates are manufactured what we call intermediate products such as nitro-benzole, aniline oil, aniline salts, toluidine, xylidine, cumidine, benzidine, binitro-benzole, nitrobenzole, sulfo-acids, and a host of others.

INTERMEDIATE PRODUCTS LACKING

It is here that the first check in the economical manufacture of aniline dyes is encountered, for the reason that with one or two exceptions, which I will mention later, none of these intermediate products are manufactured in the United States because up to now there has not been a large enough demand for them to make their manufacture economically possible. On the other hand, Europe—Germany particularly— has so developed the demand for these intermediate products that many plants have been established for their manufacture, most of them specializing on certain compounds, so that in the aggregate they are all produced on the most economical basis. Up to within recent years, few of the aniline dye manufacturers made these products themselves, but depended largely on the aforementioned so-called specializing factories for their supplies; this is now changing, and some of the large color manufacturers are now making the principal intermediate products themselves, although none of them make everything which they use. It is then very necessary, if the United States is to be independent of Germany, that these intermediate products be manufactured on a large scale in this country, and it is here that we ask the Government to start in with a sufficient protective duty to allow the business to be developed. The present duty of 10 per cent, which was put on only in the last tariff bill, is not really sufficient for the purpose. As the group was duty-free previously, there was no incentive to begin their manufacture here.

ANILINE OIL

One exception which is made here is aniline oil, the manufacture of which was commenced about three years ago. The quantity now produced is about one-quarter and perhaps more of the total consumption of the United States, taking oil and salts as one product. The quality is very satisfactory as compared with the German and English products, and has been used by our own factory in the manufacture of aniline dyes since the beginning; in fact, if it were not being produced in this country at the present time the American dye manufacturers would not be able to continue to run as they would be unable to obtain supplies from Europe. As a result, manufacturers here are able to relieve the scarcity of aniline dyes, and have thus been of great benefit to American consumers. They will be a great factor in this relief as long as these unfortunate war conditions continue, so illustrating the great benefit to the people at large in having this class of products manufactured here, entirely independent of Europe.

Unfortunately, however, the commercial side of the manufacture of aniline oil has not been so satisfactory. In the beginning the manufacturers had no protection in the way of duty and were compelled to compete on an even basis with Europe, which could not be done successfully. They did, however, succeed in securing a duty of 10 per cent under the present tariff, which went into effect in October, 1913, but unfortunately this did not avail them anything in the beginning because the convention which controls the production of aniline oil in Europe immediately reduced their prices 10 per cent to offset our duty, so that we were no better off than before. This is a sample of what is called unfair competition on the part of European firms in their attempt to prevent the increase of the aniline industry in this country, but it could be readily checked if our Government would incorporate in their tariff what is known as the "dumping" clause, which would forbid the importation into and the selling in the United States of any product at a less price than it is sold in the country where it is produced. In spite of this check, however, the American manufacturers will continue the manufacture of oil, hoping that conditions will change in the near future so that they may be able to work at a profit. When this object is attained their plans are then to take up the manufacture of other intermediate products, until everything necessary is finally manufactured here. As a matter of further interest, I might say that our own factory in Buffalo made aniline oil thirty years ago, but we were obliged to give up its manufacture at that time owing to inability to secure benzole, which situation is, however, now changed, as it should be possible to obtain sufficient benzole to continue the manufacture under advantageous conditions.

NITRO-BENZOLE AND CARBOLIC ACID

The other exception to my statement that these intermediate products are not manufactured here is nitro-benzole, known also as crude oil of myrbane, which is in some demand from outside industries as well as the aniline industry, but not to so large an extent as aniline oil, and which is made here from time to time as conditions warrant; *i. e.*, when it can be made at a profit in competition with Europe.

There is another demand springing up for these intermediate products, which may increase their consumption to such an extent that there will be a large demand entirely outside of the aniline industry, *e. g.*, in the manufacture of smokeless powder and other explosives, the makers of which are now using such products as diphenylamine, tri-nitro-toluole, nitro-benzole, pyridine, nitro-naphthaline, etc. This will finally create a demand which will necessitate their manufacture in this country as a matter of safety, for if the Government depends on explosives made from these materials, it will in self-defense have to create some sort of subsidy or tariff protection, making it possible for their manufacture irrespective of European competition. This is also true of carbolic acid, which is a primary coal tar product and which is used in the manufacture of picric acid, and explosives used by the Government. Carbolic acid not being manufactured here at present to any extent, is now practically unobtainable from Germany or England since they have placed an embargo on this product.

NUMBER OF DYES MADE IN UNITED STATES

From these so-called intermediate products we then come to the manufacture of the actual aniline dye as sold in commerce, and their number is voluminous and complex. My good friend, Dr. Hesse, for instance, recently stated in a published lecture that there were some nine hundred different manufactured products, most of them as different each from the other as a pair of shoes is from a pair of socks. Of these nine hundred he observed that some seventy-six are now made in this country, but that this number is apparently not sufficient to meet the users' demand, in which statement I am quite ready to agree with him, except that we now make nearly one hundred types, which is more than he gives us credit for making. I will say, however, that of these nine hundred original types a great many are obsolete and probably we could get along quite well with a much less number, but as the one hundred made in America are all live types and those which can be manufactued regularly, you will see we are making really a much larger percentage of the total than is apparent at first glance. I might also venture the statement that with the hundred or so types already manufactured here together with perhaps a few more which we would be prepared to take up on short notice, we would be able to furnish the American consumers perhaps ninety per cent of their color demands (speaking now of types or shades and not of quantity), the other ten per cent, which we could not furnish, being such products as alizarines, indigo and patented specialties requiring large installations which it would take a long time to complete.

It would perhaps be interesting in connection with these colors to give a hasty sketch of their beginning and development into the great chemical industry of Germany, with its investment of millions of dollars and employment of thousands of people.

HISTORY OF DYE INDUSTRY

The first color discovered was mauve, a sort of violet, by Perkin in 1856; then followed magenta and fuchsine in the same year, and a small establishment for the manufacture of the same in England, which was not, however, very successful. In 1862 came the discovery of Soluble or Water Blues, then Hoffman's Violet about 1863, Bismarck Brown in 1863, Naphthol or Martius Yellow in 1864, and the Nigrosines in 1867.

It was about this period that the Germans became actively interested in these products, and commenced their patient, intelligent, and careful researches into the subject, which later resulted in most wonderful discoveries and the development of this industry in their country.

Then followed the discovery of Orange, Fast Red, Chrysoidine, Malachite Green, Ponceau (Scarlet), Methylene Blue, Eosines, and Metanil Yellow about the years 1875, 1876, 1877 and 1878, and the manufacture then became one of recognized merit and importance.

After 1880 followed in rapid succession the discoveries of Auramine in 1883, Tartrazine in 1884, Benzo Purpurine in 1884, Congo Red in 1885, Benzo Azurine in 1885, Naphthol Black in 1885, Diamine Red in 1886, Rhodamine in 1887, to mention only a few of the best known and most successful colors.

From 1880 to 1890 might be called the golden period of the business. Just prior to that time alizarine had been discovered, red in 1871, blue in 1877, patented, and successfully produced and sold at high prices with correspondingly large profits. It was about that time that our German friends discovered the advantage of securing an exclusive market in the United States through their patents which enables them to sell at high prices here, although continuing the manufacture in Germany. The profits were enormous from such patented products as alizarine, benzo-purpurine, diamine red and other direct dyeing cotton colors, Auramine, Rhodamine, Tartrazine, and other such colors, which were discovered and put on the market in that period, and put the German industry immediately on such a high pinnacle of success that it has continued until the present time.

In the nineties came the discovery of such important products as direct blacks for cotton, and acid and chrome blacks for wool, the total consumption of these blacks being much larger than all the other colors combined.

Also at this same period began the first of the patents on synthetic indigo, of which there are many. It was finally put on the market at a tremendous expenditure, and has been a commercial success only in the past few years, though it has now practically replaced the natural indigo.

I might say in connection with the development of colors, that in the nineties came also the development of such pharmaceutical products as phenacetine, antipyrin, etc., which paid enormous profits to the manufacturers and which were also controlled by patents.

GERMAN INVESTMENTS IN DYE INDUSTRY

Such, then, is the wonderful development of the coal tar industry, there being invested at this time in Germany something like $400,000,000, probably more, employing some 50,000 people. Some of the factories pay dividends of 25 to 30 per cent, after charging off a third of their profits to sinking funds for the erection of new plants and for other such purposes. This latter has been done for so long a period that most of the present property and plants do not appear on the books at all as assets, but have been built from the surplus profits. This statement is made on the basis of a balance sheet for 1913 issued by one of the great factories, which has a capital of 55,000,000 Marks, but whose stock is selling for over six times par value, showing that the actual capital in the business was at least four times the shares issued, or some 200,000,000 Marks. On a capitalization of 55,000,000 Marks they showed a profit of 25,000,000, or nearly 50 per cent, one-third of which was written off from their real estate and plant account, leaving about 16,000,000 Marks from which they paid a dividend of 28 per cent. Assuming that I am correct in my estimate of some $400,000,000 being invested in the industry in Germany and assuming that a fair proportion of their production is shipped to the United States, it would mean that if the United States were to develop this industry to take care of all their consumption here, they would need millions of dollars and would need to employ thousands of people, which will give you an idea of the magnitude of the business that it is now proposed that we establish here to its full extent.

VALUE OF DYES IMPORTED

It might be interesting at this point to give you the value of the aniline products imported into the United States from these European factories, the figures being for 1913: Aniline dyes, about $7,000,000; indigo, $1,000,000; alizarines, $1,500,000; a total of about $9,500,000, these figures being, however, cost prices. When the American duty of 30 per cent is added on aniline dyes, and further amounts added for expenses and profits on their sale here, it means that the American consumers are really paying something like $12,000,000 for their supplies, not counting the colors produced in America, which may perhaps reach about $2,000,000, the production in America being some 15 to 20 per cent of the total consumption. These figures do not include the importation of pharmaceutical products which are made from coal tar and which is in itself a large business.

Our German friends are entitled to all the benefits which have accrued to them by reason of their shrewd, intelligent, and careful attention to this industry, but with such a statement as the above, does it not seem as if they had had enough and that it is now time for the United States to participate in this great industry when they are so well prepared to do so by having as good, if not better, natural resources than has Germany, and being consumers of so large a proportion of the German products? We must admit at once, however, that the United States cannot compete with the German manufacturers under normal conditions, *first*, because they have a great advantage in capital, experience, and the general advantages of everything that goes with a successful and enormous business; and *second*, because the actual expenses of producing in Germany through labor conditions, and so forth, are much less in this country, so that some way must be devised to put the United States on a competing basis. Two things are necessary for this.

NEED OF PROTECTIVE TARIFF

First, a sufficient protective tariff, which does not necessarily mean, by the way, an increased price to consumers, although many people seem to think so. For instance, the *Scientific American* of September 26th falls into this common error: it states that with an average importation of about $6,000,000 worth of coal tar dyes in the last thirty years we have a total importation of $180,000,000 during that period, and assumes that had duties been 10 per cent higher it would have meant that a total of $18,000,000 would have been paid as an insurance premium against the possible event of a war such as is now disturbing commerce. Even if the *Scientific American* were correct in the statement that $18,000,000 would have been paid as an insurance premium in thirty years, this really would be cheap insurance compared with the enormous value of the colored goods manufactured, assuming that the goods could not have been manufactured without the colors, which is almost the situation as it stands to-day if colors are not soon obtained, in the necessary quantities. When I speak of goods in which aniline dyes are used, I mean the whole range including textiles, leather, paper, silk, paints, and the hundred and one other dyed manufactured products.

In my opinion, however, based on experience, just the contrary to the *Scientific American* opinion is true, for the reason that a higher tariff would have stimulated production and competition, and competition always controls the price. This is shown clearly by actual facts; *e. g.*, on indigo and alizarine colors there is no duty, and as a consequence they are not made here. Theoretically, therefore, they should be sold very cheap, but as a matter of fact, by reason of no competition here, they are controlled by conventions in Europe which make a uniform price so that consumers are unquestionably paying more than if such products were made here in competition. On the other hand, take for instance direct cotton black, an aniline dye which has a protective duty of 30 per cent; it is made in this country in large quantities and the Europeans have been obliged to reduce their selling price in this country to less than that in Europe, so that American consumers are enjoying prices as low as 17 to 18 cents for a color which sells at from 22 cents and upwards in Europe under normal conditions.

Does any one believe that the low prices would have been made in this country were it not for the competition here, and does it not therefore prove that competition here regulates the price and that it is not so much a question of duty? The American manufacturers do not want such a high duty, but they do want enough to equalize the difference in manufacturing conditions between this country and Europe and they want protection against the "unfair competition" referred to in my remarks in connection with aniline oil; in other words, the inclusion of the so-called "dumping" clause, and with a proper tariff on these lines the business could be successfully developed. If we could get our intermediate materials at the prices paid by the Germans, and then secure for our colors the prices obtained by the Germans for finished colors in other countries, plus the actual American duty, the problem would be solved, for this actual American duty, if sufficient, would cover our extra cost of manufacturing and put us in the exact position of the Germans as far as our selling prices are concerned.

NEED OF CHANGE IN PATENT LAWS

Second, our patent laws must be modified, so as to require the manufacture in the United States of all those articles for which U. S. patents are issued. England has within the past few years made such changes in her patent laws, and Germany has always required the manufacture of patented products in her own country. Her present law reads in general that the owner of a patent must work the invention to an adequate extent in Germany or at all events do all that is necessary to secure such working, and if not, then if the public interest is such that the granting of permission to others to use the invention appears needful, that is done by making some arrangement with the owner of the patent so that he receives adequate compensation—but the manufacture of the product itself is insured for Germany. About 1909 a similar clause was threatened in the patent laws of this country, and to head off such action Germany negotiated a treaty with the United States by which the German working clause was made inoperative on American inventions; in other words, in return for the United States allowing Germany to continue to manufacture her products in Germany and export them to the United States, the United States was allowed a similar latitude in exporting her patented products into Germany, but whether or not the financial results of this treaty were beneficial to the United States is a question; it certainly did not work out to the benefit of the United States as far as coal tar products are concerned.

In what I have already termed the golden period of the industry, there was from 1880 to 1883 a duty of 35 per cent *ad valorem* and 50 cents per lb. specific, which gave ample protection to the industry. As a consequence there were nine or ten factories in the United States, and the prospect of becoming independent of other nations for our supply of the aniline products was bright indeed, but the tariff act of July 1, 1883 abolished the specific duty of 50 cents per lb., leaving only the *ad valorem* duty of 35 per cent, and fixed a 20 per cent duty on the intermediate products, which left only a net protection of 15 per cent and immediately checked the industry here. No new factories were started, and within one year after the new tariff took effect five of those already established were forced out of business, leaving only four to continue the work. Those four would have gladly followed their example, but as they had invested large sums of money in plants which would be an entire loss if abandoned, they decided to continue to operate their factories, hoping for more favorable legislation in the future. Thus far they have been bitterly disappointed, and no tariff since that time has given them sufficient protection to develop their business to any large extent. Of course a specific duty of 50 cents in those days was not abnormal as the selling prices of the colors were so much higher than at present, and if a proper duty had been continued it would have had the same beneficial effect, but the abandonment of a sufficient duty has left open the admission of colors on a basis which really gives no protection at all.

In addition to the protective question as a stimulant to the creation of the dye industry in America, if the Government had in the eighties required the manufacture in this country of all products for which they issued patents, then it would have at once created a large industry here, for the European patentees would have been forced to build branch factories in the U. S. These factories would undoubtedly have developed other products even though they had originally been erected only for the manufacture of patented articles, and while this would not have helped the then American factories it would at the same time have inevitably created a large industry with beneficent results to the country at large.

As I have stated, there are now four factories in the United States manufacturing aniline dyes, our own factory having been established in 1879. While of slow development, it has been successful to the extent that it has kept in business and now manufactures practically all of the seventy-six different colors mentioned by Dr. Hesse, or to be correct, the one hundred, to which I referred in the beginning of my remarks, these colors being all of the original colors such as Bismarck Brown, Magenta, Chrysoidine, Fast Red, Water or Soluble Blues, Eosines, Nigrosines, a comprehensive line of direct dyeing cotton colors, and a comprehensive line of acid and chrome colors for wool and silk. The list could easily be extended to the manufacture of practically all of the necessary colors now demanded and not covered by patents, thus giving the consumer a large variety and insuring practical independence of Europe under any conditions. The resulting business would be large, except in comparison with the great German industries, which stand alone in their magnitude.

PRESENT WORK OF AMERICAN PLANTS

All of the American factories will continue to manufacture colors to the best of their ability, but they cannot promise any extensive increase in their production without the support of the Government in the line of tariff protection, and incidentally, the change in the patent laws. The latter, however, are not now quite so important as to colors because many of the original patents have expired and we are free to manufacture a large line of colors provided it is made commercially possible for us to do so, we having already demonstrated our ability as far as experience and willingness are concerned. I might mention that our own factory in Buffalo, known as the "Schoellkopf Aniline Works," was the pioneer in the manufacture of such products as nitro-benzole, nitro-toluole, binitrotoluole, binitro-benzole, aniline oil, aniline salts, dimethylaniline, and quite a range of sulfo-acids, some of them of our own invention, which are necessary for the manufacture of both acid and direct colors. We have also made such products as pure carbolic acid and pure naphthalene, but were obliged to give them up as well as the others because we could not compete with the European manufacturers; we are now hoping that they can be taken up again either by us or by possible manufacturers of intermediate products and their manufacture continued successfully in this country. Under the present abnormal conditions our factory is again making some of these products in order to keep in operation, since it is not a question of price but of ability to manufacture aniline dyes at almost any cost, such is the demand. But whenever conditions become more normal we shall necessarily have to give up the manufacture of these intermediate products for the same reason that we had to give them up before, *viz.*, that we can purchase them in Europe for less than we can manufacture them here.

I might mention further that our factories in Buffalo are still controlled and directed by Mr. J. F. Schoellkopf, who originally established them, being assisted a little later by his brother, Mr. C. P. Hugo Schoellkopf, so that they have had nearly thirty-five years of continuous experience in the manufacture of aniline products, and are fully competent to continue the manufacture in a large way, should favorable conditions develop.

This paper is not intended to appeal for sympathy or help from the Government or from American consumers because we happen to be so placed for the past few years that we could not develop our business as it might have been developed under different conditions, and the American factories even as they are, are prosperous and quite able to take care of themselves up to a certain point; but it is intended to show that the business cannot be extended to large proportions for the protection of American consumers, except with Government help as to tariff and patent laws, and with the assistance of the consumers themselves, which means giving the American manufacturers the preference wherever possible and assisting them to secure the necessary help from the Government.

Here then is a superficial history of the progress of the aniline industry from its inception to the present time, not only in this country but in Europe, and the situation as related to the present and future manufacture of these products in the United States is fully explained. Will the United States Government continue its indifferent policy of practically allowing this important industry to drift along as heretofore, or will it now wake up and seize the opportunity to make itself independent of all other nations in its supply of coal tar products not only for aniline dyes for commercial purposes, but for pharmaceutical products, which relieve illness and pertain to the health of its inhabitants, and for products for the manufacture of explosives which would be absolutely vital in case of war? The future alone can answer these questions.

ADDENDUM

After reading this paper, in reply to a question as to whether or not any original work had been done by the American dye manufacturers, that is, had they discovered any new products, Mr. Stone stated that sixteen patents had been taken out by the Schoellkopf Works between 1884 and 1903, comprising colors and intermediate products. One of these products, known as Schoellkopf Acid, had been taken up by one of the largest German manufacturers and used extensively by them; another product, Direct Black, had been taken up by another large German factory and also made extensively by them. Both products were used, of course, through arrangements with the Schoellkopf Works.

NEEDS OF THE TEXTILE INDUSTRY

By Alfred L. Lustig

Mr. Chairman, Members and Guests of The American Chemical Society:

I have been asked to say a few words to you on the needs of the textile industry and, as Chairman of the Dyestuff Committee of the National Association of Finishers of Cotton Fabrics, I am glad to have an opportunity to bring our needs to your attention. I would at this point like to state, however, that I am confining my remarks to the situation as it affects the dyer and printer of cotton fabrics (the branch of the industry with which I am most familiar), although I believe that the wool and silk trades are in a condition similar to our own.

As you all know, a very large proportion of the colors used by textile finishers are imported from Europe, mostly from

Germany. Owing to the war, our regular sources of supply are considerably disturbed and many of us question whether, later on, it will be possible to obtain quantities sufficient to keep us going.

When the European War broke out two months ago, two problems presented themselves to the users of coal tar colors:

I—How to secure the necessary colors and supplies to keep our plants going during the war and during the period of reconstruction following the war.

II—Realizing how dependent we have been up till now on the European makers for our supplies of coal tar colors, what steps could be taken to prevent a repetition of the present conditions in the future?

In our desire to secure the necessary supplies to keep our plants going, we undoubtedly tried to get all we could from the importers, who met the unprecedented rush of orders by apportioning the available supplies pro rata and dividing additional importations so as to keep all of us working as far as it was possible.

There has been a good deal of discussion and comment as to the ability of the importers to keep us supplied under present conditions, and there is a grave doubt in my mind whether on some special lines of colors it will be possible to meet our requirements during the next few months. But, on the other hand, I feel that everything possible is being done to facilitate importations and to secure such supplies as can be obtained in Europe, and I believe we shall continue to obtain some colors, at least for a while, unless conditions should unexpectedly change for the worse.

We have had to pay somewhat higher prices and will probably have to pay still more later on. Unfortunately, we have not been able to obtain a proportionate increase for our work in many cases, but we believe that this problem will adjust itself as soon as our present agreements, which, in most cases, were made before the first of August, are completed.

We must acknowledge the unremitting efforts made by the importers of dyestuffs and the exceptional energy, fairness and ability, with which they have handled the situation. Speaking from my own experience, I find that they showed the greatest patience under very trying conditions and worked day and night to meet the emergency.

In order to preserve the stock of colors and supplies, we have asked our customers to coöperate with us and, with their aid, we have been enabled to accomplish a good deal in preserving our color stocks.

Some of us, no doubt, grasped the opportunity to check all unnecessary waste in our own plants, which undoubtedly has also helped the situation materially.

Some of us have proceeded to replace imported coal tar colors with products of domestic manufacture. This is true to a limited extent in the use of various dyewood extracts in place of alizarines and in some cases pigments have been substituted for vat colors in printing shirting fabrics. Many experiments are being made in dye houses, trying out methods which would enable the dyer to use dyewoods and other available materials for some shades, where in the recent past coal tar colors have been used.

There is also a tendency on the part of the designers to adapt themselves to the present conditions by developing styles that can be executed without the use of coal tar colors. I refer to the strong tendency for black and white effects in printing, which can be produced with logwood; also the probability of a strongly increased demand for white goods. With all these attempts to preserve our stock of coal tar colors, with a few cases of possible substitutions and the changes of style, we are still confronted by the fact that most of us have supplies to last us for a short time only. If importations cease for any considerable length of time, we shall be obliged to curtail production and later on, in many cases, shut our plants down completely.

Having shown you the immediate effect of the conditions brought about by the European war on our industry, I shall now take up the second problem: What steps can be taken to prevent a repetition of the present conditions in the future? There seems to be only one answer to this—encourage the development of the coal tar color industry in this country.

We all know that a limited number of these products have been made here for a number of years, but we are under the impression that so far the industry has not been in a very flourishing condition. The first step, the tar distillation, had not been worked out successfully until within the last few years and our color manufacturers have depended on Europe almost exclusively for the intermediate products required to produce the finished article.

Their profit was in the possible margin between the duty on intermediate products and the duty on the finished colors, minus the cost of manufacture. I have heard it stated that this margin is not sufficient to encourage capital to embark in this branch of industry.

The next step would seem to be an increase in the duty on intermediate products and an increased margin between the duty on intermediate products and the duty on finished colors. Owing to the possibility of a change in tariff after every national election, there could be no absolute dependence on the conditions established through this method.

Then, there is a question of patents to be considered and, though hundreds of these have expired, the industry is progressing continuously and patents on a great many of the most desirable products are undoubtedly still in force. I believe, however, that with sufficient encouragement, the industry would soon attract the attention of the chemists of this country and that our research laboratories would develop new products quite as they are being worked out in Europe at the present time.

There are several ways in which the textile manufacturer can help the development of this industry. Under all ordinary methods of competition, the manufacturer will buy his products at the lowest price. It is quite conceivable that if the manufacture of certain products is taken up by domestic plants it might be necessary to pay temporarily a little higher price for the domestic article, in order to allow the development and smoothing out of these particular processes; but, later on, after the manufacture of these products is thoroughly developed, I feel that domestic competition and increased efficiency will tend to lower the prices. This has been proven in the products which are being produced in this country on a large scale and which, I am told, are meeting foreign competition quite successfully.

The textile finisher would have to sacrifice temporarily in some directions, in order to accomplish the greatest good for all, which would be a gradual development of the coal tar industry in the United States. Most of the colors which we use in our processes, representing as they do in many cases the highest development of synthetic chemistry, would be among the very last ones to be manufactured here. And yet I, for one, feel that it would be good business judgment on our part to bear additional financial burdens for some years to come, in order to help to establish an American coal tar industry, and in this way ultimately benefit ourselves.

I understand that the coal tar color manufacturers of Germany have in the past given this matter some consideration and, while I am convinced that we have the ability and energy to develop the industry, I believe that by coöperation between the German color manufacturers and those interested in developing the industry here we could gain years of time, save large sums of money and could establish the industry under the most favorable conditions.

The German people will require all their financial resources to repair the damages caused by the present war; but they can furnish us with patent licenses and with some experts, which would form a nucleus for the elaborate steps needed to work out this problem. I believe that by the resulting coöperation with the European manufacturers who, at the proper moment, might be induced to enter this field, we could help to establish the industry here and in this manner prevent a recurrence of the conditions which jeopardize textile interests at the present time. This might be done irrespective of material changes in our laws, such as, the amendment of patent laws, changes of tariff, etc., which are already being given serious consideration.

I have not attempted to illustrate the importance of textile industry by statistics. The value of the coal tar colors used is only a fraction of the value of the finished textiles and the percentage of the coal tar colors used in our industry is only a fraction of the total amount of coal tar derivatives used in this country in various lines of activity. But, I believe that the same argument, which I have tried to apply to our industry, could be successfully extended to the dyeing and finishing of other textiles and in a general way could be further applied to other industries using coal tar derivatives.

THE APPONAUG COMPANY
APPONAUG, R. I.

THE POSITION OF THE AMERICAN TAR DISTILLER

By D. W. JAYNE

Dr. Rogers asked me to respond to the question "Why doesn't the American tar distiller work up his coal tar products or sell them for the manufacture of dyestuffs?" in this discussion, and referred to the paper presented before the Berlin Congress, in 1903, by my father. I want to quote the opening paragraphs of that paper:

"The coal-tar industry, especially the manufacture of the more refined products, has not reached in the United States that degree of development which characterizes the industry of Europe, and which should be commensurate with the wealth and population of the country.

"The chief reason for this backward condition has been the *scarcity of the raw material*, the coal tar itself, due to the very general use of petroleum and electricity for illumination, and also to the large production of oil and water gas."

In the decade since this was written conditions have changed so that today it is no longer a question of the raw materials.

This subject now divides itself into two parts, under each of which the tar distiller must take into account two considerations:

I—Why doesn't the tar distiller work up his products to sell to others for the manufacture of dyestuffs?

1—Can he get a better return in dollars and cents for the separated products than for the straight distillates?

2—Has he a real demand for specific separated products by manufacturers of dyestuffs, which will assure him a constant outlet for the products if plants are erected for their recovery?

II—Why doesn't the tar distiller work up his products and manufacture the dyestuffs himself?

1—Must he find outlets for excess material now produced or to be produced?

2—Does he believe that a complete industry when established would be profitable, and is he willing to operate at no return and to invest millions based on the belief of ultimate success?

You will understand at once that all of these considerations are purely commercial ones.

Let us first realize that there are four crude coal-tar products which constitute the bulk of the material used in dye manufacture: namely, benzol, naphthalene, anthracene and phenol. Of these, but naphthalene and anthracene concern the distiller of tar, as neither benzol nor phenol occur in American tars in sufficient amount to be considered a factor by the tar distiller. Benzol and its homologues have been refined for years and available to anyone considering the manufacture of intermediate products: phenol would have to be made synthetically from benzol to obtain sufficient quantities, so that we can pass over these two basic products in this discussion.

Both naphthalene and anthracene occur in the creosote oil fraction of tar. Creosote oil finds a ready sale here, the United States consumption being about two and one-half times the production, and it is evident that naphthalene and anthracene separated from the oil must be valued at the selling price of the oil. Starting at this value, it can be shown that, considering manufacturing costs and investment, the production of these materials in such state as is required by the manufacturer of dyestuff intermediates, does not give an adequate return when the products are sold at the prices which have prevailed on them when imported. This statement is not based on generalities or theory, but on experience, for we do produce certain amounts of refined naphthalene here, and know this condition accurately. Hence, under conditions prevailing up to the present, it has been evident to the tar distiller that he could not get a better return for the separated products than for the straight distillates.

It is but just to point out at this time the distinction between the *coal-tar* industry and the *coal-tar chemical* industry, which differentiates the production and use of tar, oils and pitch, etc., from that of the dyestuffs and drugs. While it is true that Germany has a highly developed coal-tar *chemical* industry, it is but little known or realized that the United States has developed the *coal-tar* industry to extents unthought of in Germany. Remember that an average tar yields 70 per cent of pitch and that in Europe, substantially the only use they make of this pitch is for fuel, while here over 90 per cent of the pitch is used in roofing, waterproofing and road making, and the development of the industry by the tar distiller is made evident.

So far there has been no real demand from dyestuff manufacturers for the separated tar products. The present dye manufacturers in this country have made only lines of dyes for special fields, starting with the so-called intermediate products, and they apparently did not contemplate the manufacture of those intermediates, so that their inquiries of the American tar distiller were entirely for intermediates such as anilin oil, beta naphthol, etc., which inquiries naturally would bring before the distiller the consideration of the other side of this subject, Why does not he work up these products himself?

But here the first consideration is providing outlets for excess materials. Up to the present there has not yet been an excess of the basic materials so that this inducement did not exist for the tar distiller. It must also be remembered that the products of tar which can be used in the manufacture of dyestuffs form but a small percentage of the tar and even if all of such products were separated for the manufacture of dyestuffs, there would still be over 90 per cent of the original tar to be disposed of by the distiller in his regular channels. And it must not be forgotten that the use of heavy chemicals, such as acids and alkalies, enters into the manufacture of dyestuffs in volumes largely exceeding the coal tar products involved, so that any inducement to the tar distiller to enter this field is secondary to the inducements offered the manufacturer of heavy chemicals.

The last consideration is that of the ultimate success of a large industry covering the entire field of dyestuffs. The magnitude of the project is sufficient reason why the tar distiller has not acted upon it, for to those who have given the question serious thought, it has become evident that only by duplicating the scale on which the foreign manufacture is carried on can we hope to finally compete with the established factories of Germany, and what prospect of growing to this magnitude would we have without protection during the years of growth? I mean by protection, not only adequate tariff protection, but also adequate protection against competitive methods aimed to crush the infant industry. Without such protection no man or group of men, however strong commercially, has yet had the temerity to plan for the investment of the millions of dollars required to carry it through. And further, to make such a project successful, the coöperation of the textile trade, in fact, of all users of dyes, must be given. Not even a feeble indication of such coöperation was displayed before the conditions arose which showed this country's dependence on German dyestuffs.

Whether our industries shall have American-made dyestuffs from American coal-tar products depends largely on the consumers of dyestuffs. Their action or inaction will probably determine the answer.

Barrett Manufacturing Company
Frankford, Philadelphia

RELIEVING THE DYESTUFF CRISIS[1]

By Bernhard C. Hesse

In the two and a half months that have elapsed since the outbreak of the European war there has been much agitation in the press, both lay and technical, for an increased production of coal-tar dyes in the United States. All users of coal-tar dyestuffs have known for as long as 40 years that the principal source of supply is Germany and they have also known of the various attempts made in this country to produce dyes in the United States. Just as the users of dyestuffs will invariably buy in the cheapest market and will not be swayed by motives of patriotism into paying a higher price for a domestic article than they would have to pay for an imported article so do American manufacturers and capitalists invest their money in American ventures which will pay them a profit, and they do not take hold of such enterprises through motives of patriotism only or of philanthropic benevolence toward their fellow man. Business is conducted for financial profit.

It required no imagination whatever to foresee that if for any reason our coal-tar dyestuff supply was shut off from Germany that coal-tar dyes in the United States would become scarce. Nevertheless, American users of dyestuffs have continued to use the imported article. The result is that even a few weeks after the outbreak of European hostilities the users in the United States became clamorous and hysterical and called out loudly for the American chemists to go in and make dyestuffs regardless of whether the American chemists were going to make money or not. The user has suggested to the maker that he increase his facilities, that he go to Congress and get a higher tariff and that he go to Congress for a change in the patent laws; however, the user has, on his part, not made any substantial offer of any effective help throughout these last two months. The chances are that, as in the past, the greatest opponents of increased tariff on dyes would be these self-same users. The users have confined themselves largely to fault-finding with American chemical manufacturers. The users say that their position is acutely distressing and they are facing serious hardships for want of dyestuffs and they want steps taken by others to see that they are never again placed in such position of hardship—no matter what the others may stand to lose.

To date, the suggestions from the users have been merely words and so far as the public is concerned there has been no effective action.

The users themselves decline to participate actively and financially in any dyestuff venture and they further decline to contract with prospective dyestuff manufacturers for even a portion of their requirements. In other words, their position is one of passive criticism—dead weight.

The domestic dyestuff makers are increasing their production as rapidly as circumstances will permit. At or about the end of 1912, 76 different chemical dyes were made in this country; today 100 such are made—in two years a 33 per cent increase; the United States market probably has no fewer than 900 different chemical dyes, each of them in active use, some of them to a very small extent, others to a very large extent and, no doubt, many of each of these could be eliminated and their places taken by others now on the market.

If the dyestuff users wish to encourage the domestic dyestuff makers they can at least disclose to the makers the extent of the market in the United States. The exact chemical dyes on the United States market and their individual consumption and prices paid are known collectively to two different classes. The importers collectively know it and the users collectively know it. It can hardly be expected that the importers are going to hand that information over to prospective makers, that is, to competitors. If the users want increased competition among the makers or want a more assured source of supply, then the least they can do is to place before the dyestuff makers of this country a list of all such dyes as are used in this country and the amount of each that is used annually, together with the price paid therefor. With such information before them those who make dyestuffs in this country can make intelligent provision for expansion of their business. To be sure, the makers could go to each and every user and ask him for the above information, but it is quite sure that that information would be refused. The users would decline to disclose to anyone their consumption of dyestuffs and the amount of their dyestuff account. If the users are really sincere and honest in their statement that they are in a plight and that they really do want increased production of dyes in this country, then the very least that they can do is to make a full and frank disclosure of what the possibilities and probabilities in the United States market are. As said before, there are over 900 different finished dyes that have to be made and before these 900 dyes are made something like 300 substances, themselves not dyes, have to be made; to ask the domestic chemical manufacturers to go down into their pockets for the capital to make each of these 900 dyes and each of these 300 things, themselves not dyes, and then to await the pleasure of the domestic dyestuff user as to whether he will take the goods or not is asking altogether too much from the makers on the part of the users.

If the users are afraid to disclose each to the other how much dye they use and what they pay for it they are certainly in a position to select some bank or trust company as a central confidential depository for such statements and let the bank or trust company make up from these separate statements a combined statement of the market and place that before the manufacturing public. If the dyestuff users will coöperate to that extent it is morally certain that an increase in production of dyes will take place with considerable rapidity. If the users decline to coöperate to this extent it is quite likely that the number of dyes manufactured will increase even in spite of the users, but the rate will be much slower. If the users want the rate of increase speeded up they must contribute their share, and probably a plan like that outlined above is as good as can be devised.

90 William St., New York

CURRENT INDUSTRIAL NEWS

By M. L. Hamlin

THE PRESIDENT'S ADDRESS BEFORE THE CHEMICAL SECTION OF THE BRITISH ASSOCIATION FOR THE ADVANCEMENT OF SCIENCE

The address made by Professor William J. Pope, President of the Chemical Section of the B. A. A. S., is reported in the *Jour. Gas Lighting and Water Sup.*, **127** (1914), 506. The speaker pointed out that the investigator, continually occupied with his own problems, and faced with an ever-increasing mass of technical literature, ordinarily finds little time for reflection

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[1] Also printed in the *Textile Colorist*, Vol. **36**, No. 430 (Oct., 1914).

upon the real meaning of his work, and secures, in general, far too few opportunities of considering in a philosophical sort of way the past, present, and future of his own particular branch of scientific activity. He then proceeded:

"It is not difficult to form a fairly accurate survey of the position to which chemistry had attained a generation—perhaps even a few years—ago. Probably no intellect now existing could pronounce judgment upon the present position of our science in terms which would commend themselves to the historian of the Twenty-first Century. Doubtless even one equipped with a complete knowledge of all that has been achieved, standing on the very frontier of scientific advance and peering into the surrounding darkness, would be quite incompetent to make any adequate forecast of the conquests which will be made by chemical and physical science during the next fifty years. At the same time, chemical history tells us that progress is the result, in large measure, of imperfect attempts to appreciate the present and to forecast the future. I, therefore, propose to lay before you a sketch of the present position of certain branches of chemical knowledge, and to discuss the directions in which progress is to be sought. None of us dare cherish the conviction that his views on such matters are correct; but everyone desirous of contributing towards the development of his science must attempt an appreciation of this kind. The importance to the worker and to the subject of free ventilation and discussion of the point of view taken by the individual can scarcely be overestimated.

"The two sciences of chemistry and physics were at one time included as parts of the larger subject entitled 'Natural Philosophy,' but in the early part of the Nineteenth Century they drew apart. Under the stimulus of Dalton's atomic theory, chemistry developed into a study of the interior of the molecule, and, as a result of the complication of the observed phenomena, progressed from stage to stage as a closely reasoned mass of observed facts and logical conclusions. Physics, less entangled in its infancy with numbers of experimental data which apparently did not admit of quantitative correlation, was developed largely as a branch of applied mathematics. Such achievements of the formal physics of the last century as the mathematical theory of light and the kinetic theory of gases are monuments to the powers of the human intellect.

"The path of chemistry, as an application of pure logical argument to the interpretation of complex masses of observations, thus gradually diverged from that taken by physics as the mathematical treatment of less involved experimental data, though both subjects derived their impetus to development from the speculations of genius. It is interesting to note, however, that during recent years the two sciences which were so sharply distinguished twenty years ago as to lead to mutual misunderstandings, are now converging. Many purely chemical questions have received such full quantitative study that the results are susceptible to attack by the methods of the mathematical physicist, while, on the other hand, the intense complication perceived during the fuller examination of many physical problems has led to their interpretation by the logical argument of the chemist, because the traditional mathematical mode of attack of the physicist has proved powerless to deal with the intricacies exhibited by observed facts.

"The progress of chemistry during the last century has been mainly the result of the coördination of observed facts in accordance with a series of hypotheses each closely related in point of time to the one preceding it. The atomic theory, as enunciated by Dalton in 1803, was a great impetus to chemical investigation, but proved insufficient to embrace all the known facts. It was supplemented in 1813 by Avogadro's theorem—that equal volumes of gases contain the same numbers of molecules at the same temperature and pressure. These two important theoretical developments led to the association of a definite physical meaning with the idea of molecular composition, but ultimately proved insufficient for the interpretation of the ever-increasing mass of chemical knowledge collected under their stimulus.

"A further impetus followed the introduction by Frankland and Kekulé, in 1852 onwards, of the idea of valency and the mode of building-up constitutional formulae. The conception of molecular constitution thus arose as a refinement on the Daltonian notion of molecular composition. In course of time the theoretical scheme once more proved insufficient to accommodate the accumulated facts, until, in 1874, van't Hoff and Le Bel demonstrated the all-important part which molecular configuration plays in the interpretation of certain classes of phenomena known to the organic chemist.

"During the early days of chemical science—those of Dalton's time, and perhaps also those of Frankland and Kekulé—we can believe that chemical theory may have lacked the physical reality which it now seems to us to present. The attitude of our predecessors towards the theoretical interpretation of their observations was rather that described by Plato: 'As when men in a dark cavern judge of external objects by the shadows which they cast into the cavern.' In the writings of the most clear-sighted of our forerunners we can detect an underlying suspicion of a possibility that, at some time or other, the theory by means of which chemical observations are held together may undergo an entire reconstruction. A few years ago Ostwald made a determined attempt to treat our science without the aid of the molecular hypothesis, and, indeed, suggested the desirability of giving the Daltonian atomic theory decent burial.

"The last ten years or so have seen a change in this attitude. The development of organic chemistry has revealed so complete a correspondence between the indications of the conception of molecular constitution and configuration and the observed facts, and recent work on the existence of the molecule, largely in connection with colloids, with radioactivity, and with crystal structure, is so free from ambiguity, that persistence of doubt seems unreasonable. Probably most chemists are prepared to regard the present doctrine of chemical constitution and configuration as proved. Though they may turn a dim vision towards the next great development, they have few misgivings as to the stability of the position which has already been attained."

PATENT MEDICINES IN GREAT BRITAIN

Largely through the efforts of the American Medical Association and through legislation by Congress some progress has been made in the United States in limiting the dangers from the sale and use of secret remedies. The conditions are now worse in Great Britain than in this country, and in 1912 the government appointed a select committee which has just issued an abstract report. It finds [*Science*, **40** (1914), 374] that there is a large and increasing sale of patent and proprietary medicines and appliances and of medicated wines; that this constitutes a grave and wide-spread public evil and that an "intolerable state of things" requires new legislation to deal with it rather than merely the amendment of existing laws. Legislation is recommended as follows:

1—That every medicated wine and every proprietary remedy containing more alcohol than that required for pharmacological purposes be required to state upon the label the proportion of alcohol contained in it.

2—That the advertisement and sale (except the sale by a doctor's order) of medicines purporting to cure the following diseases be prohibited: Cancer, consumption, lupus, deafness, diabetes, paralysis, fits, epilepsy, locomotor ataxia, Bright's disease, rupture (without operation or appliance).

3—That all advertisements of remedies for diseases arising from sexual intercourse or referring to sexual weakness be prohibited.

4—That all advertisements likely to suggest that a medicine is an abortificient be prohibited.

5—That it be a breach of the law to change the composition of a remedy without informing the Department of the proposed change.

6—That fancy names for recognized drugs be subject to regulation.

7—That the period of validity of a name used as a trademark be limited, as in the case of patents and copyrights.

8—That it be a breach of the law to give a false trade description of any remedy, and that the following be a definition of a false trade description: "A statement, design or device regarding any article or preparation, or the drugs or ingredients or substances contained therein, or the curative or therapeutic effect thereof, which is false or misleading in any particular." And that the onus of proof that he had reasonable ground for belief in the truth of any statement by him regarding a remedy, be placed upon the manufacturer or proprietor of such remedy.

9—That it be a breach of the law: (*a*) To enclose with one remedy printed matter recommending another remedy. (*b*) To invite sufferers from any ailment to correspond with the vendor of a remedy. (*c*) To make use of the name of a fictitious person in connection with a remedy. (But it shall be within the power of the Department to permit the exemption of an old established remedy from this provision.) (*d*) To make use of fictitious testimonials. (*e*) To publish a recommendation of a secret remedy by a medical practitioner unless his or her full name, qualifications and address be given. (*f*) To promise to return money paid if a cure is not effected.

BRITISH FOREIGN TRADE IN AUGUST

As would be expected, the trade returns of the United Kingdom for August show a great reduction in both imports and exports. With Germany and Austria-Hungary trade has, of course, been extremely small, and that with other countries has been seriously interfered with. This has arisen more from the effects of the war on the foreign exchanges than from the war itself. During the month the value of the goods imported into Great Britain was $206,000,000, which is $66,000,000 (24.3 per cent) less than was imported during August, 1913 [*Engineering* (London), 98 (1914), 326]. Exports have, however, decreased from $214,000,000 in August, 1913, to $118,000,000 in 1914, the difference amounting to 45.1 per cent. The percentage drop in the value of re-exported goods is almost exactly the same. British imports from Germany have fallen from $9,100,000 in August, 1913, to $950,000 last month. More than half of this reduction —$4,140,000—is accounted for by the diminution in imports of sugar; the figures for this commodity alone were $4,350,000 in August, 1913, as against $210,000 last month. Steel blooms, bars, girders, etc., account for another $7,500,000 reduction, the imports being only $245,000 last month. The total British exports to Germany have diminished from $19,500,000 in August, 1913, to $3,880,000 during August, 1914. The principal item is coal, the amount exported last August having been worth only $368,000, whereas for August, 1913, the figure was $2,320,000. Wool and woolen goods come next, these having fallen off from $3,140,000 to $1,380,000. Cotton yarn accounts for a further reduction of $1,000,000. For iron and steel, the exports last August were $224,000 as compared with $480,000 for the same period last year. The only other item worth mentioning individually is textile machinery, which has fallen off from $293,000 to $195,000. Although these striking figures give a very good idea of the influence of the war on British trade with foreign countries, its full effects are somewhat masked by the fact that the returns include some goods imported and exported before the declaration of war. The Royal Proclamation prohibiting the exportation of certain goods has also affected the figures.

SOME DATA OF GERMAN AND AUSTRIAN FOREIGN TRADE

The following data were published in London *Engineering* 98 (1914), 300, 331, 360. (1*l* = $4.86.)

GERMANY'S EXPORTS OF SEWING AND KNITTING-MACHINES—A Board of Trade bulletin, recently issued, shows that Germany exports sewing and knitting-machines, and parts thereof, to a value of about 2,840,250*l*. per annum, while English exports are valued at 2,367,800*l*. The distribution is peculiar. England has the best of the Indian market, in which her sales amount to 128,550*l*., compared with Germany's 44,500*l*. To the Netherlands, German sales are valued at 78,300*l*., compared with England at 26,100*l*. In Sweden the respective sales are almost exactly reversed. In Belgium, Germany disposes of 117,200*l*. worth of these machines and parts; England sells there only 42,950*l*. worth. However, the tables are almost exactly turned in Spain, which buys from Great Britain to the value of 108,700*l*., and from Germany to the amount of 50,000*l*. Then, again, in Russia, England has a greater trade with sales amounting to 831,700*l*., compared with Germany's 399,300*l*.; but in Italy, Brazil and the Argentine, British business is much smaller than Germany's, as it is also in France, although in the latter country English sales amount to the considerable figure of 218,300*l*. Germany sends England machines and parts to the value of 136,200*l*. German machines find a ready sale in many countries, such as the United States, Mexico, Morocco, Bulgaria, Ecuador, etc., which markets seem to be scarcely touched by English manufacturers.

GERMANY'S EXPORTS OF PHOTOGRAPHIC MATERIALS—The value of the exports of photographic materials from Germany amounted in 1912 to 1,843,600*l*. The most important classes of goods dealt with were lenses, films, and chemicals. Sensitized paper and dry-plates were also exported in considerable, but lesser, quantities. Of photographic chemicals, Germany exported to the United States 72,900*l*. worth; to Russia, 79,950*l*.; and to England, 45,650*l*. Her largest exports of films were to France, which bought to the value of 110,550*l*., England taking 40,350*l*. worth. Next to Russia, Great Britain is Germany's largest customer for sensitized papers, taking nearly 40,000*l*. worth. The most important market for German optical glasses and lenses has been England, which took goods of this class to the value of 104,900*l*. Altogether, Germany sends England about 232,000*l*. worth of photographic goods in the year.

GERMAN AND AUSTRIAN TRADE IN BRASS AND BRASSWARE—Another white paper has recently been issued by the Commercial Intelligence Branch of the Board of Trade relating to the exports of brass and brassware by Germany and Austria. Compared with English exports in these trades, those of her rivals are enormous, though the available figures seem slightly less favorable to the United Kingdom than they actually are, since their figures cover certain articles not included in the English. As far as they form a guide, however, in a recent year, while the United Kingdom exported goods of this class to the amount of 1.6 millions sterling, Austria's exports were 1 million and Germany's nearly 6.5 millions. The principal exports of Germany were: Brass, tombac, and similar alloys, 549,650*l*.; rods, sheets, etc., of same, 1,088,700*l*.; wire of copper alloys, 314,200*l*.; lacquered and other wares of sheet brass, etc., 2,368,200*l*.; wares of copper, tombac, brass, etc., "verniert," colored, coated with nickel, etc., 1,075,000*l*. In many of these articles France and Italy are the largest purchasers from Germany, but in others Great Britain ranks as the largest buyer. In one or two cases Russia is Germany's largest market. Like previous reports, this one gives interesting information on the markets, extracted from consular reports, etc., and all interested in enlarging their business while the opportunity offers would find these well worth perusal.

GERMAN AND AUSTRIAN TRADE IN ANCHORS, GRAPNELS, AND CHAINS—Germany has a considerable foreign trade in anchors and various types of chain both for ship and general use. Her exports in 1913 had a value of 165,700*l*. Excluding bicycle chains, the corresponding trade of Austria-Hungary for 1913 had a value of 11,910*l*. These figures are considerably below that of the United Kingdom for the same class of material, which in 1913 was 687,200*l*. The trade is one, however, with which England is well equipped to deal, and any efforts made at the present time to obtain the German share should have considerable chance of success. The subject is dealt with in one of the memoranda which are being issued by the Commercial Intelligence Branch of the Board of Trade to assist British manufacturers to find new outlets for their material during the war. The tables which are published show that, as far as ships' anchors, grapnels, and cables are concerned, the trade is chiefly in the hands of the United Kingdom, but that there would appear to be small openings for the sale of British-made articles in Russia, Roumania, and Turkey. For chains, other than ships' chains and cables, the United Kingdom holds an exceedingly strong position in the Australian, Indian, South African, Canadian, Japanese, and South American markets, as well as holding a large share of the trade in the Norwegian, Spanish, and Portuguese markets. In the Netherlands, Sweden, France, Russia, Roumania, and the United States there would, however, appear to be a possibility of extending British trade in these goods.

GERMAN RAILROAD MANAGEMENT

In an article in the New York *Railway Age Gazette*, on "German Criticism of State Railway Management," it is said that Germany's State railway management is an oppressive monopoly and a political mistake. Recently this view was expressed at three different industrial congresses, and in one case the indictment was backed by a two-thirds majority. This revolt against railway nationalization comes just at the time when some Americans and Englishmen have begun to see in nationalization an easy, infallible way out of all railway troubles. What aggravates the indictment is that it is mainly directed against the Prussian State system, which of all railway systems in Germany is the most flourishing and efficient. Every charge that is customarily levelled against corporation railway ownership is now (July 19) levelled against the Prussian State system. The main charge is that the Prussian system makes for monopoly and restraint of trade. In committing all the offenses which private corporations commit, the State knows no fear, for against it the public is doubly helpless, and there are no competing roads which can be used to bring the extortionate State to reason. German experience shows that State ownership does not prevent monopoly. Monopoly remains monopoly, even though it is managed by officials, and the State is only the national organ of erring men.

GERMAN CHEMICAL INTERESTS IN RUSSIA

The many factories and subsidiary companies maintained by German chemical firms in Russia will be seriously affected by the war. The *Chemiker-Zeitung* [38 (1914), 1014] publishes a list of the more important of these. The Aktien-Gesellschaft für Anilin-Fabrikation has factories in Moscow and Libau, a subsidiary of the Höchster Farbwerke has headquarters in Moscow, the Chemische Werke Albert maintain factories in Sartana and Taganrog, and the Badische Anilin- und Soda-Fabrik has a large plant in Butirki near which are the Russian works of the Elberfelder Farbenfabriken; in 1906 the Aktien-Gesellschaft Renner, on account of tariff conditions, acquired, together with French and Russian firms, an extract factory in the neighborhood of Moscow; the Chemische Werke Riedel own a large block of the shares of the St. Petersburger A.-G. Pharmakon, and the Berlin firm of Schering has also large Russian interests.

The German iron industry also, according to the *Frankfürter Zeitung*, has important interests in Russia. Among the companies mentioned in this connection are the Milowicer Eisenwerk, the Donnersmarckhkütte, the Oberschlesische Eisenbahnbedarf, the Oberschlesische Eisen-Industrie A.-G., the Metallfabriken Hanke and the Laurahütte.

THE MATCH INDUSTRY IN RUSSIA

The match industry in Russia has undergone a striking evolution since the beginning of the twentieth century. The *Chemiker-Zeitung* [38 (1914), 1000] states that while in the year 1902 ten factories manufactured over fifteen million phosphorus matches, in 1907 eleven factories manufactured less than a million, and in 1908 the production stopped almost entirely. Of the so-called mixed factories, manufacturing both phosphorus and safety matches, there were thirty-three in 1902 and in 1911 only two. The number of safety match factories increased in proportion to this decline, growing from eighty-three in 1902 with an output of over two hundred million, to one hundred and thirteen in 1911 with an output of more than three hundred million. The matches exported in 1911 were valued at $675,000.

Russia is rich in wood suitable for matches and the manufacture of match sticks is a peasant house industry in the Government of Wjatka. The exports of these sticks in 1904, 1909 and 1911 amounted in round numbers respectively to $325,000, $274,000 and $179,000.

TEMPERATURE CONDITIONS IN COKE OVENS

An important contribution to the literature of carbonization in coke ovens has lately been made in *Stahl und Eisen* by Professor Oskar Simmersbach, of Breslau. The experiments were carried out in a Koppers regenerative oven, and the temperature conditions existing during the period of carbonization and the composition of the volatile products were carefully determined. The following abstract of the article, with the tables, has appeared in the *Engineering Review*.

The oven was charged with $8^3/_4$ tons of coal containing 22.7 per cent of volatile matter, 6.32 per cent of ash, and 12.1 per cent of water. This yielded 79.86 per cent of coke. The coal was carbonized for a period of 29 hours. The temperature rose gradually during this period, the concluding readings being

COMPOSITION OF THE GAS DURING CARBONIZATION (Per cent by volume)

Hrs. coal carbonized	2	3	4	5	6	7	8	9	10	11	12	13	15	17	19	21	23	25	27	Heating gas
CO_2	3.30	3.0	2.3	2.5	2.2	2.00	1.40	1.90	2.30	1.30	1.50	2.00	1.90	1.80	1.10	1.05	0.80	0.7	1.0	2.1
C_6H_6	1.80	1.5	1.1	1.1	1.0	0.80	0.60	0.50	0.35	0.35	0.35	0.30	0.25	0.10	...	...	...	..	..	..
C_2H_4	4.00	3.5	3.1	3.2	2.8	2.50	2.50	2.00	1.75	2.05	1.85	1.80	1.80	1.90	1.20	1.00	0.60	0.3	0.3	1.8
O_2	1.05	0.8	0.6	0.6	0.5	0.50	0.20	0.20	0.20	0.10	0.20	0.20	0.15	0.25	0.15	0.05	0.05	0.1	0.3	0.6
CO	0.90	1.9	2.9	2.8	3.0	3.95	3.40	3.10	2.80	2.80	4.15	4.10	3.90	4.15	4.70	4.00	3.80	4.9	5.8	4.2
CH_4	36.65	36.1	34.5	34.5	33.6	32.40	33.65	33.45	31.20	32.40	33.40	32.45	33.20	30.60	26.10	21.15	18.95	12.2	4.7	26.2
H_2	42.50	44.6	48.8	47.8	50.1	50.75	53.75	50.55	47.10	51.50	50.65	49.75	53.40	51.60	55.75	58.95	61.90	67.0	70.0	51.7
N_2	10.00	8.6	6.7	7.5	6.8	7.10	3.60	8.30	14.30	9.50	7.90	9.40	5.40	8.60	11.00	13.80	13.90	14.8	17.9	15.4
Min. cal. power (0° C., 760 mm.), calculated per cubic meter	5402	5271	5086	5071	4971	4802	4906	4797	4324	4583	4660	4530	4665	4369	3978	4487	3412	2960	2419	3964

1090° C. at one-fourth the distance from the charging side, 1120° C. in the center, and 920° C. at one-fourth the distance from the discharging side. These temperatures correspond to the center of the carbonized mass. In the gas space above the coal, the finishing temperatures were respectively 870°, 860°, and 810° C. The resulting coke contained 88.53 per cent of carbon, 2.56 per cent of volatile matter, and 8.91 per cent of ash.

THE DISPOSAL OF RESIDUALS IN GAS AND COKE PLANTS

Difficulties are being experienced in England, according to the *Jour. Gas Lighting and Water Sup.*, 127 (1914), 563, both in gas-works and coke-oven plants with regard to the disposal of residuals. Ammoniacal liquor is difficult to dispose of since the usual buyers have been compelled, through force of circumstances, to stop the manufacture of their various products. Consequently they have not had sufficient storage room to accommodate the bulk of liquor offered. Those who make sulfate at their own works are placed in a rather more favorable position. Even though sulfate is not selling well just now, it is not a difficult matter to store it in large quantities, the principal objection being, however, that a large amount of money soon becomes locked up in the form of stocks. The disposal of tar, too, has not been unattended with difficulty. Again, lack of storage accommodation has been an important factor, the large distillers having had to restrict their operations owing partly to the embargo placed upon the export of creosote, and partly to the fact that the demand for pitch has been below normal. As far as benzol is concerned, no difficulty is reported. The increasing use of this product as an automobile fuel has created a good market, and this is particularly noticeable as soon as there is any talk of a petrol famine, or even of a substantial rise in price.

UNITED STATES MINERAL OIL EXPORTS

The *Journal of the Society of Chemical Industry* extracts from the number for August 3, of the *Oil, Paint, and Drug Reporter* the following particulars of exports of mineral oils from the principal customs districts of the United States (representing about 98 per cent of the shipments from all parts) during the twelve months, July 1, 1913, to June 30, 1914:

	Gallons	Value
Crude oil	146,056,086	$6,808,513
Illuminating oil	1,155,809,430	74,374,091
Lubricating and paraffin oils	195,472,181	27,566,378
Naphthas, gasoline, etc	185,578,776	26,568,682
Residuum, gas oil, fuel oil, etc	586,301,600	15,562,192
Total, 1913–14	2,269,218,073	$150,879,856
Total, 1912–13	1,947,746,303	134,514,109

TESTING MOTOR-CARS WITH TOWN GAS

According to the *Scientific American*, in consequence of the comparatively high cost of gasoline, and by way of reducing factory outlay, a number of Detroit makers have taken to testing their motors with town gas instead of with gasoline. It is found that an economy of as much as $80 a day can be effected by some makers. Town gas at 45 c. per 1000 cubic feet is said to be cheaper for the purpose than gasoline at 9 c. a gallon. A comparison of costs reveals that an engine developing 19.04 horsepower consumes 458 cubic feet of gas, which costs 20.61 c. an hour, while 2.24 gallons of gasoline would be required to develop the same power, and the cost would be 33.6 c. an hour with gasoline costing 15 c. a gallon. On one test, it was proved that the cost of town gas works out at 58 per cent of the cost of gasoline.

SPELTER

The United States Geological Survey has recently issued a report that stocks of spelter increased by 23,380 tons in the first half of the year, and reached on July 1st the total of 64,039 tons. In the calendar year 1913 the production on the Continent of Europe was 655,454 net tons, about 150,000 tons being exported to England. The British spelter production was 65,197 tons. It is considered that to furnish 150,000 tons to Great Britain per year would not strain the resources of the United States. The price of spelter rose 1 cent per pound at East St. Louis between August 6th and August 20th.

MINING IN SOUTH AFRICA

The report recently issued by the Royal Commission on Mining in South Africa states, according to *Engineering* (London), 98 (1914), 300, that the coal deposits in South Africa are numerous, but comparatively undeveloped. In 1913 the total output only amounted to 8,800,000 tons, valued at about $10,000,000. The value of the output in diamonds in the Union of South Africa was $55,000,000 in 1913, and in the same year the gold output from the Transvaal was valued at $172,000,000. In regard to cost of production in the gold mines of the Witwatersrand it is said that by calculating the working capacity of two Europeans as equal to that of three natives, it is estimated that if natives at their present cost per shift—*viz.*, $0.76 per head—had to be replaced by Europeans at $2.40—and this appeared to be the minimum wage at which Europeans could live in the Transvaal—out of the fifty-two producing mines for which figures were available, twenty-six would cease to make a profit. If the white laborers replacing natives were paid at the rate of $3.00, about the current rate in Western Australia, where living is cheaper, out of the fifty-two mines, thirty-five would cease to make a profit. The average cost of native labor, $0.76 per shift, includes the cost of food, recruiting and compound expenses, in addition to money-wages. In 1913 the value of gold recovered per ton of ore, reckoned at the rate of $20.64 per fine ounce, was $6.74, in which sum the working costs per ton of ore were $4.35 and the average gross working profit per ton of ore $2.39.

The total amount paid in salaries and wages by the Rand gold-mines was $66,000,000 in 1912, and $63,000,000 in 1913. The average wage of the white employee, excluding the technical and clerical staff, was $1,540 per year. That of the native was $145. If to this latter sum there be added $50 for housing the native and for the rations he receives, the white man, who is employed almost wholly in supervision, will be seen to receive about eight times as much in wage as the native, who does the manual work. The Economic Commission has found that, when allowance is made for the cost of living, the Witwatersrand workman is better off, in a monetary sense, than the workman in Australia and America, and much better off than the workman in Europe.

PLATINUM ORE IN SOUTHERN NEVADA

A deposit of ore, containing the platinum metals in greater quantity, and entirely dissimilar in occurrence to the earlier finds, has recently been discovered in the western portion of Clark County at the property of the Boss Gold Mining Co. This deposit, according to the *Engineering and Mining Journal* 98 (1914), 641, is 10 miles west of Goodsprings, in the Yellow Pine mining district, and only four miles from the California line. The ore varies in thickness from 2 to 10 ft., the average being about 6 ft., and in appearance is a brownish granular mass, showing occasional streaks of hard quartzose material. Both walls of the ore are shattered limestone, and along these walls occurs an encasement of malachite, varying in thickness from a few inches to several feet. The main body of the ore zone carries little copper. An average of the ore, sampled at 5-ft. intervals for 200 ft. along the upper tunnel, gave the following results: Gold, 1.13 oz. per ton; silver, 5.20 oz.; copper, 0.20 per cent. It has since been learned that this ore contains 0.5 to 1 oz. of platinum per ton.

In June, 1914, a winze was started from the upper tunnel following the ore on its dip, and high-grade ore was encountered within a few feet. The appearance of the ore did not change materially except for the occurrence of small masses of greenish talc within the vein. Some of these masses were sufficiently large to be mined separately, and two small shipments, amounting to about one ton, were made, a settlement analysis of which was as follows, platinum not being determined or paid for: Gold, 124.79 oz. per ton; silver, 23.9 oz.; lead, 1.05 per cent; copper, 0.65 per cent; insoluble, 73.2 per cent; sulfur, 3.1 per cent; iron, 6.7 per cent.

On the same control sample of this shipment, the following was the result for metals of the platinum group: Platinum, 99.08 oz. per ton; palladium, 16 oz.; iridium, trace.

It has been fully determined that metals of the platinum group are present in all of the ore thus far developed, apparently as alloys of gold. It would also appear from numerous assays that the platinum metals bear a fixed ratio to the gold content, being in the proportion of about $^2/_3$ oz. platinum to 1 oz. gold. The ore is thoroughly oxidized, no sulfides having as yet been recognized, and the gold alloys have a "rusty" appearance, showing no color after panning until they have been thoroughly scrubbed or treated with acid.

The occurrence of the ore is especially peculiar in that it occurs entirely in limestone, the nearest known porphyry contact being about 600 ft. distant.

From present development it would appear that the district bids fair to become an important producer of platinum, for numerous other claims have been located in the vicinity, and are now under development. The Azurite Mining Co., whose ground adjoins that of the Boss, has developed some ore, although of somewhat different character from that of the Boss mine.

SANITATION IN VERA CRUZ

The Vera Cruz correspondent of the *Journal of the American Medical Association* writes, according to *Science*, 40 (1914), 405, that the hot season, which is also the rainy season, begins in Vera Cruz in May or June and lasts till the end of September, and as the season advances the tendency is for the death and morbidity rates for all diseases to increase, owing to the heat itself and the rapid increase in the amount of malaria; yet thanks to the effective work of our sanatoriums, this year is an exception in that the civil death rate for July is practically no greater than for June, in which month it was lower than the average. The civil death rates per thousand of population per annum for the months of June and July for the past five years in the city of Vera Cruz are given below; the improvement for July of this year is too great to be accidental or due to anything but improved sanitation.

	June	July
1910	38.86	46.86
1911	38.29	46.86
1912	44.86	49.72
1913	36.86	41.15
1914	32.00	32.58

A comparative statement of the civil deaths from communicable diseases for June and July of this year is as follows:

	June	July
Typhoid fever	1	0
Malaria	8	2
Smallpox	4	1
Dysentery	12	4
Tuberculosis	19	26
Diarrhea and enteritis, under 2 years	19	14
Diarrhea and enteritis, 2 years and over	28	23

The increase of deaths from tuberculosis is not unusual during the hot weather; the smallpox epidemic is over and there are now no cases in the city; between May 18 and July 31, 66,432 persons were vaccinated; revaccinations are now being made when indicated but general vaccination ceased with the end of July. The principal gain is due to the fall in the death rates for malaria and intestinal diseases, and this improvement is directly due to our preventive measures.

The antimalarial measures which affect the civil population are three: the suppression of mosquito breeding, the use of the army laboratory in establishing the correct diagnosis, and the following up and treatment of all proved carriers of gametes in the blood. Mosquito breeding has been largely suppressed by the extensive and intricate system of ditches in the environs of the city, totaling about twenty-five miles in length; miles of vacant lots and hundreds of acres of swamp at the bases of the gigantic sand-dunes behind the city have been drained by the Health Department, and it is now possible to sleep comfortably in almost all parts of the city without the use of mosquito bars, something hitherto unknown in the height of the rainy season.

Malaria has been made a reportable disease by the Health Department and demonstration of the parasite in the blood is insisted on as far as possible. All houses where proven cases of malaria have occurred have been visited by inspectors trained in mosquito extermination, and secondary cases have been so far practically unknown. As a result of a partial malarial survey of the city, it has been found that the disease is principally localized along the railroad and railroad yards. Further investigations along this line are now under way. The work has advanced far enough to demonstrate that there is very much less malaria now than is usual at this time of the year; the Mexican physicians are unanimous in saying that the amount of *paludismo* is now very small.

The other group of diseases which have been brought under control are the dysenteries and diarrheas, and the preventive measures which seem to be directly responsible for the improvement are the following: the suppression of flies and the protection of food-stuffs in the market by screening, the improvement in the milk supply, and the disinfection and isolation of dysenteric cases. The number of milk venders in the city is approximately 150, and 200 samples of milk have been examined for dirt, adulteration and the percentage of fat. The milk examinations are made at irregular intervals on unannounced dates, each vender's milk being examined at least once quarterly. The measure, however, which seems most directly responsible for the diminution in the number of cases and deaths from intestinal diseases is the antifly campaign. The city water has been frequently examined in the laboratory and found uniformly good. No cases of yellow fever have originated in Vera Cruz or been brought to that port.

NOTE

The description of the Fullagar internal combustion engine published in the last issue of THIS JOURNAL, 6 (1914), 862, was largely quoted from an article in the *Journal of Gas Lighting and Water Supply*, 127 (1914), 160. A full discussion of the theoretical principles involved can be found in *Engineering* (London), 98 (1914), 103.

NOTES AND CORRESPONDENCE

NOTE ON ANTISEPTICS

Editor of the Journal of Industrial and Engineering Chemistry:

The recent discussion in these columns as to what ozone will or will not do to bacteria under different conditions suggests that many of the commonly accepted notions as to chemical sterilization might be revised somewhat. In this connection, a few years ago, Owen,[1] of the Louisiana Experiment Station, showed that several of the well-known bacteria of the potato bacilli group—*i. e., Bacillus vulgatus, Bacillus mesentericus fuscus, Bacillus mesentericus niger* and *Bacillus mesentericus*

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[1] THIS JOURNAL, 3, 481.

granulatus—were capable of growing in raw sugars and that the spores of two of the above species could withstand a temperature of 100° C. for two hours. Russel[1] recently recorded the fact that certain bacterial species tolerate phenol, cresol and hydroquinone, in fact appear to feed upon these substances. The author well remembers having seen well-developed mosquito larvae swimming about in a jar of bichloride of mercury solution, which had been made up in the usual manner for disinfecting utensils in a laboratory where investigations on cholera and other infectious diseases were being carried on. The director of the laboratory was so impressed that he had the solution analyzed in order to satisfy himself that there had been no mistake made in its preparation. What seems like a more remarkable case was noticed recently in this laboratory; *i. e.*, a mold growing on a solution containing 11.8 per cent of copper sulfate, $CuSO_4.5H_2O$. Fragments of the mold growth first discovered grew on other samples of copper solution, showing that the first fully developed mold film had not accidentally dropped into the solution. Dr. Raymond F. Bacon, of this laboratory, states that he has observed molds derived originally from spoiled tomatoes, growing in a 10 per cent solution of sodium benzoate and also in a 10 per cent sulfuric acid solution. Perhaps these facts are not more remarkable than the oxidation of free sulfur to sulfate or the assimilation of atmospheric nitrogen and, doubtless, others could contribute equally noteworthy instances where certain bacteria, molds or low forms of life have appeared not to mind the presence of some of our commonly accepted antiseptics.

BENJAMIN T. BROOKS

MELLON INSTITUTE OF INDUSTRIAL RESEARCH
UNIVERSITY OF PITTSBURGH
October 8, 1914

NOTE ON WATER PURIFICATION BY OZONE

Editor of the Journal of Industrial and Engineering Chemistry:

The writer was much interested in the article on "Water Purification—with Report of the Ann Arbor Plant," by R. W. Pryer, that appeared in the October issue of THIS JOURNAL.

In reference to this report I would like to say that in April, 1910, I made a test of the Ann Arbor Plant for The Baltimore County Water and Electric Company, which was at that time installing an ozone plant somewhat similar in design to the one in question. The result of that test showed that the system, as it was then installed, was a failure as far as bacterial efficiency was concerned, although this inefficiency was ascribed to other causes than explained in Mr. Pryer's report. I do not know what changes have been made in the design or method of operation in the Ann Arbor plant since 1910, but the failure to produce efficient results (at that time) was due mainly to the intermittent action of the aspirators which caused a poor mixture of the ozone and water. No tests were made at that time as to the concentration of ozone produced at the plant, but from the odor it was not greater than 0.5 g. per cubic meter. The bacterial efficiency was practically nil and in some instances the number of bacteria was even greater than in the untreated water. This, as was explained by Mr. Pryer, was due to the breaking up of the suspended matter contained in the raw water, due to violent agitation in passing through the sterilizer.

The Ozone Plant of the Baltimore County Water and Electric Company, constructed under the supervision of Mr. A. E. Walden, although when first installed somewhat similar in design to the Ann Arbor Plant and built originally under the same patent right, has been greatly remodeled to overcome the faults encountered in the original design. The efficiency of the system has been greatly increased so that it is possible to obtain 99.0 to 100.0 per cent removal of bacteria, with a material reduction in color and organic matter. The concentration of the ozone can be regulated from 0.3 g. to 5.0 g. per cubic meter. It has not been found economical, however, to use a concentration higher than 1.0 g., for with proper filtration prior to ozonization and thorough mixing of the gas with the water, efficient results can be obtained.

I regret that at the present time I am not at liberty to state just what the cost of sterilization will be, but it is far below any figures quoted by Mr. Pryer.

In my opinion the failure of ozone as a sterilizing agent for the purification of water has been mainly because of (1) the failure of the systems to give a thorough mixture of ozone and water; (2) the improper preparation of the supplies (where necessary) by efficient filtration previous to ozonizing; (3) the attempt to produce high ozone concentrations, with a greatly increased cost of operation, when by thorough mixing with proper devices a much lower concentration would serve the purpose.

S. T. POWELL

BALTIMORE COUNTY WATER AND ELECTRIC COMPANY
BALTIMORE, MARYLAND
October 8, 1914

WATER PURIFICATION BY OZONE—WITH REPORT OF ANN ARBOR PLANT—NOTE

Editor of the Journal of Industrial and Engineering Chemistry:

In THIS JOURNAL, **6**, 797, the article on the purification of water by ozone with report of the Ann Arbor Plant is an interesting and painstaking description of the plant, which permits one to see clearly why it has never been a success. It is probable that the plant was built at a time when precise knowledge of the actual working of such plants was not extant or, at least, not generally available, and for this reason several errors, which at present appear obvious, were introduced into its design and construction.

The wells for ozonizing are seen to be about 3 ft. 3 in. × 3 ft. × 15 ft. deep and are 3 in number in each battery. It will, therefore, be seen that the period of contact between water and ozone is about 12 minutes and 45 seconds, which is far in excess of what is necessary to produce good ozonation, but on the other hand, the quantity of ozone used, namely, 0.227 g. per cm. of water, is perhaps $^1/_8$ of what would be required in a system of the character of that in question. Also, it will be noted that the ratio of water to ozone is 1 to 2.2 and it is now known that the air should be in much larger quantity, both for the reason that the air itself is a value in the oxidation of organic matter and because the generation of ozone at high concentrations is decidedly uneconomical.

There are two types of ozone water purifiers used abroad to a considerable extent. I refer to the Otto and Siemens-de Frise methods. In the former, the ozonized air is introduced under the water by means of aspirating action of the latter in passing through a suitable suction pump, and as the amount of air that can be moved with a given flow of water is limited, we find that high ozone concentrations are made use of in this method of operating. In the de Frise method, as the ozonized air is introduced independently of the water by means of a separate compression pump, the amount of air that can be used is independent of the quantity of water that is used and we find, therefore, that large quantities of air are made use of and with benefit.

It will be noted that in the Ann Arbor Plant mica tubes are used in the ozone generators instead of glass, and we have found in our own experience that this is a very uneconomical form of ozone generator dielectric, the losses in mica being many times greater than the corresponding losses in glass. Furthermore, it will be noted that little or no effort has been made for cooling the generators, Mr. Pryer specifically mentioning

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[1] *J. Soc. Chem. Ind.*, **1913**, p. 1136.

that there is no water jacket provided for this purpose. This would have a decided adverse influence upon the economy of the ozone generators. The concentration of ozone generation, namely, 0.5 g. per cm. average, is not too high but on the contrary it is not as high as it should be to insure economical use of air.

While the plant as it stands is a failure, I should not hesitate to state that with the substitution of a new ozone generating plant of 10 kw. capacity, designed according to present knowledge along these lines, it could be made a complete success, using all of the structural work such as filter, fore bay, rear bays and ozone wells. In fact, one bank of wells, and perhaps two could be eliminated entirely and all of the ozone introduced efficiently into the water in one, or at most two, of the units now used.

M. W. FRANKLIN

SPRAGUE ELECTRIC WORKS, GENERAL ELECTRIC CO.
BLOOMFIELD, N. J., October 20, 1914

PRELIMINARY NOTE ON IRON IN FLORIDA SOILS

The total iron in seventy-three samples of Florida soils and other formations ranged from 0.23 to 11.53 per cent calculated as ferric oxide (Fe_2O_3), the lowest figures representing material from the overburden of a phosphate mine and the latter a garden soil. The second largest amount was 7.44 per cent and only slightly greater than some succeeding ones. This indicates that the highest amount was probably due to added iron. The average iron content from all sources was 2.92 per cent.

Humus and iron, in general, were found to be present in direct proportion. Soils having much humus contained about 5.72 per cent iron oxide; those containing little humus contained about 3.72 per cent; those containing a trace of humus had 2.57 per cent; and those containing no humus contained about 1.57 per cent of iron oxide.

Untilled soils at depths of 3 and 9 inches contained comparatively more or less iron depending apparently upon the kind of plant life.

Roughly the amount of vegetation upon untilled soils was proportional to the iron content. Live oaks and hard woods were found to grow on soils containing 4.29 to 5.72 per cent iron oxide; cypress on soils containing about 5.7 per cent of iron oxide; long and short leaf pines and scrub oaks on soils containing 1.43 to 4.29 per cent iron oxide.

This work is being continued and the quantities of other elements are to be considered in relation to the iron.

We express our thanks to Dr. E. H. Sellards, State Geologist of Florida, and to Dr. J. McNeill of this Institution for samples of soil.

STATE COLLEGE FOR WOMEN
TALLAHASSEE, FLORIDA
August 18, 1914

C. A. BRAUTLECHT
A. B. PARLIN

NOTE ON COLORIMETRIC METHOD FOR VANADIUM

The writer has learned that some parties have not been successful in the use of the colorimetric method for vanadium in steel, described in THIS JOURNAL, **5**, 736. It is stated that the colors as developed are dissimilar and therefore not comparable.

This difficulty is due to failure to thoroughly oxidize carbonaceous matter and to completely expel sulfur dioxide after reduction of the permanganate. In carrying out the determination, heat the solution strongly for 4 minutes after addition of permanganate; add sufficient dilute ammonium bisulfite to clarify the solution and continue heating 3 minutes, or until sulfur dioxide is entirely expelled. Upon cooling and finishing as directed, the colors are found to be very satisfactory for comparison.

LIMA, OHIO
October 13, 1914

C. R. MCCABE

LUBRICANT FOR STOPCOCKS, ETC.

Editor of the Journal of Industrial and Engineering Chemistry:

An excellent lubricant for use with burette stopcocks, desiccators, etc., can be made by melting together equal parts of paraffin and vaseline. The paraffin gives body to the mixture which is therefore superior to vaseline alone, especially in places where high temperatures prevail.

632 DALE AVE., CLARKSBURG, W. VA.
August 20, 1914

E. W. OSGERBY

THE AMERICAN INSTITUTE OF MINING ENGINEERS

The annual meeting of the American Institute of Mining Engineers was held in Pittsburgh, Pa., on October 8th–10th, 1914.

After registration at the Hotel Schenley, the members in attendance were welcomed to the lecture hall of the Carnegie Institute by Dr. W. J. Holland, director of the Carnegie Museum; a technical session followed. The afternoon session of October 8th was devoted almost entirely to the presentation and discussion of papers. L. C. Morganroth discussed "The Occurrence, Preparation and Use of Magnesite," and then a paper on "The Iron Industry in Brazil," prepared by E. C. Harder, was read by Bradley Stoughton. During the course of Mr. Harder's paper, it was pointed out that few mineral deposits have in recent years attracted such wide-spread attention as the Brazilian iron ore deposits, owing mainly to the quantities of rich ore occurring there, in contrast to the ever-decreasing grade of ores shipped from many large producing iron ore districts. The Brazilian ore is of good grade, yielding 67 to 68 per cent of iron, and several hundred million tons are in sight. Up to the present, however, no iron ore has been exported from Brazil and only a very insignificant quantity has been used to supply the small domestic demand. G. S. Rice spoke on "Investigations of Coal-Dust Explosions," in the course of which he told of the history of investigations into various mine explosions from 1884 to the present time. In the evening of October 8th a formal reception was held in the lecture hall of the Carnegie Institute, after which T. T. Read exhibited a series of pictures illustrating "Ancient Methods of Manufacture of Iron in China;" this was followed by a lecture on safety methods in coal mining by J. W. Paul, and then Edward Higgins explained two reels of pictures showing the mining of iron ore at Mineville, in the Adirondack region of New York.

The second day of the meeting opened with sectional sessions and closed with an informal dinner at the Hotel Schenley. In the interval between these assemblages, the 300 engineers in attendance were taken on inspection trips to various industrial plants and to the Government experimental mine at Bruceton. Albert Sauveur presided at the meeting of the iron and steel section. John Birkinbine read a paper on "Reserves of Iron Ore for the United States," in the course of which he stated that as far as the supply of ore is concerned there need be no fear for the future of the steel industry in this country. A report on "Finishing Temperatures and Properties of Rails," by George K. Burgess and others, and papers by J. K. Furst on the duplex process for making steel and by A. Sauveur on manganese steel, were next presented. At the meeting of the coal and coke section, R. V. Norris presided; papers were read by H. N. Eavenson, on coal mine explosions caused by gas and dust and by T. T. Read on the manufacture of coke. Heinrich Ries presided at the meeting of the section on non-metallic minerals, at which D. T. Day read a paper by W. C. Phalen on "Salt Making by Solar Evaporation." J. A. Dresser and O. B. Hopkins presented papers dealing with asbestos deposits, D. T. Farnham spoke on "Quarrying Shale by the Tunnel System," and H. A. Gardner and G. B. Heckel discussed paint pigments.

The meeting closed on October 10th after three sectional meetings and a visit to the oil and gas district about Oakdale and to the Pittsburgh Station of the Bureau of Mines. Edward Higgins read an interesting paper on the safety movement in the Lake Superior iron region; he said in part: "There are five organizations engaged in this work, namely, the mining companies, the county mine inspectors, the co-operative range committees, the Lake Superior Mining Institute, and the Federal Bureau of Mines. The unity of purpose and the strong co-operation that has characterized the work of the five bodies has been a factor in the development of the work. The bulk of the cost has been and still is borne by the mining companies. Mainly their work has been to provide protective devices in and about the mines and to educate the miners to protect themselves from injury." G. S. Rice read a paper prepared in conjunction with H. H. Clark, dealing with the dangers attending shot firing in coal mines when it is done without undercutting; he referred to the measures taken against this danger. J. C. H. Ferguson spoke of the evolution of grinding devices from the time of their preparation from cast iron to the present day of rolled steel shells. S. S. Rumsey spoke on centrifugal motor-driven mine pumps, and O. P. Hood discussed the use of gasoline locomotives and their effect upon the health of miners; Harrison Souder explained a new detonating fuse; J. V. Emmons read a paper on the surface decarbonization of tool steel, and R. H. Rice reported on a system of blast-furnace blowing. At the meeting of the section on petroleum and gas, C. H. Washburne presented a paper on "The Capillary Concentration of Gas and Oil," and L. Edelneau described his method of refining petroleum. These papers were followed by a general discussion of gas and oil wells.

W. A. Hamor

THE NATIONAL COUNCIL FOR INDUSTRIAL SAFETY

The third annual meeting and congress of the National Council for Industrial Safety was held in Chicago on October 13th–15th, 1914. Over 2,000 delegates, representing various industrial concerns that are now giving practical demonstration of the "safety first" movement in their plants, were in attendance.

In addition to the formal meetings, there were round table sessions and exhibits of safety devices. The Congress was presided over by R. W. Campbell, chairman of the Central Safety Committee of the Illinois Steel Company, while W. H. Cameron, formerly of the American Steel Foundries Company, acted as secretary.

L. B. Burnett, assistant to the president of the Carnegie Steel Company, discussed "Effective Co-operation between Employer and Employee;" H. M. Wilson, engineer-in-charge, Bureau of Mines, Pittsburgh, Pa., spoke on "How Government Agencies May Best Co-operate with Manufacturers, Transportation Companies, and Others;" "Efficiency in Safety Work" was discussed by D. R. Kennedy, special agent of the Youngstown Sheet and Tube Company; R. H. Newbern read a paper on "The Safety Problem of the Railroads." A round table conference on the methods of educating workmen in accident prevention was led by L. R. Palmer, of the Pennsylvania Department of Labor and Industry; the economics sessions were presided over by C. B. Connelly. Addresses were made by Ida M. Tarbell on "Effects of Safety on the Community," and by J. P. Jackson on "Safety First in Europe."

More than 2,000,000 serious accidents occur in the industries of the United States every year, and safety engineers are inclined to the belief that at least half of these may be avoided; the National Council for Industrial Safety has pledged itself to employ every known agency to co-operate in reducing these to a minimum.

W. A. Hamor

AMERICAN LEATHER CHEMISTS' ASSOCIATION

The eleventh Annual Meeting of the American Leather Chemists' Association, in conjunction with the Annual Meeting of The National Association of Tanners, was held at the Hotel Sherman, Chicago, on October 28–31, 1914.

PROGRAM

President's Address. W. K. Alsop.

Report of the Secretary-Treasurer. H. C. Reed.

Committee Reports.

Color Valuation of Tanning Materials. George A. Kerr.

Laboratory Apparatus for Leaching Experiments. Lloyd Balderston and W. K. Alsop.

The Relation between Green Salted Weight and White Weight of Various Portions of the Hide. F. A. Loveland.

Lime. E. H. Bachtenkircher.

Dyes and Dyestuffs. Allen Rogers.

Leach House Efficiency. John H. Yocum.

Sewage Disposal and Use of Tannery Wastes. C. C. Smoot, III.

A Résumé of the Methods of Tannery Sewage Disposal. A. Roth. Rogers.

The Bating of Hides and Skins. Allen Rogers.

The Availability of Tannins in Liquors of Various Strengths. Thomas A. Faust.

Determination of Insolubles in the Analysis of Tannin Extracts. W. K. Alsop.

Spruce Extract. Sigmund Saxe.

The Clarification of Leather Extracts for the Determination of Reducing Sugars. F. P. Veitch and J. S. Rogers.

General Meeting National Association of Tanners.

Discussion—TanningSchool, Etc.—Joint Meeting with National Association of Tanners.

THE CHEMICAL SOCIETIES IN NEW YORK CITY

1914-1915 SEASON—RUMFORD HALL, THE CHEMISTS' CLUB

American Chemical Society—October 9.

Society of Chemical Industry—October 23.

American Chemical Society—November 6.

Society of Chemical Industry—November 6.

Joint Meeting—American Chemical Society, Society of Chemical Industry and American Electrochemical Society—December 11.

Society of Chemical Industry: Perkin Medal Award—January 22.

Joint Meeting—American Electrochemical Society, American Chemical Society and Society of Chemical Industry—February 5.

American Chemical Society: Nichols Medal Award—March 5.

Society of Chemical Industry—March 19.

Society of Chemical Industry—April 23.

Joint Meeting—Society of Chemical Industry, American Chemical Society and American Electrochemical Society—May 21.

American Chemical Society—June 11.

PERSONAL NOTES

The New York Section of the A. C. S. has appointed a committee composed of B. C. Hesse (Chairman), H. A. Metz, I. F. Stone, J. B. F. Herreshoff, D. W. Jayne, J. M. Matthews and A. Rogers to examine into the feasibility of expanding the manufacture of chemicals and dyestuffs in the United States and to report to the Section on November 6th.

The first meeting of the Maryland Section of the A. C. S. was held at Hopkins Hall, Druid Hall Avenue, Baltimore, on October 10th. Dr. C. Glaser read a paper on "The Catalytic Decomposition of Bornyl Chloride by Copper."

The Society for the Promotion of Engineering Education will hold its 1915 meeting at the Iowa State College, Ames, Iowa, June 22–25th. Dean Marston of the Iowa State College is President of the Society.

The Pittsburgh Section of the A. C. S. met on October 15th at the Central Turn Verein where the following program was given: "The Separation of Gases by Fractional Distillation at Low Temperatures" demonstrated by experiments with Special Apparatus—G. A. Burrell; "The Uses of Hydrofluoric Acid in the Arts"—Dr. K. F. Stahl.

The Pittsburgh Section has offered its services to the manufacturing interests of Pittsburgh which are hampered by the present shortage of imported chemicals and other materials.

An addition is being built to the chemistry building of the University of California, costing, with its equipment, $40,000. It will provide laboratory accommodation for 250 students.

The Rochester Section of the A. C. S. heard a lecture by Mr. H. E. Howe on "The Manufacture of Optical Glass" at its October 5th meeting.

The Wisconsin Section of the A. C. S. met on October 14th, when Prof. S. T. Acree, of the Forest Products Laboratory, spoke on "The Reactions of Both the Ions and the Molecules of Acids, Bases and Salts."

The office of the Secretary of the Society for the Promotion of Engineering Education has been moved to Pittsburgh and is now located in Thaw Hall, School of Engineering of the University of Pittsburgh.

The 27th meeting of the Nashville Section of the A. C. S. on Oct. 16th was a Memorial Meeting to William Lofland Dudley, with a paper on his life and work by Prof. J. T. McGill of Vanderbilt University.

The University of Illinois Section of the A. C. S. was addressed at its September 29th meeting by Prof. Edward Bartow, Director of the State Water Survey on "Some European Practice in Water and Sewage Purification, and Some Experiences in Europe after the Outbreak of War."

The Southern California Section of the A. C. S. met on October 15th at the Hollenbeck Hotel, Los Angeles. Mr. Edgar S. Baruch presented a paper entitled "Ethics and the Chemical Profession." The Committee on Oil Tests rendered an interesting report of their work of the past summer.

W. F. Monford has resigned from the St. Louis Water Works Staff and has established a laboratory at 506 North Vandeventer Ave. Mr. Monford will limit his work to the supervision and control of water supplies.

The Chicago Chemical Bulletin issued monthly by the Chicago Section of the A. C. S. presents an 8-page pamphlet, containing editorials, personals, advertisements, an employment column, correspondence and other items of interest to the Section.

The next meeting of the Chicago Section of the A. C. S. will be held on November 13th at the Hotel Sherman.

The Lexington Section of the A. C. S. held its 18th regular meeting on October 14th. Drs. Jos. H. Kastle and G. D. Buchner gave an Experimental Illustration of the Chemical Changes Occurring in the Accumulator by the Electrolysis of Cuprous Chlorid.

The University of Illinois reports that its enrollment in Chemical Engineering and Professional Chemistry courses is forty per cent larger than ever before. There is also a large increase in graduate students in chemistry, particularly in industrial lines.

The Rochester Section of the A. C. S. met on October 19th, the subject for the evening being "What Can This Society Do for You?"

The St. Louis Section of the A. C. S. considered "The Effect of the War on American Chemical Industries" at its October 12th meeting. The discussion was led by Dr. F. W. Frerichs of the Herf and Frerichs Chemical Co., Dr. F. W. Russe of the Mallinckrodt Chemical Works, Mr. Gaston Du Bois of the Monsanto Chemical Works and Dr. J. R. Macpherson Klotz of the Barrett Manufacturing Co.

Mr. Luciano Selmi, formerly with the Lake Superior Iron & Chemical Co. at Ashland, Wisc., has accepted the position of Chief Chemist and Metallurgist with the Otis Steel Co., Cleveland, Ohio.

The San Francisco and Southern California Sections of the A. C. S. are considering the formation, jointly, of a Bureau of California Chemists to act as an Advisory Committee to manufacturers who may wish to engage in chemical industries on the Pacific Coast.

The Connecticut Valley Section of the A. C. S. holds its meetings the first Saturday of every month, October to May, inclusive, at the City Club of Hartford, 7 Central Row, Hartford, Conn. at 8 P.M. At its 26th meeting on October 3rd, Mr. Edwin C. Scott of the Solvay Process Co., Syracuse, N. Y., talked on Electro Cleaners and the general topic of cleansing.

On October 9th the corner-stone to the addition to the Chemical Laboratory of the University of Illinois was laid. The Hon. W. L. Abbott, President of the Board of Trustees, presided. After addresses by Prof. W. A. Noyes of the University and Mr. William Hoskins of Chicago, the corner-stone was laid by President Edmund J. James. When completed, the entire laboratory will be 231 feet long and 202 feet wide and will contain 164,288 square feet of usable space.

At the October 9th meeting of the Indiana Section of the A. C. S. at the Indianapolis Chamber of Commerce, Dr. W. M. Blanchard, President of the Section, spoke on "Diacetyl and Some of Its Derivatives," giving the account of his research work in the University of Berlin last year.

The University of Michigan Section of the A. C. S. met on October 20th. Prof. E. E. Ware read a paper on "The Relation between China Wood Oil and Modern Varnishes."

Prof. Harry N. Holmes has resigned from the chair of Chemistry at Earlham College, Earlham, Indiana, where he has been since taking his doctor's degree at Johns Hopkins in 1907. Prof. Holmes is now head of the Department of Chemistry at Oberlin College.

At a joint meeting of the Pittsburgh Sections of the American Electrochemical Society and American Institute of Electrical Engineers, Prof. A. F. Nesbit, formerly of the University of Pittsburgh, discussed the Electrical Precipitation of Smoke, Dust, etc., and Mr. A. F. Weston, of the Research Corporation of New York City, showed lantern slides illustrating practical applications of the precipitation apparatus.

At the October 15th meeting of the Philadelphia Section of the A. C. S. the following papers were presented: "Glass and the Glass Industry" (illustrated), George E. Barton of the Whitall Tatum Co., Millville, N. J.; "Cork: Its Origin and Uses" (illustrated), H. W. Prentis, Jr., of the Armstrong Cork Co., Philadelphia.

The Kansas City Section of the A. C. S. will meet on November 14th at the University of Kansas, Lawrence, when Prof. C. F. Nelson will speak on "Osmosis" and Prof. G. W. Stratton on "Chlorophyl."

Dr. David T. Day has resigned his position with the U. S. Geological Survey in order to engage in private practice.

The Second Pennsylvania Industrial Welfare and Efficiency Conference will be held in the State Capital at Harrisburg on November 17 to 19, 1914, under the auspices of the Pennsylvania Department of Labor and Industry and the Engineers' Society of Pennsylvania. The first conference, last year, was attended by about 2000 persons, many of whom were leaders in the labor and industrial world. An unusually effective Safety, Welfare and Efficiency Exhibition will be open from November 16th to 18th.

Mr. John D. Northup has been placed in full charge of gathering the statistics on petroleum and compiling this Government Report for the U. S. Geological Survey. Mr. Northup succeeds Dr. David T. Day, recently resigned.

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.

DEPARTMENT OF AGRICULTURE

Arsenical Cattle Dips: Methods of Preparation and Directions for Use. Robert M. Chapin. Farmers' Bulletin 603, from the Bureau of Animal Industry. 16 pp. A popular write-up suitable only for the parts of this country infected with the Texas fever tick.

The Application of Refrigeration to the Handling of Milk. John T. Bowen. Department Bulletin 98, from the Bureau of Animal Industry. 88 pp and 37 figs. Paper, 10 cents. This paper "discusses the application of refrigeration in the operation of the modern milk plant and describes the various forms of mechanical and other systems of cooling." It is of interest to producers, shippers, dealers, and consumers of milk generally, and also to manufacturers of refrigeration machinery and appliances.

Harmful Effects of Aldehydes in Soils. Oswald Schreiner and J. J. Skinner. Department Bulletin 108, from the Bureau of Soils. 26 pp. Paper, 10 cents. "This bulletin deals with the discovery and properties of aldehydes in soils. These are shown to affect crops unfavorably and decrease the yield greatly. The results are of interest to agricultural experimenters and those practical farmers whose training interests them in the advance of scientific agriculture."

The Inorganic Composition of Some Important American Soils. W. O. Robinson. Department Bulletin 122, from the Bureau of Soils. 27 pp. Paper, 5 cents. "This bulletin gives the results of chemical and mineralogical investigations of certain important soils. The inorganic part alone is considered and special attention is given to the so-called rare elements. It is technical and intended for the use of research workers in agricultural chemistry and teachers in the same field. It will also be found of secondary interest to practical agriculturists."

Absorption of Fertilizer Salts by Hawaiian Soils. Wm. McGeorge. Bulletin 35, of the Hawaii Experiment Station. 32 pp. Paper, 5 cents.

Oxidases in Healthy and in Curly-dwarf Potatoes. H. H. Bunzel. Separate from the Journal of Agricultural Research, **2**, 373–404. A contribution from the Bureau of Plant Industry.

Moisture Tester for Grain and Other Substances and How to Use It. J. W. T. Duvel. Circular 72, reissued with supplement. 16 pp. Paper, 5 cents.

Composition of Roquefort-cheese Fat. James N. Currie. Separate from the Journal of Agricultural Research, **2**, 429–34.

The Effect of Strongly Calcareous Soils on the Growth and Ash Composition of Certain Plants. P. L. Gile and C. N. Ageton. Bulletin 16 of the Porto Rico Agricultural Experiment Station. 45 pp. Paper, 10 cents.

Density of Wood Substances and Porosity of Wood. Frederick Dunlap. Separate from the Journal of Agricultural Research, **2**, 423–8.

Effects of Certain Cooking Conditions in Producing Soda Pulp from Aspen. Henry E. Surface. Department Bulletin 80, from the Forest Service. 63 pp. Paper, 15 cents. The detailed information presented is of interest in connection with laboratory experimental work as well as to those endeavoring to improve the efficiency of commercial paper-making plants using the soda process.

Relative Resistance of Various Conifers to Injection with Creosote. C. H. Teesdale. Department Bulletin 101, from Forest Service. 43 pp. Paper, 15 cents. This bulletin is intended to show "how woods should be graded in order that they may give uniform results when subjected to treatment with preservatives; it is intended for those interested in wood preservation."

Yields from Destructive Distillation of Certain Hardwoods. L. F. Hawley and R. C. Palmer. Department Bulletin 129, from the Forest Service. 16 pp. Paper, 5 cents. This bulletin gives the results of laboratory distillation tests; it is of interest to manufacturers of by-products.

HYGIENIC LABORATORY

Bulletin 96, dated August 1914, contains the following articles of chemical interest. 124 pp. Paper, 15 cents.

(1) **Report of Investigation of Coastal Waters in the Vicinity of Gulfport and Biloxi, Miss., with Special Reference to Pollution of Shellfish.** R. H. Creel.

(2) **Comparison of Methods for Determination of Oxygen in Waters in Presence of Nitrite.** Elias Elvove.

(3) **Some New Compounds of the Choline Type, Including the Preparation of Monoacetate of α,β-Dioxy-β-methyl Butane.** G. A. Menge.

(4) **Detection of White Phosphorus in Matches.** Earle B. Phelps.

(5) **Chemical Composition of Rubber Used in Nursing Nipples and in Some Rubber Toys.** Earle B. Phelps and Albert F. Stevenson.

(6) **Analysis of Thymol Capsules.** Atherton Seidell.

(7) **Seasonal Variation in Composition of Thyroid Gland.** Atherton Seidell and Frederic Fenger.

(8) **Note on New Apparatus for Use with Winkler Method for Dissolved Oxygen in Water.** Hyman L. Shoub.

(9) **Pharmacological Action of Some Serum Preservatives.** Carl Voegtlin.

PUBLIC HEALTH SERVICE

Studies on the Self-purification of Streams. Earle B. Phelps. Reprint 214, from the Public Health Reports. 5 pp. Paper, 5 cents. This article describes the physico-chemical principles upon which are based the investigations of re-aeration of streams and the limits of permissible pollution without nuisance. It is a condensed form of the paper presented at the Cincinnati meeting of the American Chemical Society. (See This Journal, **6**, 682.)

Biological Products Establishments, Licensed Propagation and Sale of Viruses, Serums, Toxins, and Analogous Products. Reprint 206, from the Public Health Reports. 4 pp. Paper, 5 cents.

SUPERINTENDENT OF DOCUMENTS

Lists have been issued recently by this office giving the government publications for sale by the Superintendent of Documents on various phases of Agricultural Chemistry (Price list 40, 6th edition) and Forestry in the United States (Price list 43, 6th edition). Either of these lists can be obtained on request.

BUREAU OF FOREIGN AND DOMESTIC COMMERCE

Cost of Production in Pottery Industry, Summary of Results Miscellaneous Series 16. 43 pp. Paper, 10 cents.

Cottonseed Products and Their Competitors in Northern Europe. Part 2, Edible Oils. ERWIN W. THOMPSON. Special Agents Series 89. 31 pp. Paper, 5 cents.

Those interested in South American and similar trade conditions will find information of value in the following four publications:

(1) Banking and Credit in Argentina, Brazil, Chili, and Peru. EDWARD N. HURLEY. Special Agents Series 90. 72 pp. Paper, 10 cents.

(2) Important Details in South American Trade. Separate from Daily Consular and Trade Reports, August 28, 1914. 4 pp.

(3) Publications on Latin America and West Indies. Miscellaneous Series 17. 15 pp. Paper, 5 cents. This gives a brief review of the information available to manufacturers and exporters in the bulletins issued by the Bureau.

(4) Commercial Relations of the United States with Foreign Countries, calendar year 1912. (A special unnumbered publication). 272 pp. Cloth, 40 cents.

The Monthly Summary of Commerce and Finance of the United States has become the **Monthly Summary of Foreign Commerce of the United States**; the number for July, 1914, is the first of this new title; it is also No. 1 of the 1914–15 series.

BUREAU OF STANDARDS

The Relation of the Horse-power to the Kilowatt. Circular 34, 2nd edition. 16 pp. This circular includes a full discussion of the present practice in power ratings; the use of the kilowatt instead of the horse-power is urged.

The Testing of Potentiometers. FRANK WENNER AND ERNEST WEIBEL. Scientific Paper 223. 40 pp. This paper includes a discussion of the theory of potentiometer measurements as well as the methods of testing which are described.

The Emissivity of Metals and Oxides. I. Nickel Oxide (NiO) in the Range 600° to 1300° C. G. K. BURGESS AND P. D. FOOTE. Scientific Paper 224. 24 pp. Results for the monochromatic emissivity or absorptivity are given for the above range, and for the dispersion for 4 temperatures.

Adjustments of the Thomson Bridge in the Measurement of Very Low Resistances. F. WENNER AND E. WEIBEL. Scientific Paper 225. 4 pp. A description of two methods of procedure for making this adjustment.

BUREAU OF MINES

Experiments with Furnaces for a Hand-fired Return Tubular Boiler. SAMUEL B. FLAGG, GEORGE C. COOK AND FORREST E. WOODMAN. Technical Paper 34. 32 pp. The investigation reported was confined to the construction and operation of furnaces of this one type; the results are of greatest interest to the mechanical engineer.

Waste of Oil and Gas in the Mid-continent Fields. RAYMOND S. BLATCHLEY. Technical Paper 45. 57 pp. This report "describes the general amounts and kinds of wastes, and attempts to show the importance of conserving these natural resources. It does not present general rules and regulations for reducing the waste of gas and oil, except in two extreme cases, but suggestions are made that are intended to help the operator meet the situation. The right kind of cooperation should accomplish more than the enactment of drastic regulations."

Report of the Committee on Resuscitation from Mine Gases. W. B. CANNON, GEORGE W. CRILE, JOSEPH ERLANGER, YANDELL HENDERSON AND S. T. MELTZER. Technical Paper 77. 36 pp. This report discusses the several manual and mechanical methods for artificial respiration, including recommendations.

Prevention of Accidents from Explosives in Metal Mining. EDWIN HIGGINS. Miners' Circular 19. 16 pp. A non-technical discussion of the subject.

Supplementary List of Permissible Explosives. (Unnumbered circular). 1 p. The additions to the list up to August 1, 1914, are given.

Origin of Coal. DAVID WHITE AND REINHARDT THIESSEN. Bulletin 38. 390 pp. including 54 plates. Paper, 80 cents. The following articles on phases of the general subject make up this bulletin: Geologic relations of the coals. Analyses of the coal samples studied under the microscope. Physiographic conditions attending the formation of coal. Rate of deposition of coal. Regional metamorphism of coal. Origin and formation of peat. Microscopic study of coal.

GEOLOGICAL SURVEY

Geology of the Phosphate Deposits Northeast of Georgetown, Idaho. R. W. RICHARDS AND G. R. MANSFIELD. Bulletin 577. 76 pp. Although largely of geological interest, this bulletin includes a brief statement of the chemical character, specific gravity, and possible sources of these phosphate deposits.

Advance chapters of "Contributions to Economic Geology" have recently been issued as follows, the first seven titles being from the second part of the issue for 1912, the remainder from the first part for 1913:

(1) **Geology and Coal Resources of the Sierra Blanca Coal Field, Lincoln and Otero Counties, New Mexico.** CARROLL H. WEGEMANN.

(2) **Coal near Thompson, Grand County, Utah.** FRANK R. CLARK.

(3) **Coal near Wales, Sanpete County, Utah.** FRANK R. CLARK.

(4) **Rhode Island Anthracite.** G. H. ASHLEY.

(5) **Coking Coal in Powell Mountain, Scott County, Va.** M. R. CAMPBELL.

(6) **The Coal Resources and General Geology of the Pound Quadrangle of Virginia and Kentucky.** CHARLES BUTTS.

(7) **The Coal Resources of a Part of Northeastern Missouri.** F. C. GREENE. Each of these articles includes analyses of the coals and data of economic interest.

(8) **Some Deposits of Mica in the United States.** DOUGLAS B. STARRETT. Bulletin 580F. 60 pp. This paper reports on the investigations made of a number of mica deposits studied during 1913; it does not give a general report on the whole country, but some information of a general nature as to the production, uses, value, and nature of mica is included.

(9) **Gold Placers on Wind and Bighorn Rivers, Wyoming.** FRANK C. SCHRADER. Bulletin 580G. 20 pp.

(10) **Carnotite near Mauch Chunk, Pennsylvania.** EDGAR T. WHERRY. Bulletin 580H. 5 pp.

Colorado Ferberite and the Wolframite Series. Bulletin 583. 75 pp. with 49 figures and plates. This bulletin is made up of two articles: "The mineral relations of ferberite" by F. L. Hess and "Crystallography of ferberite from Boulder County, Colorado" by W. T. Schaller.

Bibliography of North American Geology for 1913. J. M. NICKELS. Bulletin 584. 193 pp. The list is arranged alphabetically by authors' names, but a subject index is included. It contains a list of chemical analyses reported and of the minerals, rocks, and formations described.

Our Mineral Reserves—How to Make America Industrially Independent. G. O. SMITH. Bulletin 599. 48 pp. This bulletin is issued "for the purpose of furnishing to the public in convenient form a summary of the mineral resources available for utilization under the pressure of present conditions, in the hope of encouraging their development and discouraging the importation of raw material and products which can be supplied at home."

Mineral Resources of Alaska, 1913. Bulletin 592. The advance chapters of this annual publication are now being issued. The whole report is made up of 21 papers by 11 authors; one of the papers is an administrative report, two are general summaries, and the others deal more specifically with the economic geology of certain districts. Separates have been issued for the following parts of this report:

(A) The Mineral Deposits of Alaska and the Alaskan Mining Industry in 1913. ALFRED H. BROOKS. 57 pp. In the first part of this are described the geologic occurrence of the following: Gold, copper, silver, zinc, lead, tin, tungsten, iron, chromite, antimony, other metallic minerals, coal, petroleum, peat, structural materials, and miscellaneous nonmetallic minerals. In the second section the details are given of operations for 1913, which show some falling off of mineral production as measured by total value of the output. The following gives the more interesting data:

MINERAL PRODUCTION OF ALASKA IN 1913

	Quantity	Value
Gold (fine ounces)	755,947	$15,626,813
Silver (fine ounces	362,563	218,988
Copper (pounds)	21,659,958	3,357,293
Coal (short tons)	2,300	13,200
Marble, gypsum, tin, lead, petroleum, etc.	.....	200,000
Total		$19,416,294

(C) Marble Resources of the Juneau, Skagway, and Sitka Districts. ERNEST F. BURCHARD.

(D) A Barite Deposit near Wrangell, Alaska. ERNEST F. BURCHARD.

(E) Mineral Deposits of the Yakataga District, Alaska. A. G. MADDREN.

(K) Mineral Resources of the Yukon-Koyukuk Region, Alaska. HENRY M. EAKIN.

Most of the other separates are primarily of mining interest, having little of chemical interest.

Quality of the Surface Waters of Washington. WALTON VAN WINKLE. Water-Supply Paper 339. 105 pp. This is one of a series of papers frequently issued by the Geological Survey, treating of the water supplies of some part of the United States. This paper gives many analyses and includes "a brief discussion of the constituents, uses, and purification of natural waters and a detailed consideration, by drainage basins, of the quality of the streams of Washington, showing the nature and the amount of the material which they hold in solution."

Surface Water Supply of the United States, 1912. This series of papers for different parts of the country contain results of stream flow measurements and other data gathered at the numerous gaging stations. Little data of chemical interest is given; the papers of this series should not be confused with those of the series described just above.

CONSULAR REPORTS—SEPTEMBER, 1914

The production of **geranium oil** in Algeria and its chemical constants and adulterants are described. (P. 1195.)

Perfume essence from the Reunion Islands include geranium oil, cananga oil, and verti-vert. (P. 1197.)

A new **paper factory** is being constructed at Maracay, Venezuela. (P. 1223.)

Portland cement factories of Japan are exporting cement to Manchuria and China. (P. 1227.)

The annual production of **ammonium sulfate** in Japan is nearly 20,000 tons; the imports are about 120,000 tons. (P. 1228.)

It is reported that the embargo on exportation of **potash** from Germany *via* Holland has been removed. (P. 1261.)

Plans have been completed for the new **University of British Columbia** to be located near Vancouver. A contract has been let for a science building to cost $600,000.

The Chilean government will introduce **oil-burning locomotives** on 125 miles of the government railway as an experiment. (P. 1295.)

Both oil and electric **safety lamps** are used in the Cardiff (Wales) coal mines, though the miners do not readily accept the electric lamps. (P. 1342.)

Gas is being made from low-grade coal mine refuse at Nanaimo, Canada, and is piped 60 miles to Victoria. (P. 1366.)

Exportation of **potash** from England has been forbidden. (P. 1457.)

The use of **high pressure gas** for street lighting is being considered for Bombay. (P. 1461.)

The methods of mining **graphite** in Ceylon are described and the trade conditions and uses of graphite are discussed. (P. 1462.)

Imports of **dyestuffs** into the United States have been practically constant in amount for the past five years, about $10,000,000 annually. In 1909 there were manufactured in this country about $16,500,000 worth of dyestuffs, making the total consumption over $25,000,000 worth. (P. 1469.)

The frequency of lead poisoning in the British **pottery industry** has decreased from 66 per 1000 employees in 1898 to 14 per 1000 in 1912. (P. 1477.)

DEMANDS FOR AMERICAN GOODS OWING TO THE WAR (PP.)

HONDURAS—1224 and 1361
Crockery
Enamel ware
Essential oils
Cornstarch
Bluing
Candles
Medicines
Vegetable oils

BIRMINGHAM, ENGLAND—1311, 1414, 1484 and 1629
Wire rods
Steel billets
Spelter
Copper and brass tubes
Brass wire and sheets
Bottles
Sulfur
Print paper
Gold leaf
Gas mantles

VENEZUELA—1343
Bottles
Paper
Leather
Drugs
Iron
Paint
Kerosene
Stearin
Copper plate
Olive oil

WEST INDIES—1550, 1591, and 1677
Electrical supplies
Chemicals
Metal goods
Cement
Drugs
Cotton-seed oil
Kerosene
Gasoline
Coal

CANADA—1550, 1591, and 1613
Drugs
Chemicals
Metal ware
Rubber
Paint colors
Plate glass
Zinc
Lead
Tin
Dyes

NORWAY—1551, 1590, and 1594
Sugar
Tin plate
Materials for oleomargarine
Hardware
Rubber
Zinc
Chemicals
Dyes
Sulfur
Soda

EGYPT—1551
Beer
Mineral waters
Oleomargarine
Copper
Brass
Iron and steel
Scientific instruments
Glass
Petroleum
Coal
Chemicals
Paints
Paper

JAPAN—1551 and 1591
Aniline dyes
Malt
Potassium chlorate
Phosphorus
Rosin
Aluminum
Copper, zinc, nickel, and iron articles
Dynamite
Paper

GREECE—1590 and 1614
Sugar
Copperas
Coal
Paper
Iron manufactures
Cotton-seed oil
Oleomargarine

SPAIN—1590 and 1614
Coal
Iron and steel
Phosphate
Glass
Cement
Starch
Dyes
Photographic supplies
Petroleum
Paper

ARABIA—1590
Dyestuffs
Gasoline
Kerosene
Soap
Cement
Glass
Iron
Coal
Pottery

BELGIAN CONGO—1591
Wine
Petroleum
Coal

CHOSEN, KOREA—1591
Kerosene
Paper
Drugs
Dyes
Explosives
Metals

NEW ZEALAND—1591
Drugs
Chemicals
Glass
Enameled ware
Paper
Aluminum

SWITZERLAND—1615
Cotton-seed oil
Petroleum
Gasoline
Sugar

INDIA—1615 and 1661
Glass
Chemicals
Drugs
Dyes
Metals
Lubricating oil
Cement
Ceramics
Rubber goods

NETHERLANDS—1626
Hides
Enameled ware
Petroleum
Tin plate
Paper

CHINA—1616, 1627, and 1661
Dyestuffs
Chemicals
Paper
Enameled ware
Glass
Phosphorus
Potassium chlorate
Fertilizers
Sugar

PORTUGAL—1626
Drugs
Chemicals
Coal
Glass
Linoleum
Paper
Paints

JAMAICA—1628
China
Drugs
Glass
Gas mantles
Matches
Iron, tin, copper, galvanized, and enameled ware

ARGENTINE—1633–42
Coal
Paper
Galvanized iron
Enameled iron
Glassware
Crockery
Photographic supplies
Drugs
Chemicals
Cement
Plate glass

SWEDEN—1661
Sulfur
Chloride of lime
Sodium and potassium carbonates
Gasoline
Petroleum
Coal
Copper
Rosin
Oil cake
Sodium hydroxide

SOUTH AFRICA—1674 and 1677
Explosives
Asbestos
Cement
Calcium carbide
Carbon dioxide
Potassium and sodium cyanides
Disinfectants
Sugar
Tartaric acid
Glass
Glycerine
Iron ware
Fertilizers
Nitrates
Lubricating oil
Paper
Photographic supplies
Silver plate
Sheep dip
Tar
Tin ware
Zinc

NICARAGUA—1725
Iron ware
Chemicals
Paper
Drugs
Soap

STATISTICS, ETC., ON EXPORTS TO THE U. S. (PP.)

GHENT, BELGIUM—1191
Chicory
Glue stock
Matches
Naphthalene
Cocoa oil
Copra oil
Creosote oil
Paper stock

PERU—1218
Sugar
Rubber
Guano
Hides
Silver
Copper
Vanadium
Gold

SYRIA—1237
Brandy
Butter
Olive oil
Pistachio nuts
Hides

TSINGTAU, CHINA—1274
Soya-bean oil
Egg products
Ground-nut oil
Hides
Silk
Walnuts

ASIATIC TURKEY—1301-2
Colocynth
Puer
Galls
Skins
Licorice

HONDURAS—1313-27
Hides
Gold
Silver
Liquid amber
Peruvian balsam
Rubber
Sarsaparilla

HONGKONG—1304
Aniseed oil
Camphor
Cassia
Cassia oil
Cement
Earthen ware
Glass ware
Lard
Matches
Peanuts
Peanut oil
Silk
Sugar
Tin

PANAMA—1328-38
Balata
Cocobolo
Copper
Hides
Ipecac
Ivory nuts
Pearls
Rubber

VENICE—1431
Beet pulp
Garlic
Glass
Glycerine
Hemp
Hides
Jute
Marble

GREECE—1345-58
Drugs
Laurel leaves
Marble
Olive oil
Chrome ore
Magnesite
Pumice
Rosin
Skins
Emery

BRAZIL—1377-95
Brazil nuts
Cotton seed
Carnauba wax
Gold
Hides
Manganese ore
Monazite sand
Rubber

SIAM—1419
Gamboge
Stick-lac
Sapphires

NICARAGUA—1436
Balsam
Copper
Dyes
Gold
Hides
Rubber
Silver
Sugar
Tan bark

FRANKFORT, GERMANY—1445
Asbestos
Celluloid
Antipyrin
Benzoic acid
Bleaching powder
Bronze powder
Coal tar dyes
Naphthol
Potash
Quinine
Resorcin
Sodium cyanide
Clay
Gelatine
Glue
Mineral water
Platinum
Artificial silk
Hides
Wine
Wood pulp
Zinc

WIESBADEN—1447
Antimony salts
Citric acid
Tartaric acid
Oxalic acid
Sodium bisulfate
Cream of tartar
Sodium formate
Potassium oxalate
Rochelle salt
Aniline dyes
Cement
Fertilizer
Mineral water
Stone ware
Wine

AIX LA CHAPELLE—1452
Bleaching powder
Fire brick
Chemicals
Cocoa butter
Dyestuffs
Paint driers
Fertilizers
Fuses
Paper
Soap
Steel
Tin ware
Mineral water
Wine

JAPAN—1489-1501
Albalone
Antimony ore
Soya-bean oil
Camphor
Coal and coke
Copper
Graphite
Hides
Vegetable isinglass
Drugs
Paper
Peanuts
Peppermint oil
Silk
Sulfur
Vegetable wax

BARMEN, GERMANY—1456
Chemicals
Dyes
Coke
Hides
Nickel

MAGDEBURG, GERMANY—1505-17
Barium hydroxide
Carbon tetrachloride
Bone-black
Copper products
Fertilizers
Kainite
Kieserite
Magnesium chloride
Magnesium sulfate
Peanut oil
Potassium carbonate
Potassium hydroxide
Potassium cyanide
Potassium chloride
Potassium sulfate
Sugar
Urea
Tungsten ore
Zinc

QUEBEC—1518-29
Aluminum
Asbestos
Creosote oil
Sodium nitrate
Coal
Copper ore
Mercury fulminate
Fertilizer
Gas liquor
Hides
Iron oxide pigment
Maple sugar
Sulfur ore
Tankage
Wood pulp

STATISTICS, ETC., ON EXPORTS TO THE U. S. (PP.)—(*Concluded*)

HANOVER—1449
Ammunition
Celluloid
Antimony sulfide
Arsenic acid
Creosote
Mesothorium
Phosphoric acid
Thorium nitrate
Cerium nitrate
Cobalt
Glycerine
Hides
Infusorial earth
Inks
Potash
Rubber
Wine
Wool fat

ROME—1460
Aluminum
Chemicals
Cork
Glue stock
Hides
Meat extract
Olive oil
Sienna

ERFURT, GERMANY—1544-8
Glass
Hides
Manganese ore
Scientific instruments

MOROCCO—1553-62
Hides
Gum sandarac

BRITISH COLUMBIA—1569-80
Bullion
Cascara bark
Fertilizer
Hides
Tin
Wood pulp
Gold ore
Zinc ore
Copper ore
Blister copper
Copper matte

MERSINA, TURKEY—1601-6
Gum tragacanth
Sesame oil and seed

CHILI—1617-25
Copper ore
Iodine
Sodium nitrate
Silver ore
Tin ore

BURMA—1655
Hides
Mineral wax
Lac
Cutch (dye wood)
Copper matte

BAHAMAS—1665-72
Bark
Hides
Sisal

NEWFOUNDLAND—1681-90
Cod oil
Seal oil
Whale oil
Guano
Iron ore
Flint pebbles

GUATEMALA—1714-17
Hides
Rubber
Sugar

Zinc refining in Japan has increased so that not only the domestic demand is supplied, but also some zinc is shipped to England. (P. 1487.)

Annual imports of **mineral waters** into the United States are over 3,000,000 gallons, valued at $1,000,000. As these have come principally from Germany, France, and Austria-Hungary, domestic waters will probably soon replace the foreign. The production in this country is about 57,000,000 gallons, valued at $5,500,000. (P. 1483.)

High-grade **iron ore** deposits have been discovered on the Copper River, near Hupert, B. C. (P. 1529.)

The **peanut and peanut-oil industry** of South Carolina are discussed. (P. 1534.)

Tungsten mines in Chosen, Korea are being operated on a small scale. (P. 1549.)

A new **pig-iron furnace** is to be erected in Chosen, Korea, at a cost of $2,750,000. (P. 1606.)

The regulations regarding the grading of **Manila hemp** are discussed. (P. 1607.)

A company has been organized in Ceylon to manufacture **sugar** from the palmyra palm. (P. 1610.)

A **branch laboratory** of the Canadian Department of Internal Revenue is to be opened in Vancouver. (P. 1628.)

A plant for making **sublimed white lead** in Australia is being enlarged. (P. 1628.)

A substitute for **ichthyol**, to replace the supply from Austria, has been placed on the market. (P. 1675.)

Developments of **potash deposits** near Barcelona, Spain, have been interrupted by the war. (P. 1717.)

BOOK REVIEWS

Chemistry in America: Chapters from the History of the Science in the United States. BY EDGAR FAHS SMITH. New York: D. Appleton and Co. 1914. Pp. xiii + 356. 24 half-tones. Price, $1.00.

This volume, on the development of chemistry in the United States, may be described rather as a source-book than as a history. It consists largely of biographies of individual chemists, although inter-relations and groupings are not neglected, and the institutions in which chemistry was especially cultivated receive more than incidental mention. The book contains two general addresses, which give an excellent idea of the interests of chemists at the opening of the nineteenth century, and extensive extracts from several original papers.

The earliest contribution to chemistry printed in America seems to be one published in 1768 by John de Normandie. The balance is frequently mentioned in this paper. It is surely time that the absurd misstatement, to the effect that Lavoisier was the first to use this instrument, should cease to appear in almost every paper and address professing to deal with the history of the science.

It is interesting to note that the Chemical Society of Philadelphia (1792–1809) and its successor, the Columbian Chemical Society, founded in 1811, antedated the European societies devoted to the cultivation of the same science.

The biographical chapters give vivid characterizations of many interesting men. They begin with James Woodhouse, professor of chemistry in the University of Pennsylvania, a vigorous and emphatic personality whose lectures rarely exceeded forty minutes and were often much shorter. Priestley and his relations with American chemists during the last ten years of his life (1794–1804) occupy much space and constitute one of the most interesting parts of the volume. Thomas Cooper (1759–1841) was probably the first of the large number of chemists who have become college presidents.

The biographies include John Maclean of Princeton, Samuel L. Mitchell of Columbia, Robert Hare of Philadelphia, perhaps the most influential American chemist of his day, and a group of mineralogical chemists headed by Archibald Bruce from whom brucite derives its name.

The concluding part of the volume deals with Guthrie, an independent discoverer of chloroform and the first to use it in medicine, Rogers who experimented in dialysis, T. Sterry Hunt, preëminent as an original thinker, J. Lawrence Smith, Wolcott Gibbs, Mallet, Carey Lea, Cooke of Harvard and Willard Gibbs of Yale.

The work gives an excellent idea of the place of American chemists in the history of chemistry, and we owe a debt of gratitude to the author for publishing the valuable material originally collected for his lectures on the development of the science.

Alexander Smith

Chemical Reagents. Their Purity and Tests. Authorized translation of Pruefung der Chemischen Reagentien auf Reinheit (Zweite Auflage) Von E. Merck. By Henry Schenck, A.B. (Harvard). Second edition. 8vo. pp. ix + 199. Cloth. D. Van Nostrand Company, New York. 1914. Price, $11.00 net.

This latest edition of Merck's Chemical Reagents follows the same general lines as the first edition, which in turn was preceded by the Krauch editions on "Die Pruefung der Chemischen Reagentien auf Reinheit," which have appeared successively since 1888. In this edition is appended for the first time a table for the preparation of test solutions commonly used, with general directions and approximate strengths.

The general treatment of the subject matter consists in a brief description of the familiar appearance of the particular reagent, along with detailed tests for the more common impurities. These tests are to be made in the examination, both qualitative and quantitative. In many places are added the use and solubility along with references to such literature as in the author's judgment are the most important new contributions upon the uses and methods of testing reagent chemicals. This listing of references is of particular value to the analytical chemist who is frequently called upon to make a more elaborate examination of his reagents than is described in the ordinary manual. In this connection it is noted, however, that under Sodium Oxalate (Soerensen's Oxalate) the valuable work of Blum of the U. S. Bureau of Standards, one of the most elaborate investigations on a chemical reagent, is not mentioned. It is possible that inasmuch as this work was published in 1912, the translator overlooked this important article. It is to be noted that the Tests of Purity applied to oxalic acid and the oxalates do not call attention to calcium which is so likely to be present.

On the whole this standard handbook treats the testing of the more common reagents in a highly satisfactory manner for a small book and it is gratifying to know that frequent editions of this valuable manual appear from time to time.

Victor Lenher

Sammlung Vieweg, Heft 2. Anorganische Peroxyde und Persalze. By Dr. C. Freiherrn von Girsewald. 98 pp. Paper, M. 2.40. **Heft 6. Brennereifragen.** By D. Sidersky. Illustrated. 49 pp. Paper, M. 1.60. Friedr. Vieweg & Sohn, Braunschweig, 1914.

These two recently issued books are among the first six volumes issued of the "Sammlung Vieweg," a collection which, it is planned, shall cover all the branches of pure and applied science and shall present in each subject its strictly contemporaneous state of development.

Dr. von Girsewald has divided the main part of his book into two divisions, one dealing with hydrogen peroxide and the other with derivatives such as the true metal peroxides, persalt like the perborates, etc. While the theoretical part of the subject is not neglected, the chief interest of the book is in the development of the practical applications of peroxides to industry.

In the theoretical part the discussion of the formula of hydrogen peroxide (that preferred by the author is $H - O : O - H$) is not always thoroughly convincing and it appears a mistake to insist so strongly on any detailed structural formula.

The book is on the whole interesting and instructive, and the author is to be commended for introducing the necessary feature—sometimes omitted in such books—of profuse references to original sources, especially patent literature; the work is sufficiently exhaustive to give a true picture of the present-day status of peroxides and persalts, as well as point out the probable lines of future development.

"Brennereifragen" deals with the questions of modern, chiefly French and Austrian, distilling practice. The first part treats of the continuous fermentation of beet juice (the chief source of spirits in France and Austria as opposed to Germany where potatoes and grain are the commonest raw materials), while the second part takes up distillation and rectification. The book is well illustrated with microphotographs and many pictures and diagrams of apparatus.

M. L. Hamlin

Rapid Method for the Chemical Analysis of Special Steels, Steel-Making Alloys, and Graphite. By Charles Morris Johnson, Ph.M., Chief Chemist to the Park Steel Works of the Crucible Steel Co. of America. Second edition. xi + 437 pages, 39 figures. John Wiley & Sons, Inc., New York. Price, $3.00 net.

The first edition of Mr. Johnson's book, published in 1909, met with a hearty reception and a ready sale to those who were interested in alloy steels. An important feature of the first edition was the incorporation of methods of analysis of alloy steels, wherein the author gave actual methods used in control work of operations. The methods were based on experimental data covering years of experience.

In the introduction to the second edition special attention is called to the following general statement: "If iron be combined by fusion with notable quantities of an element whose melting point is very much below that of iron, the tendency is to produce a metal of inferior physical properties, but if iron be combined with an element whose melting point is nearly that or higher than that of iron, then the tendency is to produce a metal of superior physical properties."

Attention is also called to the author's methods for the determination of phosphorus in tungsten-bearing materials; tungsten in ores; for sulfur in alloy steels by heating the insoluble carbides, which carry the major part of the sulfur, to a yellow heat in a stream of acid-carrying hydrogen, evolving the sulfur as hydrogen sulfide from sulfates; modification of Brunk's method for nickel in steel; the titration of iron or vanadium or both in the presence of uranium; uranium in ores; ferro uranium and steels; cobalt steels and cobalt metals: to the author's investigation of the cause of bark in pipe-annealed steel, tapered clay combustion tubes, milling machine, one piece nichrome triangle, and the plan and views of laboratory rooms.

The second edition is enlarged, the author elaborating on methods given in the first edition. He has also added new methods based on more recent experience, and has brought the book up to the latest and best analytical practice in iron, steel and its alloys. Additional chapters give methods for the testing of lubricating oils, coal, iron ore, fluorspar, limestone, sand and brick. The aim of the author has been to produce methods that combine speed, simplicity and accuracy.

William Brady

NEW PUBLICATIONS

By John F. Norton, Massachusetts Institute of Technology, Boston

Air: Pumping by Compressed Air. By E. M. Ivens. 8vo. 244 pp. Price, $3.00. John Wiley & Sons, New York.

Analysis: Chemical Analysis, Qualitative and Quantitative. By G. L. Gardiner. 8vo. 504 pp. Price, $2.00. Black, London.

Analysis: Introduction to Qualitative Chemical Analysis (Anleitung zur qualitativen chemischen Analyse). By H. v. Pechmann. 14th Ed by W. Prandtl. 8vo. 138 pp. Price, $0.50. Munich. (German.)

Analysis: Principles of Quantitative Analysis: An Introductory Course. By W. C. Blasdale. 12mo. 394 pp. Price, $2.50. D. Van Nostrand Co., New York.

Analysis: Tables for Qualitative Chemical Analysis. (Tafeln für qualitativen chemischen Analyse.) By H. v. Pechmann. 14th Ed by W. Prandtl. 8vo. 39 pp. Price, $0.35. Munich. (German.)

Analysis: Technical Methods of Ore Analysis. By Albert H. Low. 6th Ed. 8vo. 362 pp. Price, $2.75. John Wiley & Sons, New York.

Brewing: The Modern Brewery. A Practical Handbook for the Brewer (Die Bierbrauerei der Neuzeit). By S. Zimmermann. 8vo. Price, $2.50. Bartenstein. (German.)

Experiments. By Philip E. Edelman. 250 pp. Price, $1.50. Philip E. Edelman, Minneapolis, Minn.

Food: Foods and Sanitation, a Text-book and Laboratory Manual for High Schools. By Edith H. Forster and Mildred Weigley. 12mo. 396 pp. Price, $1.00. Row, Peterson & Co., Chicago.

General Chemistry: Foundations of Chemistry. By Arthur A. Blanchard and F. B. Wade. 12mo. 446 pp. Price, $1.25. American Book Co., New York.

General Chemistry: Laboratory Experiments in General Chemistry. By H. B. North. 2nd Ed., revised. 12mo. 205 pp. Price, $1.00. D. Van Nostrand Co., New York.

Household Chemistry: Elementary Household Chemistry. By John F. Snell. 12mo. 307 pp. Price, $1.25. The Macmillan Co., New York.

Inorganic Chemistry: Text Book of Inorganic Chemistry. By A. F. Holleman. 12th Ed. 8vo. Price, $2.00. Leipzig. (German.)

Inorganic Chemistry: The Principles of Inorganic Chemistry. By Wilhelm Ostwald. Translated by Alex. Findlay. 4th Ed. 8vo. 836 pp. Price, $4.50. The Macmillan Co., New York.

Iron: Iron Ores, Their Occurrence, Valuation and Control. By E. C. Eckel. 8vo. 427 pp. Price, $4.00. McGraw-Hill Book Co., New York.

Oils: Mineral Oils and Their By-products. By Iltyd I. Redwood. 2nd Ed. 8vo. 336 pp. Price, $3.00. Spon & Co., New York.

Oils: The Hydrogenation of Oils: Catalyzers and Catalysis: and the Generation of Hydrogen. By Carleton Ellis. 8vo. Price, $4.00. D. Van Nostrand Co., New York.

Physical Chemistry: A Manual of Practical Physical Chemistry. By F. W. Gray. 12mo. 211 pp. Price, $1.25. The Macmillan Co., New York.

Physical Chemistry: Hydrogen Ion Concentrations. (Die Wasserstoffionen-Konzentration.) By L. Michaelis. 8vo. 210 pp. Price, $2.00. J. Springer, Berlin. (German.)

Physiology: A Text-Book of Physiological Chemistry. By Olof Hammarsten. Translation by John A. Mandel. 7th Ed., English. 8vo. 1014 pp. Price, $4.00. John Wiley & Sons, Inc., New York.

Rubber: The Rubber Industry in Brazil and the Orient. By C. E. Akers. 8vo. 33 pp. Price, $1.50. Methuen, London.

Tanning: Handbook for Tannery Laboratories (Handbuch fuer gerberei-chemische Laboratorien). By G. Grasser. 8vo. 395 pp. Price. $4.00. Schulze & Co., Leipzig. (German.)

Textiles: The Chemical Technology of Spun Yarn (Chemische Technologie der Gespiustfasern). By K. Stirn. Price, $3.50. Borntraeger, Berlin. (German.)

Tinplate: The Tinplate Industry. With Special Reference to Its Relations with the Iron and Steel Industries. By J. H. Jones. 8vo. 302 pp. Price, $2.00. P. S. King. London.

Welding: A Practical Manual of Autogenous Welding (Oxy-Acetylene). By R. Granjon and P. Rosemberg. 8vo. 256 pp. Price, $1.25. C. Griffin, London.

Wines: Faults and Diseases of Wines, Their Causes, Recognition, and Remedies. (Fehler und Krankheiten des Weines, deren Ursachen, Erkennung und Heilung.) By J. L. Merz. 8vo. 108 pp. Price, $0.75. Wien. (German.)

RECENT JOURNAL ARTICLES

Analysis: Improved Apparatus for the Analysis of Mixed Gases. By A. C. Wilson. *The Analyst*, Vol. 39, 1914, No. 462, pp. 391–2.

Analysis: Studies on the Determination of Tungsten. By Hans Arnold. *Zeitschrift für anorganische Chemie*, Vol. 88, 1914, No. 3, pp. 333–40.

Analysis: The Perchloric Method of Determining Potassium, as Applied to Water Analysis. By Clarence Scholl. *Journal of the American Chemical Society*, Vol. 36, 1914, No. 10, pp. 2085–88.

Carbon: Energy of Vaporization of Carbon. By Carl Hering. *Metallurgical and Chemical Engineering*, Vol. 12, 1914, No. 8, pp. 526–8.

Colloids: The Theory of Colloid Chemistry. By Wilder D. Bancroft. *The Journal of Physical Chemistry*, Vol. 18, 1914, No. 7, pp. 549–58.

Combustion: Coal Flames with Ether. By Alan Leighton. *The Journal of Physical Chemistry*, Vol. 18, 1914, No. 7, pp. 619–23.

Combustion: Surface Combustion. By W. A. Bone. *The Chemical Engineer*, Vol. 20, 1914, No. 3, pp. 99–109.

Creosote: Efficiency of Various Parts of Coal-Tar Creosote against Marine Borers. By Clyde H. Teesdale. *Engineering Record*, Vol. 70, 1914, No. 11, pp. 302–3.

Electrochemistry: The Electric Furnace in the Foundry. By W. L. Morrison. *The Iron Age*, Vol. 94, 1914, No. 14, pp. 777–9.

Gas: Catalysis in the Gas Industry. By Rudolf Lessing. *The Chemical Trade Journal and Chemical Engineer*, Vol. 55, 1914, No. 1426, pp. 241–2.

Gas: The Recovery of Gas Works By-products. By C. C. Tutwiler. *Journal of the Franklin Institute*, Vol. 178, 1914, No. 4, pp. 383–415.

Illumination: Recent Developments in the Art of Illumination. By Preston S. Millar. *Journal of the Franklin Institute*, Vol. 178, 1914, No. 4, pp. 435–64.

Leather: Clarification of Leather Extracts for the Determination of Reducing Sugars. By F. P. Veitch and J. S. Rogers. *The Journal of the American Leather Chemists' Association*, Vol. 9, 1914, No. 10, pp. 421–36.

Oils: The Creosote Oil Situation and the Treatment of Crossties. By S. R. Church. *Engineering News*, Vol. 72, 1914, No. 13, pp. 658–9.

Potash: Potash Salts: Summary for 1913. By W. C. Phalen. *The Chemical Engineer*, Vol. 20, 1914, No. 3, pp. 89–98.

Sanitation: Collection and Disposal of City Refuse, Washington, D. C. By J. W. Paxton. *Engineering News*, Vol. 72, 1914, No. 14, pp. 671–4.

Sanitation: Refuse Destruction. By R. O. Wynne-Roberts. *Canadian Engineer*, Vol. 27, 1914, No. 13, pp. 466–70.

Sewage: Electrolytic Sewage Treatment. By Maurice E. Connolly. *Municipal Engineering*, Vol. 47, 1914, No. 4, pp. 279–85.

Sewage: Report on Electrolytic Sewage Treatment at Elmhurst. By P. M. Travis. *Engineering Record*, Vol. 70, 1914, No. 11, pp. 292–4.

Sewage: The Sewage Disposal Problem in Villages and Small Cities. By George C. Whipple. *American Journal of Public Health*, Vol. 4, 1914, No. 9, pp. 758–66.

Sewage: Sewage Treatment. By Rudolph Hering. *Journal of the Franklin Institute*, Vol. 178, 1914, No. 4, pp. 417–33.

Soda: A New Theory of the Ammonia Soda Process. By William Mason. *Metallurgical and Chemical Engineering*, Vol. 12, 1914, No. 9, pp. 571–2.

Steel: The Electric Arc Furnace and the Development of the Steel Casting Industry. By Ivar Rennerfelt. *Metallurgical and Chemical Engineering*, Vol. 12, 1914, No. 9, pp. 581–3.

Steel: Titanium Nitride in Steel. By G. F. Comstock. *Metallurgical and Chemical Engineering*, Vol. 12, 1914, No. 9, pp. 577–80.

Sugar: The Reserve Factory Process of Making White Granulated Sugar. By B. Sandmann. *The Louisiana Planter and Sugar Manufacturer*, Vol. 53, 1914, No. 14, pp. 222–3.

Tanning: Notes on the Application of Tungsten Salts to the Analysis of Tanning Materials. By Alexander T. Hough. *Journal of the Society of Chemical Industry*, Vol. 33, 1914, No. 17, pp. 847–8.

Textiles: Oils and Soaps Used in Textile Manufacturing. Anonymous. *The Textile American*, Vol. 22, 1914, No. 3, pp. 34–6.

Tungsten, Studies on the Analytical Examination of. By Hans Arnold. *Zeitschrift fuer anorganische Chemie*, Vol. 88, 1914, No. 3, pp. 333–340.

Turpentines, Detection and Determination of, Petroleum Derivatives in. By C. Grunaldi and L. Prussig. *Chemiker Zeitung*, Vol. 38, 1914, No. 95, pp. 1001–1002.

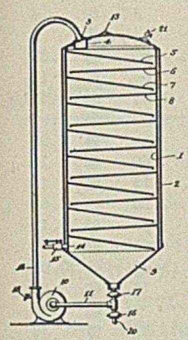
Water: Applications of Water Analysis. By Edward Bartow. *American Journal of Public Health*, Vol. 4, 1914, No. 8, pp. 633–37.

Water: Conservation of Potable Water and the Dual System of Distribution. By Henry C. Hodgkins. *Journal of the American Water Works Association*, Vol. 1, 1914, No. 3, pp. 554–64.

Water: Disinfecting 200,000,000 Gallons of Water a Day—Experience with Chloride of Lime and Liquid Chlorine. By Francis D. West. *Journal of the American Water Works Association*, Vol. 1, 1914, No. 3, pp. 403–55.

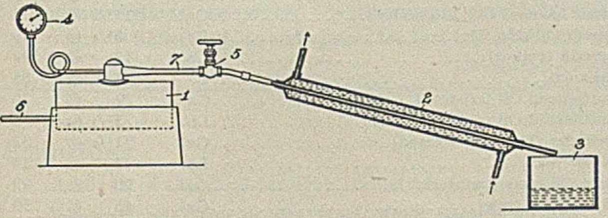
RECENT INVENTIONS

By C. L. Parker, Solicitor of Chemical Patents, McGill Building, Washington, D. C.



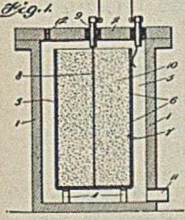
Hydrogenating Oils, Fats, and Fatty Acids, Etc. J. N. Humphreys, June 23, 1914. U. S. Pat. 1,100,735. The oil to be hydrogenated is mixed with a finely divided catalytic agent and caused to move in a film relatively slowly and quietly over a circuitous path in an atmosphere containing hydrogen.

Treatment of Petroleum Hydrocarbons. Bacon and Clark, June 23, 1914. U. S. Pat. 1,101,482. This process is designed for converting into gasoline petroleum hydrocarbons from which the usual gasoline content has already been removed by fractional distillation or hydrocarbons normally free from gasoline. The process consists in producing saturated gasoline hydrocarbons (*i. e.*, hydrocarbons having boiling points ranging from about 30° C. to 150° C., at atmospheric pressure), by simultaneously decomposing and distilling under a pressure of from 100 to 300 pounds per sq. in. petroleum hydrocarbons having a boiling point of about 250° C. and upward, the operation being continued at a rate to give a yield of saturated gasoline hydrocarbons of a minimum volume of 18 per cent of the distilling charge, and subsequently treating the distillate thus obtained for the separation of the saturated gasoline hydrocarbons.



Carbon-Remover. C. B. Longenecker, June 30, 1914. U. S. Pat. 1,101,646. This is a compound for treating cylinders of internal combustion engines consisting of sodium chlorid and sulfur.

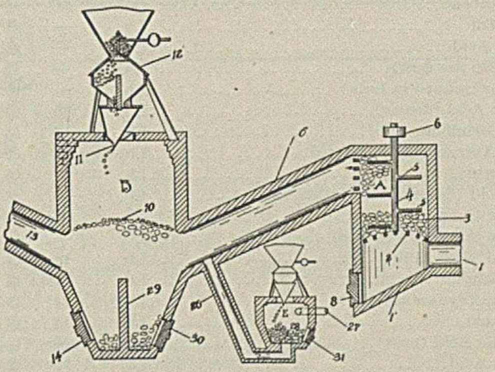
Sulfur and Sulfates from Sulfites. C. Hansen, June 30, 1914. U. S. Pat. 1,101,740. Sulfur and sulfates are produced by heating solutions of a mixture of two molecules of a bisulfite with one molecule of a sulfite under pressure and with continuous stirring.



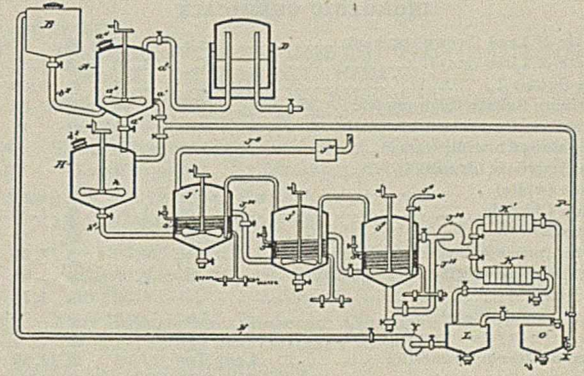
Method and Means for Fixing Nitrogen. W. S. Landis, July 14, 1914. U. S. Pats. 1,103,060 and 1,103,062. Calcium carbid contained within a bag of loosely woven fabric is placed within porous vessel 3 in the chamber 1 and electrically heated, nitrogen being admitted through pipe 11 during the heating operation.

Fertilizer. F. S. Washburn, July 14, 1914. U. S. Pat. 1,103,115. The phosphoric acid contained in phosphate rock is rendered available as a plant food by treating the rock with sulfuric acid to obtain a crude solution of phosphoric acid and then feeding the crude solution so obtained to a solution containing di-ammonium phosphate.

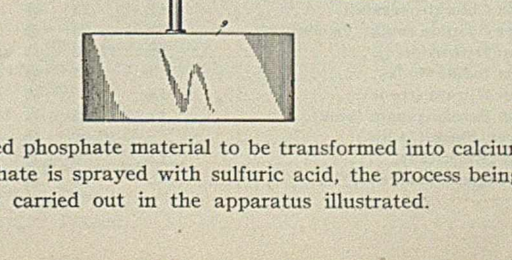
Rendering Smelter Fumes Useful and Recovery of Their Values. C. S. Vadner, July 14, 1914. U. S. Pat. 1,103,165. The smelter fumes are purified of their mechanical impurities by passing them through the mechanical filter in the chamber "A." They are then mixed with hydrocarbon gases and the mixture heated to a high temperature in the gas converting chamber "B," thereby rearranging them in their combinations. Combustible gases in the remaining mixture are recovered by cooling, whereby part of the impurities and the moisture are eliminated.



Process of Making Bisulfite of Soda. H. Howard, July 28, 1914. U. S. Pat. 1,104,897. Lime-mud is reacted upon with sodium bisulfite, thereby forming calcium sulfite and sodium sulfite. Sodium sulfate is added and the resulting mixture is reacted upon with sulfur dioxid at a temperature between 45° C. and 65° C., thereby forming calcium sulfate and sodium bisulfite.



Calcium Acid Phosphate. E. W. Reed, July 28, 1914. U. S. Pat. 1,105,304. A moving body of air laden with the finely divided phosphate material to be transformed into calcium acid phosphate is sprayed with sulfuric acid, the process being preferably carried out in the apparatus illustrated.



MARKET REPORT

AVERAGE WHOLESALE PRICES OF STANDARD CHEMICALS, ETC., FOR THE MONTH OF OCTOBER, 1914

ORGANIC CHEMICALS

Acetanilid	Lb.	30	@	32
Acetic Acid (28 per cent)	C.	1.50	@	1.65
Acetone (drums)	Lb.	11½	@	12½
Alcohol, denatured (180 proof)	Gal.	33	@	35
Alcohol, grain (188 proof)	Gal.	2.60	@	2.65
Alcohol, wood (95 per cent)	Gal.	45	@	47
Amyl Acetone	Gal.	2.50	@	2.75
Aniline Oil	Lb.	—	@	—
Benzoic Acid	Lb.	—	@	—
Benzol (90 per cent)	Gal.	—	@	—
Camphor (refined in bulk)	Lb.	—	@	60
Carbolic Acid (drums)	Lb.	36	@	38
Carbon Bisulfide	Lb.	10	@	15
Carbon Tetrachloride (drums)	Lb.	—	@	15
Chloroform	Lb.	30	@	35
Citric Acid (domestic), crystals	Lb.	70	@	72
Dextrine (corn)	C.	3.07	@	3.32
Dextrine (imported potato)	Lb.	—	@	—
Ether (U. S. P., 1900)	Lb.	15	@	20
Formaldehyde	Lb.	8½	@	9½
Glycerine (dynamite)	Lb.	24	@	25
Oxalic Acid	Lb.	15	@	18
Pyrogallic Acid (bulk)	Lb.	1.90	@	2.10
Salicylic Acid	Lb.	1.20	@	1.25
Starch (cassava)	Lb.	3¼	@	4
Starch (corn)	C.	2.39	@	2.50
Starch (potato)	Lb.	—	@	—
Starch (rice)	Lb.	—	@	—
Starch (sago)	Lb.	—	@	—
Starch (wheat)	Lb.	5	@	10
Tannic Acid (commercial)	Lb.	60	@	66
Tartaric Acid, crystals	Lb.	50	@	55

INORGANIC CHEMICALS

Acetate of Lead (brown, broken)	Lb.	7¼	@	7½
Acetate of Lime (gray)	C.	1.50	@	1.55
Alum (lump)	C.	2.75	@	3.00
Aluminum Sulfate (high-grade)	C.	1.50	@	2.00
Ammonium Carbonate, (domestic)	Lb.	10	@	11
Ammonium Chloride, (gray)	Lb.	6¼	@	6¾
Aqua Ammonia (drums) 16°	Lb.	2¼	@	2½
Arsenic (white)	Lb.	5	@	6
Barium Chloride	Ton	1.20	@	1.30
Barium Nitrate	Lb.	—	@	—
Barytes (prime white, foreign)	Ton	20.00	@	27.00
Bleaching Powder (35 per cent)	C.	2.00	@	3.00
Blue Vitriol	C.	4.50	@	4.75
Borax, crystals (bags)	Lb.	3¾	@	4½
Boric Acid, crystals (powd.)	Lb.	7¼	@	8
Brimstone (crude, domestic)	Long Ton	22.00	@	22.50
Bromine (bulk)	Lb.	40	@	50
Calcium Chloride (lump)	Ton	11.80	@	12.00
Chalk (light precipitated)	Lb.	8	@	10
China Clay (imported)	Ton	14.00	@	16.00
Feldspar	Ton	—	@	—
Fuller's Earth (powdered, foreign)	Ton	—	@	—
Green Vitriol (bulk)	C.	55	@	60
Hydrochloric Acid (18°)	C.	1.15	@	1.65
Iodine (resublimed)	Lb.	3.75	@	4.00
Lead Nitrate	Lb.	8¼	@	8½
Litharge (American)	Lb.	5	@	5¼
Lithium Carbonate	Lb.	1.25	@	1.30
Magnesium Carbonate	Lb.	5	@	6
Magnesite "Calcined"	Ton	45.00	@	50.00
Nitric Acid (36°)	Lb.	3⅞	@	4¼
Phosphoric Acid (sp. gr. 1.75)	Lb.	28	@	28½
Phosphorus	Lb.	35	@	95
Plaster of Paris	Bbl.	1.50	@	1.70
Potassium Bichromate (50°)	Lb.	13	@	15
Potassium Bromide	Lb.	70	@	80
Potassium Carbonate (calcined), 80 @ 85%	C.	12	@	15
Potassium Chlorate, crystals	Lb.	15	@	16
Potassium Cyanide (bulk), 98–99%	Lb.	25	@	30
Potassium Hydroxide	C.	32.00	@	40.00
Potassium Iodide (bulk)	Lb.	3.15	@	3.25
Potassium Nitrate (crude)	Lb.	—	@	—
Potassium Permanganate (bulk)	Lb.	35	@	40
Quicksilver, Flask (75 lbs.)		50.00	@	—
Red Lead (American)	Lb.	5½	@	6
Salt Cake (glass makers')	C.	55	@	65
Silver Nitrate	Oz.	33	@	35
Soapstone in bags	Ton	10.00	@	12.00
Soda Ash (48 per cent)	C.	67½	@	72½
Sodium Acetate	Lb.	5	@	7
Sodium Bicarbonate (domestic)	C.	1.00	@	1.10
Sodium Bicarbonate (English)	Lb.	3½	@	4
Sodium Bichromate	Lb.	4¾	@	5
Sodium Carbonate (dry)	C.	60	@	80
Sodium Chlorate	Lb.	—	@	14
Sodium Hydroxide (60 per cent)	C.	1.55	@	1.57½
Sodium Hyposulfite	C.	1.60	@	1.90
Sodium Nitrate (95 per cent, spot)	C.	—	@	1.90
Sodium Silicate (liquid)	C.	60	@	70
Strontium Nitrate	Lb.	15	@	17
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.	9¾	@	10
Tin Oxide	Lb.	37	@	38
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.	45	@	57
Black Mineral Oil, 29 gravity	Gal.	13½	@	14
Castor Oil (No. 3)	Lb.	8¼	@	9
Ceresin (yellow)	Lb.	12	@	22
Corn Oil	C.	5.45	@	5.55
Cottonseed Oil (crude), f. o. b. mill	Gal.	29	@	30
Cottonseed Oil (p. s. y.)	Lb.	5½	@	6
Cylinder Oil (light, filtered)	Gal.	21½	@	32
Japan Wax	Lb.	13	@	14
Lard Oil (prime winter)	Gal.	90	@	92
Linseed Oil (raw)	Gal.	45	@	50
Menhaden Oil (crude)	Gal.	33	@	—
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.	4.05	@	—
Rosin Oil (first run)	Gal.	25	@	—
Shellac, T. N	Lb.	17	@	18
Spermaceti (cake)	Lb.	28	@	30
Sperm Oil (bleached winter), 38°	Gal.	70	@	71
Spindle Oil, No. 200	Gal.	18	@	19
Stearic Acid (double-pressed)	Lb.	9	@	11
Tallow (acidless)	Gal.	64	@	66
Tar Oil (distilled)	Gal.	30	@	31
Turpentine (spirits of)	Gal.	47½	@	48

METALS

Aluminum (No. 1 ingots)	Lb.	18	@	18½
Antimony (Hallet's)	Lb.	12	@	12½
Bismuth (New York)	Lb.	2.10	@	2.15
Bronze powder	Lb.	—	@	—
Copper (electrolytic)	C.	11.15	@	—
Copper (lake)	C.	11.67½		
Lead, N. Y	C.	3.50	@	—
Nickel	Lb.	—	@	—
Platinum (refined)	Oz.	50.00	@	52.00
Silver	Oz.	50½		
Tin	C.	28.75	@	30.00
Zinc	C.	4.80	@	4.90

FERTILIZER MATERIALS

Ammonium Sulfate	C.	2.55	@	2.62½
Blood (dried)	Unit	3.15	@	3.20
Bone, 4½ and 50 (ground, raw)	Ton	27.50	@	—
Calcium Cyanamid	Unit of Ammonia	2.22½	@	2.40
Calcium Nitrate (Norwegian)	C.	—	@	—
Castor meal	Unit	—	@	—
Fish Scrap (domestic, dried)	Unit	3.00	&	10
Phosphate, acid (16 per cent bulk)	Ton	7.50	@	—
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	nominal		
Pyrites (furnace size, imported)	Unit	13	@	—
Tankage (high-grade)	Unit	3.15	&	10